

PYROLYSIS 2008

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ADVANCES IN ANALYTICAL AND APPLIED PYROLYSIS 2006-2008

**Book of Abstracts of the Communications presented to the
18th International Symposium on Analytical and Applied Pyrolysis
Lanzarote - Canary Islands. May 18-23, 2008**

J.A. González-Pérez & F.J. González-Vila Eds



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***Editors:
J.A. González-Pérez & F.J. González-Vila***

Maquetación: Rocío González Vázquez

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FOREWORDS

During the 17th Symposium on Analytical and Applied Pyrolysis, held in Budapest, our research group from IRNAS-CSIC was proposed as organizer of the next Symposium. Now, two years after, and on behalf of the Organizing Committee I have the great honour to welcome all you to the 18th International Symposium on Analytical and Applied Pyrolysis (PYR08) held in the Canarian village of Tegui, Lanzarote, Spain, during May 18-23, 2008. Lanzarote is known as the land of fire, one of Spain's most beautiful areas and an ideal place to host this meeting.

This PYR edition is organized under the auspices of the Spanish Ministry of Science and Innovation (MICINN), Spanish Council for Scientific Research (CSIC), Canarian Government, Canarian Universities of Las Palmas de Gran Canaria (ULPGC) and La Laguna (ULL), and the local authorities from Lanzarote (Cabildo de Lanzarote and Ayuntamiento de Tegui).

The Journal of Analytical and Applied Pyrolysis (JAAP) is a prestigious Elsevier journal that serves scientists who study thermal processes of materials. Every other year, this group of scientists organizes this International Meeting that is among the most prestigious conference in the field. We are expecting that PYR08 in Lanzarote will continue the tradition as the premier forum for the presentation and discussion of cutting-edge scientific advances in basic and applied pyrolysis, setting the trend for the development of this discipline.

This edition of the Symposium has exceptional exposure in fields like novel applications of pyrolysis in the environment and forensic sciences, the search for new materials, polymers, alternative energy source and in the structural elucidation of complex organic materials that may help in a better comprehension of the carbon cycle and Global Climatic Change. More than 200 top scientists and industry professionals from more than 30 countries from all over the world will attend PYR08. This edition has a very intense programme that include 10 Invited Key Lectures, 66 Oral and 180 Poster presentations.

We will like to thank PYR08 Organizing Committee for their constant work in the hard tasks needed for a successful meeting, the Scientific Committee for valuable advice and the production of our solid and outstanding Scientific Program and to all donors, sponsoring companies and expositors for their support without which the Lanzarote PYR08 would not have been possible.

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ORAL PRESENTATIONS

SESSION 1 OPENING

K1: Pyrolysis in geosciences: application to exobiology questions

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This lecture will show the application of pyrolysis techniques in the area of exobiology. Two topics will be approached: the organo-synthesis in meteorites and the search for traces of life in the most ancient terrestrial rocks. Two types of samples will therefore be presented: carbonaceous meteorites and archean siliceous rocks (cherts).

In both types of samples, carbon mostly occurs as insoluble organic matter (IOM) and this organic fraction is considered to be less affected by mobile contaminants (either of anthropogenic or natural post-depositional origin) than the soluble one. IOM therefore contains major information recording its origin and formation pathway. However, IOM analysis is made more difficult because IOM is tightly associated with the mineral matrix and it is chemically inert. Pyrolysis thus appears as a powerful tool for deciphering the chemical structure of such macromolecular organic matter.

The primitive carbonaceous chondrites contain substantial amounts of carbon (up to 3%) and this organic matter is considered as a record of interstellar synthesis and to contain precursors of prebiotic molecules possibly deposited on earth by meteoritic bombardments. For these reasons, meteoritic organic matter has been raising interest for long.

The most ancient rocks on Earth are cherts. They contain traces of organic matter, the origin of which is much debated: abiotic formation under hydrothermal conditions or organic microfossils? The chemical structure of the IOM from an archean chert was investigated so as to yield biomarkers that are of the age of the deposit.

These studies led (i) to reveal a different origin than commonly considered for the meteoritic organic matter and (ii) to support a scenario according to which life was present on Earth 3.5 billion years ago.

K2: Feedstock recycling of synthetic and natural rubber by pyrolysis in a fluidized bed

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Today's high oil price increase the interest in feedstock recycling of plastics and rubber to recover monomers, oil and gas from these hydrocarbon source [1]. Another goal is to protect the environment from landfilling of these polymers that decompose very slowly. The problem for cracking rubber into suitable products in the low heat transfer, the high heating energy needed for cracking and the high content of fillers such as carbon black, silica, and zinc oxide.

We use a smaller indirectly heated fluidized bed process with a capacity of 500 – 3000 g/h and a pilot plant for the pyrolysis of whole tires [2]. It was one goal of the study to investigate how much monomers such as butadiene and isoprene can be recovered from synthetic and natural rubber. The heart of the pilot plant is a fluidized bed reactor with an inside diameter of 450 mm and a height of 900 mm. Sand is used as a fluidizing medium with a size of 0.3 – 0.7 mm. The temperature, kind of the fluidizing gas, and composition of the rubber feed was varied. The table summarizes the results.

Table. Pyrolysis of rubber in a fluidized bed

Feed:	tire	rubber	natural rubber	whole tires
Pyrolysis temperature	600 °C	650 °C	600 °C	700 °C
Fluidizing gas	pyro-gas	steam	steam	pyro-gas
<i>Products:</i>				
Gas (wt%)	16	22	18	14
Butadiene	0,2	1,1	0,5	0,3
Isoprene	2,2	6,7	22	0,4
Oil	31	34	47	19
Tar	18	6	11	15
Carbon black	32	30	1,5	40
Steel cord	-	-	-	11

The yield of oil can be increased using steam instead of pyrolysis gas for fluidizing. It is possible to receive 22 wt% of isoprene from natural rubber. The whole amount of oil and isoprene is 69 wt%. Tar is the high boiling product fraction. The quality of the carbon black recovered from tire rubber with a yield of about 30 % was superior and useful as filler for rubber.

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SESSION 2 BIOMASS I:
Characterization, Fuel & Chemicals Production

K3: Applied Pyrolysis of Biomass for Energy and Chemicals

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The shortage of fossil fuels, political imponderabilities and the climate change are main drivers for the increasing interest in using renewable feedstocks for energy and as source for chemical feedstocks. To replace fossil raw materials, wood and other lignocellulosics must be subjected to either biological or thermochemical conversion. These processes degrade the polymeric constituents into smaller molecules, which can subsequently be used as basic materials for energy or chemicals production. Of the available combustion and gasification technologies for biomass, fast pyrolysis is the least developed, but offers the benefits of a liquid fuel (bio-oil) with concomitant advantages of easy storage and transport as well as higher power generation efficiencies than fossil fuelled systems at the smaller scales of operation that are likely to be realised from bioenergy systems. Furthermore, the bio-oil can serve as source for chemicals and add value to the whole process chain.

Especially fast pyrolysis systems are today in the focus of interest as they provide high yields of bio-oils in the range of 65-70 wt.%. The most important fast pyrolysis systems for bio-oil production will be presented and discussed, two of them are located in Canada and the other three are based on European technologies. Energetic applications of the bio-oils, ranging from simple combustion in boilers to combustion in diesel engines will be presented and discussed. In addition, latest developments in biomass-to-liquid (BTL) progress will be shown where biomass pyrolysis is an important integral part prior to the production of a synthesis gas.

New developments in pyrolysis-based biorefineries will also be presented combined with the new concepts developed in an European integrated project and in PyNE, the traditional European Network on biomass pyrolysis.

The recovery of chemicals from pyrolysis liquids is also an issue and latest developments will be shown ranging from the extraction of a single compound such as acetic acid to a complex mixture used as liquid smoke aroma in food industry. Last but not least, analytical tools for the characterization of bio-oils will be presented and discussed.

L1: Interactions between Cellulose- and Lignin-derived Pyrolysis Products in Wood Gasification

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Wood gasification is a two-stage process. The primary pyrolysis products (volatiles and char) which are formed in the initial stage are converted further to the gaseous products in the second stage. Polysaccharides (cellulose and hemicellulose) and lignin as the major wood consistent polymers form the pyrolysis products with different chemical structures. Wood polysaccharides form anhydrosugars, furans, aldehydes, ketones and carboxylic acids as the primary volatile products, while the primary volatiles from lignin are mainly low molecular weight phenols with the aromatic nuclei which are originally included in wood lignin as like guaiacyl (4-hydroxy-3-methoxyphenyl)-unit in softwood lignin. Because of these different chemical structures, reactivities of the volatile products are quite different between polysaccharides and lignin (unpublished data); polysaccharide-derived volatiles are easily gasified in vapor-phase, while gasification rates of lignin-derived volatiles are quite low and rather similar to those of char fractions. In this paper, interactions between cellulose and lignin (Japanese cedar milled wood lignin) are presented as studied under the conditions of N₂/ 600°C/ 40-80s.

Two interaction modes are possible, ie. direct solid-solid and vapor-phase interactions. To distinguish these interactions, a dual-space ampoule reactor was used. In this reactor, direct solid-solid interaction is not allowed between cellulose and lignin (milled wood lignin from Japanese cedar). Thus, careful comparison of the results with those of cellulose-lignin mixtures gives some insights into the solid-solid and vapor-phase interactions separately.

From the quantitative determination of the pyrolysis products with ¹H-NMR and GC-MS analyses, the influences arising from the interactions on product formation were clarified as summarized in Table 1. The direct solid-solid interactions enhanced the volatile products formation from both cellulose and lignin, with reducing the char yield. The vapor-phase interactions reduced the yield of cellulose-derived volatiles and increased the yield of lignin-derived volatiles. The gas (CO, CH₄, CO₂, H₂) yields increased significantly. These results indicate that gasification of the cellulose-derived volatiles is enhanced under the influence of the lignin-derived vapor. Methane formation from lignin was also enhanced. Secondary carbonization of lignin-derived volatiles was also effectively inhibited, and the ratio of catechol / *o*-cresol increased substantially.

An interaction mechanism is proposed to explain these results. In this mechanism, the cellulose-derived volatiles act as H-donors and the lignin-derived volatiles (radicals), especially obtained after the O-CH₃ bond homolysis, act as H-acceptors.

Table 1 Summary of the influences of the direct solid-solid and vapor-phase interactions (N₂/ 600 °C).

Direct solid-solid interactions		
Gas		+/-
CH ₄ from lignin		-
Tar		+
From cellulose		+
From lignin		+
Char		-
Vapor-phase interactions		
Gas		+
Gas from cellulose		+
CH ₄ from lignin		+
Tar		+/-
From Cellulose		-
From Lignin		+
Catechols		+
<i>o</i> -Cresols		-
Char		(-)
Secondary char from lignin		-

+: enhanced , -: suppressed

L2: On the catalytic steam reforming of the aqueous fraction of bio-oil: acetol and 1-butanol as model compounds

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Lignocellulosic residues may be upgraded through pyrolysis of biomass. Particularly, bio-oil, the liquid fraction obtained in the fast pyrolysis of biomass, may constitute an attractive feedstock for both energetic purposes and for the production of certain fine chemicals. Bio-oil can be separated into two different phases: ligninic, that can be used as a substitute for phenol in phenol-formaldehyde resin formulations; and the aqueous fraction, which can be converted to hydrogen by steam reforming.

Ni/Al coprecipitated catalysts had been previously tested in the steam reforming of acetic acid as a model compound of bio-oil showing adequate reforming activity and selectivity towards hydrogen, though a decrease in activity with reaction time took place due to carbon deposition. The present work is the following step in the study, testing the catalytic steam reforming of acetol and 1-butanol as model compounds. These chemicals have been chosen since they are the major constituents identified in the ketonic and alcoholic fractions of the aqueous fraction of bio-oil respectively.

The experimental setup consists of a fixed bed inside a tubular quartz reactor operating at atmospheric pressure. The bed is constituted by a mixture of sand (used as inert filler) and a Ni-based catalyst (hidrotalcite-like nickel aluminate). Three catalysts with relative atomic percentages of nickel ($\text{Ni}/(\text{Ni}+\text{Al})$) of 23, 28 and 33 % were prepared by coprecipitation. The experimental procedure implies in-situ reduction of the catalyst with hydrogen and further reforming of the model compound. The exiting flow is forced into a condenser and finally the remaining product gases are analysed on-line with a Micro GC before venting. Typically, 20-30 mg of catalyst were used and the organic flow rate fed by means of a HPLC metering pump ranged from 0.1 to 0.17 mL/min. The weight of catalyst/organic flow rate ratios, W/m_{org} , were selected after preliminary runs with both compounds and fixed at values of 0.89 (g catalyst min)/g of acetol and 3.43 (g catalyst min)/g of butanol.

The results obtained at 650 °C show a significant non catalytic reforming of acetol, yielding a carbon conversion as high as 24 %, though negligible in the case of 1-butanol, which may lead to conclude that acetol is easier to be reformed. In the case of catalytic steam reforming, both the influence of the temperature and the nickel content in the catalyst on product gas yields were studied. At 550 °C both chemicals became poorly catalytically reformed, whereas at 650 °C showed acceptable yields, close to equilibrium conditions, though a progressive decrease was observed. The best results were obtained in both cases for the catalyst with a 28 % Ni content. These results are concordant with those previously obtained in the catalytic steam reforming of acetic acid as a model compound, where the highest hydrogen yields were also obtained with the 28 % Ni catalyst.

L3: Biomass Pyrolysis - Secondary reactions of primary pyrolysis products

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Gasification of biomass is of growing interest because of its potential as one future source for energy supply. In the first step up to 500°C, solid biomass is converted to primary pyrolysis products. The primary product composition of biomass pyrolysis depends on the amount of the main components hemicelluloses, cellulose and lignin [1]. In a second step at higher temperatures, the primary products are gasified to raw gas, secondary and tertiary tars [2, 3]. Tar impurities of the raw gas cause considerable effort of gas cleaning before further use, e.g. for the conversion to methanol or Fischer-Tropsch synthesis.

In this work, tar formation by secondary reactions is investigated in the temperature range between 500°C and 1100°C in a plug flow reactor system (figure 1). The thermal degradation of guaiacol (2-Methoxyphenol), a model compound for the primary lignin products, and furfuryl alcohol (2-Hydroxymethylfuran), a model compound for the primary carbohydrate products, are studied at residence times in the isothermal reaction zone between 0.1-0.6s. Products are analyzed by online-MS and by offline GCMS measurements.

Formal kinetic parameters of guaiacol and furfuryl alcohol decomposition are determined. The product distribution is analyzed dependent on temperature and residence time for both compounds. Possible reaction pathways for the thermal degradation and the tar formation are discussed.

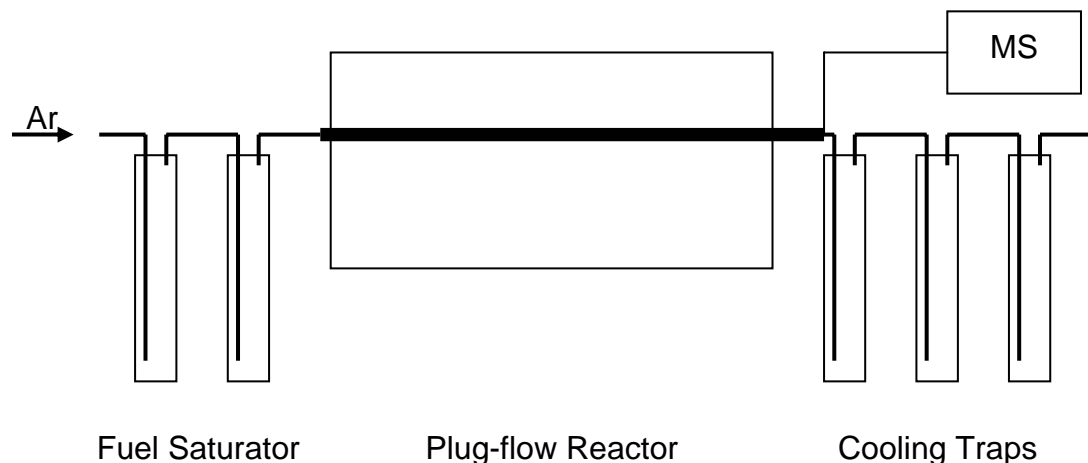


Figure 1. Plug flow reactor system for guaiacol and furfuryl alcohol pyrolysis experiments.

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L4: Rapid pyrolysis of biomass for the production of fuel gas: effect of the nature of biomass, of particle size and of the gaseous atmosphere

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Biomass is today considered as a renewable fuel whose use would help to reduce greenhouse gases. Over the past two decades, worldwide interest has been growing in the thermochemical conversion of renewable resources through pyrolysis and gasification. Rapid pyrolysis of biomass at high temperature is a way to produce very large quantities of gas and small amounts of char and liquids. Among pyrolysis gases, H_2 and CO are very interesting for cogeneration, fuel cell or the Fischer Tropsch synthesis for example. On contrary, it is preferable to limit the formation of CO_2 (which is not a fuel gas) and of CH_4 which is known to be very hard to reform.

In this work, a series of experiments has been performed in an Entrained Flow Reactor (EFR) in order to investigate the effect of the nature of biomass and of the gaseous atmosphere (N_2 or N_2 + steam) on the production of gases during rapid pyrolysis at $950^\circ C$ of small particles (125-200 μm). Additional experiments have then been performed in a tubular reactor in order to investigate the effect of particle size on the production of gases and char. The gas species CO , H_2 , CH_4 , C_2H_4 , C_2H_2 and CO_2 were quantified with FTIR, NDIR, FID and TCD.

Five biomasses were pyrolysed: beech wood, a mix "spruce and fir", bark, grass and rice husk. Results showed that the two woody biomasses produce approximately the same quantities of each gas. They formed more CO , CH_4 and H_2 than the other biomasses. The grass formed less H_2 and CO but more CO_2 than the other biomasses. Previous works showed that it is not possible to predict gas yields of a biomass from its composition in cellulose, hemicellulose and lignin, because of interactions between components and catalytic effects of minerals [1].

The effect of gaseous atmosphere on gas yields was investigated with experiments using beech wood under nitrogen and under 20% vol. of steam in nitrogen. Results showed that when the atmosphere contains steam: a) the yield of CO_2 increased; b) the yield of H_2 increased; c) the yield of C_2H_2 increased; d) the yield of C_2H_4 decreased.

Yields of CH_4 and CO are similar under nitrogen and in presence of steam. Results concerning the impact of steam on H_2 , CO and C_2H_4 yields are in accordance with the results of Dupont [2].

Experiments of pyrolysis of beech wood particles of 125-200 μm , 1 mm, 10 mm and 20 mm of diameter were performed in the tubular reactor. Results showed that larger particle size leads to: a) higher CO_2 yield; b) higher char yield; c) lower CO yield; d) lower C_2H_4 yield.

The total gas quantities formed are approximately similar whatever the particle diameter.

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L5: Fast, intermediate or slow pyrolysis for fuels production, power generation from various Biomasses or as pre-conditioning unit for gasifiers

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Pyrolysis of biomass is of different kind in terms of feedstock, applied reactors as well as applied type of pyrolysis - fast, intermediate or slow pyrolysis. The classical approach on slow pyrolysis leads to charcoal or even finally to activated carbon, starting from wood. The opposite of this is fast pyrolysis of wood in creating a maximum of liquid phase for this specific feedstock.

The main target of intermediate and fast pyrolysis is the production of liquids for direct application in heat and power or for biorefinery purpose. At least the option to transport the liquids from pyrolysis of fast growing biomasses as for instance straw - while higher in energy density than the feedstock - from decentral areas of production to more central applications is of interest. Under this aspect a typical application of the fast pyrolysis is the pre-conditioning of gasifier feedstock, producing liquids and gases as well as char or even slurry.

More difficult as the pyrolysis of wood is the pyrolysis of non-woody biomass and the application of its products. Non-woody biomass often leads to high reactive liquids and depending of the feedstock often rich in high tars. Some of these products are of bituminous character and, therefore, solid at room temperature, what creates problems at storage or within the process itself. Some fast pyrolysis/gasification approaches are dealing with production of syngas from straw or empty fruit bunches from oil palms, others are dealing with straw application in ablative (fast) pyrolysis for heat and power. In general the maximisation of liquid is no longer valid for fast pyrolysis in general but strongly dependant on the feedstock and the used reactor.

A new type of pyrolysis is the intermediate pyrolysis, even in between the reaction conditions of slow and fast pyrolysis it offers much different product qualities. The distribution of the product phases is affected as well as the composition of the liquid phase. Tar production can be very low and liquids, therefore, suitable for the application in engines. It is of importance that the reaction conditions for intermediate pyrolysis offer a wide range of variation for the process optimisation. Topics of interest are biorefinery, enhancement of gas production for difficult feedstock generating non suitable oils for heat and power or the running of mixtures of various biomasses and finally the conditioning of cokes for combustion.

This paper will offer some aspects on application of ash rich feedstock to combustion, gasification and direct heat and power applications via pyrolysis. Furthermore, it delivers strategies for three planned energy parks in Europe.

SESSION 3 FUNDAMENTAL STUDIES:
Kinetics & Mechanisms of Pyrolysis

K4: Kinetic Triplet of Pyrolysis Reaction

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The first question when one intends to design a pyrolysis process is how fast the pyrolysis reaction can be accomplished. To this end, we have to understand chemical decomposition pathways of a substance. In addition, recent studies offered an insight that physical processes may also play an important role in pyrolysis kinetics of thermoplastics. However, many previous kinetic studies have only focused on estimating the decomposition rates of polymers without considering their decomposition characteristics. This paper tried to bring an issue that the pyrolysis kinetics should not be confined just with the thermal decomposition rates under specific conditions, but with physico-chemical processes of pyrolysis reaction.

Single step kinetics of solid state decomposition takes the following kinetic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

Arrhenius equation generally expresses the explicit temperature dependency of the rate constant:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha)$$

where A , E , and $f(\alpha)$, respectively, represent pre-exponential factor, activation energy, and reaction model. The A , E , and $f(\alpha)$ are called as kinetic triplet that can characterize a unique pyrolysis reaction.

Many kinetic studies assumed that the reaction model of pyrolysis reaction of polymers would be accounted for by reaction order function without verification. Fixation of reaction model could allow a force-fitting of Arrhenius parameters. It is, hence, essential to estimate the correct form of reaction model that reflects the physico-chemical processes of pyrolysis reaction.

It was demonstrated that reduced-time-plot (RTP) using isothermal decomposition data was useful to determine the reaction model. Applying the RTP, the reaction model of high density polyethylene (HDPE) was determined to be “contracting cylinder” model, whereas that of linear low density polyethylene (LLDPE) was accounted for by “Avrami-Erofeev” model. Pyrolysis reaction model of polypropylene (PP) varies with reaction temperature. At lower temperatures (683~693 K), the “contracting cylinder” model is responsible for the reaction model of PP. Bubble nucleation may be a major reaction mechanism of PP pyrolysis at higher temperatures (728~738 K). High generation rates of volatiles lead to the accumulation of volatiles in the melt until reaching a critical concentration where bubble nucleation sets forth, thus mimicking “Avrami-Erofeev” model.

It is suggested that the pyrolysis kinetics as well as reaction model of polymers should be evaluated in accord with physico-chemical characteristics of pyrolysis reaction.

L6: Comparison between the pollutant emission in the pyrolysis and combustion of different wastes

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Thermal decomposition of wastes can take place both in controlled (incinerators, cement kilns...) and non-controlled conditions, for example, during fires or open-air burning. The substances emitted during non-controlled plastic thermal degradation may create a serious hazard for human health and for the environment.

Since 1984, the Department of Chemical Engineering of the University of Alicante has been working on different research projects involving the pyrolysis of some organic wastes such as polyethylene (PE), tyres, sewage sludges, poly vinylchloride (PVC), waste paper, cotton textiles, polyester textiles, meat and bone meal (MBM), varnish based on polyurethane, *orujillo* (olive pomace) and waste lube oils. These wastes are first of all studied from a kinetic point of view by using a thermobalance, which is not the aim of the present work. The wastes are also studied by analysing the pollutant emitted in different experimental conditions. In this last case, the appliance used is a quartz tube that is place inside of a horizontal furnace; such has been described previously. The atmospheres used throughout these years have been, on the one hand a pyrolytic N₂ flow, and in other cases synthetic air in order to simulate combustion conditions. The temperatures of the runs are in the range 500-1100 °C.

In this work, a comparison between the different yields obtained relative to the wastes is presented. The analysis and discussion comprises several compounds such as hydrocarbons, PAHs and PCDD/Fs (dioxins), taking the experimental results obtained at 850 °C, both pyrolysis and combustion.

Figure 1 shows the emissions of some compounds and Figure 2 the fingerprints of the emissions of PCDD/Fs for some wastes.

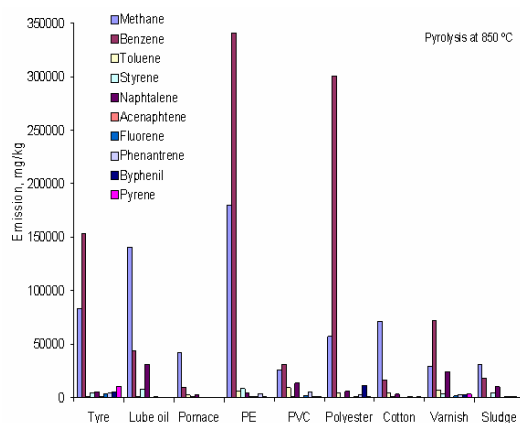


Figure 1. Pyrolysis runs at 850 °C.

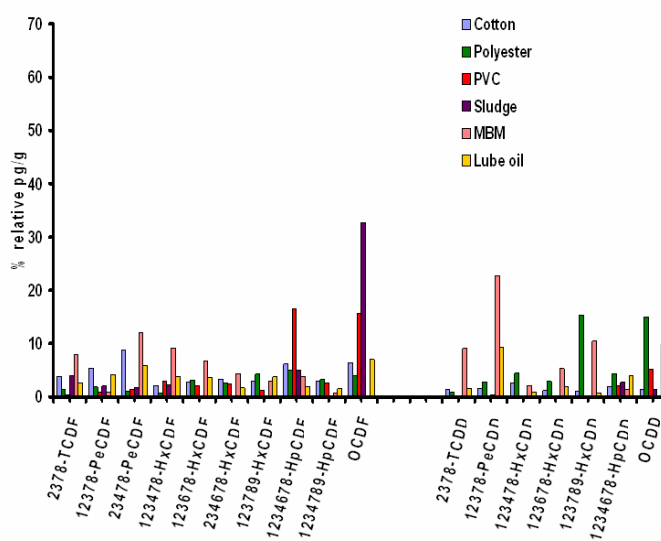


Figure 2. Combustion runs at 850 °C.

L7: Pyrolysis Behavior of Cellulose Fibers Modified for Composites

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Natural fiber composites are recognized as an alternative to conventional glass or carbon-fiber reinforced composites. Key advantages of cellulose fibers are: low cost, low density, renewable nature, biodegradability and less abrasion during processing. The limitations of using lignocellulosic fibers as reinforcing fillers in plastic composites are the low degree of dispersion and poor interfacial adhesion. Therefore various treatments are applied to modify the surface of the cellulose fibers to increase the compatibility between the fibers and the plastics. Substitution of some hydroxyl groups of cellulose with bulky carboxymethyl groups results in significant improvement of the accessibility of molecules, moreover, a subsequent heat treatment decreases the hydrophilic character of the fiber due to hornification¹. Zn and Ca salts of polycarboxylic acids were proved to be β -nucleants for polypropylene², hence Zn and Ca salts of carboxymethylcellulose as cellulose based polycarboxylic acid might positively influence the crystallization of polypropylene on the fiber surface. Coatings with some hydrophobic materials, like paraffin, can also improve the interfacial adhesion.

The objective of the present work was to understand the structural and thermal decomposition relationship of cellulose fibers with treatment methods. The thermal behavior of partially carboxymethylated cellulose (CMC) was investigated. Furthermore we studied the effect of Zn^{2+} and Ca^{2+} ions introduced into CMC and untreated cotton fibers. The effect of a waterproof agent, zirconium stearate has also been studied on the thermal stability of the CMC fibers. Simultaneous thermogravimetry/mass spectrometry was applied to study the thermal decomposition of the samples in inert atmosphere. The detailed analysis of the volatile products has been carried out by pyrolysis-gas chromatography/mass spectrometry.

It is concluded that low degree of carboxymethyl substitution ($\text{DS}=0.06$) already results in significant changes in the thermal properties of cellulose. The yield of the high molecular mass products is reduced, while the gas evolution and the char formation are enhanced. Zn^{2+} ions have similar effects on the original and carboxymethylated (CM) cellulose due to its Lewis-acid character. The decomposition shifts to lower temperature, the char formation is enhanced and levoglucosan evolution is reduced. Ca^{2+} ions present high impact on the decomposition of CM-cellulose, enhance the effect of carboxymethylation. However, Ca^{2+} ions have smaller effect on the original cellulose. The waterproof agent seems to decompose independently from the cellulose samples.

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L8: Quantitative and Kinetic TG-FTIR study of biomass residue pyrolysis: DDGS and Chicken Litter

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New energy policies all over the world are trying to tackle high oil prices and climate change by promoting the use of biomass to produce electricity, heat and liquid transportation fuels.

Dry Distillers Grains and Solubles (DDGS) is a by-product of ethanol production from corn by means of dry-grind process. Due to its high content of proteins it is widely used as feed for cattle but the dramatic increase in corn-ethanol production brought the feed market to a saturation point [1] accelerating the need to explore new markets and applications [2].

Chicken litter is another biomass waste that is produced in large quantities in several areas of the World and whose disposal on farm land is limited due to pollution issues. Incineration is often applied as a treatment method, but combustion of such a fuel is troublesome in boilers due to its high ash and Nitrogen content causing corrosion, slagging, fouling and harmful emissions.

The fuels tested here were received from industrial partners. In order to reduce the ash content and improve the ash behaviour for plant operation, the fuels were pre-treated using the leaching pre-treatment method developed by Arvelakis et al. [3].

Pyrolysis of these fuels has been monitored through a coupled TG-FTIR set-up. The fuels are heated in a thermobalance at different heating rates (10 – 30 - 100°C/min), in Helium flow, up to a temperature of 900°C. Evolved gases are analyzed with a coupled FTIR spectrometer. A quantitative method has been developed and quantification of the following volatile species is possible: CO, CO₂, CH₄, HCN, NH₃, HNCO, H₂O.

In this paper we present the results from the devolatilization of DDGS and Chicken Litter. A kinetic analysis has been performed using a Distributed Activation Energy Model (DAEM) so that kinetic parameters have been retrieved for the global devolatilization process and for the release of single species.

Weight loss curves together with the composition of each step and kinetic parameters are compared between the pre-treated and untreated fuels.

This work will thus give a better insight into the mechanisms of reaction of these fuels that nowadays bear high commercial potential but for which also little knowledge is available

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L9: Pyrolysis and Gasification of Biomass / Validation of a Predictive Model

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The occurrence of residual biomass in Greece could be a real opportunity in producing substitution fuels. Among agricultural residues and in particular, olive tree pruning, rapeseed residues, and soya residues are concerned in this study. The aim of this work is to help in the choice of sustainable technologies in order to produce valuable alternative fuels. Both, proximate and ultimate analyses have been performed on each of the three products. The different samples have been characterized by TGA analyses. Pyrolysis has been performed in a captive sample reactor [1] and gasification in a fixed bed reactor [2]. Mass balance and characterisation of pyrolytic and gasification products are presented. These results are compared with those obtained by the use of a predictive model [3].

Flash pyrolysis was performed by heating each sample (~0,3g) at temperatures between 500°C and 600°C, at atmospheric pressure in He (30ml/min), with an average heating rate of 40-50°C/s. The solid (char) and the condensed hot gases (liquid hydrocarbons and tar) were determined gravimetrically. Gasification was performed with air in a laboratory scale batch fixed bed reactor (63cm³). The air factor (λ) in the gasification experiments was between 0.2 and 0.4. The temperatures ranged from 750°C to 950°C, with a heating rate about 15°C/min. Gas sample is taken during experiments in order to proceed to the gas composition analysis. As an example, the table below shows results of laboratory scale pyrolysis experiments compared to those obtain by running the predictive model (with carbonisation rate $\alpha=0,75$) for olive tree pruning (500 °C).

Pyrolytic products	Pyrolysis Experiments	Predictive model
Kg char/t biomass	250	243
%ash/ char	4	1
HV char (MJ/kg)	25	22
Kg gas/t biomass	770	757
% VM/gas	93	94
HV gas (MJ/kg)	19	21

For flash Pyrolysis, the comparison of the different samples shows results in accordance with a 75% of the carbonization. The deviation is within the range of 1 to 12% except of the value percentage of ashes in the char for olive tree pruning. For gasification, when comparing the results, the deviations were higher as different considerations were taken in both experiments and predictive model. Further investigations are proposed.

In conclusion, this work shows that, in the case of agricultural residues, it is possible to use of a simple predictive model to evaluate the proportion of solid and gaseous pyrolytic products, their calorific values and the percentage of volatile matter knowing their proximate and elemental analyses. This method could therefore contribute in the choice of a feasible technology to produce substitution fuels from specific residues.

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L10: Kinetic study of the thermal cracking of the products of the biomass gasification

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Different techniques of biomass gasification exist in the pilot ladder, but for advanced applications, as production of bio combustibles or of cogeneration by means of a fuel cell, the quality requested on the composition of biogas is constraining (weak content of tar, of particles, of organic and inorganic species), what leads to choose innovative pathway of gasification. The high temperature way (> 1300 K) is promising and seems to be a credible alternative to other already explored resolutions, as the catalytic way. A resolution would be to combine a classical system in fluidized bed with a high temperature reforming stage. It is so necessary to understand the reforming kinetics at high temperatures in a reducing atmosphere. Detailed kinetic mechanisms already exist for combustion of hydrocarbons but the sensitive reactions would be different in our case. Experiments will allow us to determine the important ways of reaction and to improve the models.

An entire experimental study of the methane reforming has therefore been performed in a plug flow mullite reactor under a near atmospheric pressure (1,07 bar). The kinetic influence of the different gases present in the biogas (H_2 , CO ,...) on methane conversion has been observed firstly individually followed by the study of complex mixtures representative of the outlet of a biomass gasification. The profiles of reactants and reaction products (CH_4 , CO , CO_2 , H_2 , C_2 , C_3) versus temperature (from 1200 to 1800 K) or versus reactant concentration, for a constant residence time (0,68 s), have been measured by gas chromatography.

The analysis of the results shows that hydrogen has an inhibiting effect on the methane reforming while CO has no kinetic effect. Water seems to accelerate the methane conversion below 1500 K and to slightly inhibit it above. CO_2 makes the conversion easier being a radicals OH source via the reaction: $CO_2 + H = CO + OH$ by reduction with H atoms. In presence of H_2 , water has a promoting influence at any temperature. Methane is converted mainly into C_2 . To be converted entirely with a residence time of 1 second, methane should be warmed at 1700 K.

We have used to model the experimental results a kinetic mechanism developed for methane combustion in our laboratory. The main trends are reproduced and the sensitive reactions have been highlighted. The reactor has been modelled with a plug flow reactor with CHEMKIN II. Carbon reforming appends mainly by reaction of OH radicals with unsaturated C_2 molecules, which are soot precursors. Process conditions necessary for high temperature methane reforming would then be favourable to undesirable soot formation.

L11: The Effect of Pyrolysis Temperature on Thermal Degradation of Polysiloxanes and Microstructure of the Derived Glasses: Correlation between Mass Loss, Gas Release and Fracture Morphology

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Manufacturing of polymer-derived ceramic materials from polysiloxanes attains interest because of high shaping properties and low fabrication temperature [1]. The pyrolysis process of polysiloxanes is accompanied by a large amount of gas generation and significant volume shrinkage of the derived glasses [1, 2]. Correspondingly it is important to find structural sensitive factors allowing control of structural properties of the glasses by pyrolysis conditions.

The present work studies the thermal degradation behavior of polysiloxanes in inert atmosphere up to 1200°C by thermogravimetry interfaced to mass spectrometry. The chemical composition of the derived glasses was determined by elementary analysis while the microstructure was studied by optical microscopy combined with scanning and transmission electron microscopy.

The degradation of polysiloxanes proceeds by a three-stage thermal interval characterized by different mass losses as well as by different amounts and type of evolved gaseous species. The degradation behavior correlates with the content of Si, C, O and H in derived glasses.

The derived samples contain networks of pores and bubbles with diameters in excess of 0.5 mm. The inner glass macrostructure is revealed after fracturing in compressive mode. High-developed rough fracture surfaces containing delaminated filaments are frequently observed in samples pyrolyzed at 400°C at which the highest amount of gas release and mass loss takes place. Transmission electron microscopy study shows that the filaments are composed of isotropic distributed SIOC-nanodomains.

According to calculation of formal kinetic parameters, the first degradation step lying below 400°C is characterized by the lowest apparent activation energy of around 60 kJ/mole. This energy attributes to evolving of low-molecular gaseous species like ethanol, water and siloxanes. Especially siloxanes effect tremendously the degradation of the initial polymer precursor. Polymer swelling accompanied by pore coagulation is believed to be responsible for the spatial material separation in form of filaments. A glass formation mechanism based on deformation of viscous polymer during gas release is proposed.

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L12: Oxidative Thermal Degradation of LDPE and The Determination of Some Thermodynamic Quantities

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The pyrolysis of polyolefin wastes is one of the possible way to obtain chemical feedstocks. In this work, the thermal degradation of low density polyethylene, (LDPE), which is a major product within plastics, was investigated in a semi-batch reactor system. First-order rate kinetics approach was chosen and reaction rate coefficients, k , and some thermodynamic quantities determined as activation energy, reaction enthalpy, free activation enthalpy, and entropy of degradation of LDPE for different air flow rates. We found that the maximum value of reaction rate coefficient is $0,0243 \text{ min}^{-1}$ at 600 mL min^{-1} air flow rate and the free activation enthalpy (ΔG^\ddagger) is $148,66 \text{ kJ mol}^{-1}$ at 450 mL min^{-1} air flow rate. Moreover, we found that the oxidative degradation of LDPE is not spontaneous and has low energy necessary (for degradation) than non-oxidative degradation processes.

Key words: Thermodynamics quantities, thermal degradation

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SESSION 4 SYNTHETIC POLYMERS:
Characterization and Recycling

K5: Characterization of Cross-linking Structure in Recycled Polymeric Material by Pyrolysis-Gas Chromatography

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The wasted polymer materials, subjected to the material recycling process, are often deteriorated compared with those of the virgin materials. This deterioration can be often caused by the formation of cross-linking structure during the recycling process, as well as the oxidation and/or the cleavage of the polymer main chains. Moreover, in the case of rubbers materials, the degree of devulcanization during the recycling process could be critical for the properties of the recycled products. However, the characterization of the cross-linking structure in the polymer materials has not been an easy task even using the most advanced spectroscopic methods mainly because of their insoluble nature.

On the other hand, pyrolysis-gas chromatography (Py-GC) has been one of a powerful technique for the characterization of insoluble cross-linking polymer materials. Recently, Py-GC in the presence of organic alkali such as tetramethylammonium hydroxide (TMAH) can be successfully applied to characterize the branching and cross-linking structures in condensation-type polymers. During the reactive pyrolysis in the presence of TMAH, the polymer chains are decomposed selectively at carbonate and/or ester linkages to yield quantitatively the methyl derivatives of the components reflecting the cross-linking structures.

In this work, the cross-linking structures formed in poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) during the material recycling process were first studied by Py-GC in the presence of TMAH. In the pyrograms of the thermally treated PET and PBT, an additional peak was commonly observed. Based on the observed spectra obtained by Py-GC-MS and GC-FTIR measurements, this peak was assigned to the product reflecting a biphenyl type cross-linking structure. Furthermore, in the pyrograms of the kneaded PET and PBT samples, which were prepared to simulate the material recycling process, the same peak for the cross-linking structure was also observed, although its intensity was lower than that in the thermally treated samples. This fact verified that the biphenyl-type cross-linking structure might be formed to some extent during the material recycling process of the wasted PET and PBT.

Moreover, recycled rubber materials were characterized by Py-GC equipped with a sulfur-specific detector. Here the recycled natural rubbers (NR) and ethylene-propylene-diene rubbers (EPDM) obtained by a new continuous rubber recycling technology using a modular screw type reactor were studied. In the sulfur-specific pyrograms for the rubber samples, characteristic sulfur containing pyrolysates to the cross-linking structure were observed, such as methylthiophenes for NR and cyclopentathiophenes for EPDM. The observed intensities of the specific products were interpreted in terms of the changes in cross-linking structure and devulcanization reaction mechanism during the new recycling process.

L13: Analysis of some new Polyurethane Products by Py-GC/MS

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Polyurethanes exist in a wide variety of physical forms including elastomers, coatings and foams, and are used in the manufacture of paints, varnishes, textiles, furniture, and many other common products. A pure polyurethane is synthesized using a diisocyanate and a polyol, and when pyrolyzed, these polymers regenerate the diisocyanate and provide much information about the nature of the macromolecule. Many products called polyurethanes are actually blends of several polymers, especially paints [1], coatings and varnishes for home use.

Polyurethane finishes are typically applied using an organic solvent. With growing concern about the release of solvent vapors, however, emphasis has been placed on the development of water-based polyurethane coatings. These products are substantially different from solvent formulated polyurethanes in several ways, including the amount of actual polyurethane in the product and the diisocyanates used. Figure 1 compares a typical solvent based finish to a new water based one. The main peak in the solvent based product is the diisocyanate, while the largest peak in the water based product is actually styrene.

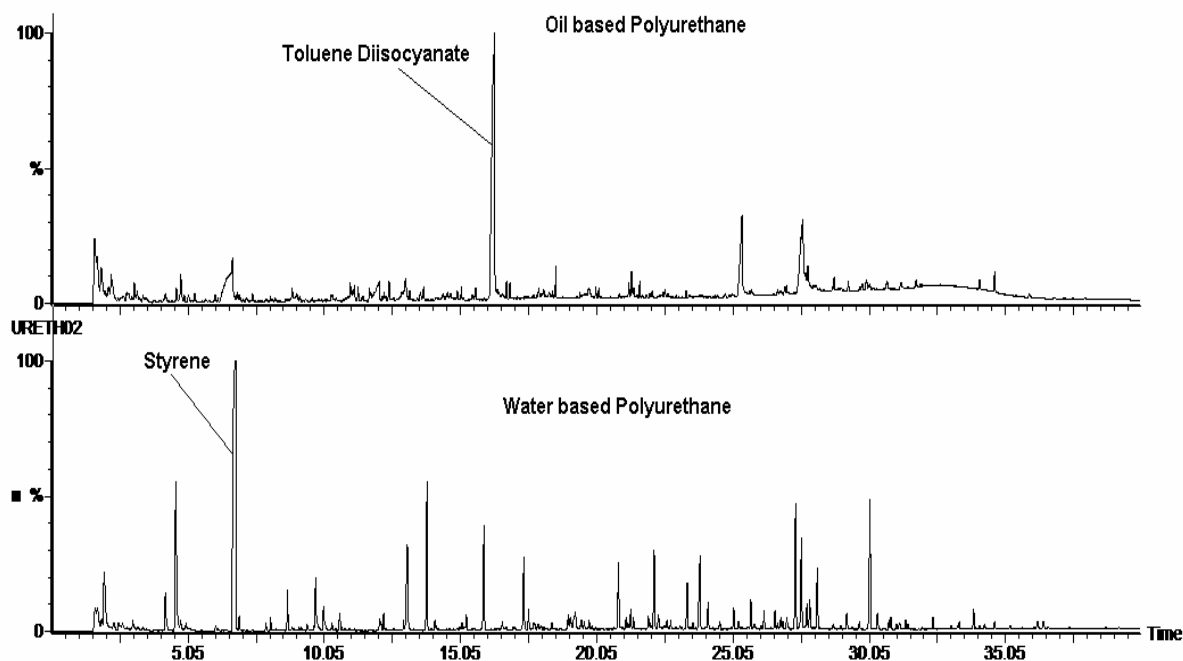


Figure 1. Traditional polyurethane finish (top) and water based (bottom).

This paper will present data on several new polyurethane finishes, contrasting the results to those obtained from earlier formulations.

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L14: Analysis of Wood Polymer Composites by Two Stage Pyrolysis

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The combination of woody materials with thermoplastic polymers to wood polymer composites (WPC) is gaining more and more attraction in USA and Europe and a wide range of commercial products are already available on the market. The combination of different wood types, chemically modified wood, and various polymers results in a wide product distribution and thus the analytical characterization with one single method is hard to accomplish. In our study we have investigated a set of commercially available WPCs and WPCs produced from different polymers (PE, PP, PVC, and melamine resin) and wood types (spruce and beech), as well as from acetylated and propionated wood particles. To separate wood from the polymer matrix and enable an easier identification of both components a two stage pyrolysis approach was carried out [2].

By screening of pyrolysis conditions an optimum combination of temperatures was found resulting in an almost perfect separation of wood and polymer matrix, regardless of the type of matrix polymer (Fig. 1). Thus, a general procedure for the easy identification of WPC constituents as well as possible chemical modifications with Pyrolysis-GC/MS was developed.

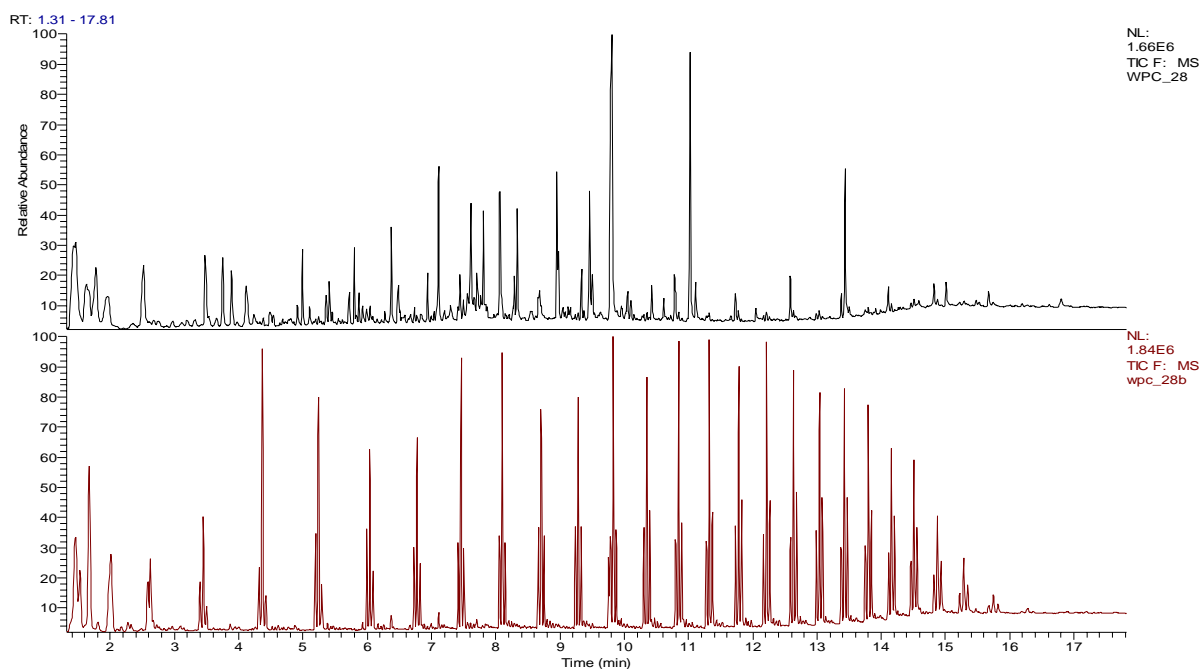


Figure 1. Pyrolysis of a WPC (spruce/polyethylene) at 550°C (upper chromatogram) showing the wood profile and at 700°C (lower chromatogram) showing the polymer profile.

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L15: Removal of organobromine compounds from the pyrolysis products of flame retarded plastics using zeolite catalysts

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In recent years there has been intensive research into using pyrolysis to process flame retarded plastics. Flame retarded plastics are used extensively in electronic and electrical equipment (EEE) and often contain brominated flame retardants, some of which are considered to be extremely toxic. Therefore, it is important that during the pyrolysis of flame retarded plastics, all of the brominated compounds are destroyed.

In this work, we have pyrolysed two flame retarded plastics in the presence of two Zeolite catalysts to remove the organobromine compounds from the derived pyrolysis oil. The flame retarded plastics were, acrylonitrile – butadiene – styrene (ABS) that was flame retarded with tetrabromobisphenol A and high-impact-polystyrene (HIPS) that was flame retarded with decabromodiphenyl ether. The two catalysts investigated were Zeolite ZSM-5 and Y-Zeolite. Pyrolysis was carried out in a fixed bed reactor at a final pyrolysis temperature of 440 °C. The pyrolysis gases were passed immediately to a fixed bed of the catalyst.

The Zeolite catalysts, especially Y-Zeolite, were found to be very effective at removing volatile organobromine compounds. However, they were less effective at removing antimony bromide from the volatile pyrolysis products, although some antimony bromide was found on the surfaces of the spent catalysts. It was found that the presence of Zeolite catalysts increased the amount of gaseous hydrocarbons produced during pyrolysis but decreased the amount of pyrolysis oil produced. In addition, significant quantities of coke were formed on the surface of the catalysts during pyrolysis. The Zeolite catalysts were found to reduce the formation of some valuable pyrolysis products such as styrene and cumene, but other products such as naphthalene were formed instead.

L16: Thermal Degradation of Cobalt- poly(styrene)-block-poly(2-vinyl pyridine)

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The synthesis of organometallic polymers by coordination of metals to plastics or other polymeric materials has gained significant interest as a consequence of their uses as conductors, liquid crystals, light emitting diodes and their interesting optical, magnetic and catalytic characteristics. On the other hand the use of organometallic polymers for the preparation of nano structural metallic composites increases the importance of these materials even more. The literature work indicates that the use of block copolymers, with interesting morphologic characteristics, in the synthesis of organometallic polymers yields several advantages in the preparation of nano structural metal composites [1]. Though several studies on preparation and application of these important materials have been carried out, the knowledge of reaction mechanism and thermal characteristics that are very important for investigation of synthesis routes and application areas is still limited. Furthermore, it is also known from the previous studies that the temperature control has significant importance in the preparation of nano structural metallic composites. The reaction temperature should be high enough to decompose precursor, yet, it should be sufficiently low to avoid degradation of the polymeric structure. The decomposition of the polymer leads aggregation of the nano particles. Thus, the knowledge of the effect of temperature on organometallic polymer precursor has significant importance. Application of TGA for the purpose of determination of thermal characteristics is very common, yet, the results obtained are insufficient for investigation of thermal degradation mechanism and products.

In this work, thermal degradation characteristics of cobalt-poly(styrene)-block-poly(2-vinyl pyridine), prepared according to the literature methods, was investigated via direct pyrolysis mass spectrometry [2,3]. In order to determine the effect of metal on thermal behavior, pyrolysis mass spectrometry analyses of the homopolymers, polystyrene and poly(2-vinyl pyridine), the copolymer, and poly(styrene)-block-poly(2-vinyl pyridine) and cobalt-poly(styrene)-block-poly(2-vinyl pyridine) were performed. The thermal characteristics of poly(styrene)-block-poly(2-vinyl pyridine) changed significantly in the presence of cobalt.

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L17: Thermal decomposition and flame retardancy behaviour of nano SiO₂-phenolic nanocomposite

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The present investigation describes the preparation of novolac type phenolic resin and its nanocomposite through in-situ polymerization. The geminal hydroxyl group present in the nano SiO₂ particles reacts with the phenolic resin to form chemical bonding. The network structure of nano SiO₂ particle was identified by using CP MAS ²⁹Si NMR. The formation of linkage between organic and inorganic phase was confirmed by CP MAS ¹³C NMR and FTIR.

The nanocomposite exhibits good transparency. Moreover, the thermal and flame resistant property exhibited significant improvement. The complete degradation of nanocomposite takes place at 50°C above the degradation of neat phenolic resin. The char content of nanocomposite at any intermediate temperature is higher than that of neat resin. The limiting oxygen index of the neat resin is 38 whereas there is an increase in the value to 43 in the case of nanocomposite. Consequently this material possesses excellent flame retardant property.

The difference in degradation products on isothermal pyrolysis followed by GC-MS studies also favours the exceptional flame retardant behaviour of nano SiO₂-phenolic nanocomposite.

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L18: Py-GC/MS Study on the Conversion of Pyrolysis Oil of Waste Plastics for Obtaining Halogen and Nitrogen Free Product

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Most of the pyrolytic waste plastic recycling research is focused on the recovery of valuable products from polyolefins. However, the proportion of automotive shredder residue and waste electronic and electric equipment (WEEE) is increasing globally at the fastest rate. Taking into consideration the complexity of these wastes that makes recycling of their plastic content complicated or impossible, pyrolysis seems to be an adequate option for handling them. Nevertheless, the critical point of the pyrolysis processes of flame retarded and nitrogen containing plastics is that environmentally intolerable compounds are formed together with useful products [1]. Pyrolysis-GC/MS combined with online catalytic conversion [2] has been applied for screening the possibilities of upgrading pyrolysis oil of automotive plastics waste and EEEW by conversion of halogen- and nitrogen-containing components over inexpensive catalysts. Since poisoning of catalyst is highly probable by waste components, no noble metal or other special catalysts were taken into consideration, but zeolites of various structure and cation content.

Waste samples and typical polymer components of them, namely styrene copolymers, polycarbonate, epoxy resin, polyamides, and polyurethanes have been pyrolysed and the conversion of their volatile products was studied over Y and β zeolites of hydrogen, ammonia and sodium form. It was found that sodium-zeolites have significant debrominating activity, however their dechlorinating power is restricted to chlorine attached to aliphatic carbons. Protonic zeolites are able to denitrogenate pyrolysis oils of aliphatic polyamides and of styrene-acrylonitrile copolymers, their activity is not much influenced by the zeolite structure and acidity in the range of the studied zeolites. Although zeolites lose their activity sooner or later due to coke deposition, their activity can be fully regenerated by thermal treatment in air.

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L19: Influence of FCC catalyst steaming on HDPE pyrolysis product distribution

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In recent years, production and consumption of plastics have increased continuously and is expected to continue increasing in the next years. The present demand exceeds 70 million tonnes per year [1]. Thermal degradation of waste plastics in an inert atmosphere has been regarded as one of the most feasible solutions at industrial scale. Moreover, catalytic pyrolysis of plastic wastes gives way to hydrocarbons that can be used as either fuels or chemicals [2,3].

A commercial FCC catalyst (supplied by *Albemarle*) based on a zeolite active phase has been used in the catalytic pyrolysis of HDPE. Different treatments have been applied to the catalyst to improve its behaviour. This paper deals with the optimization of catalyst treatment and pyrolysis conditions to optimize the production of diesel-oil fraction. Runs have been carried out using the fresh catalyst and once it has been subjected to mild steaming (760 °C for 5 h) and severe steaming (816 °C for 8 h).

The pyrolysis reactions have been carried out in a pilot plant conical spouted bed reactor provided with a pneumatic system for continuous feeding of plastic. The bed was initially made up of 30 g of catalyst. The plastic feedrate was 0.5 g/min to ensure a good heat transfer and avoid bed defluidization.

The product stream components have been grouped into three lumps: Gas (C_1 - C_4 hydrocarbons), light liquid fraction (C_5 - C_9 hydrocarbons) and medium and heavy liquid (C_{10+} hydrocarbons). The first runs have been carried out using the fresh catalyst at 500°C and this catalyst gives way to a 51.6% gas yield, 35.0% of light liquid fraction and a low yield of C_{10+} fraction (13.3%). With the aim of reducing the gas yield and increasing the liquid production, a mild steaming was applied to the commercial catalyst. Subsequently, runs have been carried out at 500 °C. The results show a significant improvement in product distribution. Thus, the gas yield decreases to 22%, the yield of light liquid is similar as with the fresh (37.7%) but the yield of the desired C_{10+} fraction increases to 37.9%.

The results obtained using the mild steamed catalyst suggested that a more severe treatment can reduce the gas yield and increase the diesel fraction production. Likewise, a slightly lower temperature has also been used in the catalytic pyrolysis (475°C instead of 500 °C) to reduce the content of aromatics in the diesel oil fraction. It must be noted that operation below 450 °C can be risky because reaction rate is drastically reduced and bed defluidization occurs.

Using the catalyst subjected to severe steaming treatment (816 °C for 8 h) and carrying out pyrolysis at 475°C there is a significant reduction of the gaseous fraction to 8.2%. The light liquid fraction has also been reduced to 22.1% but the yield of diesel fraction increases to 69.1%. Nevertheless, the diesel fraction obtained contains a high content of aromatics, which implies that it should be mixed in a refinery with other streams to obtain commercial fuels.

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L20: Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes

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As most plastics are not biodegradable, their deposition in landfills is not advisable. There is a lot of controversy about the incineration of these wastes, as well as its impact in the environment, due to the release of toxic and greenhouse gases. Another disadvantage of the traditional incineration of these wastes is that it completely destroys all its organic matter, which could be otherwise valuable for different applications. Additionally, the biomass residues that can be found in forests and that accumulate on the ground posing a risk of fuel for forest fires can be processed in order to retrieve its organic matter in a useful form. Another problematic waste stream is the used tyres. One of the most promising ways of taking profit of all these wastes energetic content is by pyrolysis.

The effect of the experimental conditions of pyrolysis of mixtures of plastics (PE, PP and PS), biomass (pine) and tyres residues was studied in this work. Experimental trials were made in a 1L stainless steel autoclave, in which the experimental conditions like: initial pressure, waste mixture composition, temperature and time of reaction were varied and optimized. The three product fractions obtained (liquids, solids and gases) were collected and analyzed with the appropriate means: Liquids were distilled into three fractions and analyzed by Gas Chromatography (GC) and GC/MS (Mass Spectrometry), gases were also analyzed by GC and its density was also measured. The remaining liquid in the solid phase was extracted with solvents and analyzed by GC. Ecotoxicological tests were done in pyrolysis solids to determine the necessity of any special pre-treatment.

The average HHV of the obtained gases was 35 MJ/m³. Two immiscible liquid phases were formed in the tests where pine was present, one being mainly water with traces of compounds commonly produced by fast biomass pyrolysis, and the other being a less dense organic phase. The average HHV of these organic phases was about 40 MJ/kg. The char resulting from the pyrolysis tests showed an average HHV of 34 MJ/kg (daf) and the residue from liquid distillation (solid at room temperature) an average 45 MJ/kg (daf).

The effects of experimental conditions in products yield and composition were also studied. The rise of reaction temperature decreased liquid yields, by increasing solids and gases yields and also led to higher alkanes content on the produced gases. The increase of initial pressure led to small variations in products yields and composition. On the other hand, the parameter that showed a more significant effect on pyrolysis products and composition was the pine and tyre contents on wastes mixture. The rise these amounts led to higher solid and gas yields, being the last one richer in CO and CO₂ when higher amounts of pine were used.

L21: Effects of ITQ 21 and ITQ 24 as zeolite additives on the oil products obtained from the catalytic pyrolysis of waste tire

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Pyrolysis has recently been considered as a promising process to recycle waste tire whose amount generated globally is approximately 6×10^6 tons per year. The products obtained from the pyrolysis of waste tire, solid, liquid and gas, have potentials to be reused. H-Mordenite (HMOR) was reported to have a high activity for production of paraffins in the pyrolysis of polypropylene [1]. In addition, for some applications it is desirable to have a zeolite with a three-dimensional system of large pores, since it greatly facilitates the diffusion of relatively large molecules in and out of the zeolite void space, minimizing pore blockage.

The two ITQ21 and ITQ24, which have 3D dimensions of large pores, were successfully synthesized in order to be used as additives in HMOR for the catalytic pyrolysis of waste tire. In an autoclave reactor, a tire sample was first pyrolyzed in the lower zone, and then the evolved products were further treated catalytically in the upper zone. The liquid products were separated by liquid adsorption chromatography [2], and analyzed by a SIMDIST GC (ASTM D2887).

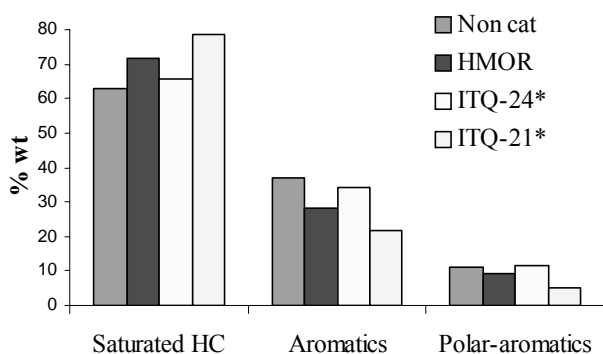


Figure 1. Composition of liquid products.

Comparing with the non catalytic pyrolysis, the experiment results indicated the obvious reduction of aromatics in the liquid products when the ITQ21 additive was used whereas only slight decrement was observed in the case of ITQ24 (Figure 1). In addition, the ITQ21 additive also helped reduce polar aromatics dramatically. This was explained by the particular topology of ITQ21, favoring the diffusion of the large molecules out of the pores [3]. However, as compared with pure HMOR catalyst, the use of both types of ITQ led to a decrease in

gasoline and kerosene productions, but the amounts of these fractions were higher than those produced in the non catalytic pyrolysis (Table 1). The different effects of the additives were mainly attributed to the different properties and topology of the catalysts which were characterized by XRD, TPD-NH₃, and BET using nitrogen adsorption.

Table 1. Main fractions in the liquid products (%wt)

Fraction	Non cat	HMOR	ITQ-24*	ITQ-21*
Gasoline	12.969	30.353	26.377	20.086
Kerosene	31.494	36.485	33.293	38.813
Gas Oil	34.124	27.842	31.160	31.927

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L22: Thermal Degradation Studies on PMMA-HET Acid Based Oligoesters Blends by TG-FTIR and Off-line Pyrolysis GC-MS Methods

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Polymethyl methacrylate (PMMA) is widely used in the general consumer products, especially in electrical fittings, insulations and in all outdoor applications where light transmission is important. Besides, it has better physical and chemical properties like higher softening point, better impact strength, better weatherability and an excellent corrosion resistance than polystyrene [1]. But PMMA burns readily in air when subjected to heat. Reducing the flammability of PMMA without affecting its optical clarity is a real challenge. 1,4,5,6,7,7-hexachlorobicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid (HET acid) is one of the well known halogenated reactive flame retardants for polymers [2]. In the present investigation, four different HET acid based oligoesters are synthesized by condensing HET acid with four different diols, ethylene glycol (EG), 1,2-propane diol (1,2-PD), 1,3-propane diol and 1,4-butane diol separately using melt condensation technique in vacuum [3]. Methyl methacrylate (MMA) and blends of MMA with 5% and 20 % of the four different HET acid based oligoesters are separately bulk polymerized using azobisisobutyronitrile as the initiator. Glass clear rods of blends are obtained. The thermal degradations aspects of the blends are investigated using differential scanning calorimetry, thermogravimetry, TG-FTIR and off-line pyrolysis GC-MS. DSC and TG studies show the degradation temperatures of the oligoesters and PMMA lie nearly in the same temperature region (220 – 420 °C). FTIR-TG studies provided the complete evolution profile of the different degradation products (CO, HCl, CO₂, H₂O, hexachlorocyclopentadiene (HEX), HET acid/anhydride and MMA). The maximum evolution of MMA from PMMA and HET acid/anhydride from the oligoesters lie in the region 350 – 400 °C. The retro Diels-Alder product HEX from HET acid/anhydride is formed in detectable quantities indicating chain transfer and flame cooling action in this temperature region. The off-line isothermal degradation of PMMA and its blends with 20 % of oligoesters in nitrogen atmosphere at 400 °C for 10 min followed by the GC-MS studies of the volatile products show HET EG and HET 1,2-PD can effectively interfere the unzipping reaction of PMMA.

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L23: The thermal degradation mechanism of poly(methyl methacrylate)-TiO₂ nanocomposites

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In the last years, the potential of using metal oxides as fillers in polymer has become appreciated in several applications. The obtained composite might exhibit improved thermal, electrical, mechanical, optical and fire resistance properties. However, to gain a better knowledge of the influence of these fillers on the thermal degradation of the polymer still needs further studies. Among the papers published about this subject, it appears that the majority of the works performed concern particularly the poly(methyl methacrylate) (PMMA) filled with silica particles. Our team performed some previous studies about the influence of Fe₂O₃ and TiO₂ nanoparticles on the thermal degradation of PMMA. It was proposed that the improvement of the thermal stability was the result of two main factors: (i) restriction of mobility of the polymer chains caused by the steric hindrance due to the presence of particles and (ii) bonds due to the adsorption of polymer on the oxide surface via methoxycarbonyl groups (—C(O)OCH₃) [1, 2]. Accordingly, it was also proposed that the adsorption phenomena could modify a key step of the reaction mechanism involved. The aim of the present work was to study the effect of the amount of TiO₂ nanoparticles on the degradation mechanism of PMMA in order to confirm the preceeding interpretations. Brief description of the methods applied, and of the materials studied.

The influence of TiO₂ nanoparticles on the mechanism of thermal degradation of PMMA was investigated. Following techniques TEM, SEM, TGA, DSC and Py-GC/MS were used for the characterization of studied materials. PMMA-TiO₂ nanocomposites were prepared by melt blending with different (5, 10, 15 and 20 wt% TiO₂) load rates. According to TGA results and the activation energy (determined by the model-free isoconversional method of Vyazovkin), the incorporation of 5 wt% of TiO₂ nanoparticles in the PMMA stabilizes this polymer (more than 40°C). However, for very high load rates a catalytic effect has been observed which increases with increasing load rate. The results obtained by Py-GC/MS showed clearly that TiO₂ increases the formation of methanol, methacrylic acid and propanoic acid methyl ester during the degradation of PMMA. This catalytic effect could be explained through the interaction of the methoxy group of the methacrylate function with the hydroxyl groups present at the surface of the oxide particles.

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L24: Kinetic studies of the Decomposition of Flame Retardant Containing High Impact Polystyrene

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High impact polystyrene (HIPS) is used for casings of computers, telephones or refrigerators. Fire retardants are added in general to reduce the flammability of these technical devices. However, brominated fire retardants, which are still frequently used, can produce toxic and carcinogenic products during combustion or recycling. Therefore, it is essential to obtain knowledge of the degradation behavior of these materials.

Five samples of HIPS, containing Decabromodibenzyl (DDB) and Decabromodiphenyloxide (DDO), respectively, as fire retardants and Sb_2O_3 as synergist, were degraded at different heating rates (2.5, 5, 7.5, 10K min^{-1}) by thermogravimetry. The product gases were analysed online by mass spectrometry. The activation energies E_A were determined after the method of Miura [1] and the distribution function of the activation energies were obtained.

The plot of the logarithm of the frequency factor $\lg(k)$ versus E_A results in general in a straight line as long the mechanism of the reaction is unchanged. However, during the degradation of these samples, in general several lines were observed indicating the change in the mechanism. These changes are accompanied by a decreasing E_A and k resulting in the step like structure of the TGA-plot.

The steps can be linked to the evolution of different products detected by TG-MS. HIPS degrades in one step with a distribution maximum E_{AD} at 210 kJ mol^{-1} in the absence of fire retardant and Sb_2O_3 . The $\lg(k)$ - E_A plot indicates in the presence of fire retardant the presence of two steps. E_{AD} is located at the beginning of the second step at 178 and 192 kJ mol^{-1} for DDO and DDB, respectively. In the presence of Sb_2O_3 , the E_{AD} of DDO containing HIPS is further reduced (141 kJ mol^{-1}) even if it remains at a weight loss X of ca. 45 wt%. On the contrary, DDB containing HIPS shows two maxima (149 kJ mol^{-1} , 159 kJ mol^{-1}) during the first step.

The activation energies obtained from the TGA can be used to simulate the TGA-plots. Best results were achieved using the a power law:

$$\frac{dX}{dt} = k \exp\left(-\frac{E_A}{RT}\right) * 4X^{3/4}$$

Several brominated products were identified by GC-MS and TG-MS. The samples without Sb_2O_3 produced mainly 1- and 2-Bromo-1-phenylethane as the addition product of HBr and styrene. In the presence of Sb_2O_3 less of these products were observed and more polybrominated benzenes, toluenes, phenols, benzofuranes and dibenzyls.

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L25: Validation of the TD-GC/MS method for the determination of decabromo diphenylether (DeBDE) in polymeric materials

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Obtaining accurate data on the levels of polybrominated diphenylethers (PBDE) in consumer products is a challenging task. The difficulty can be attributed to two factors. First of all, PBDEs are normally solvent extracted from the matrix, a process which is time consuming, expensive and often leads to poor recoveries. The second source of error is due to the high boiling point of DeBDE (RI > 4200). These two factors often result in unduly low analytical precision and force the analyst to use a number of surrogates, internal standards and calibration check samples, in order to achieve the desired data quality.

In 2006, the National Institute of Advanced Industrial Science and Technology (AIST) in Japan sponsored a “round robin” survey of laboratories routinely analyzing polymeric samples for Decabromodiphenyl ether (DeBDE). The DeBDE concentration in the polystyrene test sample was 317ppm. Samples were provided to a number of analytical laboratories performing the determination of PBDEs using the prescribed RoHS method which is based on Soxhlet extraction and GC/MS analysis. The results of the study clearly demonstrated the shortcomings of the RoHS method. As practiced, the results obtained using the RoHS method were inaccurate and the precision was greater than 50%.

The audit sample was also analyzed using a method based upon thermal desorption (TD) of the DeBDE from the matrix followed by GC/MS analysis[1, 2]. The TD-GC/MS method requires no sample preparation. The sample is analyzed as received. This eliminates the tedious extraction step and avoids errors normally associated with solvent extraction. A special column is used for the analysis which is designed to elute DeBDE under 300°C eliminates thermal degradation during the separation step.

This work will present a summary of the TD-GC/MS method, the calibration curve, and the AIST standard results [3]. Factors influencing the accuracy and precision of the DeBDE analysis will be discussed.

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SESSION 5 BIOMASS II:
Characterization, Fuel & Chemicals Production

KL6: Quality of Biomass Fast Pyrolysis Oils

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Fast pyrolysis liquid is one feasible candidate for renewable energy. There are advantages when comparing use of pyrolysis liquid to use of solid fuel. One clear benefit is logistic. Small-scale fast pyrolysis plants may be located adjacent, like in forest areas or integrated with a pulp mill. Energy density of pyrolysis liquid is higher than that of solid biomass and when properly designed the transportation and storage of pyrolysis liquid is easier than that of solid fuel. In combustion, the emissions from pyrolysis liquid are much lower than those from use of solid biomass, especially the particulates. Pyrolysis liquid may be used with small modifications to replace heavy fuel oil.

Typical product yields from white wood (wood without bark) are 64 wt % organic liquids, 12 wt % product water (chemically dissolved in organic liquids), 12 wt % char, and 12 wt % non-condensable gases. Variations in organic liquid yields are mainly due to differences in both physical and chemical composition of feedstock, when operated within normal fast pyrolysis regime (fast heat-up of feed, short residence time of solids, rapid cooling of product vapours). Reactor configuration plays a minor role for product liquid quality.

In order to promote the acceptance of a new fuel into markets to replace light or heavy fuel oil, fuel characterisation methodology should be as similar as possible. Standard fuel oil analyses of ASTM, DIN, and EN originally developed for mineral oils have been modified for pyrolysis liquids and some new methods have been developed. In 2007 Dynamotive (Canada) has made a Biooil Standard Initiative for ASTM/TC/D02 'Petroleum products' for standardisation of pyrolysis oil as fuel.

The instability of pyrolysis liquids is one determining factor when considering the handling, transport, storage, and use of pyrolysis liquids. In order to understand and control this property the changes in chemical composition of pyrolysis liquids are critical. Because only a small part of pyrolysis liquids can be characterized using conventional methods like GC/MSD, a chemical characterization scheme based on solvent extractions was developed. Through this scheme, the changes in various chemical fractions of the liquid were followed. This scheme was also adapted for results obtained by Pyroprobe-GC/MSD and/or AED.

L26: Catalytic Pyrolysis and Liquefaction of two Different Lignin Extracts

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Fluidized bed pyrolysis systems using sand as the bed material have become the method of choice for the liquefaction of biomass. These systems tend to be large enough to collect gaseous, liquid, and solid (char) fractions in quantities which allow accurate measure of the yield and composition of each. A drawback to the large size is the limits on using these systems as screening systems to test bed materials other than sand for their impact on product yield.

We have built a small scale system that mimics the fluidized bed and allows us to measure all three components as bed materials are tested. The system consists of a 3-ml cell which is charged with catalyst and lignin and swept with helium. The cell is rapidly heated to 600°C and the fluidized components are swept out with the condensable fraction collected in a cold trap and the non-condensable fraction collected in loops for later analysis. At the end of the reaction, the solid remaining in the cell is combusted with the weight loss representing char. Pyrolysis and liquefaction of two different lignins have been examined over H-ZSM-5, K-ZSM-5, and solid phosphoric acid in the reactor system. H-ZSM-5 has been the most effective in deoxygenating the aromatic components in the liquid fraction and also increases the yield of hydrogen and methane in the gas fraction.

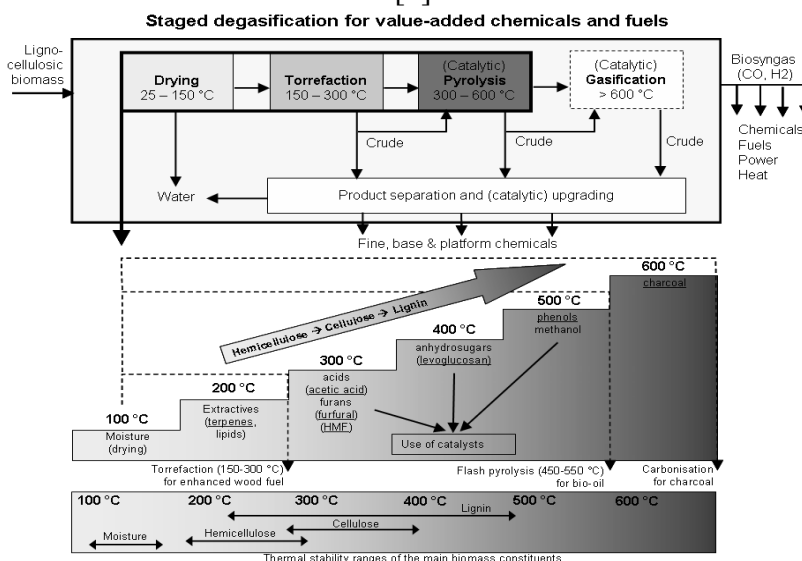
L27: Biomass Valorisation by Staged Degasification

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Pyrolysis of ligno-cellulosic biomass leads to an array of useful solid, liquid and gaseous products [1]. Staged degasification is a pyrolysis-based conversion route to generate value-added chemicals from biomass. Because of different thermal stabilities of the main biomass constituents hemicellulose, cellulose and lignin, different temperatures may be applied for a step-wise degradation into valuable chemicals [2].



Staged degasification experiments were conducted with deciduous (beech, poplar), coniferous (spruce, pine) and herbaceous (straw) biomass. Thermogravimetry was used to estimate appropriate temperatures for a two-stage degradation process that was subsequently evaluated on bench-scale by moving bed and bubbling fluidised bed pyrolysis experiments. A mechanistic study was conducted, using solid-state ^{13}C -NMR techniques.

Degasification in two consecutive stages at 250°C-300°C and 350°C-400°C leads to mixtures of degradation products that originate from the whole biomass. The mixtures that were generated at 250°C-300°C, predominantly contain hemicellulose degradation products, while the composition of the mixtures that were obtained at 350°C-400°C, is more representative for cellulose. Lignin derived fragments are found in both mixtures. Yields up to 5 wt% of the dry feedstock are obtained for chemicals like acetic acid, furfural, acetol and levoglucosan. Certain groups of thermal degradation products like C_2 - C_4 oxygenates and phenols are formed in yields up to 3 wt%. Highest yields have been obtained for beech wood.

Staged degasification is a promising and elegant pyrolysis-based route to valorise lignocellulosic biomass. Clear opportunities exist to increase product yields and selectivities by optimisation of reactor conditions, application of catalysts and specific biomass pretreatments like demineralisation and pre-hydrolysis.

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L28: Biomass pyrolysis: kinetic modeling study and experimental validation under high temperature and flash heating rate conditions

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In the present energy context, there is a growing interest for the development of processes that produce synthesis gas (H_2 , CO) from biomass gasification with enough purity for liquid fuel synthesis. However, biomass gasification is still poorly understood and therefore modeled under typical conditions of gasifiers ($T=800-1000^\circ C$; flash heating rate).

This study is an attempt to model the first step of this transformation, namely biomass pyrolysis, through a molecular description of the biomass, and then to test the model on flash pyrolysis experiments at high temperature ($T=800-1000^\circ C$).

The specificity of the modelling approach is to describe the biomass pyrolysis as a decomposition of its constitutive polymers. Existing models have already tried to follow this approach, but their effort was mainly focused on coal (FG-DVC, CPD and Flashchain). Their extension to biomass remains uncertain (Bio-CPD, Bio-Flashchain) [1,2] or is limited to primary pyrolysis (FG Biomass) [3]. Moreover, the model proposed here couples an accurate description of the solid devolatilization chemistry with a kinetic description of the secondary gas phase reactions and also with the description of the heat and mass transfer phenomena. Therefore the model is able to predict not only the intermediate products but also the light gases obtained at the outlet of a gasifier, notably H_2 , not on an empirical basis but in a phenomenological way.

The validation experiments have been performed on wood in an entrained flow reactor of laboratory (wood mass flow rate: $1\text{ g}\cdot\text{min}^{-1}$). The influence of the particle size (0.4;1.1 mm) and of the temperature ($T=800-1000^\circ C$) has been tested versus the solid residence time in the reactor (0.3-1 s). Under these conditions, the particle size is the most crucial parameter that influences decomposition. For 1.1 mm particles, pyrolysis requires more than 0.5 s and heat transfer processes are limiting. For 0.4 mm particles, pyrolysis seems to be nearly finished before 0.5 s, with more than 70 wt % of gas release.

The agreement between modelling and experiments appears to be encouraging, notably regarding the trends with temperature and the results on minor species (C_2H_4 and C_2H_2). It has to be noticed that the model was used without any particular fitting. This proves the robustness of the model and its potential use under realistic gasifier conditions.

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L29: Flash (co-)pyrolysis of biomass: The influence of biopolymers

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The flash pyrolysis of biomass (waste) is a promising method to obtain both energy and value-added materials (e.g. chemicals), without competing with basic food supply. The obtained bio-oil shows the most potential to be applied as a source of energy and materials. Flash pyrolysis breaks biomass into smaller molecules with pyrolytic water as an unavoidable reaction product. In view of the applicability of bio-oil in general, water is defined as detrimental. The flash co-pyrolysis of willow and the biopolymers: polylactic acid (PLA) and polyhydroxybutyrate (PHB), respectively induce interactions resulting into a synergetic reduction in the amount of pyrolytic water. Additionally, a synergetic increase in pyrolysis yield and in energy recuperation is obtained [1,2]. Even though biopolymers are biodegradable and/or renewable, they are still considered as waste.

The influence of a variety of biopolymers (PLA, Corn Starch, PHB, Biopearls, Eastar, Solanyl and Potato Starch) on the pyrolysis of willow (target biomass) during flash co-pyrolysis at 450°C with a semi-continuous home-built pyrolysis reactor is investigated. The flash pyrolysis of pure willow serves as a reference. Besides bio-oil, the flash co-pyrolysis of willow and PHB additionally results in the production of crystals of crotonic acid, which offers added value as a source of chemicals. Based upon some predefined objectives (e.g. water content, water-free bio-oil yield, ...), the different flash co-pyrolysis experiments are compared: no single biopolymer option performs the best on all objectives.

A multi-criteria decision aid (MCDA) software tool 'Decision Lab' is applied to construct an evaluation table summarising the biopolymer options in terms of the predefined objectives. Decision Lab evaluates the different biopolymer options with the PROMETHEE and GAIA methods, which are two MCDA outranking methods based on the principle of pairwise comparison [3]. In order to properly analyse the evaluation table and to generate most relevant results, suitable preference functions and specific thresholds are defined. A GAIA plane provides a global view of the decision problem. The PROMETHEE partial and complete rankings sort the best actions from the worst, taking into account the priorities. Additionally, sensitivity and robustness analysis are performed.

The flash co-pyrolysis of biomass and biopolymers results in improved pyrolysis characteristics. Based on the predefined objectives, the flash pyrolysis of pure willow seems to be the least interesting option. The most performant biopolymer options are the ones with PHB, PLA, Biopearls and Potato Starch.

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L30: Comparison of Gasification and pyrolysis of thermal pre-treated wood board waste

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Taking onto account problems of greenhouse effect together with the decrease of fossil resources, what kind of solution can be provided by human society to satisfy its own increasing need for energy? Biomass gasification is one of the few options which can provide a substantial part of this share in the near future. Nevertheless, the industrial development of such a biomass gasification process is slowed down by the expensive cost of wood and biomass. The idea would then be to substitute this natural feedstock by waste, such as wood board. Indeed their low or even negative cost would improve the economic efficiency of the gasification process and favour its development. Nevertheless, this type of waste contains huge amount of nitrogen coming from urea – formaldehyde and melamine – formaldehyde resins associated with wood and which are responsible of the production of nitrogen species (ammonia, isocyanic acid, hydrogen cyanide, NO_x) during classical thermo – chemical conversion (combustion, pyrolysis, gasification). Previous studies [1, 2] shows that it is possible to remove thermally around 70 % of initial nitrogen through a low temperature pyrolysis between 250°C and 400°C. A two step process of thermo – chemical conversion can thus be imagined. A first low temperature pyrolysis step which aims to remove nitrogen and a second step which aims to produce combustible gases for different applications (combustion, cogeneration, bio – oil).

The aim of this work is to study and to compare two classical ways of thermo – chemical conversion (pyrolysis and gasification under water) of the pre – treated materials produced during the first step of the process.

Experiments were achieved in a quartz tubular furnace and produced gases were analysed by FTIR spectrometry and gas chromatography.

This study shows that for pyrolysis and gasification, the thermal pre – treatment of wood board waste prevent the production of hydrogen cyanide and that the best results are achieved with the 250°C pre – treated wood board waste from an energy recovery point of view.

Gasification is the process which gives the best results in terms of energy recovery but which release all remaining nitrogen under polluting gases form.

The best way to prevent the production of nitrogenous species is the pyrolysis process. It assumes an energy recovery 2 times lower than in the gasification process but produce two times lower quantity of pollutants. Moreover, the char then produced which contains remaining nitrogen can be converted in active char enriched with nitrogen functions and which could show good capabilities for water treatment (organic compounds removal) or gas cleaning (sulphur removal).

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L31: Co-Pyrolysis of biomass and HDPE (High-Density Polyethylene) waste

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The disposal of waste plastics is an important environmental problem in developed countries. For instance, polymeric waste materials i.e. plastics, tires are the main difficult disposal wastes since they are not biodegradable. The utilization of these waste materials is indeed of importance from economic and environmental aspect. Especially, packing materials make up the 50-70 % of the total plastic disposal. Of this amount, 89 % are polyolefins (polyethylene, polypropylene, polystyrene, polyvinyl chloride). The reuse of these materials becomes a problem of sorting or isolation of a pure form. Nevertheless, decomposition of polyethylene and polypropylene do not give high yields of ethylene and propylene with the ordinary recovery techniques [1,2]. The chemical recycling of these waste materials is one of the best methods for energy recovery and environmental protection. Pyrolytic processes are suitable to convert polyolefins and cellulose (or lignin) derived materials into valuable feedstock and the specific benefits of this method potentially include: the reduction of the volume of waste; the recovery of chemicals and the replacement of fossil fuels [3].

In this study, co-pyrolysis of biomass sample (almond shells) with hdpe waste is investigated. The biomass: polymer mixtures were prepared various ratios such as 1:0, 1:1, 1:2, 2:1 and 0:1. The co-pyrolysis reactions were carried out at 500 °C under various sweeping flow rates of 400 cm³min⁻¹. Addition of waste hdpe increased liquid and gas products whereas it caused the reduction of solid yields. Co-pyrolysis of polymer and biomass enhanced liquid yields when comparing the biomass pyrolysis yields. The maximum oil yield was obtained while the ratio of waste hdpe/biomass mixtures was 2:1. Obtained bio-oils were analyzed in detail with various spectroscopic and chromatographic methods. It is concluded that addition of waste hdpe improves the quality in terms of hydrocarbon distribution and quantity of obtained bio-oil.

Keywords: Bio-fuel, co-pyrolysis, waste hdpe.

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L32: Sequential Pyrolysis and Catalytic Low Temperature Reforming of Wheat Straw

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Recently the interest of energy recovery from renewable and sustainable sources is exceeding due to the global warming and CO₂ emission discussions. Energy recovery from biomass has two striking characteristics. First, biomass fixes carbon dioxide from atmosphere by photosynthesis, secondly, especially lignocellulosic by-products from crops – straw - from agriculture or biogenous residues from food processing industry are abundant and should be made accessible for energy recovery. Therefore, various processes are in development in which the pyrolysis of biomass is applied for power generation in combined heat and power applications (CHP) [1] or combined with gasification to produce hydrogen [2] or sequential catalysis to produce methanol or synthetic fuel [3]. The quality and characteristics of pyrolysis products from biomass change dramatically with the feed stock and residence times.

The pyrolysis of wheat straw with intermediate pyrolysis at 450 °C, that means with solid phase residence times from 1 to 10 minutes, leads to 28 % char, 24 % gas and about 48 % condensate, which separates in a water phase and a organic phase. The organic phase is liquid but not homogeneous and contains viscous compounds which could accumulate and polymerize with age due to the phenolic structure. This is also typical for other lignocellulosic biomasses and could lead to solid tars depending on the pyrolysis conditions. With a sequential reforming unit after the pyrolysis these compounds could be converted in lower alkanes as methane, hydrogen and carbonoxides and could increase the heating value of the formed pyrolysis gases and, therefore, find an application in gas engines. Since, the pyrolysis of biomass is in any case connected to the formation of water, not only from the moisture content of the feedstock, but also due to the formation of water during thermal degradation of biomass, the reaction partner water is abundant. The aim of this investigation is to apply a low temperature reforming unit after the intermediate pyrolysis of wheat straw, in the temperature range between 420 °C and 490 °C. From the energetic point of view a reforming unit at temperatures below 500 °C as sequential step to the pyrolysis of biomass is striking in comparison to a gasification which needs temperatures about 800°C-1000°C. The used catalyst is a commercial pre-reforming catalyst from Südchemie, which is optimized temperatures about 400°C-500 °C. Changed reaction parameters are temperature, inert gas flow and, therefore, residence times and amount of catalyst. Hydrogen contents up to 12 % and the increase of heating value of the non condensable pyrolysis gas about 1.5 in comparison to pyrolysis without reforming are achieved.

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SESSION 6 PYROLYSIS TREATMENTS:
Pulp & Paper, Fossil Fuels & other Industrial Applications

KL7: Pyrolysis Technology for Wastes Treatment and Energy Production. An overview

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Thermochemical processes such as Pyrolysis and Gasification have been considered since the 80's as a promising technical option for wastes and residues treatment. So, by implementing these processes is possible to reduce the volume of the final residues to dispose, and at the same time to produce energy.

From the industrial point of view, the pyrolysis process presents advantages over the other thermochemical processes. Advantages such as, a lower operating temperature and a severe reduction atmosphere. The first one allows reducing the well known ash melting problems and the second one to reduce the dioxin and furans formation. Obviously, it is necessary to talk about the disadvantages, among them the most critical one is the endothermic character of this process.

However, and spite of this requirement of energy, quite critical at the present, pyrolysis still being a good industrial option for the treatment of many residues. Some industrial installations, to optimize the whole process, also consider a joint scheme pyrolysis – gasification in order to exploit its advantages.

In this context, an overview about the industrial implementation of the pyrolysis technology will be done during the presentation.

L33: Determination of Nonylphenol and Nonylphenol Ethoxylates in Pulp Samples by Py-GC/MS

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Nonylphenol polyethoxylates (NPEs) are detergents that are effective as dispersing or stabilizing agents. Consequently, up until lately, these products were widely used in the manufacture of pulp and paper products. NPEs break down into nonylphenol (NP), which is more toxic than the NPEs. NP and other breakdown products of NPEs have been found in water, sediment, wastewater, sludge from municipal and industrial wastewater treatment plants, and soil on which the sludge has been spread. Acute adverse effects from exposure to NPEs have been reported in invertebrates, fish, mammals and algae. Concentrations of nonylphenol as low as 0.017mg/L (17µg/L) have been shown to be lethal to winter flounder in 96 hour exposures. These substances are not found to be bioaccumulative, or to transfer up the food chain. NPEs have also been identified as a possible endocrine disrupting substance, capable of interfering with the development and reproduction of fish and wildlife.

As a result of these concerns, Europe effectively banned NPEs in the 1990s for all down-the-drain applications [1]. No legal prohibitions exist for these compounds in North America. However, the pulp and paper industry voluntarily reduced/eliminated the use of NPEs [2,3] in advance of either regulatory requirements or a comprehensive environmental assessment of their effects. Unfortunately, some companies were slow to phase out the use of NPEs mainly because of performance and cost factors of NPE free products. For example, NPEs are very effective deresination agents in the manufacture of pulp from resinous wood species such as aspen, and it has been difficult to find NPE free products that are as effective as NPEs. Consequently, some mills continued using NPEs to meet the needs of markets that required pulps with very low amounts of extractives, e.g., pharmaceutical grade products.

Since Europe has banned the use of NPEs in pulp and paper production, companies selling to the European market are required to demonstrate that their products do not contain NPEs. One of the main reasons for this is that workers are reluctant to handle pulps that contain NPEs as they believe that handling such pulps will result in them breathing pulp particles loaded with NPEs that will be harmful to their health. This then raised the question of how to ascertain that pulp and paper products do not contain NPEs.

We have developed a method for ascertaining the presence of NP and NPEs in pulp samples at very low levels. The method entails pre-concentration of the compounds and their detection by Py-GC/MS. Solvent extraction of the compounds from pulps with acetone gives better recoveries than desorption of the compounds from the pulps by gas stripping. The detection limit for NPEs with our technique is as low as 0.003 ppm in pulp sheets.

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L34: Analytical pyrolysis study of biodelignification of Cloned *Eucalyptus globulus* and *Pinus pinaster* Aiton kraft pulp and residual lignins

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Cloned eucalypt is now being investigated in Portugal. The advantages of clonal forestry are vividly illustrated by its large-scale adoption during recent years in Brazil, South Africa and some other tropical and subtropical countries. The goal of this research is ongoing quest to increase our knowledge on Portuguese hardwood and softwood. In the face of mounting the complexity of macromolecules studies, it is essential that we promote the joy of learning. Cloned *Eucalyptus globulus* and *Pinus pinaster* have been used for producing conventional kraft pulp, with a kappa number of 34.5 and 15.5, respectively. Biodelignification using fungal laccase-violuric cid (LMS) has been carried out on the two types of kraft pulps. The original milled woods, milled wood lignins, kraft pulps and treated kraft pulps samples have been characterized by Py-GC/MS. They were pyrolyzed at 600°C for 20 s in helium atmosphere using a Pyroprobe 2000 pyrolyzer interfaced to an Agilent 6890A/5973 gas chromatograph/mass spectrometer. The pyrolysis products were separated on an HP-5MS (Agilent Techn.) capillary.

Based on the results of analytical pyrolysis, the pyrograms indicates that the lignin composition of the two wood species and corresponding pulps are very different. The chemical structure of cloned eucalypt is more complex than that of pine. The high phenolic content in kraft lignin is due to the degradation of aryl–ether linkages under the kraft cooking conditions. Phenol derivatives are more dominant in softwood than hardwood. Pentose marker decreased in the pulps in comparison with the wood, for eucalypt. In the case of pine, this xylan marker appears unchanged. The selected ion chromatograms for *Pinus pinaster* are more difficult to interpret because hydroxybenzene may be formed from carbohydrates and extractives (polyphenols) in addition to lignin. However, the amount of 4-methylguaiacol and 4-vinylguaiacol strongly decrease with biodelignification.

Pinus pinaster milled wood lignin contains elevated levels of vanillin and a 2-methoxybenzaldehyde derivative. These two structures contribute to the aldehyde content of the lignin and to the reduction in the number of β linkages. The pyrograms of the residual lignin from the pulps treated by LMS illustrate differences from brownstocks. LMS also degrade β -dimers and β -O-4 dimers via $C\alpha$ oxidation, alkyl-aryl cleavage and $C\alpha$ - $C\beta$ cleavage. Laccase also catalyze the cleavage of aromatic rings. Laccase-violuric acid biodelignification is capable of reacting with the last vestiges of residual lignin, which are typically very unreactive.

L35: Efficient analysis of Py-GC/MS data by an automatic database approach in large extend – Example: white pitch detection in pulp and paper industry

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Hyphenated techniques like Py-GC/MS (pyrolysis - gas chromatography/mass spectrometry) are used to analyze small sample amounts (~100µg) in a fast and reliable way. One advantage of this technique is the high information content of the chromatograms, but it is often difficult and very time consuming to extract meaningful information. Especially with automatic sampling, data evaluation becomes a major bottleneck. An effective approach to automate the characterization of chromatograms is presented.

The developed database approach has been tested on compounds belonging to "white pitch". These are chemicals which derive from paper coating processes. A set of designed mixtures has been produced consisting of carboxymethylcellulose (CMC), poly(vinyl alcohol) (PVAL), two kinds of styrene-butadiene (SB), acrylate and non measurable pigments. The database approach consists of basically three steps:

1. Measuring and establishing a database with reference substances
2. Measuring problematic or unknown samples
3. Using the database for the identification of problematic or unknown samples

The database establishment is done by extracting the relevant information from each reference substance. The chromatograms are processed automatically to dump background and to deconvolute overlapping peaks [1]. In a further step all relevant pyrolysis products of a reference substance are extracted. Kováts type retention time (RT) indices are calculated. The relevant pyrolysis products from each reference substance are stored in a database. After compilation the database contains a collection of information, for example the appearance of pyrolysis products in one or more reference substances.

To evaluate the approach, a set of different mixtures has been tested. All pyrolysis products from a distinct mixture are matched with the database entries. This results in information about the sources of the detected pyrolysis products. The presence or absence of pyrolysis products compared to the database helps to determine composition details of the examined mixture. It was possible to determine the composition details of each mixture. All substance classes could be discriminated. Even the presence or absence of the two kinds of styrene-butadiene could be detected. All examinations have been done with amounts of each measurable substance at 10%, 5% respectively 2% giving an idea about the detection limit.

The described methodology enables a nearly automated treatment of unknown samples. The approach can be used to solve typical problems in industry, for example with impurities. Py-GC/MS as a fast and reliable method, giving qualitative and quantitative information about complex mixtures, and only small sample amounts (~20-200µg) for analysis are key assets of the technique that are enhanced by fast and more comprehensive data evaluation routines.

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L36: Characterization of Slow Pyrolysis Products Obtained from Linseed (*Linum usitatissimum* L.)

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This study presents the characterization of pyrolysis products obtained from linseed (*Linum usitatissimum* L.) produced by slow pyrolysis in the maximum yield. The char and liquid product were analyzed to determine their elemental composition and calorific value. The chemical composition of the pyrolysis oils and fractions were investigated using chromatographic and spectroscopic techniques (¹H NMR, IR, and GC). The chemical class composition of the oils was determined by liquid column chromatographic fractionation. The oils were separated into pentane soluble and insoluble fractions by using pentane. The column was eluted successively with n-pentane, toluene and methanol to yield aliphatic, aromatic and polar fractions, respectively. The results of the adsorption chromatography of the oils showed that the pyrolysis oil consists of 80wt% n-pentane soluble. The aliphatic aromatic and polar fractions of oils obtained in slow pyrolysis are 30, 34, 36wt%, respectively. The aliphatic and aromatic subtraction make up ~64wt% in slow pyrolysis oil. This seems to be more appropriate for the production of hydrocarbons and chemicals.

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L37: Effect of Pressure on Pyrolysis of n-Heptane

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Petrochemical industries are often concerned with maximizing the yields of light olefins. Due to this, extensive studies have already been carried out on pyrolysis of straight and branched-chain alkanes. However, little information is available in the published literature on high pressure pyrolysis of these compounds. Data on high pressure pyrolysis will be particularly useful in successful operation of scramjet engines where this type of endothermic reactions provide active cooling to the engine components, thereby allowing flight at high Mach number[1]. Therefore, it seems appropriate to study pyrolysis at both subcritical as well as supercritical conditions. Studies on pyrolysis of n-heptane at atmospheric pressure are already available [2]. In this study pyrolysis of n-heptane was investigated in a laboratory-scale tubular stainless steel flow reactor up to a pressure of 1.48 MPa in the temperature range of 813 to 953 K. Argon was used as an inert diluent. Nitrogen was used as an internal standard for gas chromatographic analysis of the samples. The gaseous and liquid products were analyzed offline using three GCs. The major paraffinic products obtained were methane, ethane and propane; whereas the major olefinic products were ethylene, propylene, 1-butene and 1-pentene. Conversion of n-heptane increased with increasing pressure mainly due to the longer residence time of the reactants, resulting due to the higher density of the reactants. Pressure also had a pronounced effect on the product selectivities (defined as moles of product over 100 moles of n-heptane cracked). Selectivities of paraffinic components increased with increasing pressure presumably due to the higher rate of radical recombination reactions at higher pressure. It was observed that the selectivity of ethane depended significantly on the inlet partial pressure of n-heptane. It was also observed that the selectivity of hydrogen decreased with increasing pressure. On the other hand, selectivities of propylene and 1-butene passed through a maxima whereas that of ethylene decreased with increasing pressure. This is most likely due to the secondary reactions of higher α -olefins with small radicals to produce C_nH_{2n-1} radicals. These radicals produce aromatics via decomposition to olefins or diolefins, followed by dehydrogenation.

Chemical initiators are known to increase the rate of pyrolysis reactions. In n-hexane pyrolysis [3], it was observed that some phosphorus containing compounds increase the rate of reaction to an appreciable extent. However, data on the effect of initiators at high pressure are very limited. Hence, experiments were also conducted using triethylamine as an initiator, at high pressure. It was observed that addition of small amount of this initiator considerably enhanced the rate of reaction, without affecting the product distribution.

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L38: Pyrolysis of Mixed Waste Plastics Using Azoisobutylnitrile (AIBN) - An Initiator

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The quantum growth of living standards and drastic increase in use of plastic products had a remarkable impact on the environment. Thermoplastic polymers make up a high proportion of waste and this amount is continuously increasing around the globe. The main consumption of plastic products is packaging, household and domestic products, electrical and electronic goods and also there is significantly increased consumption of plastics in building, construction and automotive industries [1-2]. The pyrolysis of mixed plastics has been considered as an effective way to convert waste plastics into useful hydrocarbon liquid products [3]. In this study, for the first time, we used Azoisobutylnitrile (AIBN) in the pyrolysis of most widely used domestic plastics and tried to understand its effects on the products distribution. The pyrolysis of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) plastic wastes with Azoisobutylnitrile was carried out individually under nitrogen atmosphere. A series of single (plastic/AIBN) and binary (mixed plastics/AIBN) reactions were carried out in a 25-cm³ micro autoclave reactor under different conditions of weight, time duration, pressure and temperature. The optimum conditions selected for our work were: 5% AIBN by weight of total waste plastics, time 60 minutes, pressure 650 psi and temperature 420 °C. It was found that HDPE, LDPE, PP underwent to a maximum cracking and produced maximum amounts of liquid and gaseous products. Pyrolysis of PET and PS plastics with Azoisobutylnitrile afforded comparatively significant amount of inorganic solid materials. In other thermal reactions, various ratios of mixed plastics were pyrolyzed with Azoisobutylnitrile that afforded excellent yields of liquid hydrocarbons and gaseous products. The results obtained from of this study were compared with the results obtained by thermal and catalytic reactions of the same plastics in our previous work. This result shows a very significant increase in the liquid portions of the products on using Azoisobutylnitrile in the pyrolysis of mixed waste plastics. The thermal coprocessing of waste plastics with Azoisobutylnitrile is seems to be a feasible process by which waste plastics can be converted into liquid fuels or chemical feed stocks in higher amounts.

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L39: Experimental study of pulverized coal combustion in O₂/CO₂ mixtures using TG-FTIR coupled technology

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Pulverized coal combustion in conventional power plants produces large amount of carbon dioxide which contributes to the greenhouse effect. Mitigating the emission of greenhouse gas CO₂ becomes an international and imperative issue. Oxy-fuel combustion technology (also called O₂/CO₂ recycled system) of pulverized coal is one of new promising methods, which offers a low risk step development of existing PC power generation technology to enable CO₂ capture and storage. This technology involves the combustion of pulverized coal in the mixture of oxygen and recirculated flue gas (mainly CO₂) in order to reduce the net volume of flue gases from the process and to substantially increase the concentration of carbon dioxide (CO₂) in the flue gases. Compared to the normal pulverized coal combustion in air, CO₂ concentration of the off-gases using oxy-fuel combustion technology could be increased from around 15% up to a theoretical 95%. Although oxy-fuel is potentially competitive with other technologies, there are still a lot of uncertainties for the proposed oxy-firing of PC boilers just for this technology involves many modifications to familiar PC technology. The chemical kinetics of coal combustion in O₂/CO₂ mixtures is quite different from traditional coal combustion process in air. In the work reported here, Thermo-Gravimetric (TG) analyzer and Fourier Transform Infrared (FTIR) coupled technique was used for studying the combustion characteristics and evolved gaseous compounds of pulverized coal in different combustion environments. The effects of combustion environment, oxygen concentration, particle size of pulverized coal and heating rate were considered and the differences of pulverized coal pyrolysis, combustion and gaseous compounds release under two environments were analyzed. Results show that the pyrolysis process of coal in CO₂ environment can be divided into three stages: moisture release, devolatilization and char gasification by CO₂ in higher temperature zone. In the lower temperature zone, the mass loss rate of coal pyrolysis in CO₂ environment is lower than that in N₂ environment. When temperature increases to or over 800°C, mass loss rate increases sharply for the char gasification by CO₂. Combustion experiments show that the burning process of pulverized coal in O₂/CO₂ environment is delayed compared with that in O₂/N₂ environment for equivalent oxygen concentrations. It means that the combustion characteristic of coal char is changed due to the presence of high concentration carbon dioxide. The replacing of N₂ only by CO₂ is unfavorable to the burning and burn-off of coal char. But this performance can be improved by increasing O₂ concentration. When O₂ is increased, the DTG curve of pulverized coal combustion shifts to lower temperature zone. The combustion rate increases, as a result, the burnout time is shortened. The pulverized coal combustion performance can also be improved by reducing the particle diameter. With smaller coal particles, the burning rate increases and burnout time is shortened. It indicates the refinement of pulverized coal is propitious to the improvement of combustion process. Results also show that coal particles are sharply heated in a shorter period of time and burnt in a higher temperature region as the heating rate increase. But the increase in heating rate has almost no obvious effect on the combustion processes of pulverized coal. FTIR experimental results show that during the programmed heating process, H₂O and CO₂ as the major species combined with small account of CO, CH₄, SO₂ and NO were determined and considered from the FTIR spectra. Differences in the absorbance of FTIR bands depend on combustion environments. Compared with pulverized coal combustion in O₂/N₂ environment, much more CO is produced in O₂/CO₂ coal combustion process, but the releases of SO₂ and NO are less than those released in O₂/N₂ environments. The results might have important implications for understanding the intrinsic mechanics of pulverized coal combustion in O₂/CO₂ environment.

Keywords: Oxy-fuel; Pulverized coal; O₂/CO₂ Environment; Combustion characteristics; TG-FTIR.

L40: Investigation into coke formation from pyrolysis of heavy refinery residues: Effects of hydrocarbon and water additives

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Abstract

Thermal pyrolysis is a well established process for upgrading heavy oils and residues in the petroleum refinery and visbreaking is currently in its frontline. Unfortunately, the process is challenged with the formation of unwanted pyrolytic coke [1-3]. In order to identify suitable additives that may prevent coke formation, visbreaking experiments have been conducted on a refinery vacuum residue at 410°C with residence times of up to 60 minutes in mini-autoclave reactor. Under anhydrous conditions, an induction period of 40 minutes was observed prior to start of coke formation. Experimental results which show how coke induction period and coke yields are affected when different additives were introduced have been equally examined. Introducing 5 wt% of tetralin, naphthalene and phenanthrene resulted in coke yields of 2.8, 3.1 and 3.6 wt% coke respectively which were all higher than 2.4 wt% was obtained under anhydrous conditions. Coke yields further increased when more naphthalene or phenanthrene were used. In contrast, more tetralin input resulted in lower coke yields and subsequently reduced to minimum in excess tetralin. This shows that tetralin is an exogenous source of hydrogen and can mitigate coke formation in reacting streams, but must be above a certain threshold level to avoid increased coke formation. Water when added in small quantities proved to be useful as well for reducing coke levels suggesting effective utilization of water hydrogen to mitigate coke at pyrolysis temperatures. The extent of cracking was also generally improved with tetralin and water additives.

Keywords: Visbreaking, Coke, Polyaromatic Hydrocarbon (PAH), Hydrogen donor.

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L41: Pyrolysis and combustion of oil shale for oil recovery

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Oil shale are sedimentary rocks that can be found in many places over the world; they contain typically 20% of organic matter. The recovery of this matter as a liquid oil or as gas presents a considerable potential in energy supply.

Among the processes to achieve this, in-situ combustion or the combustion in special reactors are very promising techniques. They both involve the propagation of a combustion front that heats the porous medium and extracts oil as a product of pyrolysis. This front is supplied in energy by the oxidation of the so called fixed carbon resulting from the pyrolysis of the organic matter, and potentially by the direct oxidation of part of the organic matter or of the gas – condensable or not – resulting from the pyrolysis. In this work, an oil shale was characterized in details using ThermoGravimetric analysis, Differential Scanning Calorimetry, and the standard proximate and ultimate analysis. The permanent gases produced during its pyrolysis were characterized using NDIR, GPC and FID, from experiments under N₂ atmosphere.

An experiment was then realized where a combustion front propagated downward through a 300mm high bed of oil shale. The extracted oil was recovered and the flue gas was analyzed. A mass balance for the propagation of the front enables to quantify the fraction and nature of the organic matter that was oxidized. The front removes more than 96 % of the organic matter. A mass fraction of 52 % is recovered as liquid oil, resulting from the condensation of some devolatilisation products. The flue gas is rich in CO, CO₂ and Non-Methanic Hydrocarbons; some CH₄ is found while H₂ is negligible.

L42: Modeling Study of Pyrocarbon Formation Obtained by Propane Pyrolysis - Chemisorption of Aliphatic and Aromatic Species

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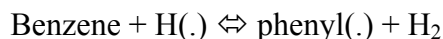
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A detailed heterogeneous kinetic mechanism modeling deposition reactions involved in pyrocarbon formation has been developed. The present model consists of about 370 elementary surface reactions involving about 100 surface phase species whereas the homogenous model developed and validated previously [1,2] is composed of about 600 reversible elementary steps.

Deposition reactions are assumed to occur at the edges of “Basic Structural Units” (BSU) on both “bay” and “zig-zag” like structures. The surface site density (where pyrocarbon deposition by chemisorption takes place) is estimated by assuming the surface behaves as a graphitic structure and by considering the simultaneous growth of several BSU over the portion of a graphene flat plane. Since both ways of calculation give similar results the site density is assumed to be constant ($1,6 \cdot 10^{-9}$ moles.cm⁻²). Elementary heterogeneous processes are believed to be similar to reactions occurring in gas phase pyrolysis, ie H-abstraction, bond dissociation, termination, addition, β -scission and cyclization.

Kinetic parameters of heterogeneous reactions are estimated by assuming that the surface chemisorption reactions are similar to elementary steps in the gas phase involving aromatic species. For example, the creation of an active radical site at the edge of a BSU by a hydrogen atom is assumed to be similar to the following gas phase reaction:



The activation energies of the surface reactions and the gas phase prototype reactions are considered to be equal whereas the probability of reaction is taken into account in the surface reaction pre-exponential factor estimation.

The results of simulation using the Surface Chemkin[®] package are compared with experimental results obtained by Chemical Vapour Deposition (CVD) on carbon fibres at low pressure (< 50 torr). The experimental set up consists of a perfectly stirred reactor (volume 87 cm³) fed with a propane/nitrogen mixture, with temperature ranging from 900 to 1050 °C and residence time ranging from 0.5 to 4 seconds [1,2]. Calculations demonstrate the absence of external and internal diffusion limitations within the carbon fibres preform during the time of deposition. The present model shows good agreement for deposition rates as well as gas phase composition within the temperature and residence time ranges studied. Experimental and simulated results seem to indicate that pyrocarbon is mostly formed by deposition of light unsaturated species such as acetylene and ethylene, which is coherent with a global deposition model developed previously [3].

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L43: Steam Activation of Pyrolytic Tyre Char at Different Temperatures

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The pyrolysis of tyres has merited considerable attention in the literature for the last 20 years, but most studies address aspects concerning the quality and possibilities of the liquid and gaseous products. Nevertheless, the char or solid residue accounts for 30 to 40% of the original tyre mass, which means that finding a commercial application for that product is of great interest. In fact, certain authors [1] affirm that the profitability of the tyre pyrolysis process at industrial scale depends on the char application.

In this paper, the activation of tyre char has been addressed using steam as activation agent. The effect of the temperature and activation time has been studied. The char samples used in the activation have been obtained by continuous flash pyrolysis carried out in a conical spouted bed reactor at 500 °C, operating under conditions in which the char yield reaches 34% (mainly the carbon black contained in the tyre). The activation has been carried out at 850 °C and 900 °C in a fixed bed reactor. Two grams of pyrolytic tyre char have been used in each run. The char sample is heated at inert atmosphere (nitrogen) until the activation temperature is reached. Nitrogen flow is maintained at the activation temperature for one hour in order to complete sample carbonization. The activation gas mixture, which is made up of steam and nitrogen at a ratio of 75:25, is then continuously fed into the reactor. Finally, when the reaction is finished, the activation mixture is replaced by nitrogen and the reactor is cooled.

The results have shown that the main effect of temperature is the increase in the activation reaction rate. Thus, the evolution of burn-off with time is approximately twice faster at 900 °C than at 850 °C. Similar evolutions of BET surface area with burn-off have been observed at the two temperatures studied. The maximum BET surface areas are above 500 m²/g for both temperatures, which is consistent with the results obtained by other authors [2]. The maximum BET surface area values have been obtained for a burn-off of around 60%. It should be noted that an increase in burn-off above these values gives way to a decrease in the BET area obtained. During the activation process, a mesoporous structure is developed, with a predominant pore diameter around 500 Å. The microporosity of the materials obtained is very low and an acid treatment of the char is required in order to increase the contribution of small pores. The mesoporous carbon obtained in the tyre char activation is suitable for use in the adsorption of different pollutants [3].

Steam activation has another important advantage, as is sulphur removal from the char during activation. The initial sulphur content of the original char is higher than 3% and it has been reduced to less than 1% at the end of steam activation treatment. This reduction in sulphur content can be the key for the industrial application of tyre derived carbons, either as active carbons or as carbon blacks for tyre manufacturing.

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L44: On-line detection of organic components in biomass flash pyrolysis off-gas by means of soft photo ionisation time-of-flight mass spectrometry

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Flash pyrolysis of biomass can be applied to produce a variety of oils and oil/coke slurries for the fabrication of synthesis gas as the first step of a process chain for the production of chemicals and synthetic fuels. However, relatively little is known about the primary products in the pyrolysis off-gas or the mechanisms of the pyrolytic decomposition of the various educts. In the framework of a joint project funded by the German ministry for education and research organic components of the flash pyrolysis off-gas from biomass produced by a flash pyrolysis experimental plant at Research Center Karlsruhe, Germany (throughput 10 kg/h) have been analyzed in real time applying time-of-flight mass spectrometry. Thereby, resonance enhanced multiphoton ionisation (REMPI) as well as single photon ionisation (SPI) applying a novel electron beam pumped argon excimer lamp (EBEL) as photon source have been utilized as soft ionisation methods to suppress fragmentation otherwise caused by the many species present in the gaseous matrix. Wheat straw, a mixture of spruce and fir wood as well as beech wood served as educts. Pyrolysis temperature with every educt was 500 °C with a residence time of a few seconds.

Since REMPI is a very sensitive detection method for aromatic compounds, phenolic species such as phenol, cresol, guaiacol and vinylguaiacol are detected in real time. In addition, a typical marker substance for wood related matrices, the PAH retene, was also monitored during the pyrolysis of the spruce/fir mixture, but the signal vanished when beech wood was filled in as educt instead. Due to the fact that REMPI ionisation is wavelength dependent, with the used wavelength of 266 nm all aromatic pyrolysis products are not accessible. However, with SPI-TOFMS further lignin products such as syringol and eugenol could be monitored. Furthermore, SPI allows the detection of aliphatic hydrocarbons, mainly alkenes, carbonylic compounds such as acetone, and furan derivatives such as furfural, furfuryl alcohol and hydroxymethylfurfural. Due to their similar structures, the overall picture for the three educts is comparable; however, there are qualitative differences such as the appearance of retene and the allocation of peak patterns.

**SESSION 7 ADVANCES IN PYROLYSIS METHODS &
INSTRUMENTATION**

KL8: Thermochemolysis and GC-MS for Identification of Bacterial Endospores

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Members of the bacterial genus *Bacillus* demonstrate quite diverse biological activities. For example, in sporulated form, *B. anthracis* (the anthrax pathogen) can be lethal to humans, while *B. thuringiensis* is commonly dispersed as a natural pesticide. The ability to rapidly identify sporulated bacteria on location is highly desirable. Thermochemolysis (i.e., thermal hydrolysis/methylation) followed by analysis by gas chromatography-mass spectrometry (GC-MS) has been previously employed to produce volatile biomarkers from bacterial species. Typically, a sample is combined with methanolic tetramethylammonium hydroxide (TMAH), dried, and rapidly heated using pyrolysis. Such analyses of *Bacillus* endospore biomarkers have been performed using Curie point, infra-red, and resistively-heated pyrolyzers. Direct pyrolysis alone has also been used to obtain biomarkers from endospores.

In this work, we report a novel, simple, pyrolyzer-free approach to thermochemolysis of biological samples followed by analysis of biomarkers using a hand-portable GC-MS system. A coiled Pt wire that can be retracted inside a syringe needle similar to a solid phase micro-extraction fiber is used to sample a suspension containing endospores and TMAH. The coil is retracted inside the needle, the needle is inserted into the heated GC injection port, and the coil is re-extended. Thermochemolysis products (biomarkers) are immediately swept onto the GC column, while non-volatile residues remain on the Pt coil. This procedure reduces thermal degradation products generated at typical pyrolysis temperatures. Treatment of endospores with methanolic sulfuric acid prior to addition of TMAH facilitates the generation of biomarkers by perforating the robust spore structure and complexing with metal cations associated with the key endospore biomarker, dipicolinic acid.

L45: Development of On-line Ultra Violet Radiation Pyrolysis-GC/MS (UV/Py-GC/MS) System using Multi-functional Pyrolyzer

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The physical and chemical performances of most polymeric materials gradually degrade due to external effects such as heating, photoradiation, oxidative atmosphere and mechanical stress. During the degradation process, not only the decomposed compounds formed from the sample but also the structural alternation of the polymers has been important targets to analyze. By getting this information, it would be possible to prepare the advanced materials by modifying its molecular structures and/or selecting appropriate additives. For these analyses, innovative analytical methods have to be developed.

In this work, a new analytical instrument using an on-line micro-ultra violet (UV) radiator combined with the multi-functional micro-furnace pyrolyzer (PY-2020iD, Frontier Lab, Japan) attached to a capillary column GC/MS was developed. A UV beam was radiated on a small amount of polymer sample set in the pyrolyzer through a fiber cable under oxidative and slightly heating atmosphere. The trace amounts of evolved gases from the irradiated polymer sample were on-line analyzed by GC/MS, and then the residual polymer was pyrolyzed in the pyrolyzer at high temperature typically at 600°C to give a specific pyrogram or subjected to conventional evolved gas analysis (EGA) typically by temperature programming up to 700°C to give a thermogram in order to characterize the thermal characteristics. Based on both information obtained, the deterioration mechanism of the polymeric material during photo, thermal and oxidative decomposition and the effect of additives such as photostabilizer and UV-absorber can be evaluated using sub-milligram order of minute polymer sample with a relatively short test period. Here the basic performance of this system was examined using representative polymeric materials such as polystyrene and polycarbonate.

L46: Determining the best reaction conditions for yields and composition of “oil” from lignin in a new solvolytic pyrolysis technique

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Background: We have recently developed a new procedure for converting lignin residues from lignocellulosic ethanol production into organic liquids with a high H/C ratio [1] in a process that can be termed pyrolysis, solvolysis or liquefaction in a non-aqueous medium [2]. The process consists of batchwise heating of the lignin in a hydrogen-donating reaction medium in a high-pressure reactor. The procedure gives very high yields of an organic or “oil” phase that has suitable chemical properties for use as a blending component in motor fuels. The chemistry of this conversion are described elsewhere. [1,3]. The yield and composition of the oil is a function of several experimental factors which need to be evaluated to find the best conditions for the reaction, so that high yields of good quality oil is produced using as little as possible of the hydrogen donor and solvents at technologically acceptable temperature, pressure and reaction duration.

Methods: Solvolysis/pyrolysis has been performed on selected lignins at a temperature of 380 °C with formic acid and ethanol or iso-propanol as co-solvents. The lignins are residues from weak acid hydrolysis or enzymatic hydrolysis of wood for the preparation of sugars for ethanol fermentation. Pyrolysis experiments have been run at different durations and volumetric relations between alcohol, hydrogen donor and lignin, and the masses of gas, organic liquid, aqueous/ethanol phase and char have been determined. The oil has further been separated into two major fractions by flash chromatography on silica and analysed by GC-MS. Reaction conditions were selected using a statistical experimental design and the best conditions in terms of yields and composition of the oil phase were determined.

Results: Very high yields of “oil” can be obtained due to incorporation of solvent units into the product. Maximum yields comprise nearly 200 % of the lignin input by weight, which in this experiment is 34 % of the total organic mass in the reactor. The H:C ratio of the liquid is increased to above 1.5 during the process, and the oil is immiscible with water and soluble in non-polar solvents. Coke formation can easily be completely suppressed. However, unwanted decomposition of the solvents can give high yields of gas-phase product in certain experimental domains. Interpreting the experimental designs has resulted in finding conditions that balance the requirement for a high H/C and low O/C ratios in the oil against a good yield of liquids in a boiling point range that is suitable for motor fuel use.

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L47: Evolved gas analysis in thermogravimetry by a novel photo-ionisation mass spectrometer: Organic signatures of polymer Pyrolysis and crude oil distillation

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Thermogravimetry – mass spectrometry (TG-MS) is a well established technology for analysis of thermal decomposition products from materials such as chemicals, polymers food or bio mass samples. Conventionally electron impact (EI) MS is applied in TA-MS, giving information on evolved small molecules such as CO, CO₂, NO or CH₄. More complex organic molecules often are not detectable due to the fragmentation associated with EI. Single photon ionisation with VUV-light is a well suited ionisation technology for direct mass spectrometric analysis (SPI-MS) of complex organics mixtures (i.e. combustion effluents). In this work the coupling of thermogravimetry (TA) and a novel SPI-MS technology is described which allows the analysis of the evolved pattern of (non-fragmented) organic molecules up to 400 m/z. The novel SPI-MS approach used for TG-SPI-MS coupling is based on an innovative VUV-light source (electron beam pumped rare gas excimer lamp – EBEL). In the EBEL, a 13 keV electron-beam is injected through a 300 nm thick SiN_x-membrane into a dense rare gas, forming a small but very bright VUV-emitting spot. The VUV-light is focussed into the MS-ion source by MgF₂ lenses or parabolic mirrors. An ultra-compact orthogonal-acceleration-TOFMS is used as MS. The new EBEL-SPI-oaTOFMS instrument achieved low ppb detection limits for organics. Initial applications on combustion effluent-monitoring (tobacco smoke, car exhaust) were already reported. In this work the first coupling of thermogravimetry (TG) and EBEL-SPI-oaTOFMS is described. A newly developed interface guarantees the non-retained transfer of larger organic compounds. The newly developed prototype of a thermogravimetry–EBEL single photon ionisation oaTOF-mass spectrometer coupling (TG-EBEL-SPI-oaTOFMS or short TG-SPI-MS)) was applied to study the molecular signatures of the evolved gases from thermal decomposition of plastics, biomass fractions and coals as well as in simulated distillations of different crude oil sorts. Plastics such as polyethylene (PE), polyvinylchloride (PVC), ABS or polystyrene (PS) were investigated individually as well as mixtures. The analysis of the data from the TG-SPI-MS of the plastics reveals that – unlike to common TA-MS couplings with EI – it is possible to detect the full chemical signature of the organic pyrolysis products. Long homologous series of the released oligomers as well as other pyrolytic products are detectable. While e.g. decomposition of PE takes place in a one step process at ~510°C under emission of long homologous series of alkenes, PVC decomposes in a two-step mechanism were firstly hydrogen chloride and benzene is eliminated in a hydrodechlorination reaction (~300°C). In the second step (~500°C), the residual cross-linked polyolefin moieties decompose under release of heavily alkylated aromatics, including alkylated larger polycyclic aromatic hydrocarbons. In the case of the crude oil analysis, the profile of the evolved alkanes, alkenes, dienes and aromatics etc. is shifting to larger molecular masses with increasing temperatures (distillation). At higher temperatures (~450°C) the pyrolytic decomposition of the higher molecular residue (~ 5% mass) begins. The temperature – m/z contour plot gives a graphical impression of the distillation and pyrolytic residue decomposition behaviour which is characteristic for specific crude oil sorts. A pixel based statistical analysis was applied for analysis of similarities/dissimilarities of crude oils from Europe, Middle East and the US.

L48: Application of high temperature oscillatory-shear rheometry and ^1H NMR techniques for understanding the microstructure of coal during pyrolysis/carbonization

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The metastable plastic region that forms during coal pyrolysis and carbonization is generally considered to be the most important stage in establishing both coke quality and oven wall pressures. In order to gain greater insight into the microstructural changes taking place, from which to understand how high quality cokes occur and why excessive oven-wall pressures occur, we have developed high temperature oscillatory shear rheometry techniques. By combining measurements obtained using both 25 mm and 8 mm diameter plates we have characterised the entire plastic and resolidification regions. During softening, phase angle (δ) increases from near 0° (corresponding to a completely elastic solid), and can reach a maximum of 90° (which corresponds to a completely newtonian liquid). Bubble nucleation and growth, as evidenced by plate expansion or axial force measurements, was found to occur when δ exceeded 45° or the complex viscosity (η^*) dropped below 5×10^5 Pa.s. Bubble coalescence occurred when δ exceeded 65° or η^* dropped below 5×10^4 Pa.s. For coals that pass through the bubble growth boundary but don't reach the bubble coalescence boundary, or take a long time to reach it, the plastic region is essentially a thick low gas permeability region which is thought to disrupt the flow of volatiles and hence allow pressure to build up. During resolidification, δ decreases back to 0° and η^* increases above 10^8 Pa.s. The relationship between δ and η^* is different for different coals and thought to reflect the degree of cross-linking in the aromatic network formation. Furthermore, the relationship between fraction of rigid hydrogen (ϕ_{rh}), obtained from ^1H NMR measurements, and η^* also gives characteristic curves. We are currently identifying whether these relationships provide an indication for coke quality. These techniques could also be useful in many other pyrolysis applications, where an understanding of microstructure is needed.

L49: Polymer degradation studies using Laser pyrolysis-FTIR microanalysis

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Due to the demand for better understanding of the polymer degradation mechanism, solid- and gas phase analysis have been carried out using a Laser pyrolysis-FTIR/ATR method [1]. The use of a laser in a pyrolysis system for investigation the thermal degradation of polymers has several advantages over the traditional filament or furnace pyrolyzers [2].

The concept behind the method is the combination of the micro scale modelling of fire circumstances applying CO₂ laser and analytical monitoring techniques: FTIR analyzing the chemical changes in the gas phase and ATR-IR in the solid phase.

In this study ethylene-vinyl acetate copolymer (EVA) and polypropylene (PP) based nanocomposites were analyzed. Pristine and surface modified nanofillers such as montmorillonite and needle-like sepiolite were applied to obtain composites and to investigate their influence on the degradation. In order to get a complex picture about the degradation of the samples thermal analysis (TGA), combustion tests have been performed as well.

The initial experiments were carried out - by means of pristine polymers - in order to optimize the variable parameters of the method such as laser performance and treatment time, flow rate of purge gas etc.

Nanofillers containing samples were exposed to laser beam, the evolved gases were collected in a gas cell and continuously monitored. The characteristic peaks of the EVA degradation at 1730 cm⁻¹ (C=O), 2918 cm⁻¹ (-CH₂), 1290 cm⁻¹ (C-O-C), 2355 cm⁻¹ (CO₂), 2162 cm⁻¹ (CO) can be clearly attended: through the split of the acetate groups and oxidation in the gas phase; and double bonds formation (965 cm⁻¹) in the solid phase was established by ATR-IR. The most significant effect has been observed in case of metal (Fe, Cu) modified montmorillonite contained EVA samples by accelerating the decomposition. The same effect has been noticed also in case of polypropylene.

A CO₂ laser pyrolysis system combined with FTIR served for investigation of the gas phase degradation product of polymers. The results suggest that the designed and developed new LP-FTIR system has several advantages: easy sample handling; sample size and sample pretreatment are minimized; modelling of different fire scenario is feasible through the varied intensity, duration of treatment time, rapid temperature rise; reduced secondary reactions. The method contributes to the understanding of degradation mechanisms including fire retardancy.

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L50: Pyrolysis as a Characterization Technique for Monitoring the Interaction in Polymer Nanocomposites

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Composite materials usually have a discontinuous component, the filler, embedded in a continuous phase, the matrix. If one of the dimensions of the filler is below 100 nm the filler is considered in the nanoscale, and the resulting materials are called nanocomposites. The resulting properties are only enhanced with respect to the original matrix if the nanofillers are properly dispersed into the matrix. Thermogravimetric pyrolysis was reported for monitoring the interaction of carbon nanotubes with polymer matrices in composite materials [1]. Because of the small dimensions of carbon nanotubes, the carbon interfacial surface per unit volume is very high, which may induce a polymer phase with a different pyrolysis mechanism. According to this, the higher the nanotube loading, the higher the effect if the filaments are adequately dispersed. In addition, the thermal stability of the polymer should improve and the temperature of decomposition of the final material should increase if the nanofiller interacts adequately through covalent bonding [2], creating a new polyme phase.

The present work analyses the quantitave effect of carbon nanofilament concentration of well-dispersed polypropylene nanocomposites in thermogravimetric pyrolysis. Nanofilaments studied are carbon nanotubes (CNT) and two commercial stacked-cup carbon nanofibers (CNF). The stability clearly rises with the filament concetration, as seen in figure 1a, which proofs the usefulness of TG in nanocomposite characterization. It can also be observed that the use of a micrometric size carbon fiber does not promote a higher decomposition temperature with respect the matrix.

The present work also analyzes the effectiveness of nanofiber functionalization. Figure 1b shows the TG curves of nanocomoposites of PMMA composites with a constant concentration of 1%vol in pristine CNF, carboxylated CNF, and amino functionalized CNF. Although changes in the temperature of decomposition are slight, adding as far as the dispersion is better (as shown through TEM), the thermal stability is higher.

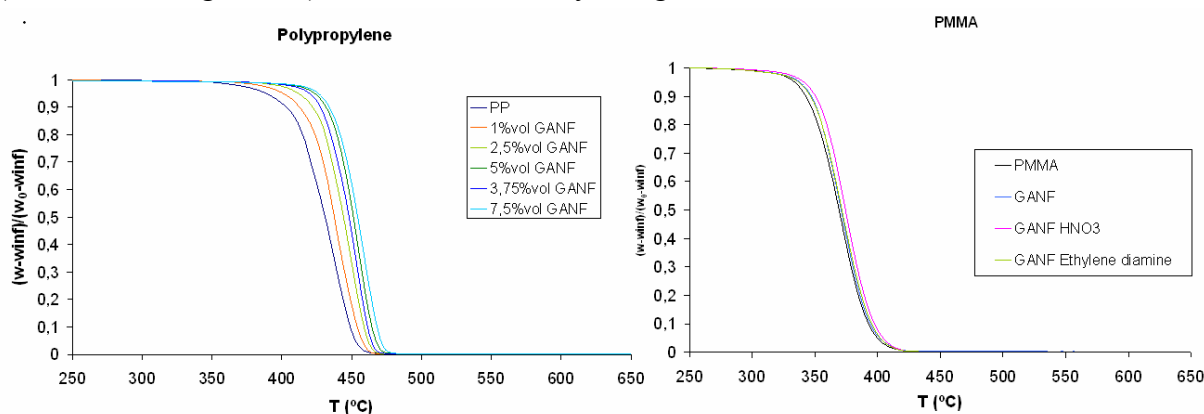


Figure 1. TG curves of nanocomposite materials. 1a) PP matrix; 1b) PMMA matrix

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L51: Micro-Pyrolysis of technical lignins in a new modular rig and product analysis by GC-MS/FID and GCxGC-TOFMS/FID

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A new off-line pyrolysis rig has been designed to allow multifunctional experiments for preparative and analytical purposes. The system conditions can be set and monitored, e.g. temperature, its gradients and heat flux. Experimental options available are:

- Addition of internal standards for exact quantification.
- Integration of a catalytical active zone.
- Selection of different atmospheres and various mixing ratios.
- High speed heating rates up to 190 C/s with pyrolysis temperatures up to 850 C at variable pyrolysis times.
- Complete mass balance of products and reactants (gas, liquid and solids) by gravimetrical methods and subsequential chromatographic analysis.

During the experiment there is an adjustable transport gas flow through the closed system, which allows for quick removal of pyrolysis products from the hot reactor zone into a cold trap and a gas absorption trap. Solid products remain in the reactor. All collected fractions can be individually analyzed by e.g. GC-MS/FID and GPC.

In the present work the pyrolytic behaviour and the decomposition products of lignin related compounds were studied under different conditions: heating rate (from 2.6 C/s up to 120 C/s), pyrolysis temperatures at 500 C and 800 C in different atmospheres (N₂, H₂, mixtures of N₂ and acetylene). Kraft lignin (Holmen AS, NO), soda lignin (Granit, CH), organosolv lignin (Alcell, USA), pyrolytic lignin from pine bio-oil [1], residues from wood hydrolysis (Etek Etanoltechnik AB, SE) and also fermentation residues from biogas production (Haak, DE) were studied.

The obtained pyrolysis products were classified in three general groups: charcoal, liquid phase and gas phase (volatile organic compounds (VOC) and permanent gases). The liquid fraction was analyzed by GC-MS/FID. Also comprehensive two dimensional GC [2] was applied to characterise the pyrolysis liquid fraction. VOC's were semiquantified by a redesigned headspace technique and subsequential GC-MS/FID analysis.

The obtained results by the modular off-line pyrolysis rig will be shown for several technical lignins at different process conditions. The micro-pyrolysis rig proved to be an efficient and useful device for complex pyrolysis applications.

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**SESSION 8 ANALYTICAL PYROLYSIS APPLICATIONS I:
Soil, Geochemistry and Environmental Sciences**

KL9: Analytical Pyrolysis of Soil and Natural Organic Matter

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The objective of the review is to summarize the progress in analytical pyrolysis of soil organic matter (SOM), various SOM fractions and related natural organic matter that potentially enter soils. It covers the time period 1998 to 2008. The techniques applied include the traditional Curie-point pyrolysis gas chromatography/mass spectrometry (Cp-Py-GC/MS), the newly developed multi-step pyrolysis or double-shot technique used *on-line* in combination with GC/MS, and various soft ionization techniques (field ionization, field desorption mass spectrometry). Examples for applications of analytical pyrolysis techniques include various soil types that are characterized by types of organic matter association with minerals such as Vertisols or Andisols. Among organic-mineral fractions those with high stability that may be sinks for organic C received particular attention. Several publications linked the thermal stability of SOM and compound classes to their biological stability and resistance against biodegradation. This will be shown for various analytical pyrolysis techniques and types of soil materials. Although dissolved organic matter (DOM) can be characterized by diverse wet chemical techniques, analytical pyrolysis has been used in recent years to get insight into the composition and pathways of DOM. The scale of DOM investigations ranged from nanolitres collected in the plant rhizosphere to river systems in landscapes of thousands of square kilometres. Thus, analytical pyrolysis methods contributed to urgent research needs such as risk assessment of genetically modified crops, soil remediation and effects of global warming on SOM turnover and DOM mobilization. Finally, an outlook will be given how new, complementary analytical techniques such as synchrotron-based X-ray absorption spectroscopy and ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) will improve the basis for the interpretation of analytical pyrolysis data.

L52: The Effect of Afforestation on the Soil Organic Carbon (SOC) of a Peaty Gley Soil Using On-Line Thermochemolysis in the Presence of ^{13}C -Labelled Tetramethylammonium Hydroxide (TMAH)

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Afforestation may have a significant effect on soil organic carbon (SOC). In Britain substantial areas of both deep and shallow peatland have been afforested with conifers since the 1950s. However, information on the effects of afforestation on the properties of SOC is lacking.

During afforestation the contribution of lignin to SOC will obviously be significant. The physiochemical recalcitrance of lignin in classical litter decomposition studies has led many to assume that it is relatively resistant to degradation in soils. However, more recent findings suggest that it is more easily degraded in soil than conventionally perceived [2].

Investigating the geochemical changes that take place when lignin is degraded and incorporated into SOC will provide us with an insight into soil carbon dynamics at the molecular level. In this study peaty gley soil cores were obtained, firstly from a second rotation Sitka spruce stand from Harwood Forest (Northumberland, UK) and secondly from an adjacent, undisturbed moorland soil. The Forest had originally been established on treeless moorland with a peaty gley soil. Following preparation, the soils were analysed using on-line thermally assisted hydrolysis and methylation (THM) coupled to GC/MS. ^{13}C -labelled TMAH allowed us to assess the relative contributions of lignin and non-lignin phenolic compounds [2].

Both soils were composed of guaiacyl, syringyl and *p*-hydroxyphenyl (G, S and P) lignin derivatives. Semi-quantitative analysis revealed a decrease in the amounts of lignin-derived products with increasing burial depth, with the most significant decrease occurring between the F and upper H horizon. The changes in the quantities of other components of SOC will also be discussed, e.g. the methylated carbohydrate derivatives [3].

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L53: Free and occluded light SOM fractions in soils under cerrado, tilled and untilled fields, Minas Gerais, Brazil – a pyrolysis-GC/MS study.

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In a previous study [1, 2] we studied the isotopic composition of soil organic matter in an Oxisol under cerrado forest, and adjacent fields that had been under maize-beans rotations under conventional tillage (CT) and no-tillage (NT) for 30 years. The study was carried out at the Miaze and Sorghum National Research Centre (Embrapa-CPMS), Sete Lagoas-MG, Brazil. For the present study, we studied the Free Light fraction (FL), the Occluded Light fraction (OL) and extractable OM (Ex) of the same soils by pyrolysis-GC/MS (Curie temperature = 600°C). Samples were taken of 0-7.5 cm and 7.5-15 cm depth. Together, there were 35 samples of the FL fraction, 36 of the OL fraction, and 35 of the Ex fraction. 166 Pyrolysis products were identified and quantified. The quantified data were subjected to factor analysis.

In factor space, the three fractions plotted in three fully separated clusters, with the FL fraction between the OL and Ex fractions. This indicates that the decomposition of the OL fractions takes a different path from normal OM decomposition in the soil. The Ex fraction was characterized by the strongest degradation, the largest content of N-containing products, and the highest fraction of microbial OM. The OL fraction showed a relative increase of recalcitrant components such as n-alkanes and alkenes, aromatics and polyaromatics. Such a relative increase of recalcitrant products was absent in the Ex fraction.

A maize-beans rotation supplies a litter that is chemically different from that of the cerrado forest. Roscoe and Buurman (2003) [2] calculated that in topsoils under maize/beans about 28% of the FL fraction was maize derived under NT, and 47% under CT, while the occluded fraction (OL) contained 13% maize-derived OM under NT and 17% under CT. Nevertheless, the chemical difference between OL and FL fraction is larger than that due to land use system. Further, the chemical variation of the three fractions was OL>FL>Ex, with the Ex fraction containing the smallest fraction of fresh litter. Differences between the two depth fractions were not found.

The FL and OL fractions contain a large number of fragments that can be attributed to charred material (polyaromatics, alkylbenzenes, alkylphenols, etc.).

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L54: Specific extraction of soil lignins: evaluation with pyrolysis/GC/MS

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Lignin is the second most abundant compound in plant tissues after cellulose. Due to its polyphenolic structure, lignin is not easily biodegradable by microbial activity. Using the CuO oxidation method, which releases simple methoxy phenols, we recently reported that lignin turnover in soil can be estimated by compound-specific ¹³C analyses of naturally-labeled lignin molecules in agricultural soils under C3 to C4 crop succession (Dignac et al., 2005).

However, CuO oxidation gives access only to a part of the lignin molecule. To obtain a more complete characterisation, an isolation procedure of intact lignin has been adapted for soil samples, which includes grinding to generate fine particles followed by enzymatic attack to remove cellulose and final extraction of the "Milled maize enzymatic lignin (MMEL)" (Pew, 1957). This method has been used abundantly to characterise plant lignin but was never used for soils.

The objectives of this study were to use pyrolysis/GC/MS to 1) evaluate the purity of the extracted lignins by characterizing the chemical composition of MMEL extracted from soils and plants and 2) estimate the efficiency of the extraction procedure by searching for lignin markers remaining in the extraction residues.

The pyrolysis of lignins extracted from soil lead to a major contribution of lignin-derived pyrolysis products such as methoxyl and dimethoxyl phenols, suggesting that they are primarily composed of lignin units. In the pyrogram of MMEL extracted from maize stems, several peaks originated from polysaccharides (furancarboxaldehyde, OH-propanone,...). In the pyrogram of MMEL extracted from soil, only one peak (furancarboxaldehyde) was found to be specifically derived from carbohydrates, suggesting that lignins are less bound to celluloses in soil than in plant material. Many non-specific pyrolysis products were also observed. However, many of them were phenols (phenol, methyl phenol, etc), and might be lignin derived. Styrene and methyl styrene, possibly originating from degraded lignin were more abundant in the pyrolysate of soil MMEL than in that of maize stems.

The extraction residue of plant material displayed a number of lignin-derived pyrolysis products, while the residue from lignin extraction from soil mainly displayed nitrogen containing and polysaccharide derived products, and only two minor lignin derived peaks. The lignin extraction from soil thus appeared rather complete and the extracted lignins might be representative of the total lignins present in the soil sample.

MMEL may be used in addition to CuO oxidation to characterize lignin present in soils and estimate their dynamics.

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L55: Pyrolysis-GC/MS of Black Carbon: fresh knowledge on the molecular structure of aged charcoal

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The product of incomplete biomass combustion is referred to as black carbon (BC). Black C is relatively resistant against biodegradation and may therefore constitute an important fraction of recalcitrant soil organic matter, and thus play a significant role in global C cycling. Pyrolysis-GC/MS is a molecular characterisation technique often used in studying complex mixtures of natural organic matter. It is thought to be unsuitable for analysis of BC because the pyrolysis step itself causes thermal modifications that may interfere with the chemical signature of natural burning, and because a significant fraction of BC is not pyrolysable.

We analysed many 1000 to 6000 yrs old charcoal fragments using Pt-filament coil probe pyrolysis at 750 °C and subsequently 1000 °C for 10 seconds, and identified the pyrolysate using GC/MS. Analysis of lignin-rich peat showed that demethoxylation and cyclisation did not frustrate analysis under these pyrolysis conditions. Charcoal produced a large suit of aromatic compounds that can be considered characteristic of BC: benzene, toluene, PAHs (a.o. naphthalene, fluorene, phenanthrene, 2-phenylnaphthalene and pyrene) and N- and O-substituted (poly)aromatics (benzofuran, dibenzofuran, pyridine, benzonitrile, benzodicarbonitrile and naphthalene carbonitrile). Uncharred carbohydrate material in the charcoal was recognised as levoglucosan and levoglucosenone, or as a set of furans and furfurals when the carbohydrate fraction had been subjected to significant biodegradation. Charcoal fragments of different plants (*Quercus* sp., *Erica* sp., *Arbutus unedo*, *Fabaceae*) produced similar pyrolysates. With age, more oxygenated (ketonic) compounds were observed and a general increase in pyrolysability of the material is observed. The large amount of nitrilic N, especially in the 1000 °C series, suggested that N is a significant component of condensed BC moieties. Pyrolysis-GC/MS had hitherto been underestimated as a tool for BC characterisation at the molecular scale.

L56: Impact of landuse change on the molecular composition of soil organic matter

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The transformation of grassland into cultivated land is a common practice in many parts of the world. This management commonly leads to decrease of the soils organic matter content. In this study, we analysed the quantitative and qualitative changes occurring in the soil organic matter composition on a molecular basis using Curie point pyrolysis. The aims of the study were (1) to assess the field variability of pyrolysis data, (2) to evaluate the suitability of analytical pyrolysis for studying the molecular composition of organic matter in different landuse systems, and (3) to follow the development of SOM in grassland soil, after conversion into agricultural land.

Soil was sampled at the long-term observatory for environmental research in Poitiers, France. At this site, grassland was converted to cultivation in 2004. Three replicates samples were taken 3 weeks, 3 months, 1 year and 2 years after conversion, as well as from cultivated and grassland control soils. The samples were treated with 10 % HF to remove mineral material before being subjected to analysis of the bulk chemical composition by Curiepoint pyrolysis coupled to gas chromatography and mass spectrometry. Our gas chromatograph was equipped with a rather polar (wax-coated) column, because we hypothesised that polysaccharides and proteins were likely to be the first components to be affected by land-use change. The relative contributions of single molecules were obtained by integration of the total ion chromatogram.

Analysis of three replicated soil samples after HF treatment by Curiepoint pyrolysis showed an acceptable variation (about 10 %) of relative contribution of single pyrolysis products to the total ion chromatogram. Pyrolysis products derived from lignins, proteins and polysaccharides were identified in all samples. Significant differences in molecular composition were noted between SOM composition from grassland compared to cultivated soil. In agricultural soil protein-derived pyrolysis products such as pyrrole and pyridine were most abundant, whereas in the prairie, lignin, polysaccharide and protein derived pyrolysis products showed similar abundances. Principal component analysis showed that agricultural, prairie and converted prairie had distinct molecular characteristics. The first component, which accounted for 58 % of the variability, was mainly determined by the contribution of polysaccharide and lignin derived pyrolysis products, such as 2-cyclopentene-1-one, furfural and 2-methoxy-phenol. The second component, which explained 23 % of the variability, was due to contributions of unspecific compounds from a range of chemical families, such as benzene, ethanol and styrene.

We conclude that Curie point pyrolysis can be used to follow alterations of soil organic matter composition on a molecular level.

L57: Hydropyrolysis as a new tool for radiocarbon pretreatment and the quantification of Black Carbon

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The first results concerning the potential of hydrogen pyrolysis (hypy) as a new tool for the quantification and isolation of Black Carbon (BC) for radiocarbon analysis are reported. BC comprises the most stable form of carbon within the pyrogenic carbon continuum, fixed within samples such as charcoal. Isolation and quantification of this component is therefore of great interest in radiocarbon measurement, particularly for more ancient samples, where contamination issues become more critical. The fact that hypy can reduce labile organic matter to volatile products in a controlled manner makes it an attractive new approach for the rapid isolation of the most resistant carbon fraction from carbonaceous samples. This suggests that hypy represents a promising new approach not only for BC quantification as an end in itself, but also for ¹⁴C dating where purified BC is the target material for dating.

In this study, we have used a range of samples containing BC to assess the use of hypy for this purpose, including pyrogenic carbon samples of various antiquity and from different soil matrices. One key factor is whether it is possible to determine the point, in terms of operational conditions, at which removal of the labile organic matter is complete, and further hydrogen pyrolysis results in degradation of the purified BC via hydrogasification to form methane. We have therefore assessed the reproducibility and reliability of the method to isolate BC, and used ¹⁴C measurement of the hypy residue and removed products to test its potential utility as a pre-treatment procedure for ¹⁴C analysis.

The results show that hypy can effectively and reproducibly isolate the most resistant carbon fraction within a variety of sample types and thus provides a rapid and robust pre-treatment technique for radiocarbon analysis. Hypy has the additional advantage that the non-BC fraction removed from a sample can be quantitatively collected for subsequent further analysis. The technique represents a promising new approach not only for ensuring reliable decontamination of pyrogenic carbon samples prior to radiocarbon dating but also for BC quantification in a variety of environmental matrices.

L58: Curie-point Pyrolysis / Gas Chromatography / Mass Spectrometry of standard dipeptides and oligopeptides in the presence of Tetramethylammonium hydroxide

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Nitrogen-containing organic compounds represent the second most abundant reservoir of nitrogen on earth. Despite the important implication of nitrogen in environmental processes, its chemical structure and origin remain widely unknown likely due to the refractory nature of its source macromolecules. Recent studies [1], using ¹⁵N NMR spectroscopy, pointed to the dominance of amide functions in natural environments, thus suggesting that N is engaged in polar building blocks. For a few years, TMAH-Py/GC/MS has been applied to the study of refractory OM from different sources, and focused on nitrogen-containing macromolecules.

For a better understanding of the pyrolysis results of these materials, the pyrolytic behaviour of model compounds has been investigated. Thus the twenty protein amino acids (AA) have been recently pyrolysed in the presence of TMAH and a data base has been constituted [2].

As nitrogen mainly occurs in high molecular weight structures and not as free amino acids, the influence of the peptidic linkage on the pyrolytic behaviour of amino acids has been investigated and seventeen dipeptides have been studied along with a few oligopeptides, containing four to nine amino acids.

TMAH-pyrolysis of dipeptides revealed that they do not behave as the mixture of the corresponding amino acids. In the pyrochromatograms of dipeptides the major pyrolysis products of free amino acids are generally only detected at trace levels. The most abundant compounds correspond to higher molecular weight derivatives, mainly methylated diketopiperazines (DKPs) as well as methylated derivatives of the dipeptides. More complex DKPs constituted from three amino acids were also identified in several cases, sometimes as the major product. According to their structure, these DKPs can be classified in two different types depending on their formation, two mechanisms have been propounded. Moreover, to precise the role of the peptidic bond on the pyrolytic behaviour of the amino acids, pyrolyses of symmetrical pairs of dipeptides were performed. They demonstrated that the functional group involved in the peptidic bond has no influence on the formation of methylated derivatives of the amino acid. However, depending on the reactivity of its side chain, one amino acid can react to form more complex cyclic products either when it is C-terminal or N-terminal. Results obtained upon TMAH-pyrolysis of oligopeptides underlined the important formation of cyclic products. They established the possible formation of DKP not only from N-terminal sequential amino acids pairs as previously observed (AA₁-AA₂ + AA₃-AA₄) [3], but also from AA₂-AA₃. Complex DKPs were also identified as main pyrolysis product for a pentapeptide.

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L59: Assessing soil organic matter alteration in fire affected soils by PY-GC/MS

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Forest fires are the main disturbance in the Mediterranean basin [1] and exert both immediate and lasting environmental impacts. This is in part caused by the transformation of soil physical, chemical and biological characteristics associated to changes in soil organic matter (SOM) [2] which in turn is reflected in the structure of the whole system.

In this investigation a comparative direct analytical pyrolysis approach was used to evaluate the effects of fires in SOM using samples from soils affected and non-affected by wildfires. Samples were taken from a variety of scenarios from Andalusia (Southern Spain) that included different soil types under different vegetation and affected by wildfires between 1999 and 2004. As control (non-affected) samples were taken from nearby areas with similar soil characteristics and vegetation type but with no recent history of forest fires.

Analytical pyrolysis (Py-GC/MS) was performed using 10 mg of the fine earth soil fraction (<2.0 mm) in a Frontier Laboratories Double-Shot Pyrolyzer (mod. 2020iD) directly connected to a GC-MS system Agilent 6890. The detector consisted of an Agilent 5973 mass selective detector (EI at 70 eV). The GC-MS conditions were the same for all the experiments. The identification of individual compounds was achieved by single ion monitoring for different homologous series, low-resolution mass spectrometry and comparison with published and stored data (NIST and Wiley libraries).

The analysis of thermo-evaporation products released from whole soil samples using sub-pyrolysis temperature (280 °C) show differences in the most labile SOM fraction (mainly furan derivatives) between the fire affected and not affected soils. The analysis of products released at pyrolysis temperature (500 °C) show very clear differences, with a relative enrichment in aromatic compounds in fire-affected soils at the expense of *n*-alkane/alkene pairs, polysaccharides or lignin derived compounds that dominate in pyrolysisates from fire non-affected soils.

Analytical pyrolysis is revealed as a valuable tool for the direct analysis of SOM. The analysis minimizes sample handling and can be applied directly to sieved soil samples. In this work, the differential characteristics found between burnt and control samples have potential as markers to assess the effect of fire on soil and to monitor the recovery after wildfire events.

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L60: Use of thermal analysis in the characterisation of biochar and soils containing biochar

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Biochar is a fine-grained, porous charcoal substance that, when used as a soil amendment in combination with sustainable production of the biomass feedstock, effectively removes net carbon dioxide from the atmosphere [1]. Biochar can be produced by pyrolysis or gasification systems. The bioenergy produced during biochar production may be in the form of thermal energy, a synthesis gas (syngas), or a bio-oil. Biochar and bioenergy co-production from urban, agricultural and forestry biomass can help combat global climate change by displacing fossil fuel use, by sequestering carbon in stable soil carbon pools, and by dramatically reducing emissions of nitrous oxides, a more potent greenhouse gas than carbon dioxide [2,3].

Characterisation of biochar in soil is important for several reasons. First, for carbon accounting purposes it is essential that the amount of biochar is known that remains in soil over the long term. Secondly, it may be important to be able to 'fingerprint' specific biochars, so that different manufactured products are traceable. Third, it is important in research to be able to characterise biochar within soils, so that its longevity, reactions and impact on the soil system are understood. Finally, it is important from a practical point of view to determine the characteristics of biochar using methods that are sufficiently rapid and inexpensive that their widespread use becomes possible.

Thermal analysis methods (thermogravimetry, differential scanning calorimetry (DSC) and evolved gas analysis) have been applied to three sample suites of biochars and related materials: (1) a batch of samples prepared from pine and peanut husk at approximately 500°C under different pyrolysis conditions for research purposes by Eprida Inc. (Athens, GA); (2) opportunistically-sampled biochars and charred plant material, and (3) well-studied soil samples from terra preta (soils to which char was added in prehistoric times).

The pine and peanut husk biochars gave similar results for each material, and differed subtly. In both cases, thermal analysis shows that weight losses cease after 550°C, with residual masses between 10 and 16%. DSC traces for the pine biochars show a broad peak between 490 and 550°C; for biochar produced at higher pressure (6 psi compared with 1.4/0.4 psi) there is a peak at 490°C and a shoulder at 550°C. The peanut husk samples show very similar results, with consistent residual masses of 15-16%, and DSC traces that show peaks at 510 and 480°C with a shoulder at 440°C. Evolved gas analysis shows evolution of water at approximately 100°C (drying), at 350°C (dehydration of cellulose) and at 500°C (dehydration of char). The opportunistic samples showed similar patterns, with biochar from a gasification plant showing higher temperature reactions.

The soil samples clearly show differences in results for thermal analysis of terra preta compared with adjacent oxisols (soils that had no char added). In addition to having a higher organic matter content, DSC traces for the terra preta soils clearly show the presence of a biochar-like material, that is stable at high temperatures (up to 500°C) during thermal analysis. Evolved gas analysis shows the evolution of water at 100-120°C, at around 350°C (cellulose dehydration) and at around 500°C (kaolinite plus char dehydration), and evolution of carbon dioxide at 500°C, clearly displaced to higher temperatures compared to adjacent oxisols. Thermal analysis confirms (and offers scope for quantifying) that terra preta soils up to 2000 years old contain stable forms of carbon that resemble modern biochar.

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**SESSION 9 ANALYTICAL PYROLYSIS APPLICATIONS II:
*Art, Forensics and Natural Products***

KL10: Analytical pyrolysis: a unique tool for rapidly diagnosing works of art

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Diagnosis in art and archaeology entails a chemical study designed to reveal the composition of materials used along with the secrets of the past, by highlighting the molecular composition of the artwork.

Used in conjunction with related information from historical sources, the chemical characterization of organic materials has in the last few years considerably improved our knowledge of the painting techniques of the past and of the function of archaeological objects. Moreover, the chemical composition helps to assess the state of conservation along with any potential risks of degradation.

To achieve such aims, direct and rapid analytical methods that avoid sample pre-treatment are particularly welcome in the field of the cultural heritage, where the availability of samples is often limited and contamination must be avoided.

This lecture describes the analytical pyrolysis procedures that are able to identify specific organic materials from molecular patterns. This enables us to assess the role that these substances once played and to determine the use of artefacts. The identification of materials is mainly based on the principle of “chemotaxis”, that is on the detection of one or more specific molecular biomarkers which have survived ageing or which are formed over the centuries as stable products of ageing processes.

In this field, pyrolysis gas chromatographic techniques in combination with mass spectrometry (Py-GC/MS) and direct in-source Py-mass spectrometric technique, namely direct exposure electron ionization mass spectrometry (DE-MS), have been proven to be of particular interest in the study of natural materials and macromolecules.

In particular, Py-GC/MS provides useful data on the chemical structure of material components. During pyrolysis, the macromolecules are depolymerised by heat and the pyrolysis products can be identified by mass spectrometry, after gas chromatographic separation. For instance, in the case of lignin, pyrolysis produces a variety of phenolic products, which consist of guaiacyl and syringyl structural units with an aliphatic side chain in position 4 of the aromatic ring: the pyrolysis products represent, to a greater or lesser extent, the structural units that make up the macromolecule.

In DE-MS the sample undergoes resistively controlled heating on a rhenium filament within the ion source of the mass spectrometer. The sample components are desorbed or, in the case of macromolecules, pyrolysed over the heating range, and are ionised and analysed as a function of time. DE-MS is a fast fingerprint tool that is able to discriminate, for instance, between plant resins or between hardwood and softwood in archaeological artefacts by using a very limited amount of sample without any pre-treatment.

Basically, this lecture outlines such methods and shows several significant case studies related to statues (the restoration of bas-reliefs of S. Antonio Chapel in Padua), wall paintings (Monumental Cemetery of Pisa) and archaeological objects (Roman amphorae, Palaeolithic flints, archaeological wood).

L61: Biomacromolecules of Fossil Algae and Zoomorphs as Revealed by Curie Point Pyrolysis-Gas Chromatography-Mass Spectrometry

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Fossil organic matter, i.e. prasinophytes (*Tasmanites* and *Leiosphaeridia*), Chitinozoa and scolecodonts, from predominantly Paleozoic sedimentary rocks were investigated for their chemical composition in order to reveal potential relationships of individual families/taxa by biomarkers. Samples originate from SE Turkey, Oklahoma and Virginia (USA) and from Gotland (Sweden). All samples arise from relatively low-temperature time windows. After kerogen separation from the sediment, about 300 individual handpicked palynomorphs per analysis were cleaned by dichloromethane to remove soluble hydrocarbon, and then subjected to Curie point pyrolysis-gas chromatography-mass spectrometry.

Tasmanites from all geographical localities are dominated by a series of *n*-C₆₋₂₂ alkene/alkane doublets which are typical of pyrolysis products of algaenan, the microbiological resistant algal biopolymer. The pyrolysates of the *Tasmanites* from Tasmania show a normal tricyclic terpenoid compounds. No traces of tricyclic terpenoids have been detected from the pyrolysates of *Tasmanites* from Hazro area, Oklahoma and Virginia, however. Like *Tasmanites*, *Leiosphaeridia* are characterised by a series of *n*-C₆₋₂₂ alkene/alkane doublets, too, and they also exhibit monounsaturated and diunsaturated tricyclic terpenes as well as monoaromatic tricyclic terpanes. Within the composition of the biomacromolecules of the investigated Chitinozoa, aromatic moieties dominate over aliphatic ones, although a series of *n*-alkene/*n*-alkane doublets up to C₂₂ was found as well. Alkyl-benzenes, naphthalenes, phenols and phenanthrenes represent the major aromatic compounds. No pyrolysis products diagnostic of or related to chitin or proteins were detected. The pyrolysis products of scolecodonts (fossilized jaws) include aromatic hydrocarbons such as alkylbenzenes, alkyl-naphthalenes, alkylphenols and the aliphatic hydrocarbons are represented by a homologous series of *n*-alkenes and *n*-alkanes. Thus hints on amino-acids are solely provided by phenol compounds.

Thus, based on this study of pyrolysates from *Tasmanites*, *Leiosphaeridia*, Chitinozoa and scolecodonts, we conclude:

1. An inherent source-biomarker relationship between the *Tasmanites* and tricyclic terpenoids does not exist because all *Tasmanites* except Tasmanian ones are devoid of tricyclic terpenoids. Furthermore, *Leiosphaeridia* contain these compounds, too.
2. It is very unlikely that the original macromolecules of Chitinozoa consisted of chitin because no related chemical compounds could be detected.
3. Phenols represent the only compounds which can be related via degradation processes during diagenesis to amino-acids and related compounds commonly found in extant polychaete jaws of scolecodonts.

L62: Direct Analysis of Alkylphenols in *Ginkgo biloba* Leaves by Thermochemolysis–Gas Chromatography/Mass Spectrometry in the Presence of Tetramethylammonium Hydroxide

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Ginkgo biloba extracts (EGb) are mainly used for the improvement of the blood circulation, both peripherally and centrally. However, alkylphenols including ginkgolic acids and ginkgols in *Ginkgo* leaves and extracts are claimed to be allergenic, cytotoxic, mutagenic and slight neurotoxic. Accordingly, a requirement for a maximum concentration of ginkgolic acids in EGb had been included in the draft monographs of US [1] and European pharmacopoeias [2] by establishing a limit value of 5 $\mu\text{g}\cdot\text{g}^{-1}$. Therefore, it is requested to develop a practical method to determine the alkylphenols in *Ginkgo biloba* leaves or extracts rapidly and precisely.

In this work, thermochemolysis–gas chromatography/mass spectrometry in the presence of tetramethylammonium hydroxide was applied to determine alkylphenols in *Ginkgo biloba* leaves directly using a vertical microfurnace pyrolyzer. On the pyrograms of *Ginkgo biloba* leaves obtained at 300 °C in the presence of TMAH, a series of sharp peaks of alkylphenols including ginkgolic acids and ginkgols as their corresponding methyl derivatives could be observed clearly. On the basis of the relative intensity of these peaks on the pyrogram obtained, chemical composition of the alkylphenols in *G. biloba* leaves was determined rapidly and precisely without using any tedious and time-consuming pretreatment such as solvent extraction and purification, with RSD less than 3.4%. Furthermore, the separation of the positional double bond isomers ($\Delta 8$ or $\Delta 10$) of C15:1 and ($\Delta 10$ or $\Delta 12$) of C17:1 ginkgolic acids was also achieved.

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L63: Thermal decomposition, characteristics and behaviour of microalgae during slow pyrolysis

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Background

Aquatic microalgae have been identified as potential candidates for the production of high volume, low cost biomass and it has long been established that microalgae offer a promising route to crude oil and petro-chemical feedstock substitution¹. Pyrolysis of microalgae offers a processing method that presents opportunity to maximize utilisation of algae biomass through the production of 'carbon neutral or better' oil, gas and char products in an integrated value-chain².

Introduction

This work aims to establish a base level of understanding of the thermo-chemical properties of 6 different microalgae species, selected for their inherent characteristics and industrial potential. This analysis is designed to provide a clearer picture of the behaviour of microalgae biomass under slow pyrolysis conditions and to characterize the resulting oil, gas and char.

Method

Each sample was first ground then pre-dried for 90 minutes at 60°C in a vacuum oven to remove excess moisture. The samples were then subjected to slow heating conditions in a pyrolysis oven, with a heating rate of 10°C per minute, driven to a maximum of 750°C.

Gas chromatography/mass spectrometry (GCMS) was used to characterize the gas species that evolved from dried algae samples. Computer-aided thermal analysis (CATA), utilizing a method devised by Strezov et al.³, was then undertaken to establish the inherent heat balance and heat content of non-volatile gases. Molecular weight distribution of pyrolysis oils was also established to identify tar composition and finally, thermo-gravimetric analysis to infer the percentage (on a dry weight basis) of pyrolysis char produced from algae was carried out.

Conclusion

The cell structure and inherent composition of algae species gives rise to differences in observed behaviour during pyrolysis and is reflected in resulting oil, gas and char outputs. Of particular interest is the capacity of certain algae species to produce gas under these conditions of sufficient quality and quantity to drive the pyrolysis process itself.

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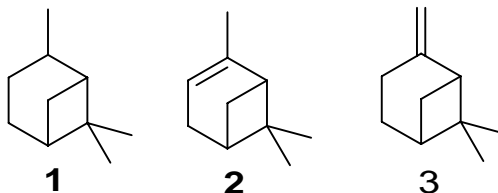
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L64: Prediction of the Isomerization Behavior of some Monoterpenoids based on the Thermal Rearrangement of Three Major Pinane-Type Monoterpenes

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Pinane-type monoterpenes (**1**) are from special interest in the field of thermo-organic chemistry from various points of view. First of all, monoterpenes like α - (**2**) or β -pinene (**3**) are renewable resources for the syntheses of building blocks leading to flavors and fragrances [1, 2]. Secondly, these compounds have the great advantage, that they are mostly available in enantiomeric pure form [2]. Syntheses based on **1-3** often include an isomerization step which can either be thermally induced or acid-catalyzed. Thermally induced rearrangements are from special interest because they are often stereo- and enantiospecific reactions without the need of any additional reagent (catalyst, solvent).



With respect to their reactivity and the formed main products pinane-type monoterpenes and terpenoids can be divided into three main groups represented by the title compounds (**1-3**) investigated herein. The presented work deals with the thermal behavior of **1-3** in a flow type pyrolysis apparatus using nitrogen as carrier gas in a temperature range from 300-600 °C at different residence times [3]. Reactions carried out exclusively yielded isomerization products, without the formation of any degradation or polymerization products. Experiments allow for the calculation of kinetic parameters (acc. to Arrhenius-Eq.) for the main reactions giving the opportunity to model the thermal rearrangement of **1-3** in dependence of reaction temperature, residence time and of surface-to-volume-ratio. Additionally, comparison of the results found for the title compounds allow for the prediction of the rearrangement behavior of derivatives of **1-3** (e.g. verbenone, verbenene, 2-pinanol) concerning reactivity and product spectra.

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L65: On the formation of a hydroxylactone from the catalytic pyrolysis of carbohydrates over nanometric metal oxides

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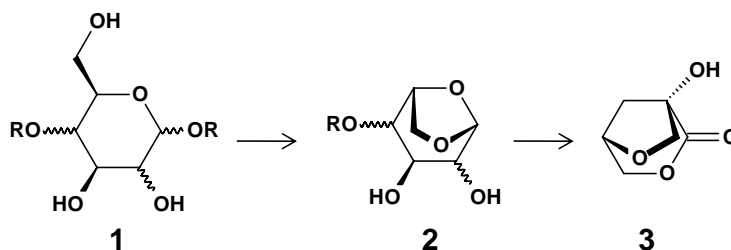
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There is a growing interest in developing novel chemical intermediates from renewable resources. Most of the proposed platform chemicals are derived from plant polysaccharides by bio/chemical transformations. Pyrolysis is an alternative route to break down polysaccharides into smaller molecules, among which anhydrosugars possess structural attributes (chirality, multifunctionality) useful for their conversion into fine chemicals.

Recent works have demonstrated that the pyrolytic production of chiral anhydrosugars from cellulose is influenced by the presence of nanopowder (NP) metal oxides [1]. Preparative pyrolysis of cellulose mixed with NP aluminium titanate (AlTi) allowed the isolation of hydroxylactone **3** (abbreviated LAC) [2]. LAC has the potentiality to be a chemical intermediate in the synthesis of high value products and specialties, such as enantiopure tetrahydrofuran derivatives and biodegradable polyesters. The formation of LAC was fully demonstrated in the literature only for cellulose. The pyrolytic production of LAC from other sugar precursors with and without NP AlTi was investigated in this study along with the catalytic activity of MCM-41 mesoporous materials doped with Ti and Sn. The yields of LAC from the thermal degradation of D-hexoses **1** and monoanhydrohexoses **2** were determined by analytical off-line pyrolysis, employing a heated filament pyrolyser and GC-MS analysis. The effect of nanometric catalysts on the thermal behaviour of carbohydrates was further investigated by TGA and DSC.

The results obtained from off-line pyrolysis show that all the investigated sugars produce LAC upon pyrolysis. The yield of this lactone is generally enhanced when the sugar is pyrolysed in the presence of the catalyst. Starch and cellulose exhibit the highest yields (5-7%), while monosaccharides (glucose, galactose, mannose) the lowest. As a general rule, non-reducing sugars give higher yields than reducing ones.

TGA and DSC experiments evidence the occurrence of carbohydrate/catalyst interactions and indicate that the thermal degradation is complete below 400 °C.



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L66: Characterisation of archaeological waterlogged wood by direct exposure mass spectrometry (DE-MS) and Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

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Anaerobic erosion bacteria, in presence of wet environment, can slowly degrade waterlogged archaeological wooden objects, as shipwrecks. This action mainly lead to the formation of pores and cavities filled with water, caused by the loss of cellulose and hemicellulose, of extractable compounds and also by the alteration of lignin. This soft and fragile structure, mainly composed of residual lignin, can easily collapse when drying. Due to this reason, the chemical characterization of archaeological lignin is surely an aspect of primary importance in the diagnosis and conservation of waterlogged wood artefacts [1, 2]. At present, the knowledge of lignin degradation processes in historical and archaeological wood is extremely inadequate, and further studies are required. Archaeological wood samples of different species and age have been examined in this study. The majority of them were collected during the excavations at the Ancient Harbour of San Rossore (Pisa, Italy), where twenty one shipwrecks dating from 2nd cent. B.C. to 5th cent. A.D. have been discovered from 1998 until now. The aim of this work is to study the chemical composition of archaeological waterlogged wood, with particular attention to lignin, by means of direct exposure electron ionisation - mass spectrometry (DE-MS) and analytical pyrolysis/gas chromatography/mass spectrometry (PY/GC/MS) using hexamethyldisilazane (HMDS) for the in-situ thermally assisted derivatisation of pyrolysis products. Principal component analysis (PCA) has been exploited to do unsupervised pattern recognition analysis of DE-MS mass spectral data. DE-MS combined with PCA analysis of mass spectral data is a fingerprint method for the screening, the evaluation and the comparison in short time of wood samples. This integrated PCA / DE-MS analytical approach is a reliable and powerful tool which allows to estimate the degrade of waterlogged wood by evaluating the syringiyl/guaiacyl ratio. Instead, Py-GC/MS with HMDS can easily elucidate the chemical modifications of lignin molecules in archaeological objects.

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POSTER PRESENTATIONS

SESSION 2 & 5 BIOMASS:
Characterization, Fuel & Chemicals Production

Analytical pyrolysis as a direct method to determine the lignin content in wood.

Part 3: Evaluation of species-specific differences in lignin composition using Principal Component Analysis

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The chemical characterization of wood using traditional analytical techniques is normally a tedious procedure that requires a large amount of sample, not always available. Analytical pyrolysis is being increasingly used as a qualitative and also quantitative method in the wood and pulp field to assess chemical composition of lignocellulosics with the main advantages over classical wet-chemical methods: (i) easy sample preparation (drying and milling), (ii) rapid analysis, and (iii) the low amount of sample required (micrograms range) [1].

In Part 1 of this series a method for the quantification of the lignin content (Py-lignin) of Maritime pine (*Pinus pinaster* Aiton) and spruce wood (*Picea abies* [L.] Karst.) samples directly from the pyrograms was presented [2]. The good correlation found between the Py-lignin and Klason lignin content gave a common model for both species. In Part 2 [3] five subspecies of larch wood (*Larix* sp.) were used to evaluate this common model, revealing only small differences between the measured and the predicted Klason lignin contents. Compression wood was included due to the difference in lignin composition and content compared to normal wood. As the influence of compression wood was small a so-called "softwood model" including all samples was calculated which can be used for pine, larch, and spruce wood with the limitation of the highest and lowest values were the species-specific models lead to better results. However, slightly different slopes of the linear regression lines of pine and larch, and especially the one of spruce suggested possible differences in lignin and/or carbohydrate composition that should be investigated.

In this work Principal Component Analysis was used to evaluate the pyrolysis results with respect to differences in lignin composition focusing on species-specific differences. By using the G-related peaks from the pyrograms, species were clearly separated in the PC1-PC2 scores plot. Moreover, it was additionally possible to separate the pine samples according to site. The PC2-PC3 scores plot revealed a clear separation of the larch wood samples from the other species which could be related to the fact that larch differs genetically more from the others. In the PC2-PC4 scores plot the two spruce samples with high H/G ratio were far from the others. The discussion of these results together with the loadings will help to reveal the differences in lignin composition between the species and sites.

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Monitoring the chemical composition of developing xylem by analytical pyrolysis and FTIR spectroscopy

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Xylogenesis is a complex and dynamic process that consists of the successive addition of secondary xylem that differentiates from the vascular cambium. Environmental conditions and developmental stages of the plant play crucial roles on each step of xylogenesis. As a consequence, wood forming tissues retain environmental and developmental signatures at the cell organisation, as well as at the individual cell level (size, shape, cell-wall structure and chemical composition), resulting in a highly variable raw material, not only among different genotypes, but also within a single individual. Indeed, different types of wood with contrasting properties can occur within the same tree, i.e. compression and opposite woods, juvenile and mature woods, early and late woods.

Analytical pyrolysis and Fourier transform infrared (FT-IR) spectroscopy were used as rapid analysis tools to evaluate differences in the chemical composition of *Pinus pinaster* developing xylem samples collected from: 1) the beginning (early wood) to the end (late wood) of the growing season and, 2) from the base to the top of straight 30 years old trees.

The pyrograms of developing xylem show the presence of toluene a characteristic pyrolysis product of phenylalanine that is absent from that of fully developed wood. Another striking difference is the lower amount of lignin products $14.9 \pm 3.1\%$ (12.5 ± 3.7 G-units) in differentiating xylem compared to an average of 26 % for wood. These findings were corroborated by FTIR spectroscopy.

The comparison of the FTIR spectra of differentiating xylem and developed wood show that besides the usual features found in the spectra of fully developed wood (i.e. the characteristics bands of polysaccharides and lignin), wood forming tissue show additional bands (amide I, II, III) attributed to the presence of amide vibrations from the peptide group.

Analytical pyrolysis data were combined in multidimensional analysis, in order to characterise the cell wall chemical composition. Data analysis revealed sample groupings due to differences in chemical composition. The changes in the chemical composition of the developing xylem samples obtained along the growing season and along the stem can be easily and rapidly monitored with analytical pyrolysis and FTIR.

Py-GC-MS as a tool to analyse husk rice residues transformed by selected *Streptomyces* strains

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Rice husk is the protecting covering of grains of rice plant *Oryza sativa*. This residue, very abundant in developing countries such as Nicaragua, is composed of recalcitrant inorganic and organic materials, including opaline silica and lignin. Building material, filler ingredient of pet food, insulation material or fuel are some of uses described in the literature for this residue. Although rice husk can be also composted, its high lignin content can make difficult this process. To upgrade this residue the fermentation with ligninolytic microorganisms could be considered a good strategy. During the last years, several reports have demonstrated the ability of *Streptomyces* strains to modify lignin from lignocellulosic residues under solid-state fermentation conditions (SSF) [1, 2]. The main objective of this work is to analyse by Py-GC-MS the chemical modifications produced in rice husk residues fermented by selected *Streptomyces* strains under SSF conditions.

The strains were grown at 45 °C (*Streptomyces* UAH Nic-C) or 28°C (*Streptomyces* UAH 47 and *Streptomyces chattanoogensis* CECT 3336) for 10 days on a medium containing the rice husk residue supplemented with cassava and saline basal medium to get 65% humidity. The growth of the strains was estimated as the CO₂ released during the incubation period. Chemical modifications of the residue were examined through Pyrolysis-GC/MS [3].

All the strains showed an optimal colonization of the substrate reaching the maximum growth after two (*S.* UAH 47 and *S.* UAH Nic-C) or three (*S. chattanoogensis*) days of incubation. Results obtained by Py-GC/MS showed enrichment in cellulose in the fermented residues compared with the control as well as a decrease in lignin-derived compounds from *p*-hydroxyphenyl, syringyl and guaiacyl lignin units. The increase in the relative abundance of lignin units with a higher oxidation degree suggests an oxidative action of the strains on the lignin molecule. In addition, the increase in the phenylmethane+phenylethane/phenylpropane (phC1 + ph C2/ph C3) ratio would indicate the ability of *Streptomyces* strains to breakdown the C3-alkyl chain linkages once lignin units were oxidized.

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Modeling biomass pyrolysis using the Chemical Percolation Devolatilisation structural model

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The production of second generation biofuels is one of the promising processes to face the oil resources rarefaction. This is based on the production of synthesis gas, mainly composed of CO and H₂, through biomass steam gasification at high temperature. The syngas is then ducted to a liquid fuel synthesis step (e.g.: Fischer-Tropsch, methanol). Biomass pyrolysis is one of the key phenomena occurring during the gasification process: during this first step more than 75% of initial mass are released at high temperature (1000-1500°C) and high heating rates (> 1000 K/s) [1].

Hence, the numerical modeling of biomass pyrolysis is of high importance in order to optimize the process design. During the last decades, a lot of work has been done to model the coal devolatilisation. Several attempts were also performed to extend these models to the pyrolysis of the biomass components (lignin, cellulose and hemicellulose), considered independent. Among the models that have been extended to biomass, the Chemical Percolation Devolatilisation (CPD) model is one of the most promising [2]. Indeed, it allows the correct description of the mass yields from the independent component [3], and it also predicts a molecular weight distribution of the tars. Moreover, CPD has a relatively low CPU cost that enables it to be coupled with CFD codes.

The present work proposes a biomass devolatilisation modeling using CPD coupled to the GaSPar (Gasification of Solid Particles) software, developed in Commissariat à l'Energie Atomique (CEA). GaSPar is a 1D gasification physico-chemical model for a particle distribution, which includes a detailed modeling of the gas phase reactions using CHEMKIN II subroutines. The reactions between the char and O₂, H₂O as well as CO₂ are also computed, and the heat transfers phenomena are described precisely. The CPD model has been improved for the biomass by taking into account the interactions between the lignin, cellulose, and hemicellulose pyrolysis through the metaplast intermediate species and the cross-linking phenomenon. The composition of the released gases is obtained using empirical correlations. The modeling results are compared with experimental results obtained under different heating and temperature conditions (drop tube furnace, TGA).

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Experimental study of fast pyrolysis of biomass at high temperature: influence of particle size and temperature

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Pyrolysis, as the first step in all biomass thermo-conversion processes, is a very important issue nowadays. A lot of investigations concerning the interaction between the chemical and physical processes during pyrolysis, in particular the relative importance of heat transfer and intrinsic kinetics, have been done in the past decades. According to the operating conditions (mainly sample size, heating rate and final temperature of reactor), pyrolysis process can be controlled by chemical kinetic, external heat-transfer (thermally thin regime), or external plus internal heat transfer (thermally thick regime). However, only few experimental results under the typical heating conditions encountered in fluidised bed or entrained flow gasifiers, namely millimetric particles, fast heating rates (hundreds of °C.s⁻¹) and high temperatures (800-1000°C) can be found in the literature [1, 2, 3]

A free fall reactor and a horizontal tubular furnace have been used as experimental facilities to investigate the influence of particle size and temperature on biomass pyrolysis behaviour under the following operating conditions.

	Free fall reactor	Horizontal tubular furnace
Temperature	800°C; 950°C	
Pressure	Atmospheric	
Type of biomass	Beech wood	
Carrier gas	N ₂	
Average particle size	400µm; 600µm; 800µm; 1,1mm	1.1mm; 2mm; 3mm; 5mm; 10mm
Solid residence time	< 3s	3s ~ several minutes

First results tend to show that the yields of H₂ and C₂H₂ increase with the increasing temperature; the yields of CO, CO₂ and CH₄ are not temperature-sensitive, while the yield of C₂H₄ slightly decreases with the increasing temperature. The shift in apparent kinetic rates and final product distribution for particles of different sizes reveals the influence of heat transfer limitation in the whole pyrolysis processes. A map is constructed in terms of apparent kinetic rates as a function of both particle size and reactor temperature, to locate the heat-transfer controlled regime and the transition from a thermally thin regime to a thermally thick regime.

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Influence of slow and rapid pyrolysis on the product yields and characteristics of physic nut (*Jatropha curcas* L.) waste

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Abstract

Slow and rapid pyrolysis experiments of physic nut waste using fixed bed had been carried out to determine and compare yields and compositions of products. The waste with particle size between 0.4–0.5 mm was pyrolyzed at different hold time (15 min, 30 min and 60 min) and vary temperature (500 °C, 700 °C and 900 °C) under N₂ in a vertical type reactor with a heating rate of 1 °C/min and 20°C/min for rapid and slow pyrolysis, respectively. The maximum oil yield was 30.1% at the pyrolysis temperature of 700°C with the sweeping gas flow rate 100 mL/min. Further increase in hold time after reaching final reaction temperature up to 60 minutes only caused 5% decrease of liquid yields. Appreciable differences on the residue characteristics, depending on the pyrolysis conditions, were observed. Release of volatile matter led to development of porous structure. Progressive increase in mesopore development with increasing pyrolysis temperature and short retention time took place, whereas a maximum development of larger pores occurred at 700°C. Rapid and slow pyrolysis trials indicated that increase in temperature leads to increasing gas yields from product gas measurements for reaction temperature up to 900°C by gas chromatography.

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Py-GS/MS for Characterization of Non-Hydrolyzed Residues from Bioethanol Production from Softwood

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Production of bioethanol by lignocellulosics hydrolysis has a long history, and nowadays bioethanol application as transport fuel makes it a topical task worldwide. In all configurations of hydrolysis including moderns ones, a significant amount of a raw material (up to 40-45%) remains as a rich-in-lignin non-hydrolyzed residue (LHR), and the feasible use of this residue is the necessary condition for the cost-effective operation of bioethanol production. The large potential of LHR as the raw material for obtaining products useful for environment protection, agriculture and industry is good recognized. The profound knowledge about LHRs composition and structure is needed to find methods for their converting to value added products. The aim of the present work was to study LHRs composition with emphasis on their lignin component chemical structure modification upon various stages of the bioethanol production process carried out in three different configurations: softwood acid hydrolysis (AH), separate enzymatic hydrolysis and fermentation (SHF), and simultaneous saccharification and fermentation (SSF) in pilot plant conditions in Sweden (University of Lund and Ornskoldsvik Pilot Plant by Etek Ltd.). The characterization of LHRs structure on molecular level was done applying Py-GC/MS. ESR- and FTIR-spectroscopy, and routine chemical analysis procedures were used as complementary techniques for this study as well.

High portion of the carbohydrates-derived pyrolytic products for LHR samples after SHF and AH processes indicates on non-completeness of processing or development of side reactions and *visa versa* high portion of lignin-derived compounds – up to 80% (SSF) shows the efficiency of hydrolysis process. Comparison of chemical analysis results and data obtained by Py-GC/MS of LHRs brought the direct evidence of incorporation of carbohydrates-derived fragments in lignin matrix and formation of so-called pseudo-lignin upon different stages of softwood processing. Increase in the portion of phenyl derivatives and appearance of the benzene derivatives, clearly demonstrated the condensation changes in the molecular structure of lignin component upon all stages of softwood processing, beginning with the pretreatment stage, that was in good compliance with the data obtained by other techniques (ESR, FTIR). Using Py-GC/MS the changes in molecular structure of lignin component of non-hydrolyzed residues on various stages of the technological process of bioethanol production were revealed: development of condensation reactions, ether bonds cleavage, destruction of side propane chain, oxidation.

The results of the present investigation allow to conclude that the application of Py-GC/MS opens the opportunity for prompt, detailed and reliable characterization of changes of the composition of ligno-carbohydrate complexes, that is necessary for non-hydrolyzed residues future application as well as for monitoring of carbohydrates conversion during wood hydrolysis processing for bioethanol production.

Products of fast pyrolysis of wood, their properties and applicability

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The application of renewable energy resources for energy production becomes increasingly urgent worldwide. Fast pyrolysis is one of the prospective trends of obtaining liquid fuel from solid biomass. Besides the energy purposes, the use of bio-oil for obtaining chemical products, for example, pyrolytic lignin, levulinic acid, anhydrosaccharides etc. is considered. As the feedstock for obtaining bio-oil, wood processing waste, peat and various agricultural residues such as rape and grain-crops straw, and corncobs can be used.

In this work, results of the studies on the properties of the products of fast pyrolysis of softwood and hardwood are presented. Pyrolysis was performed using a 2-chamber ablation type reactor. Optimum conditions of drying and pyrolysis regimes for obtaining bio-oil were established, the chemical compositions of bio-oils were investigated by the GC/MS method, and a comparison of heat capacity was carried out.

Separation of bio-oil into the carbohydrate and lignin fractions by the method of high-speed dispersing in water was carried out. The monomeric chemical and functional composition of the fractions was investigated, and the characteristics of the properties were investigated by the FTIR and ESR-spectroscopy methods.

It has been found that the pyrolytic lignin released from hardwood bio-oil is characterised by a decreased (twice) content of methoxy groups, which is explained by the results of Py-GC/MS. In the composition of volatile monomeric products of pyrolysis of hardwood lignin, mainly guajacyl derivatives are present. It is shown that the syringyl derivatives of lignin enter into the composition of the water-soluble fraction of carbohydrates.

The tests of the antioxidative activity of the water-insoluble and water-soluble fractions of bio-oil have shown a high efficiency of the samples, which exceeds the activity of the lignins released from wood by the alkaline delignification method ($O_2^{\bullet-}$ formation inhibition test). A possible explanation of the peculiarity of the antioxidative properties of the lignin and carbohydrate fractions of bio-oil, based on the properties of the polyconjugated system of lignin, is suggested.

Catalytic decomposition of methane over a wood char to maximise hydrogen production by biomass pyrolysis

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Hydrogen (H₂) is the greenest energy vector if produced from a renewable resource as biomass. To maximise H₂ production from biomass pyrolysis/gasification, the amount of hydrocarbon compounds (mainly CH₄) in biomass syngas must be lowered. Metal catalysts like Fe, Co and Ni were shown to be very efficient [1] to increase the kinetics of methane conversion. Because metals quickly deactivate, are sensitive to sulphur poisoning, and are prone to coking, the use of carbon-based catalysts has been proposed [2, 3]. In the present work, gathering biomass pyrolysis and the catalytic decomposition of methane over a carbon-based catalyst is studied. Catalytic activity of a wood char for CH₄ decomposition in a biomass pyrolysis gas was investigated in a fixed bed reactor to maximise hydrogen production from biomass gasification. Wood char would be the cheapest and greenest catalyst for CH₄ conversion as it is produced in the pyrolysis facility. It has been shown that raw wood char produced by slow pyrolysis of pine chips leads to a stable CH₄ conversion of 70% at 1000°C, for a contact time of 120ms (equivalent to a volumetric hourly space velocity of 3 Nl g⁻¹ h⁻¹) and in a reconstituted pyrolysis gas. For the investigated experimental conditions, ashes in wood char play a negligible role in CH₄ conversion. CH₄ conversion has been investigated as a function of pyrolysis gas composition. CH₄ in N₂ (14% vol. in N₂) leads to the rapid deactivation of the carbon catalyst, down to 10 % CH₄ conversion. This finding is interpreted by the blocking of the microporosity by pyrolytic carbon deposition. In the presence of CO₂, or H₂O, or both at once, the methane conversion is stabilised at higher values (45 to 70%). These gases concurrently activate the wood char. CO₂ and/or H₂O increase or at least maintain its surface BET area and pore texture and prevent the pores mouth blocking by pyrolytic carbon deposition. At 1000°C, oxygenated surface functions are continuously generated by the concurrent CO₂ and H₂O activation and decomposed, as evidenced by CO production, char mass losses and surface chemistry analysis (Fourier Transformed Infra Red and Thermal Programmed Desorption analysis). Functional groups are not directly the active sites of CH₄ decomposition because the raw char (N₂ pre-treated at 1000°C and thus with a very low level of oxygenated groups) has a high initial activity for CH₄ decomposition (in nitrogen without oxidizing agents). The active sites are more likely carbon atoms with dangling bonds generated by the surface functions decomposition.

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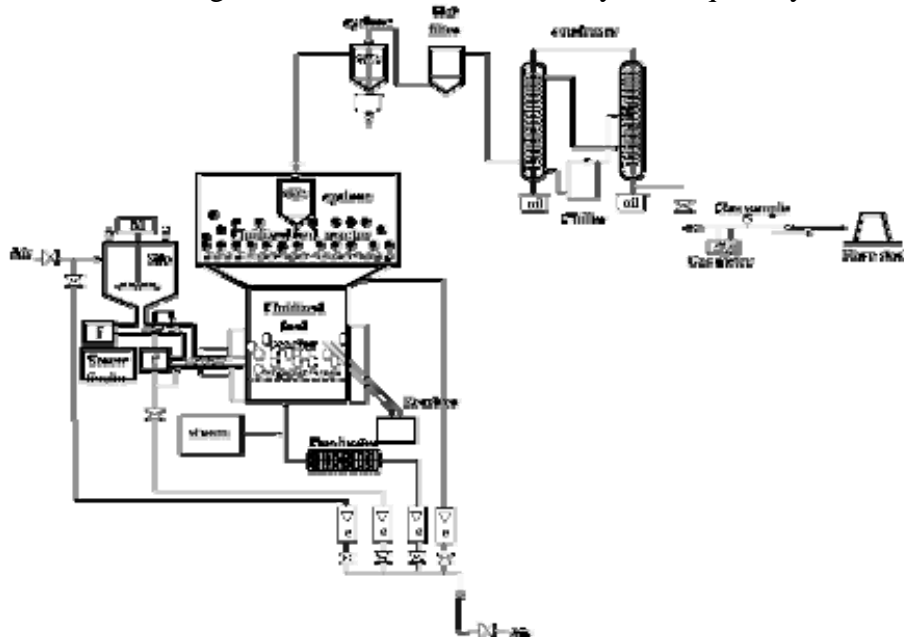
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Thermo-chemical Conversion of Sewage Sludge: Pyrolysis in a Plant with a Char Removal System and Gasification in a Two-staged Fluidized bed Reactor

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Most of sewage sludge produced in Korea is disposed by ocean dumping that London Convention, however, strongly demand to stop. Therefore, new treatment methods for sewage sludge should be found. The strong candidates of new methods are pyrolysis and gasification. The oil produced by pyrolysis, however, usually shows bad characteristics mainly due to low heating value and high content of contaminants. In this study, we performed the pyrolysis of digested and dried sewage sludge containing polymer flocculants in a temperature ranges between 446 °C and 720 °C in a pyrolysis plant equipped with a fluidized bed reactor and a char removal system composed of a cyclone and a hot filter together. In the experiments, we could obtain above 50 wt% pyrolysis oil with a maximum caloric value of 33 MJ/kg. In addition, we could reduce contaminants in the pyrolysis oils by the char removal system and calcium oxide as an absorbent to capture HCl liberated during pyrolysis. On the other hand, we performed the gasification of sewage sludge in a newly developed two-staged fluidized bed reactor. In the experiments we applied activated carbon in the second fluidized bed to reduce tar which is produced in abundance during gasification and to investigate the influence of activated carbon on the product gas composition. Producer gas obtained by applying activated carbon contained a high content of hydrogen with a value up to 22 vol% of the producer gas and methane. In addition, activated carbon acted as absorbent, which led to the strong reduction of tar in the producer gas. Therefore, the producer gas seemed to be appropriate for fuel gas in gas engine where tar content in the engine should be limited in a very small quantity.



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Study of the pyrolysis liquids obtained from different sewage sludge

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In the last 20 years, pyrolysis of different raw materials has been studied as an alternative way to produce liquid fuels and chemicals. In the University of Zaragoza pyrolysis of sewage sludge is being studied in order to valorise this waste.

Sewage sludge is the waste produced in the wastewater treatment plants when the wastewater is purified. The composition and characteristics of sewage sludge depends on several factors like the origin of the wastewater, the purification treatment of the wastewater, the stabilization treatment of the sewage sludge, the time and conditions of storage of the sewage sludge, etc. Moreover, the treatments in the wastewater treatment plants are not usually standardized and even using the same treatment some parameters as the flocculation agent or the stabilization temperature may change, what implies a change in the sewage sludge composition.

One of the most commonly used stabilization treatments of the sewage sludge in wastewater treatment plants of high capacity is the anaerobic digestion. In this work the pyrolysis of two kinds anaerobic digested sewage sludge obtained from two different urban wastewater treatment plants was studied. The elemental, the ultimate analysis, the FTIR and the content of some metals of the sewage sludge will be shown.

Pyrolysis experiments were carried out in a laboratory scale plant of fluidized bed at 550 °C and with a gas residence time of 2.4 s (from the production in the reactor to the condensation in the liquid recovery system) with these two kinds of sewage sludge. Three replicates of the experiments were made with each sewage sludge in these experimental conditions. The pyrolysis liquid obtained were studied from the point of view of its yield, water content, elemental analysis and chemical composition. The chemical composition of the liquids obtained in these experiments was analyzed by GC-MS and GC-FID.

High differences in the liquid yield and the water content of the liquids were found. These differences are thought to be related with the catalytic effect of some alkaline metals of the ash of the sewage sludge. The main chemical families found in the pyrolysis liquids obtained at these experimental conditions were aliphatic hydrocarbons, aliphatic oxygenated compounds, and steroids, apart from these, are also important but less the aromatic hydrocarbons and the nitrogen heterocyclic compounds. In this work, a reflexion about the possible toxic character of some of these families of compounds will be shown.

Effect of flow path in rice husk pyrolysis

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Obtaining energy from biomass has grown in recent years as a substitute for fossil fuels. One of the reasons for this is that energy produced from biomass has a zero increase in greenhouse gases emissions. The use of direct combustion for energy recovery presents the problems of ash agglomeration and pollutant emissions. Pyrolysis and gasification are two interesting alternatives to combustion for biomass. Using these techniques a gas and/or liquid fuel is produced which can be used to operate diesel engines or gas turbines to generate power.

In this work, pyrolysis and gasification of rice husk have been studied. Rice husk is one of the most important agricultural wastes in the world with a high energy content. The worldwide annual production has been estimated in 100 million tons [1].

Two different flow paths were studied in a horizontal laboratory reactor: parallel flow and counter flow. Substoichiometric air was used in gasification and nitrogen in pyrolysis experiments. Both the gaseous fraction and the liquid fraction were analyzed using gas chromatography - mass spectrometry (GC/MS).

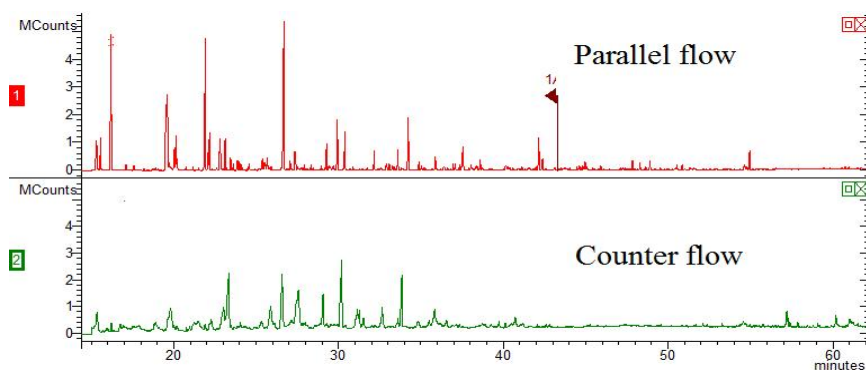


Figure 1. Chromatograms obtained in pyrolysis with parallel and counter flow.

Figure 1 shows the pyrolysis chromatograms at 850°C with the two flow paths. The differences between both operating conditions are similar in pyrolysis and gasification. Compounds obtained with parallel flow were mainly aliphatics, aromatics and polyaromatics. Since these compounds are non-polar they show symmetric narrow peaks. Compounds produced with counter flow were more polar like aldehydes, acids and esters. These compounds appear as irregular and broad peaks.

The reason of this difference between both flow paths is the gas temperature history. In the case of parallel flow all the gases pass through the hot zone, but in the counter flow once the solid has reached the decomposition temperature the gases generated move to lower temperatures, so reducing the extent of secondary reactions.

Additional experiments in batch reactors with low heating rates show similar distribution than counter flow.

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Catalytic Steam Reforming of Model Compounds of Pyrolysis Liquids in Fluidized Bed Reactor with Ni/Ca-Al and Ni/Mg-Al Catalyst

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High liquid yield is obtained when lignocellulosic biomass is processed by flash pyrolysis. This pyrolysis liquid, a renewable source also called bio-oil, has the advantage of being easier to handle than solid biomass thus improving its transportation. Steam reforming of bio-oil is an environmentally friendly way to obtain hydrogen as an energetic carrier or other synthesis gases as chemical raw materials.

As bio-oil suffers from ageing during storage an aqueous fraction is separated in order to improve its stability, thus improving hydrogen yield in the steam reforming process as well. The non soluble fraction consists of lignin derived compounds that can be used to produce highly valued fine chemicals, such as fenolic resins.

The catalytic steam reforming of model compounds of the aqueous fraction of bio-oil is studied in the present work. The performance of Ni/Ca-Al and Ni/Mg-Al catalysts in a fluidized bed reactor is compared and characteristics such as the mechanical strength to attrition are studied. On the other hand, the study is also focused on the influence of magnesium addition as a promoter that reduces the acidity of the support decreasing coke formation and modifying the nickel crystallite to improve its stability.

The experimental setup is described as follows: a one inch diameter quartz reactor is externally heated by an electric furnace. The reactor bed contains a mixture of sand and the Ni-based reforming catalyst. The catalyst is activated in a H_2/N_2 stream before steam reforming. The liquid flow (aqueous solution of model compound) is fed into the reactor by atomization. The exit product gas flow goes through a condenser system in which the excess steam and remaining organic liquids are retained. A Micro GC analyses the concentrations of gases: CO_2 , CO , CH_4 , C_2H_4 , C_2H_6 , C_2H_2 , N_2 and H_2 .

The results compare the effect of magnesium and calcium addition on coprecipitated nickel-alumina catalysts, gas yield and carbon conversion.

Studying the Conversion of Corn Fiber to Ethanol with TG/MS and Py-GC/MS Techniques

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According to the regulations of the European Union, 5.75% of all road vehicle fuel should be supplied from renewable sources by 2010. Biofuels cover a range of products from ethanol to biodiesel. The main challenge of biotechnology is the production of these fuels from renewable raw materials at low cost. At present, ethanol is the largest biotechnological product by volume. Sugar cane and corn are the dominant raw materials for bioethanol production. However, increasing fuel demands imply that the use of other feedstock materials will also be required in the future. Corn fiber, which is the residue of the corn wet-milling process, is also a potential substrate for bioethanol production [1]. It is produced in Hungary in large amounts, and is mostly used currently as a low protein animal feed product. However, it could be utilized for various other purposes, as well. A multi-step biotechnological process is available for the production of ethanol (from the starch and cellulose components of corn fiber) and corn fiber gum (corn fiber hemicellulose) [2,3]. This polymeric hemicellulose could be utilized as a new food gum, additive in plastics, dietary fiber, polymer for chemical and pharmaceutical applications, etc.

TG/MS and Py-GC/MS are frequently used in the analysis of lignocellulosic materials. The aim of our work was to find out whether these analytical techniques are applicable for monitoring the changes in the structure and composition of corn fiber in fiber processing to ethanol. Hence, the solid intermediates and products of the above biotechnological process have been studied. The destarched corn fiber has been pretreated using different alkali solutions in order to prepare a lignocellulosic substrate (pretreated corn fiber), which can further be utilized for cellulase enzyme and bioethanol production, and corn fiber gum. The chemical composition of the samples has been determined by the conventional methods.

Upon elimination of the starch fraction with amylolytic enzymes the relative amount of the other components of corn fiber increases, however, no significant changes occur in the structure of the feedstock material. This is in agreement with the fact that the starch fraction is only adhered to the corn fiber. On the other hand, the thermal behavior and the product distribution change considerably in the case of the pretreated samples compared to the destarched corn fiber. These observations imply that the alkali pretreatments result in significant compositional and structural changes. The precipitated corn fiber gums are considerably different from the variously treated corn fiber samples. The structure and composition of these polymeric hemicelluloses greatly depend on the alkali pretreatment applied prior to the precipitation step. The observed effects of the treatments are in good agreement with data determined with other analytical techniques.

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Decomposition of Levoglucosan in the Recovering Process from Cellulosic Biomass through pyrolysis

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Levoglucosan (1,6-anhydro- β -D-glucopyranose), which is a major pyrolysis product from cellulosic biomass, is a potential chemical for preparing value-added substances such as bioactive compounds and polymers. Usually high temperature $> 300^{\circ}\text{C}$ is required for the effective formation of levoglucosan from cellulose although it is also known that levoglucosan polymerizes at the temperature as low as 240°C . Accordingly, some decomposition reactions are expected in recovering levoglucosan from cellulosic biomass. Increased yield reported under vacuum conditions would be related to the stabilization against such decomposition. This paper deals with the decomposition of levoglucosan in the recovering process from wood and cellulosic materials.

A dual-space Pyrex glass reactor (Fig. 1) was used to study the influences of the pyrolysis of cellulose, hemicelluloses, lignin and wood on the levoglucosan recovery. Since direct interactions between levoglucosan and other samples are not allowed with this reactor, pyrolysis vapors from other samples interact with levoglucosan in vapor-phase and liquid/solid-phase after condensation around the reactor wall with lower temperature. In heat treatment at 400°C for 3 min under reduced pressure (30mmHg), levoglucosan (control) was completely evaporated and recovered almost quantitatively (97.4%). Under the influence of the pyrolysis of cellulose or lignin, levoglucosan recovery was reduced to 37.2% (cellulose) or 61.3-64.4% (milled wood lignins). Thus, levoglucosan itself is stable under the present heating conditions, while cellulose and lignin accelerate the levoglucosan decomposition. Interestingly, the influences of wood samples (Japanese cedar and Buna) were comparatively small (recovery: 91.0 and 82.9%, respectively). Although the action of the mixed sample of cellulose with lignin (2:1, w/w) was explained as sum of these influences, the addition of xylan (hemicellulose) to the cellulose-lignin mixture reduced the levoglucosan decomposition up to the level of the wood samples. These results indicate that hemicellulose masks the acceleration effects of cellulose and lignin on levoglucosan decomposition. In this paper, decomposition mechanism of levoglucosan in the recovering process from cellulosic biomass is also discussed.

Consequently, the levoglucosan formed from cellulosic biomass is decomposed in the recovering process, through the actions of cellulose- and lignin-derived pyrolysis products. In pyrolysis of pure cellulose, this decomposition is significant. This induced decomposition reduces the levoglucosan yield from cellulosic biomass.

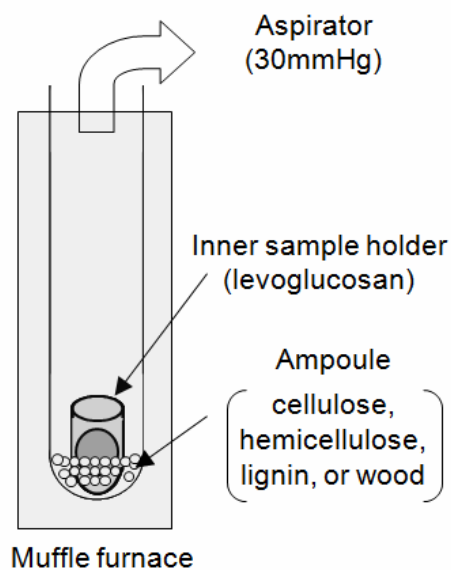


Fig. 1 A dual-space reactor.

Investigations into the pyrolytic behaviour of birch wood and its main components: primary degradation mechanisms, additivity and metallic salt effects

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Several factors may influence the thermal behaviour of biomass materials. The heating rate, the initial material composition (inorganic ions, constituents distribution, extractive compounds) are known to exert a great effect on biomass thermal degradation and these parameters could sensitively modify yields, composition, structure and other properties of the evolved products [1, 2].

It is important, for the determination of the pyrolytic behaviour and reaction pathways to analyse simultaneously the mass evolution and volatile compound profiles, during a thermal treatment. Consequently we report and discuss in this work the results of thermogravimetry (TGA) and thermal analysis-mass spectrometry (TA-MS) at low heating rate (10°C/min from 25°C to 500°C). The studied samples include: cellulose, xylan and lignin, their bi-constituents mixtures, birch wood and recomposed birch wood. In order to investigate the inorganic salt effects on the thermal behaviour, the pyrolysis of impregnated biomass main components, reconstituted biomass and natural biomass (with MgCl₂ and NiCl₂ - 1% in mass) were also studied.

Considering the large data sets collected (TG/DTG characteristics and selected MS ion intensities), principal component analysis (PCA) was used to provide a tool to simplify pyrolysis data interpretation. Moreover, additivity was evaluated through main component (same proportions as birch wood) thermal behaviours.

Our results clearly demonstrate:

- The non-additivity of the thermal behaviour of biomass samples (considering mass evolution, characteristic temperatures and produced volatile compounds).
- Specific compounds can be evidenced as representative for the thermal degradation of biomass components such as the syringol fragment for lignin pyrolysis
- Hemicellulose (xylan) has a particular behaviour among other biomass constituent polymers (as evidenced by the mineral influence and strong interactions with other constituents).
- Considering the biomass thermal behaviour, the mineral addition effect is more pronounced than main components interactions.

Finally, the primary mechanisms of the thermal degradation are discussed for single components, reconstituted biomass, and natural biomass (birch wood).

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Novel solvolytic approach of biomass pyrolysis: The lignin-to-liquid process

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The principal objective of our project was to provide the knowledge basis for the development of an industrial process for the *efficient conversion of wooden biomass into transportation fuel components*. Ethanol production alone from these feedstocks is at present not economically competitive as it exclusively uses the carbohydrate part of wood. The main challenge is to effectively convert the residual lignin fraction into either products that are suitable for use as fuels in existing motor technology or as other high value compounds. Utilising the concept of a biorefinery where all parts of the biomass feedstock are converted into value added products, is capable of turning the bio-fuel production from lignocellulose into an economically feasible approach for sustainable transportation fuels of the future [1].

Lignins from different origins have been used as input in a single pyrolytic (high pressure, high temperature) technique that simultaneously depolymerises the biomass and also significantly changes to elemental composition of the products with respect to the starting material [2]. The hydrogen/carbon ratio is increased while the oxygen/carbon ration is sharply decreased. This results in a favourable change in chemical and physical properties of the product which is compatible with conventional fossil fuels. To achieve similar conversions, existing processes exclusively apply multi-step techniques and mostly use hydro-upgrading with use of heterogeneous catalysts such as metal salts or zeolites. In our solvolysis reaction, however, a reactive solvent, which is an industrial bulk chemical, acts as hydrogen donor. It is used together with a co-solvent but without the addition of any catalysts. Problems like clogging of the catalyst surface therefore do not occur nor is solid char being formed. The solvent system has not been used in this context before and does not contain any aromatic structures like phenols, tetralin derivatives or agents known from coal liquefaction.

The immediate product is a two-phase system composed of an aqueous and an organic phase that are easily separated by decanting. The product oil contains a mixture of alkylated phenols and aliphatic hydrocarbons without any of the methoxy groups that are abundant in the source material [3]. The oils therefore show a significantly reduced amount of oxygen, are low viscous liquids which do not contain dispersed water. Elemental analyses show very low oxygen content. This provides the lipophilic character of the Lignin-to-Liquid product, which is miscible with unpolar organic solvents and petroleum. It contains deoxygenised, mostly monomeric degradation products of the natural polymer lignin. These findings will be supported by detailed information regarding methods, parameters and results of an extensive set of pyrolysis/solvolysis experiments, and possible reaction pathways will also be discussed. The products are analysed in terms of mass distribution (ESI), volatility (GC/MS), elemental composition (CHNS) and aromaticity (NMR).

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Pyrolysis-GC/MS of various acetylated wood types

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To improve the weathering stability of wood and especially the absorption of moisture chemical derivatization is widely used. In particular, acetylation with acetic anhydride [1] and isopropenyl acetate [2] was applied. The materials are used either as solid wood, in particle boards or wood polymer composites, but so far there is only little information on their pyrolytic behavior. Thus, we have analyzed six different types of acetylated soft- and hardwood and compared the pyrograms to untreated reference samples.

It was shown that besides the unspecific cleavage of acetic acid several marker compounds, such as acetylated lignin monomers and acetylated furan derivatives were released under pyrolysis conditions, which can be used to trace modified wood in complex composites (Figure 1). Besides the very few spectra presently found in libraries, we have identified several compounds as acetylated forms of lignin degradation products by interpretation of their mass spectra.

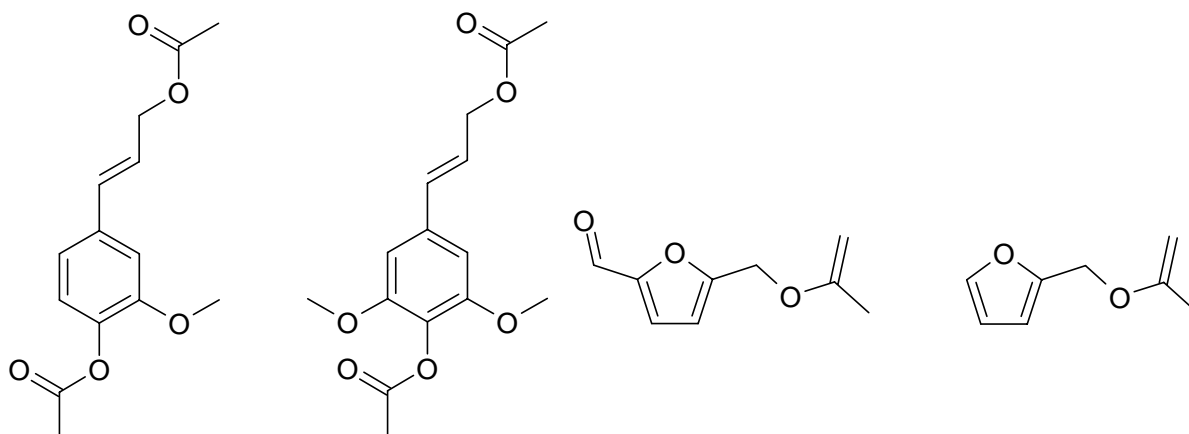


Figure 1. Marker compounds for the identification of acetylated soft wood lignin, hard wood lignin, and carbohydrates in wood samples.

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Kinetics Study by Thermogravimetry from Sugarcane Bagasse

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Biomass residues are abundant and offer many possible alternatives for practical utilization. A new generation of advanced thermal processes favoring the chemical and energy upgrading of biomass have been developing [1]. Pyrolysis seems to be a promising technology for conversion of agriculture residues. Sugarcane bagasse is a typical example of agricultural byproducts that is available in abundant quantities. In Mexico over 50 million tons of sugarcane is produced annually [2]. Kinetic study of biomass pyrolysis is of relevant importance because it constitutes the initial step of combustion and gasification process [3]. Pyrolysis kinetics of sugarcane bagasse has been investigated thermogravimetrically under dynamic and stepwise conditions at different heating rates of 1, 5, 10, 20 and 40 °C/min and in a wide temperature range 20-1000°C in N₂. Three stages of weight loss are observed, where the first two stages are overlapping. The results show that the onset temperature of mass loss is within 104-156 °C and the final reaction temperature is within 423-500°C. The average mass loss is 89.5 wt.%. There are three DTG peaks located at the temperature ranges of 135-309, 276-394 and 374-500 °C, respectively. The first two peaks might be associated with either with decomposition of the major components of the sugarcane bagasse, hemicellulose and cellulose or with different processes of cellulose decomposition. The third peak is possibly associated to a lignin. At a temperature of 460 °C, the expected amount of volatiles of this waste is within 85-89%. Friedman method and a differential parallel model were used for determinate the corresponding kinetics parameters. In this work, the yield coefficients of parallel models were examined to relate the component evolution. The knowledge of the kinetics for the thermal decomposition is needed for the design of pyrolysis reactors. Activation energies calculated were 110, 215, and 35 kJ/mol for the three stages. The total weight loss of each apparent reaction was 27 wt. %, 28 wt.% and 40 wt.% with a 5 wt.% of final residue. The simulation with the model agreed well with experimental data.

Key words: pyrolysis, kinetics, biomass, sugarcane, bagasse

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Pyrolysis of Orange Peel

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Through the last decades the fossil fuels consumption has been increased even that they are considered as one of the more important factors involved in the global warming. The worldwide scientist had been trying to generate alternatives in this topic, and the biomass, including agricultural or industrial wastes is one of them [1].

The aim of this work is to use the pyrolysis process in order to obtain information about an alternative approach of the orange peel and their potential as a source of valuable chemicals. TG analysis at 1, 5, 10, 20, and 40°C/min, suggest that there are three different overlapped steps. The main DTG peaks are located at 213, 326 and 420°C and the average mass loss is 80 wt.% within the temperature range of 114-569°C.

The bench scale experiments were carried out in a semi batch pyrolysis reactor with controlled temperature rate of 40°C/min and nitrogen flow of 100 ml/min. The average yields of the products were 53.1, 21.1 and 25.8 wt % for bio-oil, char and gases, respectively. The pyrolysis bio-oil was collected in a condensation train using iced water, limonene and liquid nitrogen baths and then characterized by GC/MS. The method used was dynamic in a HP-1 capillary column and helium UHP as carrier gas. The identified compounds include alcohols, phenols, BTX and carboxylic acids. The limonene was also collected through the pyrolysis and quantified by GC/MS.

Keywords: biomass pyrolysis, orange peel, bio-oil, pyrolysis oil.

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Pyrolysis of Textile Wastes II. Product Distribution

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The recent efforts in order to avoid land filling led to an opportunity to change the target to alternative process of solid waste treatment. The content of textiles in the Mexican MSW is around 2% they representing an important source of energy and materials taking in the view of their main cellulosic composition (cotton basis) and gross heating value of about 7,500 Btu/Lb ²[1].

Thermal behavior of textile waste was studied by thermogravimetry at different heating rates and also by semi-batch pyrolysis and the products were characterized. It was shown that the onset temperature of mass loss is within 104-156 °C and the final reaction temperature is within 423-500°C. The average mass loss is 89.5%. There are three DTG peaks located at the temperature ranges of 135-309, 276-394 and 374- 500 °C, respectively. The first two might be associated with either with decomposition of the hemicellulose and cellulose or with different processes of cellulose decomposition. The third peak is possibly associated to a lignin. At a temperature of 460 °C, the expected amount of volatiles of this waste is within 85-89%.

Bench scale pyrolysis tests at various temperatures were carried out. A system consisting of a bench scale batch reactor with a condensation train was used to collect the pyrolysis products. Textile pyrolysis results in 87.5 wt. % total weight loss, of which 31.5 wt. % is light liquid fraction, 42.5 wt. % is heavy liquid fraction, 13.5 wt.% are non-condensable gases and 12.5 wt.% is solid residue. Substituted aromatics such as toluene and xylenes (determined by GC/MS analysis) are the major products produced. The solid residue was analyzed and characterized for elemental composition, surface properties and calorific value. Char was formed with H/C ratio of 0.615 at 700°C temperature. The solid residue produced at 700°C has a high calorific value of about 38 MJ/kg with a surface area of 80 m²/g.

Keywords: Textile Pyrolysis; product analysis; cotton waste, GC/MS.

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Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin) Part IV. Structure elucidation of oligomeric molecules

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Fast pyrolysis of biomass is an advanced, promising technology for the production of liquids (bio-oils) to be used as renewable energy carriers via combustion in boilers, diesel engines, and gas turbines or via partial oxidation (gasification) in entrained flow gasifiers in biomass-to-liquids (BTL) processes. In addition, bio-oils can serve as source for various "green" chemicals (e.g. aldehydes, phenols, organic acids).

The quality, chemical stability, and application of bio-oils is very much dependent on their chemical composition [1]. In contrast to the monomeric constituents, which are well known to a great extent, the oligomeric part (pyrolytic lignin) is much less understood but contributes substantially to the bio-oil properties [2]. In our previous papers results from innovative analytical methods such as GPC, MALDI-TOF-MS and Py-FIMS were used to describe mainly the overall molecular weight distribution.

This paper deals with results from other analytical tools to get insight into the molecular architecture of pyrolytic lignins by use of wet chemical methods for functional group analysis, FTIR, ¹³C-NMR, and Py-GC/MS [3].

The results from each method were evaluated and summarized to finally derive for the first time ever structural proposals for dimeric up to octameric constituents. As an example, the structure of an octamer is presented in Figure 1.

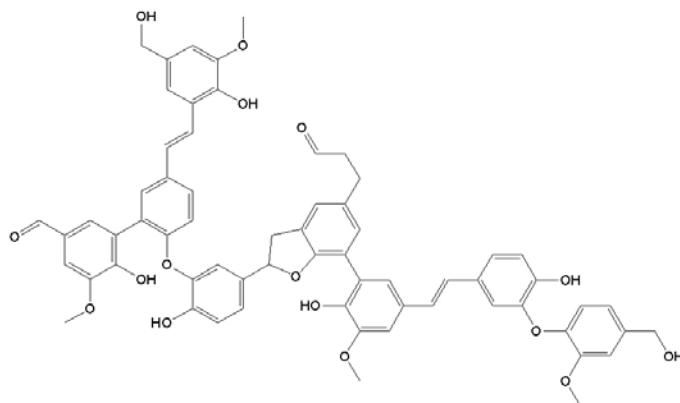


Figure 1. Octamer ($C_{64}H_{56}O_{16}$) of pyrolytic lignin with the mass of 1080 Da. The structure consists of stilbene, phenylcoumaran, biphenyl, and diphenylether.

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Identification of excavated black lacquer resin by pyrolysis-gas chromatography/mass spectrometry

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Lacquer sap is collected not only in Japan and China but also in Southeast Asia for manufacture of lacquer ware. However, the kind of lacquer tree depends on the region in which it was grown, and the lacquer saps of different trees are different.¹ Lacquer trees that grow in Japan and China belongs to *Rhus vernicifera*, and urushiol (MW=320) is the main component. On the other hand, laccol (MW=348) is the main component of the sap of *Rhus succedanea*, which grows in Vietnam and Taiwan, and thitsiol (MW=348) is the main component of the sap of *Melanorrhoea (Gluta) usitata*, which grows in Thailand and Myanmar². In order to study the history and use of the valuable ancient objects made of lacquer resin, identification of the kind of lacquer is important.³ In this study, a piece of black lacquer resin in “Shijiko” style (pottery with four ears) excavated from 17th century ruins in Kyoto, Japan, was analyzed by Py-GC/MS, and the result was compared with the standards of natural lacquer film to determine the origin of the lacquer. It was confirmed that the lacquer resin was made from lacquer sap of *M. usitata*. In addition, the use of the excavated black lacquer is discussed.

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Impact of Potassium and Phosphorus on the Physicochemical Properties of Biomass-Derived Fast Pyrolysis Liquids (Bio-oil)

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Biomass processing via thermal conversion has been investigated for many years as a source of renewable gaseous, liquid and solid fuels. Fast pyrolysis is one of the three main thermal processes, with combustion and gasification, providing a valuable product – bio-oil. This *clean* liquid can be used as an intermediate for a wide variety of applications (fuels, chemicals) [1].

In this work, short rotation willow coppice (SRC) has been investigated for the influence of potassium and phosphorus on its pyrolysis behaviour and physicochemical properties of bio-oils obtained from fast pyrolysis experiments. The willow sample was pre-treated by hydrochloric acid to remove inorganic constituents (salts and metals) [2]. The demineralised samples were impregnated with potassium (2 wt. % K as potassium acetate) and phosphorus (2% wt. % P as *ortho*-phosphoric acid). Feedstock characterisation was performed by thermogravimetric analysis (TGA) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). A comparison of product distributions and kinetics are reported. This work also describes an analytical approach (liquid-GC-MS) to determine the chemical composition of generated biomass-derived liquids during fast pyrolysis experiments.

For both potassium and phosphorus impregnated biomass the yields and distribution of pyrolysis products have been influenced by the presence of the catalyst. Potassium catalysed pyrolysis has a profound influence on the char formation stage; generally increasing the char yields. Potassium catalysis has a significant influence on cellulose decomposition markers, not just on the formation of levoglucosan, but also other species from the non-catalysed mechanism, such as 3,4-dihydroxy-3-cyclobutene-1,2-dione. Phosphoric acid has a profound influence on saccharides content in volatile products – increases the yield of anhydrosugars (i.e.: levoglucosenone; 1,6-anhydro- α -D-galactofuranose) and dianhydrosugars (e.g. 1,4:3,6-dianhydro- α -D-glucopyranose). In summary acid or base catalysts can significantly change the reaction chemistry that is occurring in the fast pyrolysis process. It is likely that future advances in understanding the reaction mechanism will help improve the reaction chemistry further and make catalytic fast pyrolysis an efficient reaction for bio-fuel and chemicals production.

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Thermo-t technique: A potentially attractive method for upgrading the quality of oils derived from biomass pyrolysis

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In order to improve the quality of bio-oil obtained from the pyrolysis of biomass, a technique known as ‘Thermo-t’ has been developed. High water and oxygen content in oil derived from biomass have been major drawbacks for its utilization as fuels. While simple azeotropic separation method can be used effectively to remove water from bio-oil, the problem of high oxygen content remains. It therefore constitutes the primary reason for differences seen between hydrocarbon fuels and oil derived from biomass pyrolysis because of chemical instability of the oil hence its susceptibility to unwanted oxidation reactions [1, 2]. In this recent study, pyrolysis of biomass was performed at different temperatures between 460 – 540°C to generate bio-oils which contained up to 35wt% oxygen. More than 76% of the oxygen contained in the oils was removed upon further treatment using the ‘Thermo-t’ technique. Significant change in the higher heating value (HHV) of the oils was also observed which increased by nearly 30%, and strongly compares with about 42MJ/kg obtainable from a conventional hydrocarbon crude oil. Furthermore, preliminary results from more tests currently suggest that water contained in bio-oil may not all be detrimental, instead, if reduced to the right amount, can beneficially contribute towards improvements in the overall quality of oils derived from biomass pyrolysis.

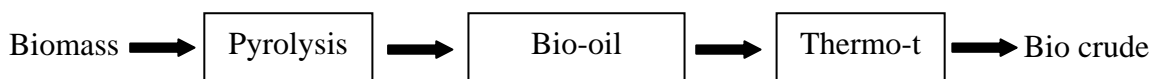


Figure 1. Summary of experimental protocol for production of improved quality bio-oil.

Keywords: Pyrolysis, Biomass, Bio-oil.

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An investigation of synthetic fuel production From Tea waste

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Contrary to the assumption that fossil fuels are the principal sources of fuels and organic chemicals, biomass in the last decade is recognized as a potential and important renewable source of energy and chemicals. Due to the negligible sulfur, nitrogen and metal content, the utilization of biomass would mean recycling mobile carbon compared to the mobilization of fixed carbon resulting from the combustion of fossil fuels [1].

Developing countries tend to have economies largely based on agriculture and forestry. Agricultural waste is one form of biomass which is readily available but is largely not utilized in energy recovery schemes [2]. Turkey is one of world's important tea producers after China, India, Sri Lanka, Kenya, Indonesia, and Vietnam. Tea plantation covers 70,000 hectares in Turkey. Tea plants (*Camellia sinensis* of the family Theaceae) are commonly grown in the Eastern Black Sea region of Turkey and 150 000 tones black tea is manufactured per year. The factories around Eastern Black Sea produce about 30,000 tones of waste annually. These wastes are not used for any purpose and stored in depository area [3].

In this study, production of synthetic fuel (bio-oil) from tea waste was investigated via rapid pyrolysis. Tea wastes were selected as a biomass source, effects of pyrolysis temperature, heating velocity, sweeping gas velocity on pyrolysis product yields and compositions were investigated in a tubular reactor. The maximum bio-oil yield was attained as % 30.40 at 500°C with a heating rate of 500°C/min and nitrogen flow rate of 200 cm³/min. Bio-oil obtained at the optimum conditions was separated into aliphatic, aromatic and polar sub-fractions by adsorption chromatography. After column chromatography, bio-oil and its fractions were subjected into elemental analysis, FT-IR spectroscopy. Aliphatic sub-fraction of bio-oil was analyzed by GC-MS. While comparing the H/C ratios, H/C ratio of bio-oil was very close to that of crude oil.

Keywords: Tea waste, Rapid Pyrolysis, Synthetic fuels.

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On and off-line oxidative PY-GC/MS studies of vegetable oils from Macauba fruit

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Since the advent of energy crisis, increasing emphasis has been placed on exploring the possibilities of recovering energy from solid wastes. In the light of this view many studies of biomass as renewable energy source have been initiated during the past two decades¹. Biomass is the only renewable source of raw material available to the chemical industry and represents the only long-term source of carbon². The chemistry of oxidative degradation is complex. Some assays rely on the measurement of effects on the sample caused by oxidation process, such as increase in weight by scission or cross-linking formation of conjugated carbonyl structures that leads to yellowing, or loss of weight by production of volatile decomposition products³.

Here we report studies which were performed to investigate the influence of some parameters such as pyrolysis time and temperature of the pyrolytic process, upon the mechanism of oxidative pyrolysis of oils from Macauba fruit. Furthermore, it was investigated how on and off-line system affect the yield and the pyrolysate composition. The on-line oxidative pyrolysis experiments were performed using a filament pyrolyser coupled to a GC/MS using a flash pyrolysis procedure. The off-line experiments were carried out using a DTA equipment coupled to a especially designed apparatus used to collect the pyrolysate material which was emerged in liquid nitrogen. Afterwards, this material was washed with CH₂Cl₂ and MeOH, the volume was reduced by nitrogen flow, the sample was redissolved in CH₂Cl₂ and injected in a GC/MS. GC/MS data acquisition was carried out using EI mode. PCI was also used and NH₃ was the gas reagent. Tripalmitic standard was used as pattern to foresee the profile that could be waited when the oils were submitted to the pyrolytic process under oxidative atmosphere. The presence of different classes of compound present in the pyrolysates was confirmed using the total ion chromatogram (TIC) and selected ion mass chromatogram (SIMC) analyses, in addition to fragmentation patterns and library matching (NIST). Identification was carried out according to pre-established criteria for the analysis of the data.

Different profiles were obtained, when on and off-line oxidative pyrolysis, were performed which can be explained by some factors: (i) temperature rate ;(ii) contact time between sample and volatiles constituents under oxidative atmosphere; (iii) how the pyrolysate was generated. The oxidative pyrolytic process generated a very complex mixture of different classes of compounds such as carboxylic acid, aldehydes, alcohols, alkenes, and alkadienes. The main differences in the yield products were the presence of γ -lactones detected only as product in the off-line pyrolysis. Furthermore, on-line flash pyrolysis does not favor the extent of the oxidative pyrolytic process because it yielded to carboxylic acids which were not detected in off-line pyrolysis. Significantly changes were observed in the yield products when any of the parameters investigated were changed

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Effect of Natural Zeolite on Flash Pyrolysis of Sewage Sludge

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Zeolites are aluminosilicate minerals with rigid, 3-dimensional crystalline structure consisting of a network of interconnected cavities. The framework aluminum and silicon are bound to each other through shared oxygen atoms. The SiO₄ units are neutral but the AlO₄ results in a net negative charge. This negative charge is balanced by mobile cations that are present during the formation.

Mobile cations and water molecules present in the structural framework of zeolite can be exchange to other cationic species, such as heavy metals in ion-exchange process. Another special aspect of this structure is that the pore and channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve.

Many other applications of natural zeolites are known. Natural zeolites are used as catalysts for example during refining of crude oil. Pütün reported positive effect of natural zeolite on bio-oil yield during pyrolysis of cottonseed cake [1]. Miskolczi reported positive effects of clinoptilolite on composition of bio-oil and temperature of thermal degradation of polyethylene and polystyrene [2].

The zeolite under investigation in our study is a natural Slovakian zeolite clinoptilolite with empirical formula: (Ca, K₂, Na₂, Mg)₄Al₈Si₄₀O₉₆·24H₂O. Sludge used in our experiments was special treated dried excessive activated sludge from wastewater treatment plant Pardubice.

Effect of this natural zeolite on flash pyrolysis of sewage sludge will be discussed in this presentation. The cracking mechanism of sewage sludge over natural catalyst clinoptilolite was investigated by TGA, TG-FTIR and pyrolysis GC-MS. Influence of dose and pretreatment procedures of natural zeolite – as calcination and acidification on flash pyrolysis were also investigated.

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Carbonisation of biomass - from pyrolysis to hydrothermal procedures

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The usage of fossil fuels (coal, oil, gas) as main source for energy and material has major drawbacks such as limited resources or its contribution to global warming. Hence the focus is shifted towards renewables and biomass. Dry biomass consists of ca. 75 % carbohydrates, ca. 25 % lignin and trace components (fats, oils, proteins, inorganic salts) resulting in a relative low energy density. The energy density can be increased by releasing water and/or CO_x through different strategies. Pyrolysis in inert atmosphere at temperatures above 500°C leads to carbonaceous residues. Pyrolysis is unfavourable due to its high energy requirements when applied to wet biomass. Water-rich biomass can directly be processed in water as reaction medium. One strategy targets at the gasification to H₂ and CO₂ at temperatures around 600°C and 250 bar [1]. In this process biomass is liquefied at temperatures between 200 and 360°C and pressures of 100 to 200 bar to gain an energy rich "biocrude" [2]. In case of the Hydro Thermal Carbonisation technique (HTC) biomass is converted at temperatures between 180 and 200°C (10 and 16 bar) at reaction times of around 12 hours and in presence of citric acid as catalyst to a solid, coal-like product [3].

The objective of this study is to gain deeper insights into the HTC process. The experiments are carried out isothermally in a commercial lab autoclave. Reaction times between 2.5 and 12 h are applied and temperature is varied from 180 to 240°C establishing the respective vapour pressure. Untreated straw as model biomass has been applied. Miscellaneous catalysts in different concentrations (citric acid, H₂SO₄ and NaCl) are tested. Intermediate reaction products in the liquid and the gas phase are characterised by means of GC-MS. The solid residue is examined by DSC (Differential Scanning Calorimetry), elementary analysis and specific surface area. With the help of GC-MS studies high amounts of furan species as intermediates are identified indicating dehydrating reactions of cellulose. Catalysis by H₂SO₄, reaction temperatures from 220 to 240°C and shorter reaction times (2.5 h) seem to be sufficient for mid-calorific residual products with lower heating values (LHV) of ca. 22 MJ/kg (LHV of untreated straw is ca. 12 MJ/kg). Elementary analysis shows a C:H:O ratio of 4:3:1, corresponding to a carbon recovery of 60 % of initial carbon mass. Applying NaCl as catalyst formation of cyclohexene-derivatives is pronounced indicating enhanced dehydrating reactions. Moreover, LHV of NaCl catalysed reaction residue is comparable to the one of H₂SO₄ catalysis. For comparison straw is pyrolysed in a thermobalance. Gaseous products are condensed and analysed by GC-MS. Pyrolysis shows a different product spectrum (mainly acetic acid) in the gas phase compared to HTC pointing at different reaction steps.

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The Production of Fuels and Chemicals from Macroalgae by Pyrolysis

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The pyrolysis behaviour of a number of brown seaweeds (macroalgae) has been investigated and the influence of inherent mineral matter on product yields and composition before and after demineralisation. Brown seaweeds contain significant proportions of alkali earth metals halogens and a range of trace heavy metals [1]. Pretreatment to demineralise the algae has been performed in both water and dilute hydrochloric acid. UK based *Laminaria* and *Fucus* species such as *L. digitata* and *F. vesiculosus* are compared with a tropical seaweed *Macrocystis pyrifera*. The pyrolysis behaviour has been studied using thermal gravimetric analysis (TGA) and Pyrolysis-GC-MS. Total mineral matter has been determined using ICP-MS before and after pretreatment. The fate of the mineral matter, halogens, heavy metals and heteroatoms during pretreatment and pyrolysis has been investigated. The pyrolysis oil at 500°C includes a range of furan derivatives and linear chain alcohols. There is also a significant amount of nitrogen containing compounds such as pyrroles and indole derivatives.

The main sugar structural unit appears to be di-anhydro mannitol. Pretreatment appears to exert a significant effect on pyrolysis behavior and significant differences are observed after mineral matter is removed. The pretreatment schemes investigated can remove a significant proportion of the alkali earth metals and halogens although can also extract some organic material. Pretreatment affects char yields and influences the nature of the char. There appears to be potential for the production of fuels and chemical from macroalgae by pyrolysis although the reduction of mineral matter and halogens by pretreatment maybe advantageous. There is also evidence that the mineral matter is exerting a catalytic influence on pyrolysis behavior.

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Pyrolysis of agricultural residues from rape and sunflower. Production and characterization of bio-fuels and biochar soil management

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Biomass sources, such as agricultural residues, are good precursors for the production of bio-oil, bio-char and gas fuels. These new and renewable fuels are the major alternatives to conventional fossil fuels (Demirbas, 2006). Pyrolysis is the most important process among the thermal conversion processes of biomass, which consists of heating the material in absence of air to produce liquid, solid and gaseous products. Rape and sunflower are one of the most commonly cultivated plants worldwide, and an important source of biodiesel technology.

Materials. Rape and sunflower are carbon and oxygen rich feedstock, containing hydrogen at a low ratio and trace amounts of nitrogen and sulphur. The volatile matter content is quite high, rape contains 78.7%, 14.02% fixed carbon and 7.28% ash. The lower heating value is 15.3 MJ/kg. Sunflower contains 74.5% volatiles matter, 17.22% fixed carbon and 8.28% ash. The lower heating value is 15.6 MJ/kg.

Experimental. Pyrolysis was carried out in a reactor; a quartz tube 40 cm long with a diameter of 7 cm placed in an electrically heated horizontal oven. A 30 g sample was pyrolyzed. Pyrolysis conditions were: heating 30°C/min, temperature to 550°C and He flow 100 mL/min.

Product yields. Under the process conditions fixed the yields were: 34% bio-oil, 25% bio-char and 41% gas for rape and 30% bio-oil, 36% bio-char and 34% gas for sunflower.

Characterization of the gases. The main components of the gas samples are H₂, CO, CO₂ and CH₄. In the pyrolysis process the heavier hydrocarbons are cracked, giving rise to lighter ones, methane and hydrogen, those of greatest interest as their heating values are higher.

Characterization of the bio-oil. Bio-oil is a carbon rich oxy-fuel containing a small proportion of nitrogen and trace amounts of sulphur. Bio-oil can be an alternative for heating fuel. The low sulphur content of bio-oil is a very important advantage (Özçimen, 2004).

Characterization of the Biochar. It is effective in retaining some nutrients and keeping them available to plants. The biochar from rape contains 0.76% N, 0.36% P₂O₅ and 4.40% K₂O and for sunflower the contents: 1.19% N, 0.44% P₂O₅ and 7.26% K₂O. The biochar persistence in soil is also important related with any other form of organic matter applied to the land.

Conclusions

The composition of the pyrolysis gas makes it suitable for use as a fuel, given the concentration of light hydrocarbons and hydrogen, and its heating value.

Bio-oil, with its very low sulphur content, may be considered from the point of view of environmental as a potential alternative to fuel-oil.

Biochar may be evaluated as an amendment to improve soil fertility and nutrient retention.

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Thermal Decomposition Study on *Jatropha curcas* L. Waste using TGA and Fixed Bed Reactor

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In this research, pyrolysis experiments on *Jatropha curcas* L. (physic nut) waste were carried out using thermogravimetric analysis (TGA) and a fixed-bed quartz reactor. The objective of this research is to investigate the effect of temperature and holding time on product distribution. It was found that the main thermal decomposition of physic nut waste generally occurred over the temperature range of 150-450°C. From the observed decomposition profile of physic nut, the parallel reaction kinetic model was applied for simulating the degradation of this waste. The three parallel reaction model agreed relatively well with the experimental data. From the model, the activation energy of hemicelluloses, cellulose and lignin were in the range of 60-150 kJ/mol, 185-235 kJ/mol and 90-150 kJ/mol, respectively. Reaction orders of those fractions were in the range of 2.35-3.50. The results from pyrolysis process using fixed-bed reactor indicated that raised in temperature and hold time lead to an increase in the production of hydrogen gas, methane gas and light hydrocarbons with highest gas production detected at 900°C. Tar (liquid oil) decomposes at higher temperatures results in lower liquid yield while gas yield and total conversion increase. Liquid oil consists of several fatty acids such as palmitic acid, stearic acid, oleic acid and linoleic acid. Their contents were in the range of 10-23 % for palmitic acid, 5-12% for stearic acid, 35-42% for oleic acid, and 29-38% for linoleic acid, respectively. The amount of char residue decreased with increasing reactor temperature and hold time. Analysis of char indicated that fixed carbon yields increase with temperature with the expense of volatile matter while there is little change on ash content.

Synthesis Gas Production during Thermochemical Conversion of Glycerol Waste in a Fluidized Bed Reactor

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Glycerol waste from production of biodiesel was subjected to decomposition under substoichiometric conditions in this study. The waste, also called crude glycerol, is a by-product of transesterification reaction between palm oil and methanol using KOH as a catalyst. Due to contamination generally occurred during production process, crude glycerol must go through expensive purification if it is to be reused as chemical feedstock. Thermochemical conversion of this waste would eliminate the need for costly treatment while producing value added fuel products. The experiment was carried out in a laboratory scale fluidized bed quartz reactor having ID of 5 cm and height of 120 cm with alumina ball as fluidizing medium. Crude glycerol was continuously sprayed from the top of reactor at the rate of 10 g/min. Oxidizing gas containing O₂ and N₂ was supplied to the reactor at air to fuel ratio of 0.0-0.8. The heat supply by electrical furnace was regulated to achieve desired reaction temperature of 700-900°C. Similar runs were also conducted using chemical grade glycerol in order to obtain base line information of this conversion process. Produced gas was passed through series of gas cleaning units and analyzed by dedicated online CO, CO₂, C_xH_y, and H₂ analyzer. Tar and char deposited in condensers and bed of reactor were collected for further examination. Gas analysis data indicated that major gas species for reaction at these temperatures are CO, CO₂, C_xH_y, and H₂ with concentration range on inert and oxygen free basis of 22.7-28.0, 8.4-27.8, 16.8-31.9, and 32.3-33.2 vol.%, respectively. Production of carbon-containing gas species greatly varied with availability of oxygen in feed stream while amount of H₂ was relatively constant. The ratio of H₂ to CO and relatively small amount of CO₂, except run at low temperature, suggested that the product gas would be fit for further production of methanol, an important reactant for biodiesel production. In practice, this means that glycerol waste would be suitable for ultimately converted to methanol via gasification and close the chemical recovery cycle of the biodiesel production process.

Thermal Characterisation of the Products of Wastewater Sludge Pyrolysis

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Due to industrialisation and urbanisation, production of wastewater sludge is increasing rapidly worldwide and this is expected to continue in the future. Consequently, disposal of wastewater sludge has become one of the main concerns for the modern society. The common disposal methods are farmland applications, land filling and incineration but none of these methods remove risk of contamination completely. Pyrolysis of wastewater sludge is receiving attention as an environmentally acceptable alternate management route. The products of pyrolysis are bio-gas, bio-oil and a carbonaceous charcoal residue, which can potentially be used as agricultural fertiliser. The aim of this work was to characterise the fundamental properties of the products of wastewater sludge pyrolysis and determine if the pyrolysis process can be energy neutral.

In this study wastewater sludge samples from different origins, including domestic, commercial and mixed sludges, were applied. All samples were pyrolysed at a heating rate of 10°C/min in a fixed bed reactor. The major gas species of pyrolysis, CO, CO₂, CH₄, C₂H₄, C₂H₆ and H₂, were monitored with gas chromatograph. Among the released species, hydrocarbons comprised half of the bio-gas fraction (50%) which suggests high potential for energy recovery through their combustion. Thermal properties of sludge samples were investigated using computer aided thermal analysis technique. The results showed that the energies required to pyrolyse wastewater sludge samples from room temperature to the carbonisation temperature of 550°C varies according to the source and origin of the wastewater sludge and ranged from 1181 kJ/kg for the domestic to, 731 kJ/kg and 860 kJ/kg for the commercial and mixed sludges, respectively. This study confirmed that in case of the commercial and mixed sludge samples, the recoverable calorific value from stoichiometric combustion of the pyrolysed bio-gas is sufficient enough to self-maintain the pyrolysis process. In case of the sample from domestic origin, the recoverable energy from combustion of the bio-gas compounds was lower than the energy required to heat the sample to the temperature of carbonisation. To pyrolyse this sample, excess energy will be required, possibly through combustion of the bio-oil fraction.

Comparison on Generation Principle of Carbon Monoxide Concentration in Pine Combustion between Plain and Altiplano Regions

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Abstract: Experiments on carbon monoxide generation principle of pine which has been widely used in the historical buildings in Tibet were conducted in a combustion cabin in high-altitude-region Lhasa and low-altitude-region Hefei respectively. Three pine samples with different sizes were adopted. The surface temperature and CO concentration under radiative heat flux of 42 kW/m^2 were measured. The effect of oxygen quantity and pressure on carbon monoxide production were analyzed. It was found from the experimental results that carbon monoxide generation had the same trend in both districts; it was first steadily released to a peak value, subsequently descended to a constant value, and then increased to a second value and decayed in the end. Comparing with those in Hefei, the two peak values and the steady value of carbon monoxide concentration in Lhasa were higher, and also, the time to them was much later. The main reason is that the quicker increasing temperature in lower-oxygen condition in Lhasa accelerated the incomplete oxidation of unburned hydrocarbons. Additionally, low mixing rate of volatile component and oxygen under the condition of low oxygen quantity and the ambient pressure was in favor of incomplete combustion of pine and therefore carbon monoxide production.

KeyWords: low oxygen quantity and low ambient pressure; pyrolysis; carbon monoxide concentration; gas phase combustion; hydrocarbon oxidation.

Catalytic conversion of biomass pyrolysis vapours over synthetic Zeolites

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Pyrolysis liquids cannot be used as transportation fuels directly without prior upgrading due to their high oxygen (40-50 wt%) and water content (15-30wt %) and the low H/C ratios. Hydrotreatment and catalytic cracking are the convenient methods for upgrading of the bio-oil. Catalytic pyrolysis is also a promising way to improve bio-oil quality such as removal of oxygen, increasing calorific value, lowering the viscosity and stability. There are many advantages of catalytic pyrolysis (in-bed mode) such as elimination of costly condensation and re-evaporation procedures in comparison with upgrading [1,2].

In this study, corn stalk, selected as raw material, pyrolysed in a fixed-bed tubular reactor with and without catalyst. The optimum pyrolysis conditions giving the highest liquid yields (29.79%) were determined as, pyrolysis temperature of 500 °C, sweeping gas flow rate of 400 cm³min⁻¹ and heating rate of 500 °Cmin⁻¹. Catalytic pyrolysis was applied using catalysts such as ZSM-5, HY and USY (10% of raw material weight) with in-bed mode at the optimum conditions. The highest liquid yield was obtained as 27.55 % with ZSM-5 catalyst. Various spectroscopic and chromatographic methods were applied for characterization of bio-oils such as elemental analysis, column chromatography, GC-MS and ¹H-NMR spectroscopy. Specifications of bio-oils and their substitution as a conventional fuel were investigated.

Keywords: Catalytic pyrolysis, bio-oils, upgrading, corn stalk.

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Upgrading of volatiles evolved during the Olive residue Pyrolysis in a two-stage fixed bed reactor

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Pyrolysis oils are complex mixtures of organic compounds that exhibit a wide spectrum of chemical groups, and generally contain some water. Their direct use as conventional fuels may present some difficulties due to their high viscosity, poor heating value, corrosiveness and instability. The upgrading of pyrolytic oils, a necessary process before using as a regular fuel, essentially involves the removal of oxygen. Hydrotreatment of bio-oil is a way for removal of oxygen. This operation requires high pressure, metallic catalysts such as Co/MoS and hydrogen donor solvents. On the other hand, a significant upgrading can be achieved by using cracking catalysts (zeolites, silica-alumina, etc.) [1]. The low pressure, zeolite catalytic upgrading of biomass pyrolysis oils is receiving increased attention as a means of converting the highly oxygenated oils into an aromatic, low viscosity premium fuel [2].

Pyrolysis of biomass is a promising way to produce bio-oil and fine chemicals. In this study, olive residue is selected as the biomass source. Turkey is an important olive producer of the world. Annually, about 1 million tons of olive is used in olive oil production and approximately 450,000 tons of olive residues are revealed. The lower calorific value of this residue is about 12.5-21 MJ/kg. It is high enough to compare with the calorific values of wood and lignite, which are 17 and 22 MJ/kg, respectively. Because of having higher calorific value and being abundant, olive residue is an inevitable biomass source in Turkey.

Rapid pyrolysis of olive residues was studied in a fixed-bed reactor under various conditions in one of our previous study. Reaction time of 5 min., pyrolysis temperature of 500 °C, heating rate of 500 °C min⁻¹, and particle size range of 0.85>Dp>0.425 mm to reach maximum bio-oil yield (46.72 %) were found to be the optimum conditions [3]. In this study, a catalyst bed was connected to the rapid pyrolysis reactor to improve the bio-oil quality. In other words, it was aimed to evaluate the performance of different types of zeolites (Natural zeolite (NZ), ZSM-5, H-Y) on the upgrading of the pyrolysis vapours in a dual system. In addition, the effects of catalyst type, selectivity on the distribution and composition of the products were investigated. The performance of the catalyst in terms of hydrocarbon formation (including aliphatics and aromatics) was investigated. The results were compared with those obtained with synthetic zeolites. Overall, this research was under taken to explore the value of upgrading as a technology to be a good alternative for cracking units in bio-refineries.

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Pyrolysis and Smoke Formation of Grey Alder Wood Depending on the Storage Time and the Content of Extractives

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With increasing amounts of industrial production of foodstuffs, also their quality control becomes more stringent. Smoked products must correspond to the standards specified in EU regulations. Special attention is paid to the content of carcinogens in foodstuffs. For smoked products, such an indicator reflecting the content of polycyclic aromatic hydrocarbons (PAH) is benzo(a)pyrene (B(a)P). The study of the chemical composition of the smoke obtained at different regimes is urgent owing to the objective of producing smoke, not containing carcinogenic hydrocarbons, as well as developing the composition of the liquid smoke, designed to impart a wood smoke flavour and taste to foods.

Grey alder (*Alnus incana* (L.) Moench) wood is the main fuel feedstock in the Baltic States and Russia, used for smoking of meat and fish. The quantity and composition of grey alder wood extractives were investigated, and, by the Py-GC/MS method, the regularities of the change in the composition of volatile products of wood pyrolysis depending on its storage time and different methods for preparing for pyrolysis have been established.

It has been shown that the quantity of the substances extracted with cold and hot water from wood does not change upon its storage during 3 years. However, in the extracts' composition upon the 3-year storage of wood, the concentration of monosaccharides grows 1.4 times.

It has been found that the content of acids and esters as well as ketones and lactones decreases and the content of aldehydes, saccharides and lignin derivatives increases in the composition of volatile products of pyrolysis of wood stored during 3 years and extracted with hot water, in comparison with freshly-cut wood.

Experiments on the isothermal smoke generation were carried out using a laboratory smoke generator at the temperature 400°C, retention time of wood in the hot zone 96 sec and the air supply factor $\alpha = 0.2$. The intensity of the formation of PAHs was determined. Their amount in smoldering condensates has been assessed from the B(a)P concentration. Wood of different storage time prior to and after extraction with water was investigated. Based on the results of GC/MS analysis of the composition of monomeric products soluble in dichloromethane and water, conclusions were made on the effect of the storage time and the content of extractives on the concentrations of both aromatisers and carcinogenic PAHs in primary condensates of the smoldering smoke.

SESSION 3 FUNDAMENTAL STUDIES:
Kinetics & Mechanisms of Pyrolysis

Kinetic reduction of mechanisms of complex pyrolytic reactions

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Detailed reaction mechanisms are available for the description of the pyrolysis of many compounds. These mechanisms may consist of hundreds of species and thousands of reactions. Thus, it is essential to reduce these mechanisms before being able to simulate mixtures of hydrocarbons. Three methods of reduction were developed and validated by comparison of the results of simulations obtained starting from the mechanisms reduced with those coming from the detailed mechanisms. In the first method (Type I), the isomers of the radicals are amalgamated, which strongly decreases the number of species and consequently the number of reactions; this is a lumping of chemical species. The second method (Type II) produces a generic mechanism where the reactions are globalized by family; the maximum degree of reduction is thus obtained, this is a lumping of chemical reactions. Lastly, in the third method (Type III) all the chains of propagations are replaced by their stoichiometric equations which eliminates all the radicals, this is both a lumping of chemical species and reactions.

We applied these methods of reduction to a detailed free-radical mechanism simulating the pyrolysis at low temperature of a mixture of five alkanes: n-pentane, n-hexane, n-heptane, 3-methylpentane and 2,4-diméthylpentane. The detailed free-radical mechanism representing the pyrolysis of this mixture of five alkanes consists of 7673 reactions and it includes 556 alkanes, 12 olefins and 420 radicals [1]. By adopting the three methods of reduction, we reduced the size of the mechanism in a considerable way (Table 1).

Table 1. Comparison of the various methods of reduction

	Mechanism			
	Detailed	Type I	Type II	Type III
Number of reactions	7673	144	61	46
Number of species	988	61	17	22

The three methods of reductions make it possible to decrease in an important way the number of reactions of the mechanism but also the number of species with a direct incidence over the computing time. It is important to notice that the reductions are based on chemical principles, it is not a mathematical reduction, and thus the reduced mechanisms, the written chemical reactions and the kinetics constants have a real physical signification.

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Evaluating the Effect of Axial Temperature Gradients in Gas Chromatography Using a Simple Plate Mathematical Model for Pyrolysis Applications

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Researchers and practitioners continue to address new temperature programming strategies in gas chromatography (GC) to improve resolution and/or analysis time for characterizing complex mixtures of volatile and semivolatile compounds such as generated by pyrolysis. In conventional temperature programmed operation, the entire column length is maintained at the same temperature, and this temperature is increased with time. By manipulating the temperature both in time and in position along the column, the movement and elution of sample components can be controlled in a unique manner, often improving resolution. As an example, a decrease in column temperature from the injector to the detector causes the front of a peak to move slower than the tail of the peak, leading to narrower, focused peaks, a behavior that is markedly different from what is experienced in isothermal and temperature programmed GC modes (Figure 1). In this presentation, a simple plate (SP) mathematical model is described for studying the effects of axial temperature gradients in GC for the separation of a mixture of normal alkanes. The partition coefficient equation for the alkanes was utilized by the SP model to predict their elution times and resolution. For validating the model, measured and calculated retention times and resolutions were compared both for isothermal and temperature programmed GC separations. The effect of different axial temperature gradient profiles on resolution and separation time for the alkane mixture was then simulated using the SP model. Comparing the different GC separation modes, we show the effect of different axial temperature gradient profiles on peak capacity. Results have demonstrated that axial temperature gradients in GC can be a good option for fast online analysis and good selectivity.

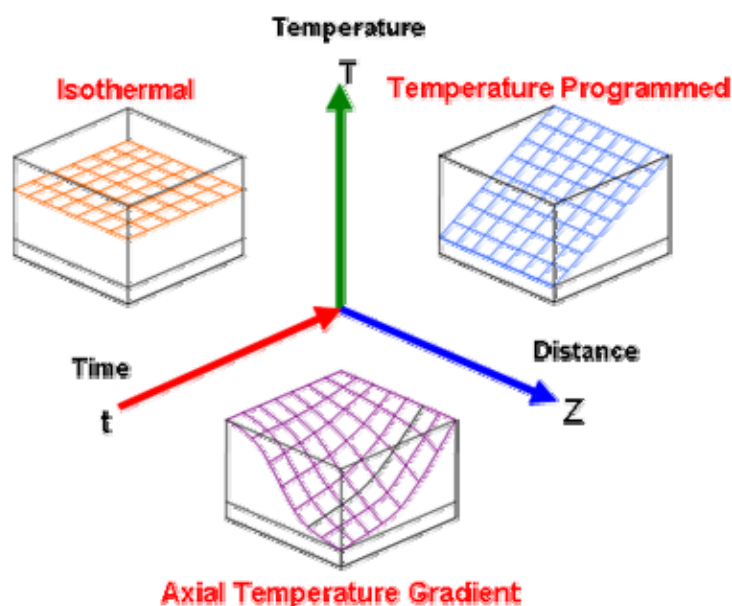


Figure 1. Three-dimensional view of the different GC separation modes.

Jerusalem artichoke pyrolysis. Energetic evaluation

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A study of the conventional pyrolysis of Jerusalem artichoke (*Helianthus tuberosus* L.) waste has been carried out. The work objective was to characterize the solid, liquid and gaseous phases for their utilization in energy generation. The influence of the operating variables has been studied, determining the optimal conditions in which the process can be developed. Also, with the object of design, a kinetic study based in the generation of the principal gases of the process, has been carried out.

The experimental set-up, consisted basically in a cylindrical stainless steel reactor provided with heating system, inlet for feeding the gas stream and accessories to collect the liquid and gas phases. The higher heating value (HHV) of solids and liquids was determined; also the proximate analysis of the solid phase was carried out. The gas phase, mainly composed of H₂, CO, CH₄, CO₂ and traces of ethane and ethylene, was analyzed chromatographically. The variables of operation studied were temperature (400-800 °C), particle size (0.63-2.00 mm of diameter), N₂ flow rate (75-300 mLmin⁻¹) and waste initial mass (2.50-10.00 g).

The temperature exercises a large influence in the process. Increasing temperature increases the production of gases and decreases the liquid and gaseous phases yield. The initial mass of waste and the particle size do not exercise a defined influence in the process. Finally, when increasing the N₂ flow rate, the yield of the liquid fraction decreases and the yield of the gaseous phase increases.

The solid phase is constituted of a charcoal with an average higher heating value of 26 MJ kg⁻¹, the liquid phase presents a HHV of 9.70 MJ kg⁻¹ at 400 °C, this value diminishes when the temperature is increased, and the gas phase has an HHV between 0.3 and 11.0 MJ (kg of raw material)⁻¹. According to the characteristics and energy contents, the solid phase can be used as fuel or precursor for the manufacture of activated carbons. The liquid phase could be used as liquid fuel or as organic-compounds source. The gas phase could be used to heat the pyrolysis reactor or to generate heat and electricity in a gas-turbine/vapour-turbine combined cycle. Finally, as previous step to the design of the industrial equipments, a kinetic study of the process, based in the generation of the principal gases, has been carried out. It has been considered that the gases are formed through parallel independent first-order reactions, with different activation energies. From this model, the rate constants for the formation of each gas and their corresponding activation energies were determined.

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Catalytic pyrolysis of exhausted olive oil waste

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A study of the pyrolysis of an exhausted waste from the extraction of olive oil has been carried out. The work objective was to characterize the solid, liquid and gaseous phases generated in the process for their possible utilization in energy generation. On the other hand, the influence of a set of variables has been studied, including the efficacy of the dolomite as catalyst. Finally, as previous step to the design of industrial installations, a kinetic study of the process (catalyzed and uncatalyzed), based in the generation of the principal gases, has been carried out.

The experimental system consists of two cylindrical stainless steel reactors connected in series. A conventional pyrolysis is produced in the first reactor. In the second reactor, the gases and liquids generated in the first one pass through a dolomite catalytic bed where the cracking of the heavier components is produced. The reactors are provided with heating system, inlet for feeding the gas and steam stream, and accessories to collect the liquid and gas phases. The higher heating value (HHV) of solids and liquids was determined; also the immediate analysis of the solid phase was carried out. The gas phase, mainly composed of H₂, CO, CH₄, CO₂ and traces of ethane and ethylene, was analyzed chromatographically. The variables of operation studied were the temperature (400-900 °C) and quantity of catalyst (0-100 g). Also, the dolomite effectiveness was evaluated for the same sample varying the number of runs (0-6 pyrolysis).

An increase in reaction temperature leads to a decrease in solid and liquid yield and to an increase in the gas phase yield. The presence and quantity of catalyst, originate an important decrease in the liquid phase yield and a high increase in the gas phase yield. The increase in the generation of gases is especially important in the case of hydrogen. In addition, the yield of liquids increases and the yield of gases diminishes when the catalyst is used repeatedly without being reactivated. In consequence, the catalyst suffers a little deactivation with use.

In the kinetic study carried out, it has been considered that the gases are formed through parallel independent first-order reactions, with different activation energies. For uncatalyzed experiments, the experimental data, once adjusted to the model, provided activation energies of 82.9, 39.6, 68.9 and 20.8 kJmole⁻¹ for H₂, CO, CH₄, and CO₂, respectively. For catalyzed experiments (following the same sequence) the activation energies were 43.0, 48.9, 49.9 and 65.5 kJ mole⁻¹.

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Analysis of the thermal decomposition of pine needles and cones by TG-MS. Kinetic parameters

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Pine needles and cones are biomass that can be used as fuel or fuel briquettes. On the other hand, thermal decomposition takes place under poor combustion conditions in forest fires.

A wide kinetic study has been carried out under different conditions in TG and TG-MS for each material. For the pine needles, four dynamic runs and two isothermal runs were carried out under pyrolysis conditions under nitrogen. For the combustion runs, seventeen runs were carried out at two oxygen: nitrogen ratios (1:4 and 1:9), both dynamic and isothermal runs. In addition, a study of the thermal decomposition was carried out in a dynamic run using TG-MS in order to observe the evolution of the major compounds, and discuss the information that can be obtained. A similar program of research was carried out for the cones.

From the overall analysis of the data, schemes of reactions and kinetic values were calculated by integration of the differential equations and minimizing the differences between the experimental and calculated ones. It is important to emphasise that the same set of parameters are proposed for the pyrolysis runs, not depending neither the heating rate in dynamic runs nor the run is carried out under dynamic or isothermal mode. For the combustion runs, only the oxygen pressure can vary the value of the pre-exponential factor. Figure 1 shows one example of the data obtained considering the variation of volatile volume evolution and its derivative, comparing the experimental points with the calculate ones, that practically overlap the previous points.

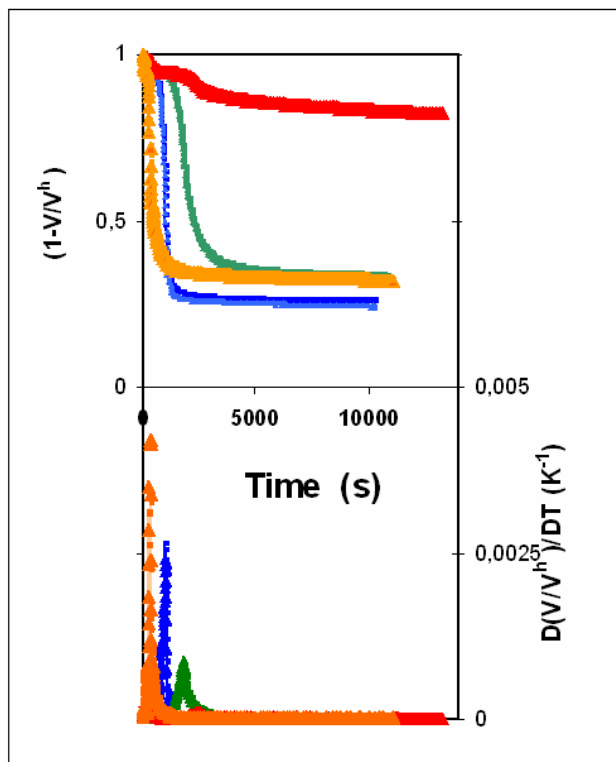


Figure 1. Dynamic+isothermal runs for pyrolysis of pine cones.

Kinetic study of the Pyrolysis and combustion of tomatoes plant

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Tomato plant is an agricultural waste that normally is decomposed and burnt on the field. Burning can be a problem due to the evolution of pollutants that can be introduced in the feeding chain through the new plant, so logically a recollection of these wastes and the exploitation of its energetic potential can be interesting.

A kinetic study, both for pyrolysis and combustion, has been carried out under different conditions in TG and TG-MS. A total of 24 runs have been performed at nitrogen atmosphere (pyrolysis runs), combustion (air) and oxidative pyrolysis or poor oxygen atmosphere (oxygen: nitrogen ratio equal to 1:9). Dynamic runs and dynamic + isothermal runs has been carried out for obtaining many data of decomposition under different operating conditions.

A scheme of five series reactions has been proposed for the pyrolysis process, although only three fraction are significant, corresponding presumably to the hemicellulose, cellulose and lignin content of the plant. For the combustion runs, four new reactions were added: two competitive oxidation reactions for the cellulose and lignin, and two combustion reactions of the carbonaceous residue obtained from pyrolysis. The kinetic values has been calculated by integration of the differential equations and minimizing the differences between the experimental and calculated ones. It is important to emphasise that the same set of parameters are proposed for the pyrolysis and combustion runs, not depending neither the heating rate in dynamic runs nor the run is carried out under dynamic or isothermal mode. The influence of the oxygen pressure is discussed. Figures 1 and 2 show some set of runs. The data obtained from the TG-MS has also been considered for testing the model proposed.

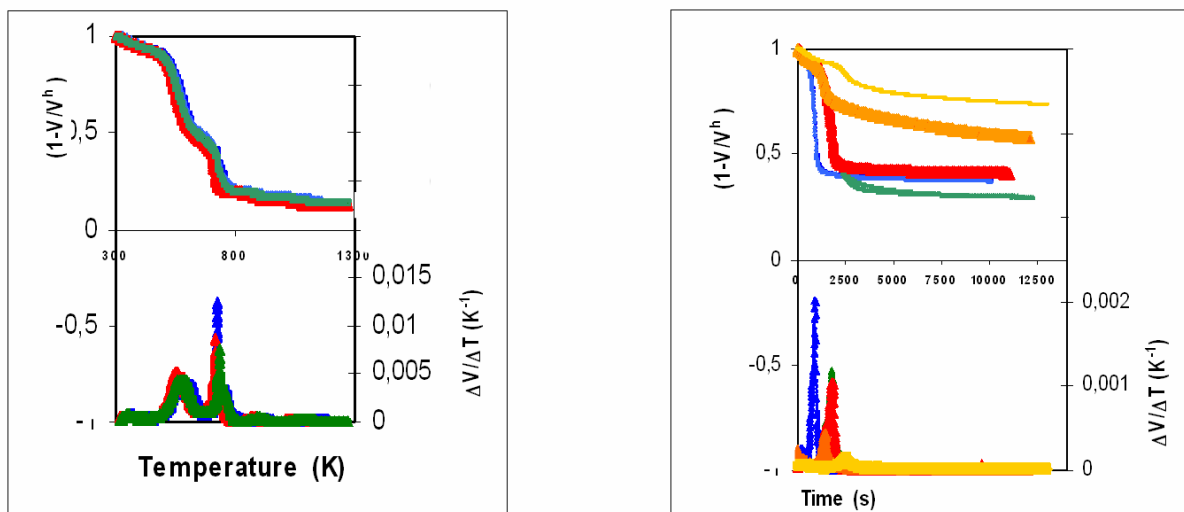


Figure 1. Dynamic runs for combustion in air. **Figure. 2.** Dynamic + isothermal runs for pyrolysis.

Polymerization and Degradation Processes of a Aromatic Amine-based Naphtoxazine Monomer

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Various polybenzoxazines can be obtained by the ring-opening polymerization of cyclic monomers, benzoxazines, which has been developed as a novel type of phenolic resin [1]. Additionally, naphtoxazines were synthesized by using hydroxyl naphthalenes as precursor to increase the thermal stability and char yield of the resulting thermosets, polynaphtoxazines. However, unlike benzoxazines, naphtoxazines suffer from low thermal stability and require autoclave since evaporation of the monomer cannot be avoided during curing [2]. Recently, allyl-functional naphtoxazines were synthesized to obtain high temperature stable polynaphtoxazine with extended network via the polymerization of allyl functionalities [3]. Yet, thermal degradation/evaporation of monomers below 200 °C during thermal treatment of monomers was also recorded. Up to this date, certain functional polynaphtoxazines were synthesized for the search of high char yield and thermally stable thermosets to be used in the development of high performance composites. But, none of the studies investigated the degradation and the polymerization mechanism of naphtoxazines during curing process.

In this study, we synthesized naphtoxazine by the reaction of 1,5-dihydroxynaphthalene, aniline and formaldehyde (15-Na) and the thermal characterization of the material was carried out in detail by using direct pyrolysis mass spectrometry technique. Degradation of the monomer was detected during the curing process while the polymerization proceeded. It has been determined that polymerization followed opposing paths yielding some thermally less stable linkages. The polymerization and degradation mechanism for were proposed for 15-Na and poly15-Na. It has been shown that pyrolysis MS is a very powerful technique to investigate the polymerization and degradation mechanism and degradation products of these samples.

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Effects of ion chemistry and mass on the electrical properties of ion implanted pyrolyzed Polyacrylonitrile

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This research describes the conductivity modifications induced by heavy ion implantation in pyrolysis products obtained by thermal treatment of polyacrylonitrile (PAN) thin films at temperatures of 435 °C (PAN435) and 750 °C (PAN750) under vacuum. Ionic species having different chemical reactivities such as Kr, As, Cl, and F ions were utilized to allow interpretation of the conductivity data either in terms of implantation induced molecular rearrangements or in terms of specific chemical doping effects. Implantation of PAN435 with Krypton, a chemically inert ion, provided conductivity increases equal to those previously reported for the implantation of arsenic ion which is a strong electron donor. Significantly larger conductivity increases were noted for the implantation of the relatively smaller but more chemically active fluorine and chlorine ionic species. Although the last observation suggested a chemical doping contribution to conductivity, other results provided evidence in favor of conductivity increases which are associated primarily with ion beam induced molecular transformations. The dose-conductivity dependence displayed a threshold behavior which can be adequately explained in terms of overlapping of the damaged regions of the individual ion tracks. The threshold, or onset of a large conductivity increase, occurred at a higher dose as the mass of the ion (or energy loss) increased. Furthermore, the implantation of PAN750 with Kr, As, Cl or F at high doses resulted in products having equal conductivity values but lower than that of unimplanted PAN750 indicating the absence of chemical doping in these products. In agreement with a disorder induced conduction, the decrease in conductivity at low applied doses of fluorine was not nearly as large as those noted for the implantation of the heavier Kr, As or Cl ionic species.

The temperature dependence of conductivity in the range between 25-300 °C followed nearly a simple activation conduction relationship from which the temperature coefficients of resistivity (α) were determined. In this temperature range, PAN750 provided the smallest α value compared to ion implanted PAN750 or to products obtained at the lower pyrolysis temperature. However, the corresponding lowest rate of conductivity change with temperatures (0.49% /°C) obtained in this study far exceeds the specification value required for thin film resistor applications (< 0.1% /°C). We are currently investigating alternative thin ceramic-metal films having small thermal coefficients of resistivity. These films are prepared by metalorganic decomposition of a mixture of metal complex and pre-ceramic polymers.

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Kinetics of Kukersite Low-temperature Pyrolysis in Autoclaves

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The organic matter (kerogen) of Baltic oil shale (kukersite) is a macromolecular resin with the empirical formula $C_{421}H_{638}O_{44}S_4NCl$ [1]. The high-molecular kerogen is insoluble in organic solvents and therefore cannot be separated from the mineral part of kukersite by simple solvent extraction. It is known that at pyrolysis of kerogen between temperatures 250-350 °C unwanted plasticization takes place resulting sticky thermobitumen (TB) and some light fractions. TB formed is a soluble in organic solvents high-molecular non-volatile intermediate product of kerogen thermal decomposition. The physical characteristics and molecular weight of TB depend on its formation conditions. At 325–350 °C begins the secondary pyrolysis of TB into oil fractions, gas and semicoke [2].

The new generation of effective hydrogenation catalyst created for hydroconversion of heavy oil and asphaltenes have encouraged concepts of successful upgrading of TB into liquid fuels. So, formation of TB from oil shale, studied intensively in the middle of the last century is again of interest. The aims of this work are systematic experimental study of the low-temperature pyrolysis of kukersite in autoclaves, and mathematical description of the co-effects of time and temperature on the yield of solid, liquid and gaseous phases.

In this work, the possibility was proved for separation of kukersite organic matter from its mineral matter by means of low-temperature pyrolysis at 340-380 °C in autoclaves and subsequent extraction with benzene of TB and oil (TBO) formed. The high yield of TBO (about 90 %) was obtained under the conditions where the initial kerogen was decomposed almost entirely into TB but the coke formation resulted from the secondary cracking of TB into oil, gas and coke was scarcely started.

A mathematical model was deduced for description of the co-effects of pyrolysis time, nominal temperature and non-linear heating rate on the yield of TBO, gas and coke in autoclaves. Rate coefficients and apparent kinetic constants estimated for the parallel-subsequent decompositions of kerogen and TBO under the low-temperature pyrolysis allowed prognosis of the conditions for the maximum yield of TBO. Agreement between the calculated and experimental yields of TBO, gas and solid residue was satisfactory.

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A New Approach to the TG-DTG Kinetic Analysis Considering a Large Number of First Order Parallel Reactions

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Kinetic analysis of thermal decomposition has focused the interest of a large number of researches all along the modern history of thermal decomposition. Many complex models have been proposed, usually involving several competing reactions and sometimes complex reactions mechanisms. However, different authors have proved that the effects attributed to heating rate can often be explained by other experimental factors, such as temperature gradients, secondary reactions, heat transfer effects, etc.

One of the approaches to deal with the complex nature of the reactions involved in the thermal decomposition of a material was to consider that it is produced by a large number of first order reactions. Such an assumption led to the distributed activation energy model that basically assumes that there is a distribution of activation energies around a central value. The main weaknesses of this approach are that one must assume a form for that distribution (usually a Gaussian distribution) and nothing is said about the pre-exponential factor that generally is assumed to be constant.

In this work it is proposed an approach which assumes that the thermal decomposition is produced by a large, but finite, number of first order reactions. Initially a set of first order reactions, numerically giving curves in the range of 'TG or DTG' curves is selected. Two methods can be used to generate this set of curves: the first one is based on the generation of sub-sets of curves centered on values (activation energy and pre-exponential factor) obtained considering that the maximum decomposition rate is obtained at a set of fixed conversions. The second method allows the graphical selection of intervals in a plot representing the logarithmic of conversion vs. the inverse of temperature. Usually between 200 and 500 first order curves are generated. Then, problem consists of selecting a subset of first order reactions (among those previously generated) that best reproduce the experimental results. If no other considerations are taking into account, the problem is a linear minimum square fitting problem. However, a large number of reactions, with small contributions, can appear if the original TG-DTG data have 'noise' due to unavoidable experimental errors. Therefore it is necessary to control the maximum "weight" of a given contribution. It could be also of interest to control the maximum number of contributions (reactions) to be considered. In that case the problem can be formulated as a Mixed integer Quadratic (Linear if a norm one is used) Programming Problem.

The procedure can be iteratively repeated in order to get a fine adjust generating a finer grid of reactions around the values obtained in previous iteration. Finally a non-linear optimization, fixing the number of contributions, can be performed to refine -even more- the final values.

Results show that the methodology allows very good reproduction of TG-DTG curves. In most cases shows families of curves with near Gaussian distributions not only of activation energies but also of pre-exponential factors.

Plastics and mixtures of Plastics and Tyres Wastes Batch Pyrolysis: A Comparison of Kinetics Studies

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Derived petroleum products like plastics and tyres have been extensively used in all modern societies in different ways producing increasing amounts of wastes with a negative impact on environment. Pyrolysis technology applied to these wastes could be a useful tool in waste valorization policies as it allows taking profit of both energetic and organic contents of these wastes, producing fuels or raw materials to chemical and petrochemical industries. A mixture of plastics composed by PE (28.5%), PP (43.0%) and PS (28.5%) and mixtures of these plastics with scrap tyres was pyrolysed in presence of an inert atmosphere and under moderate conditions of pressure and temperature. At these conditions, polymeric structure is broken down producing smaller and intermediate species, which can further react to form a complex mixture of smaller hydrocarbon molecules, being liquid and gas in nature. Previous pyrolysis studies in a 1L batch reactor [1] showed that for a similar waste blend, the optimized experimental conditions were: 420°C, 0.41MPa and 30minutes reaction time. Most kinetics studies are based on TGA measurements, measuring only weight mass loss, which result in simplified models, as only phenomena with weight losses are measured. For this study it was used six small batch reactors (0.16L) and reaction times ranging from 9 seconds till 15 minutes. The innovative aspect of the present kinetic study is that allows to follow the individual product formation (gas, liquid and solid), detecting the reaction time effect on reactions among product initial formed and identifying possible reactions routes at different temperatures. Ea and corresponding pre-exponential values were calculated for the products formed for plastics and plastics and tyres mixtures. Some products formed presented difusional effects. Experimental results were used to check and validate the proposed kinetic model. This paper will present and discuss all the results obtained so far comparing them with those of literature.

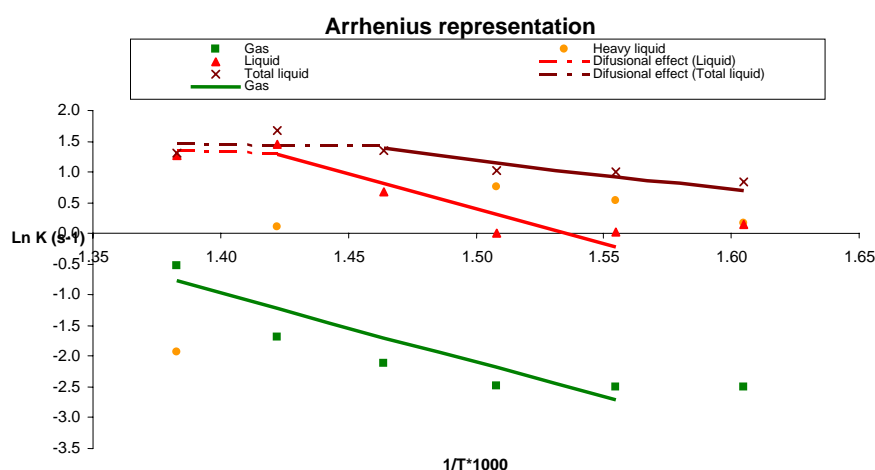


Figure 1. Arrhenius representation of different products (plastics wastes pyrolysis).

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Thermal analysis of kukersite and dictyonema oil shales

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Thermal behavior of two types oil shales – kukersite and dictyonema - from Estonia are investigated using a thermogravimetric analyzer at different heating rates. One of the oil shales, the kukersite oil shale, is one of higher oil yield and the other one, the dictyonema oil shale, is one of lower oil yield oil shales basing on the Fischer assay characterization. Several samples with different organic matter content, including concentrated kerogen samples, were studied for both oil shales.

The characteristics of volatile matter evolution were studied by a thermogravimetric-mass-spectrometric technique. Kinetic parameters were derived from non-isothermal mass loss data applying commonly used methods in oil shale pyrolysis studies. The kinetic parameters obtained are compared with each other and with those widely available in literature for different oil shales. In the case of the kukersite oil shale the thermal behavior was also investigated thermogravimetrically in high pressure (up to 40 atm) and vacuum (at pressure 10^{-3} atm) conditions.

Influence of pyrolysis temperature on the gasification reactivity of biomass chars at elevated pressures

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In recent years there has been an increasing interest in pressurised gasification systems due to their high thermal efficiency and reduced environmental impact. Moreover, gasification of biomass fuels is a promising technology that can provide chemicals and energy from renewable sources. The study of the gasification reactivity is usually focused on the reactivity of the char residue, since the volatile matter is rapidly released from the fuel and transferred into the gaseous environment. Several factors affect char properties and its reactivity during pyrolysis. Among the latter are: temperature, heating rate, pressure and residence time of the fuel particles [1]. Therefore, a clear understanding of char reactivity is required in the proper design of gasifiers from both process efficiency and environmental regulations points of view [2].

In this work, biomass chars were produced by pyrolysis of *slash pine* at elevated temperatures, 1000 and 1400 °C, in a drop tube furnace (DTF) at atmospheric pressure. A Pressurized Thermogravimetric Analyser (PTGA) was then employed (with CO₂ as the gasifying agent) to study the effect of pyrolysis temperature, total pressure and CO₂ concentration during the gasification tests at different temperatures.

It was observed that an increase in pyrolysis temperature in the DTF leads to a decrease in char reactivity. On the other hand, an increase in the total pressure of the system during the gasification tests results in a decrease of the reaction rate. With respect to the CO₂ partial pressure, it was observed that the reaction rate increases proportionally to its increase. In addition, three *n*-th order kinetic models (volumetric model, grain model and random pore model) were applied, and their validity in predicting the conversion of the samples during gasification in CO₂ was assessed. It was found that the random pore model was the only able to predict accurately the char conversion. Moreover, the Langmuir-Hinshelwood model was applied with the purpose to determine kinetic parameters and compare the experimental and calculated reactivity values, obtaining a good agreement at atmospheric and elevated pressures.

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Pyrolysis of a Polyethylene-Metal Powder Blend: Characterization of Pyrolysis Residues by Thermal and Microscopic Analysis

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Powder injection molding is a technology in which thermoplastic polymeric material with a high content of solid particles is molded into a desired shape in a closed die [1]. This green compact is subsequently processed to near full density by removing the binder and then sintering the remaining powder-binder mixture. Thermal debinding or pyrolysis in a gas atmosphere is used as conventional heat treatment to remove the binder before sintering [1]. Polyethylene is a frequently used binder component because its relatively high melt viscosity provides a good mechanical stability or the so-called pre-sintering of the green compact. However, the remaining organic material can cause molding defects within compacts [2]. At the same time, the control of the pyrolysis residues after the thermal debinding is especially difficult [1,2,3]. In particular, very little is known about the morphology and structure of the pyrolysis residues. For this purpose, a model polyethylene-stainless steel powder blend is studied in the present study by a combination of thermal and microscopic analysis.

According to pyrolysis coupled with gas chromatography and mass spectrometry, polyethylene exhibits mainly cracking of the polymer backbone into small hydrocarbon species. Thermogravimetric analysis suggests a similar (slightly higher) degradation rate of the polyethylene-metal blend compared to unfilled polyethylene. Particle surfaces without and with polyethylene residues are observed in agglomerates burnt out during the thermogravimetric experiments. The morphology of the residue is related to the particle size. About 2 µm thick amorphous films cover the particles with the size range lying between 5 and 10 µm while less than 0.1 µm thin films are found between the particles. Fibrous lamellae exhibiting a higher stacking degree of aromatic piles are observed around particles with a size of about 20 nm.

A model is argued to describe the formation of the pyrolysis residues. Herein the obtained data are considered as a product of three competitive processes: pyrolysis of the polymer backbone, chemical vapour deposition of the resulting hydrocarbon species and infiltration of viscous polymer into powder interiors.

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On-line instrumentation for investigation of PAH growth during pyrolysis and oxidative pyrolysis of biomass model compounds

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Combustion of biomass produces aerosols and particulate containing significant amounts of adsorbed polar hydrocarbons and PAH [1]. Hydrocarbon growth mechanisms based on combination of small hydrocarbon fragments such as C₂/C₄ have been postulated [2] however there is growing evidence of alternative pyrolytic and recombination pathways. In particular, the importance of resonance stabilised radicals based on cyclopentadienyl moieties [3]. Evidence of PAH growth mechanisms can be provided by analytical pyrolysis experiments using pyrolysis-GC-MS and high temperature flow cells in both pyrolysis and oxidative pyrolysis modes. The conditions employed for oxidative pyrolysis such as stoichiometry, temperature and residence time, are very critical to the formation of PAH. An on-line analytical pyrolysis method has been developed enabling pyrolysis and oxidative pyrolysis of solid biomass and representative volatile fragments known to form from fast pyrolysis of biomass. The instrumentation utilizes a micro flow cell pyrojector interfaced to an adsorbent trap for focusing of the products.

The flow cell pyrolysis unit is a useful technique in investigating PAH formation from volatile fragments. PAH can be produced from both cellulose and lignin fragments although PAH increase with phenolic content. Pyrolysis of lignin and cellulose fragments produce indene and naphthalene and it is thought that cyclopentadiene is an important intermediate.

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A kinetic study of the polychloroprene pyrolysis

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In the last years the quantity of plastic wastes has increased, result of continuous diversifying of their practical application domains. Among the treatment methods of the plastic wastes, an interesting one is the pyrolysis, a process of thermal degradation in an inert environment. This work is presenting a kinetic study of pyrolytic decomposition of polychloroprene, a common plastic material (cables insulation, gloves etc.). The experiments were made in two types of installations differentiated by the sample capacity. The experimental conditions were: temperatures up to 1000 °C, pressure 1 bar, atmosphere of flowing nitrogen, three different heating rates and two different quantities of samples.

Generally, the aim of a kinetic study is to develop a kinetic model, founded, as much as possible, on the real mechanism of the process. Regarding the pyrolysis of polychloroprene, there are two main approaches used in the published studies. The first one proposed by Caballero is assuming the existence of three solid fractions in the structure of the material, not defined as chemical structure and composition, having different pyrolysis particularities ^[1], as well as a non-decomposable inert fraction. A second approach, proposed by Faravelli, more detailed and closer to real process mechanism, considers a set of 38 intermediary radicalic and non-radicalic species involved in a set of 186 elementary reactions. ^[2] Both models proposed by the two approaches mentioned above, represent the dynamics of mass loss, by using power law reaction rate expressions. We used both approaches, fitting the model parameters to our experimental data.

The first approach presents the advantages of simplicity, but is not giving informations about the chemical composition of the products. By contrary, the second approach offers a more realistic description of the process mechanism, including more information concerning products, but with an increase of complexity, both in the stoichiometry scheme and reaction rate expressions.

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Novel effect of metal nitrates on thermal decomposition of woody biomass

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The understanding of pyrolysis behavior is of great importance for the process design of an economical thermochemical conversion of woody biomass into various useful chemicals. The addition of inorganic compounds can cause significant influences in many aspects, such as selective formation of pyrolysis products and catalytic degradation of wood. In the present paper we report a fundamental study on pyrolysis of mixture of wood – metal salts such as metal nitrates in particular.

As for the model wood sample we have used cherry wood chips with typical particle size of 1 - 2 mm. The metal nitrates of reagent grade were used in the present study without purification. Pyrolysis samples were prepared in the following way: the water-washed wood chip was dipped in the aqueous salt solution ([wood] : [nitrate] = 1 : 1 in weight ratio) for 12 hrs under mechanical stirring. The chip was then dried at 40 °C and further dried at room temperature under vacuum. Pyrolysis experiments at constant temperature and thermogravimetric analyses (TGA) have been carried out, of which details have been described elsewhere [1, 2].

Figure 1 shows typical results of TGA for various wood – metal salt mixtures. Also included in the figure is a TGA result of the simultaneous pyrolysis of wood and salt without mixing, in which case the wood chip is located on inert quartz glass wool placed on the excess amount of nitrate powder. The addition of nitrates changes drastically the TG curves. A striking observation is the abrupt weight reduction, denoted hereafter as AWR, at about 120 °C in the case of copper and zinc nitrate addition and at about 150 °C for nickel nitrate, while the wood – iron (III) nitrate mixture does not exhibit any AWR stage. It is evident from the result of the TGA with the spatial separation between wood chip and Zn(III) nitrate that the AWR stages cannot be regarded as the simple combinations of TG behavior of wood and nitrate salts.

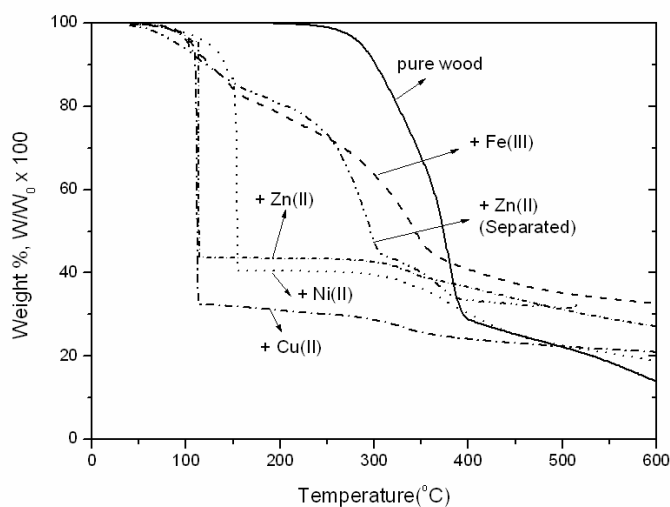


Figure 1. TG curve of the wood – metal nitrate mixtures under helium atmosphere (Heating rate = 20 °C/min). “+ Zn(II) (Separated)” means that wood chip is put on quartz glass wool under which excess amount of nitrate powder is placed on TG cell.

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Effect of Mineral Matter on the Formation of NO_x Precursors during Biomass Pyrolysis

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Gasification and power generation from agricultural biomass can contribute to solving energy and environmental problems. High nitrogen content in agricultural biomass in China may cause the emission of fuel-NO_x. Knowledge on formation of NO_x precursors is critical for minimizing the formation of NO_x. Unfortunately, the mechanisms for the formation of NO_x precursors during biomass pyrolysis are still not clear. In this paper, the release behavior tests of NO_x precursors such as NH₃, HCN, NO and HNCO of three typical kinds of biomass in China (wheat straw, rice straw and corn cob) during pyrolysis were performed using a thermogravimetric analyzer (TGA) coupled with a Fourier transform infrared (FTIR) spectrometer in argon atmosphere. Potassium and calcium, the main minerals in biomass, have different effects on the biomass pyrolysis characteristics. Different pretreatment methods, including deionized water washing to remove K⁺ and acid washing to remove K⁺ and Ca²⁺, were utilized to investigate the effect of minerals on the distribution and selectivity of nitrogen compounds during pyrolysis of wheat straw. As a comparison to the inherent minerals in biomass, KOH and CaO were loaded onto the dem-wheat straw to study the effect of the external minerals on nitrogen release by impregnating them in the corresponding aqueous solution. All the samples with pretreatments were dried before use. The loading amounts of both KOH and CaO in the samples were 5 % (wt %), and the residues of the samples after pyrolysis were characterized by X-ray diffraction (XRD) analysis. The results show that different types of biomass have distinctive formation characteristics of nitrogen-containing gases. HCN and HNCO are the main N-compounds during rice straw pyrolysis, counting for 40% and 33% of the total yields of NO_x precursors respectively, while NH₃ and HCN are the main N-compounds for wheat straw and corn cob. The N-conversion level to HNCO for wheat straw is especially low. This might be due to their different intrinsic properties, especially the different N-functionalities (mainly amino acids). HCN/NH₃ and HNCO/HCN ratios increase with the increase in H/N ratio of the three samples, but there is no correlation between HCN/NH₃ or HNCO/HCN ratio and O/N ratio in this study.

Minerals inherently present in biomass and externally added have an important influence on the formation and release of nitrogen-containing gases during biomass pyrolysis. Both the inherent and external added potassium promote N-conversion to NH₃, HCN, NO and HNCO at low temperature, but decrease the total yields of the N-containing gases during the experimental range. While the effect of calcium is more complicated, the inherent calcium decreases N-conversion to HCN, NH₃ and HNCO at low temperature (<about 330°C), while favors the total yields of the N-containing gases in the experimental range. However, the presence of added calcium restrains N-conversion to HCN, NH₃, NO and HNCO. It may be because the binding mode of the additional calcium to the components of wheat straw differs from that of inherent calcium. The coexistence of the inherent potassium and calcium promote the yields of HCN and NH₃, but inhibit the HNCO and NO formation. Compared to the original wheat straw, NH₃ and HCN are still the main N-compounds for the samples with pretreatments, but the fraction of HNCO increases obviously, and becomes worthy of attention.

**SESSION 4 SYNTHETIC POLYMERS:
*Characterization and Recycling (Cont.)***

Catalytic Cracking of Polyethylene over Zeolite Mordenite with Enhanced Textural Properties

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The worldwide polymer production has continuously grown in the last decades. Although being the worst strategy, plastics waste often ends-up in landfill, which implies in many countries the progressive depletion of the available space. Moreover, a used polymer is still a valuable raw material. Energy recovery and mechanical or feedstock recycling, are preferred options for the management of plastic wastes. Every choice possesses advantages and disadvantages, and the use of a mix of all recovery methods may be necessary in order to divert the disposal of used polymers from land-filling. Among the number of alternatives existing in the field of feedstock recycling, catalytic cracking over different solid catalysts has attracted special attention in the last years [1]. Particularly, zeolites have demonstrated to be efficient catalysts in the degradation of polyolefins into products with higher commercial value. Additionally, it has been pointed out the importance of the proportion of external acid sites, fully accessible for the polymer macromolecules, over the catalyst activity [2]. In this work, zeolite Mordenite has been chosen as catalyst in the pyrolysis of polyethylene. By means of a new synthesis method [3], different Mordenite samples with enhanced textural properties have been prepared, testing and comparing their activity on the catalytic cracking of low density polyethylene (LDPE) with a traditional Mordenite.

Cracking reactions of LDPE were carried out in a stainless steel batch reactor provided with a screw stirrer, operating at 420°C and atmospheric pressure for 2 hours under a continuous nitrogen flow. A mixture of 7.5 g of plastic and 0.15 g of catalyst (P/C = 50) were loaded into the reactor. Liquid and gaseous products leaving the reactor were separated in a condenser at 0°C and collected for GC analysis.

A number of Mordenite samples were synthesized, with BET and external surface areas from 385 and 9 m²/g, respectively, for the reference material, to 485 and 57 m²/g, for zeolites with enhanced textural properties. Thermal cracking of LDPE leads to plastic conversion lower than 30%, while values of 40% are reached when traditional Mordenite is used as catalyst. If Mordenite with enhanced textural properties is employed, a plastic conversion of 60% is attained, while turnover frequency (TOF) is twice higher than the value achieved on the reference sample (from 0.04 to 0.08 s⁻¹). In regards to the product distribution, both gas (C₁-C₅) and diesel (C₁₃-C₂₄) are formed as majority fractions when thermal and catalytic cracking over the reference mordenite is carried out. If modified Mordenite samples are used, both gas (C₁-C₅) and gasoline (C₆-C₁₂) fractions are obtained.

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Characterization of the Aqueous Fraction of Biomass Pyrolysis Oil in Chemical Families

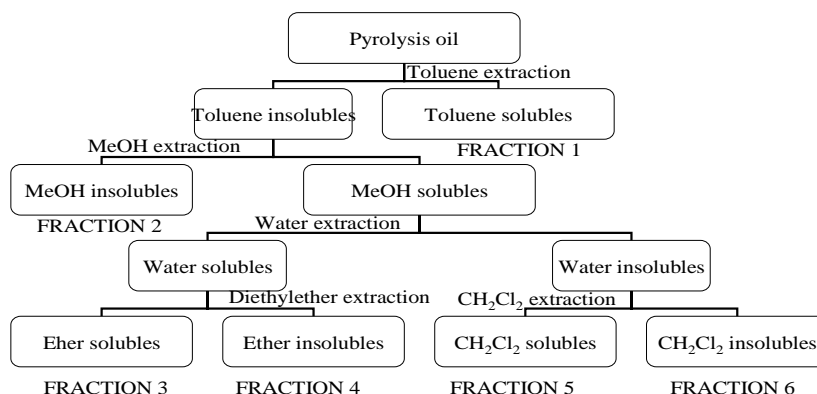
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In the last years, depletion of petroleum resources combined with petroleum demand increasing by emerging economies, biofuels obtained from flash pyrolysis of biomass could turn into a sustainable source of fuel. However, in order to introduce establish pyrolysis oil in the market, studies on composition of pyrolysis oils are of great interest. A complete analysis of bio-oil composition requires more than one analytical technique [1]. The grouping of bio-oils in chemical families characterized by a few distribution parameters could be very useful because this would enable bio-oil to be handled as a mixture of a few groups instead of hundreds of compounds [2]. Accordingly, the purpose of this work is to carry out a separation of the light aqueous fraction of the bio-oil in chemical families using a solvent extraction and then analyze these fractions using RPLC, (Reverse Phase Liquid Chromatography), GPC (Gel Permeation Chromatography) and GC-MS. Pyrolysis reactions have been carried out in a pilot plant provided with a conical spouted bed reactor and the outlet stream has been condensed in two fractions, which are a light fraction that is mainly aqueous and a heavy fraction that is mainly organic. The sample used in this study is the light one. The method proposed by M. Garcia-Perez et al. [2] has been used for fractionation in chemical families of the light fraction of pyrolysis c



Four of the six fractions proposed in the scheme have been extracted, which are fractions 1, 3, 4 and 6. No significant amount has been collected in fractions 2 and 5, given that these are made up of heavy oils [2] and the starting oil is only the light fraction of the pyrolysis oil. Average molecular weights (M_w) of the fractions have been determined by GPC using an Agilent HPLC 1100 and a TSK-GEL Alpha-3000 column. The results obtained are: 74 g mol^{-1} for fraction 1; 308 g mol^{-1} for fraction 3; 90 g mol^{-1} for fraction 4; 89 g mol^{-1} for fraction 6. The fractions have also characterized by RPLC using an Atlantis T3 column (Waters) and their chromatograms have been compared with that for the starting pyrolysis oil (the light fraction). Finally, the compounds present in each fraction have been detected by mass spectrometry using a GC-MS QP2010S Shimadzu equipment.

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Study of catalyst deactivation during the degradation of polyethylene in tube reactor

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The thermo-catalytic pyrolysis at middle temperature (400-500°C) is one of the possible ways of plastic waste recycling. This type of plastic waste handling was the topic of several researches in the last decades. These researches have shown that the catalytic cracking has several advantages compared with simple thermal treatment (e.g. higher yield of volatile products, more valuable products, etc.). However it was clearly reported too, that intensive coke formation during the degradation reaction results fast deactivation of catalysts. Catalysts life is important from process economically and environmentally aspect too.

In this study catalytic and thermal cracking of polyethylene was investigated in continued tube reactor system. HZSM-5 type and equilibrium FCC catalysts were tested and both the catalyst resistance to deactivation and the catalyst regeneration process were studied. Temperature of 500-545°C and residence time of 20 min. were used during the cracking treatment. The cracking products were separated in a distillation column, and used catalyst was filtered from the bottom product. After the first catalytic run the used catalyst was purified from the unconverted plastic and was reused again with the raw polymer, this procedure was repeated three times. The cracking products were analyzed by gas-chromatography and infrared spectroscopy. The textural properties (BET surface, acidity) of catalysts were also determined.

It was found that the using of catalysts enhanced the yields of volatile products, and the isomerisation of paraffin hydrocarbons occurred by the catalysts. Furthermore it was observed that after two and three reaction runs the FCC catalyst had activity. In case of HZSM-5 the deactivation was so intensive, that in the second reaction run was neither yield enhancing and nor isomerisation effect. The observed reduced BET surface could explain the deactivation of the used catalyst. The coke deposition was removable from the catalyst surface by the regeneration process, so the BET surface achieved the similar value as the initial was. However with the using of the regenerated catalysts initial volatile hydrocarbon yields could not be produced. There was no catalytic effect. It means that during the regeneration process the active sites of the catalyst was not reactivated. In case of the investigated cracking process the results shows that the reusing of FCC catalyst favourable, but the HZSM-5 catalyst lost all the catalytic properties in one reaction run.

Simplified evaluation of the recycling of non-mechanically recoverable waste streams by low temperature pyrolysis

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The demand of recycling alternatives, able to prevent the disposal of some non-mechanically recoverable waste streams, like highly mixed plastic ones, has motivated their testing under pyrolysis conditions [1]. The aim of the experiments was to validate the suitability of this thermal process, in absence of oxygen, as an appropriate feedstock recycling option after a simplified evaluation of the resulting products. The objective waste streams were selected because of the presence of dirtiness, the diversity of materials, the occurrence of problematic additives and fibre reinforcements or the demand of a special management.

The pyrolysis tests have been carried out in a batch operated stainless steel tank reactor at 430°C temperature in nitrogen atmosphere during 1 h. The selected plastics wastes were light packaging refuses and shreds coming from the treatment of end of life vehicles and electric and electronic equipment. The other residues were an exhausted blend of cold forging oil and solvent and sludge from a polymerization reactor bottoms. Thermogravimetric analyses of samples were run in order to get a previous trend of their thermal behaviour. The summary of tested wastes and product distributions are described at Table 1. The heating values of the liquid products, potentially applicable as fuels, were measured and their characterisation by GC/MS analysis revealed a complex mixture of organic compounds.

Table 1. Waste description and associated pyrolysis product distribution

Waste	Features description	Products		
		Gases	Oils	Solids
PP+PE (50/50 wt%)	Reference	20%	80%	---
Light packaging refuses	Dirtiness and complex material mixture	30%	30%	40%
Mixed monitor housing shreds	Presence of additives and complex material mixture	23%	55%	22%
Vinyl ester based composite scraps	Carbon fibre reinforcement and thermoset polymeric nature	13%	<1%	86%
Exhausted blend of cold forging oil and solvent	Liquid mix and special management required	23%	77%	---
Sludge from polymerization reactor bottoms	Liquid mix, dirtiness and special management required	44%	56%	---

The simplified evaluation of the pyrolysis results on dirty and mixed plastic and other organic wastes has shown that it is an attractive recycling alternative. The treatment of these wastes produced high heating value liquids applicable as fuels, gases suitable for covering the energy needs of the processes and, simultaneously, liberated valuable solids, like the carbon fibres contained as reinforcement in polymer matrixes, useful in secondary applications.

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Pyrolysis of Waste Tyres

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The problem of how to deal with wastes in general and scrap tyres in particular is becoming an important environmental and economic issue for the developed countries. It is thought [1] that more than 2.5 million tons per year are generated in the EU-15. Tyres are mainly made up of rubber, carbon black, steel and textile components. Tyres are 100% recyclable. Their chemical and physical properties make them a valuable resource. The present methods of tyre disposal include: landfill, energy recovery, export, retreading, and reuse in low value products such as sports surfaces, noise barriers and roofing materials. Although much progress has been made in recent years, efforts will inevitably intensify in the future with increasing public and political pressure for stricter legislation, such as the European Landfill Directive which strictly prohibits the disposal of rubber tyres on landfill sites. Our objective is to study the pyrolysis of granulated scrap tyres and a waste obtained from the tyre recycling industry. Tyres are made of different types of rubbers (styrene-butadiene, polyisoprene and polybutadiene), carbon black together with reinforcing fabrics and steel [2].

Two residues supplied from the tyre recycling industry were used in the study (Ty and TxTys). Polyisoprene (NR), styrene-butadiene rubber (SBR) and polybutadiene rubber (BR) were also included together with nylon and polyester. TG/DTG analysis was carried out using a TA Instruments SDT 2960 thermoanalyser. The samples were heated to 1000 °C at a rate of 3 and 10 °C/min under a nitrogen flow of 100 ml/min. The volatile matter evolved up to specific temperatures, the derivative of the mass loss and the temperature of the maximum volatile matter evolution (Tmax) were estimated from the data obtained from thermogravimetric analysis. The volatile matter evolved in a specific temperature range was calculated as the difference between the volatile matter evolved up to two specified temperatures (VMT1-T2). Gray-king pyrolysis of the raw materials was carried out following the ISO502 standard procedure. The coke, gas and liquid product yields were calculated relative to the starting material on a dry basis. The gas yield was estimated by difference. The results from the pyrolysis of the residues were studied in relation to those obtained from the pyrolysis of their main constituents.

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Effect of Metal Coated Particles on HDPE/PMMA Pyrolysate Conversion

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It is recently well documented that many metal additives can play a role at methane or another gaseous phase constituents conversion to hydrogen as an energy carrier. Thermo Catalytic Decomposition (TCD) of methane to produce hydrogen without producing CO₂ has been carried out in a fixed bed reactor at different conditions using a Ni-based catalyst. At temperature of 700 °C the concentration of hydrogen was around 80%, which corresponds to a methane conversion close to the thermodynamic values. The higher the temperature and methane flow, the shorter the life of the catalyst. Methane conversion rate has strong influence on the catalyst sustainability, so that lower methane conversion rate, i.e. the carbon deposition rate, longer the life of catalyst. The characterization study shows that catalyst become deactivated when deposited carbon prevents methane diffusion toward Ni surface. Diffusion is prevented in much higher extend by coating carbon than by filaments. Copper as a nickel dopant increases the hydrogen production leading to hydrogen concentrations over 80 % in the production gas, independent of the preparation method or the copper precursor used [1].

Mixtures of HDPE and PMMA were pyrolysed at 700 and 815°C. By Py-GC/MS method was monitored hydrogen, methane and carbon monoxide production in the system with/without metal coated particles, as an additive. Those were prepared by electrochemical deposition of Ni and Co on the small iron particles surface. Tested was their surface catalytic activity to maximize hydrogen conversion in the pyrolysate gaseous phase. Important results exhibiting in maximum hydrogen production at the highest pyrolysis temperature, and highest HDPE contents in the mixture. Powder metal additive affected production of hydrogen at 700°C, mainly with nickel coating surface. Higher content of the PMMA in the mixture led to higher production of CO and methane. Hydrogen conversion at higher pyrolysis temperature was affected by heat distribution between polymers mixture and metal powder particles. This effect as well distribution of gases during pyrolysis will be discussed.

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Pyrolysis as possible method for treatment of keratin waste

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Feather waste at poultry processing plants have high protein content hence it is used for feedstuff (e.g. chicken poultry, swine, rainbow trout and salmon); however it have low nutritional quality and digestibility. It is also used on a limited basis as nitrogen fertilizer but this could create environmental problem due to its difficult degradation. The EU regulation limits the use of feather waste for animal feed therefore new treatment methods should be found. Pyrolysis could be a viable option to recover valuable products from biomass waste. It is interesting to compare the pyrolysis behaviour of feather protein with those of wool and hair because of differences in chemical composition, solubility and molecular configuration.

Chicken feather, sheep wool and human hair were pyrolysed at 450 °C using a semi-batch operation under atmospheric pressure and a heating rate of 10 °C/min. The composition of pyrolysis products was determined by GC-MSD.

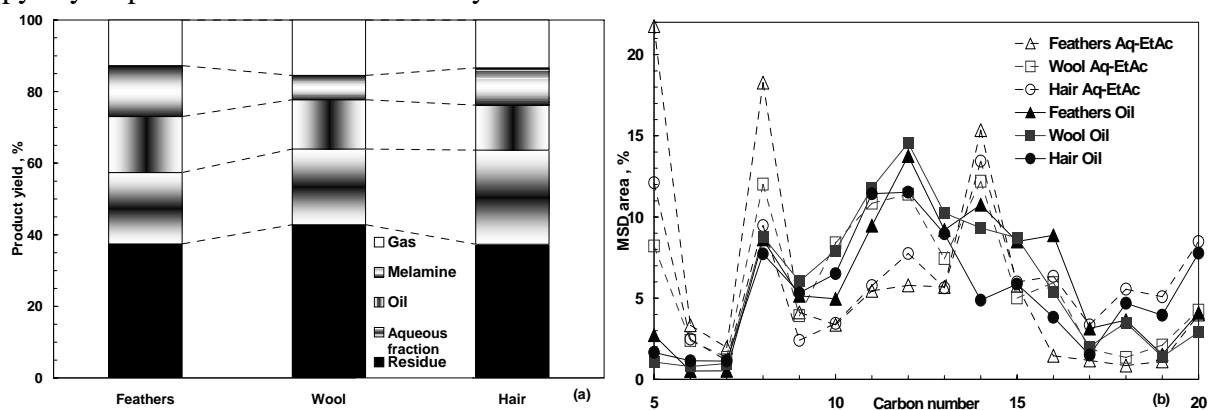


Figure 1. Product yield (a) and C-NP grams of oil and of ethyl acetate extract from aqueous fraction (Aq-EtAc) (b) resulted from pyrolysis of feather, wool and human hair at 450 °C.

Pyrolysis of feathers, wool and hair gave 13 – 15 % gaseous products, 12.5 – 15.5 % oils and 20 - 26 % aqueous fraction, the residue being of 37 – 43 %. Oil yield decreased in feathers > wool > hair order while the amount of the aqueous fraction increases in the same order. A white powder condensed at the cold outlet of the reactor. This was found to be melamine and its amount was of 7 – 14 %, higher for feathers. Part of organic compounds in aqueous fraction from pyrolysis was extracted with ethyl acetate.

Global characterisation of pyrolysis oils by C-NP grams show a wide distribution of compounds in n-C₈ – n-C₁₆ range with toluene (n-C₈), phenol (n-C₁₀), methylphenol (n-C₁₁), benzenepropanenitrile and indole (n-C₁₃) as main components. The ethyl acetate extracts contain small amounts of H₂S, CS₂, dimethyldisulfide and dimethyltrisulfide coming from disulfide bridges between cysteine units, and peaks at n-C₅ for acetonitrile, n-C₈ for acetal, and at n-C₁₄. Dimethylhydantoin coming from condensation of two alanine units as well as ethylmethylhydantoin were also found. Aliphatic nitriles (R-CN, R: C₁ – C₄) and aromatic ones (Ph-R-CN, R: C₁-C₂) were found in pyrolysis products from all samples. Hair gave heavier compounds at n-C₁₈ – n-C₂₀ in both analysed fractions.

Detailed analysis of pyrolysis products by GC-MSD revealed more differences between the three studied sources of keratin.

Influence of lignin on thermal degradation behavior of composites based on polypropylene and on poly (ethylene terephthalate)

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Lignin is an amorphous polyphenolic plant constituent, able to give a high amount of char when heated at high temperature in an inert atmosphere. This peculiarity is a basic aspect of flame retardant additives, since char reduces the combustion rate of polymeric materials.

Polypropylene (PP) and Poly(ethylene terephthalate) (PET) have been alternatively compounded with different amount of lignin by a single-screw extruder. The influence of the lignin presence and its content on crystallization behavior, on crystalline structure and morphology of the polymer composites has been investigated [1,2]. In the present work the thermal degradation of the semicrystalline polymers in the presence of lignin was studied carrying out TGA experiments in inert and oxidative atmosphere.

The lignin present in the PP composites is able to produce a high char yield that is responsible of the increase in the composite temperature degradation. The increase is more evident in the experiments carried out in air atmosphere, where, the interactions between the PP and the charring lignin lead to the formation of a protective surface shield able to reduce the oxygen diffusion towards the polymer bulk.

On the light of these interesting results we have investigated the influence of the lignin on PET thermal degradation. In fact, a recent paper reported about the good compatibility between lignin and PET, where a single glass transition dependent on composition was detected in a large range of blend ratios [3].

For the PET based composites it is observed that the initial weight loss occurs at lower temperature than that of pure polyester; the temperature corresponding to the max rate of weight loss does not depend on the lignin content and it is close to that of pure PET. The thermograms registered in oxidative atmosphere evidence that the pure lignin is completely degraded at 500°C, while, in the same temperature range, the weight loss for the composites decreases as a function of lignin content. This behaviour could be due to the interactions occurring by blending the polyester and lignin.

The influence of the lignin on the polymer composites thermal degradation resulted more emphasized for PP than for PET. These results can be due to the different condition adopted for the composites preparation, and to the higher thermal stability showed by the pure polyester compared to the pure polyolefin.-

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Catalytic pyrolysis of high density polyethylene for maximum generation of the liquid fraction

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Plastics are an important fraction of MSW and important efforts are focussed on their recovery. Mechanical recycling is limited for the management of high volumes of residues. Combustion allows energy production but contaminants treatment is difficult. Chemical recycling is one important way to generate chemical products for the industry. The generation of an interesting product such as H_2 from HDPE has been studied. Its recovery could be a possible source of H_2 in two stages, the catalytical pyrolysis followed by the catalytical reforming of the liquid fraction. In order to do so, the first stage of the process must be optimized for maximum generation of the liquid fraction.

The main goal is the selection of different catalysts for the maximum generation of pyrolysis liquids. The most important parameters to take into account are acidity and porous structure, especially their size and shape. Reaction mechanism of pyrolysis develops over catalyst surface, adsorption being the limiting step and influencing strongly on the reaction results. The catalysts studied show very different internal structures. The catalysts finally selected are faujasite zeolite, beta zeolite, clinoptilolite or natural zeolite and montmorillonite clay, that have been characterized by different techniques such as XRD, N_2 adsorption and ammonia desorption (TPD). A series of experiments were carried out at two different temperatures for the four catalysts finally selected and are shown in the following table.

Catalyst	Temperature, °C	Conversion, %	Yield liquid, g/100 g PE	Yield gas, g/100 g PE	Yield char, g/100 g PE	PE _{nd} *	L/G ratio
HUSY	400	100	51.0	33.9	15.1	0.0	1.5
	450	100	48.7	42.6	8.7	0.0	1.1
H β	400	100	42.0	45.1	12.9	0.0	0.9
	450	100	38.4	53.1	8.5	0.0	0.7
HZN	400	99.5	76.9	21.1	1.5	0.5	3.6
	450	100	84.4	14.4	1.2	0.0	5.8
AM	400	99.1	78.3	16.4	4.4	0.9	4.8
	450	100	75.0	22.1	2.9	0.0	3.4
SC	450	38	35.5	2.5	-	62.0	14.2

*PE_{nd} = Non degraded polyethylene.

The effect of the catalyst and the temperature on the conversion, distribution of gas, liquid and solid fractions and distribution of products have been studied. The main conclusions that can be obtained are that HUSY and H β are the most active and have a similar behavior, resulting in higher conversions and more efficient cracking that generates higher fractions of gases and lighter liquid compounds. AM and HZN show also similar behavior. At 450°C decompose HDPE completely, with higher yields to liquids and lower generation of char. The broad product distribution is also similar, with more olefines than paraffins and low concentrations of aromatics. This could be due to a relatively low surface area. Considering the objective of maximum yield of the liquid fraction for further dehydrogenation, it can be concluded that AM and HZN zeolite are better options for the process than HUSY and H β .

Pyrolysis of the rejects of a waste packaging separation and classification plant

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Plastic consumption has drastically increased in the last decades. Annual consumption per person in Occidental Europe is about 100 kg, this means that about 40 million tons of plastics are annually consumed. The EU Packing and Packaging Waste Directive (2004/12/CE) sets as objective for 2008 a total valorization rate (energy recover + recycling) of 80 %, with at least 55 – 85 % recycling. In Spain 60 % total valorization has been achieved, but not the minimum 55 % recycling, and it's getting more and more difficult to increase such recycling rates, since the streams left are increasingly complex and intermingled.

The general objective of this paper is to study experimentally the suitability of the pyrolysis process as an alternative for the valorisation of real streams of plastics coming from packing and packaging wastes, concretely the rejects from a waste packaging separation and classification industrial plant in which the wastes of the packing and packaging municipal container are separated in different fractions (steel, tetra-brick, aluminium, cans, different plastics) and then sent to recycling companies. The rejected fraction, about 30 % is composed of many different materials (PE, PP, PS, PVC, PET, ABS, aluminium, film, etc.), which are very much intermingled, and for which it is not technical or economically viable and ulterior separation, and therefore they can only be incinerated or land-filled.

In pyrolysis processes (heating without oxygen), the organic components of the material are decomposed generating liquid and gaseous products, which can be useful as fuels and/or sources of chemicals. The inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of the binding matter organic and therefore they could be reused in certain applications (additive or fillers for other plastics) or as a last resort it would be a minimum waste to be land-filled. Pyrolysis is especially appropriate for products or streams which contain different plastics and other ingredients both organic and inorganic, as is the fraction that has been studied in this work, since it enables to treat all the ingredients together.

The pyrolysis experiments have been carried out in a non-stirred batch 3,5 dm³ autoclave swept with 1 L min⁻¹ N₂. Different layouts for condensing the liquids and separating them from the gaseous products have been tried. The effect of catalysts has been also investigated. Pyrolysis yields (weight %) obtained is a standard pyrolysis run carried out at 500 °C for 30 minutes, were 5-6 % solids, 40-60 % liquids and 35-55 % gases.

The raw samples, as well as the solid, liquid and gaseous products obtained in the pyrolysis experiments have been thoroughly characterized (TGA, elemental composition, GC/MS, GC/FID-TCD, G.C.V., etc.). The raw sample is mainly composed of PE and PP together with lower amounts of PS, PVC, PET and ABS, and some other minority materials (Al, paper, etc.). Pyrolysis solids are composed of the fillers of the raw plastics as well as of some char formed in the pyrolysis process. Pyrolysis gases are mainly composed of hydrocarbons with a little amount of CO and CO₂, and have a very high G.C.V. Pyrolysis liquids are a complex mixture of organic compounds with a high proportion of styrene (35-40 %) and significant amounts of ethyl-benzene, toluene and methyl-styrene. The results indicate that pyrolysis may be an appropriate alternative for treating packing and packaging waste rejected streams.

Composition of the permanent gases evolved during the high-temperature co-pyrolysis of coal and plastic wastes

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The carbonization of coal to produce metallurgical coke has a special interest as an alternative route in the feedstock recycling of plastic wastes of different structures and origins. As secondary raw materials, individual plastics or mixed plastics of a domestic origin can be incorporated into typical coking blends as minor components. In the present work the aim is to evaluate the composition and the characteristics of the permanent gases evolved during the high-temperature co-pyrolysis of plastic wastes and coal. For this purpose, a coking blend used for industrial metallurgical coke production was selected for blending with individual plastic wastes (HDPE, LDPE, PP, PS and PET) and two mixed plastics from household wastes. M1 is mainly composed of polyolefins (95 %) with a small amount of PET (5 %). In contrast, M2 is a real post-consumer plastic stream which contains a low amount of polyolefins and high amounts of PET and PS (about 35 %).

The slow co-pyrolysis was conducted in a Gray-King oven (ISO 502) at a heating rate of 5 °C/min from room temperature up to 900 °C in an atmosphere of evolved gases with a soaking time of 15 min. About 8 g of the coal blend (< 0.212 mm) both with and without plastic addition was used. The addition rate for the plastic waste was 2 wt %.

Although differences are small due to the low addition rate of the plastic waste (2 wt%), the presence of the polymers clearly has the effect of producing lower coke yields (76.9-77.7 wt%) compared to the reference coal blend (78.7 wt%) and of favouring the formation of gas and tar. Generally, the yields of gas and tar are below 15 wt% and above 7 wt%, respectively. The biggest difference was found for PET. Taking into account the contribution of coal to the distribution of the products, it can be deduced that polyolefins and PS are mainly recovered as oils and waxes in the tar and as light hydrocarbons in the gas. The contribution of the polymer to the solid is less than 0.2 %, except in the case of PET, which was found to enhance the coke and gas formation. On the other hand, mixed plastic wastes behave as the main polymers in the wastes.

Evaluation of the gas fraction by gas chromatography showed that its composition varied depending on the type of the polymers present in the blend. In all cases, the main components in the gas fraction were hydrogen, ranging from 32 to 47 vol% and methane ranging from 30 to 38 vol%, with carbon oxides and light hydrocarbons ($C_{\leq 4}$) accounting for the rest. Due to the high amount of light hydrocarbons, the properties of the gas as a fuel are enhanced. The gas density was found to be in the range of 0.58 to 0.70 kg/Nm³ and the gross calorific value in the 5400 to 5800 kcal/m³.

Pyrolysis and combustion behaviour of plastic wastes and coal

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Energy recovery and feedstock recycling of plastics from municipal wastes can be useful and efficient methods for dealing with unsorted or contaminated plastics. Integrated steel plants may extend the practice of plastic recycling by using plastics at two different stages of the steel production process. The first recycling route is related to the production of iron via the blast furnace, where plastic waste is injected through the tuyeres as a fuel and the second to metallurgical coke production where plastic wastes are incorporated as minor components in coal blends. In both cases, mixed plastic wastes replace coal as a fuel and as a raw material.

In this paper, our objective is to compare the thermal behaviour, under nitrogen and air atmospheres, of the six thermoplastics (HDPE, LDPE, PP, PS, PET and PVC) contained in municipal wastes and the overlapping that occurs when the coal decomposes. The pyrolysis and combustion behaviour of various plastic wastes was studied by thermal analysis. TG/DTG/DTA analysis was carried out in a TA Instruments SDT 2960 simultaneous thermoanalyser. The samples (10 mg and <0.212 mm) were heated up to 800 °C at a rate of 10 °C/min under a nitrogen or air flow of 100 ml/min. From the results it can be concluded that the melting temperature of the polymer is not affected by the presence of oxygen. The degradation of the plastic, however, exhibits a marked dependence. The temperature of maximum volatile evolution was significantly reduced, as was the amount of carbonaceous material towards the end of the process. Moreover, the DTG profiles of LDPE and PP show a single peak (422 and 386 °C, respectively) at a much lower temperature than during pyrolysis (480 and 460 °C, respectively). Under nitrogen and air atmospheres, PVC decomposition occurs in two distinct stages, the first at 290 °C yielding hydrogen chloride and benzene and the second a mixture of volatile products (469 °C under N₂ atmosphere and 436 °C under air atmosphere). PET also decomposes in two stages, the decomposition peak occurring at 574 °C in air corresponding to the burn-off of the char formed. PET is totally degraded, leaving less than 1 wt% of carbon material vs. 18 wt% in pyrolysis conditions. On the basis of the data, it can be concluded that polyolefins are more sensitive to the presence of oxygen in the reacting gas.

The TG/DTG curves of the coal blends under nitrogen and air atmospheres were also different. In the air atmosphere, coal exhibits an increase in weight at relatively low temperature which occurs after the release of the moisture and light gases trapped in the network (around 190 °C) and before the decomposition of the macromolecular structure (350 °C), caused by oxygen adsorption. This adsorption stage overlaps with the beginning of the decomposition of the polymers (HDPE, LDPE, PP, PS and PVC). The exception is PET which starts to decompose after the oxygen chemisorption stage.

Pyrolysis behaviour of mixtures of PET with pitch and coal

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Among the thermoplastics, polyethylene terephthalate (PET) is a promising raw material for the production of activated carbon due to its high of carbon content and the textural characteristics of the pyrolysis residue. However, a drawback of the use of PET for this purpose is its low pyrolysis yield. Therefore, the co-processing with other carbon precursors may serve to improve the pyrolysis yield. Bituminous coals are the main precursors for producing activated carbons due to the porosity developed during carbonization/activation processes. In order to produce activated carbons, coals must be oxidized to destroy their coking capacity. In previous studies, it has been shown that thermoplasticity of coals can be eliminated by blending with PET, even when small amounts of PET (5 and 10 wt%) are added to coal. However, the amount of PET that needs to be added to destroy thermoplasticity depends on the fluidity of the coal. The same effect on fluidity can be achieved by mixing PET with coal-tar pitches (CTP). In other words, the co-processing of PET and coal or CTP for activated carbon production could be an alternative recycling route for this polymer. The aim of the present work was to evaluate the effect of PET addition on the thermal behaviour of bituminous coals and CTP by means of thermogravimetric analysis.

Two bituminous coals of different rank and similar fluidity (CP and CO) and a CTP with a softening point of 72 °C were chosen for blending with PET (1:1 w/w). TG/DTG analysis was carried out in a TA Instruments SDT 2960 thermoanalyser. The samples (10 mg, <0.212 mm) were heated up to 1000 °C at a rate of 10 °C/min under a N₂ flow of 100 ml/min.

PET starts to decompose at around 350°C, the maximum release of volatile matter occurs at about 430 °C (T_{max}) and the mass loss being negligible at temperatures higher than 500 °C. At this temperature the char yield is 15 wt%. Taking into account the temperature range of thermal decomposition of the raw materials, coal-tar pitch (CTP), which decomposes over a wide temperature range (160-525 °C, T_{max} at 326 °C), overlaps with the decomposition of PET to a higher extent than with the two coals, which decompose in a narrow interval and at the end of PET decomposition (coal CP -400-540 °C, T_{max} at 466 °C- and coal CO -415-540 °C, T_{max} at 485 °C-). Consequently, the degree of interaction between the starting materials and PET will be higher for CTP and much lower for coal CO, with an intermediate degree of interaction in the case of coal CP. Applying the additivity law for the blends, the differences between the experimental and calculated TG/DTG data confirm that CTP is the more active modifier. Furthermore, it can be deduced that CTP can be used as a solvent for the polymer, since CTP reduces the melting temperature of PET. Thus, the greater the interaction between components, the more the char microstructure is modified.

Continuous Catalytic Pyrolysis of HDPE over Zeolite Catalysts in a Conical Spouted Bed Reactor

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The production and use of plastics are increasing considerably, about 4% per year, due to their contribution to all daily activities. Thus, 33 million tonnes were produced in Western Europe in 2005 [1], of which 21 million tonnes were polyolefins and 6 million HDPE. At present, only a small percentage of plastic waste is recovered or recycled, less than 20% of the residual plastic. Pyrolysis is an alternative process for converting and upgrading plastic wastes.

In the pyrolysis of polyolefins, the use of catalysts in the reactor decreases the temperature required for pyrolysis and modifies product distribution. Moreover, it improves the yield of volatile products and provides selectivity in product distribution, especially for obtaining products of great commercial interest (gasoline and monomers) [2, 3].

A study has been carried out on the performance of various acid zeolites, such as HZSM-5, H β and HY catalysts, in the pyrolysis of one of the most used plastic, as is high density polyethylene (HDPE). A conical spouted bed reactor has been used in order to obtain flash pyrolysis data

Operation has been carried out continuously at 500°C. The catalyst bed consists of 30 g, and 1 g min⁻¹ of plastic has been fed into the reactor. The nitrogen flowrate is 20% in excess of that required for minimum spouting velocity (12 L min⁻¹ at room conditions). Product analysis has been carried out by means of an Agilent 6890 chromatograph provided with thermal conductivity (TCD) and flame ionization (FID) detectors, being connected on-line to the reactor by means of a thermostated line. Furthermore, product identification has been carried out by means of a mass spectrometer (Shimadzu QP2010S) and a μ GC-MS spectrometer (Agilent MSD5975B).

Reaction product analysis has been carried out every 40 minutes throughout the duration of the reactions and the product streams have been grouped into 7 lumps. These are the lumps of light olefins (C₂-C₄) and light alkanes (<C₄) in the gas fraction; the liquid fraction consisting of three lumps: non-aromatic C₅-C₁₁ compounds, single-ring aromatics and C₁₁+ hydrocarbons; wax, which is collected in the filter and quantified by weight, and the lump of coke.

Light olefins is the main lump of the reaction with the HZSM-5 catalyst, accounting for around 60 wt% yield. Propylene and butenes are the prevailing products in this lump, around 30wt% and 20 wt% yields, respectively. On the contrary, non-aromatic C₅-C₁₁ compounds are the main lump with H β and HY zeolite catalysts, around 45 wt% yield in both cases, and the lump of light olefins is the next lump in quantity, around 35 wt% and 25 wt% yields with H β and HY zeolite catalysts, respectively. Olefins are the prevailing family for both catalysts, H β and HY, in the fraction of non-aromatic C₅-C₁₁ components. The runs have been finished at the moment that wax formation caused operational problems.

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Quantitative analysis of a cross-linking agent in polycarbonate using reactive pyrolysis - GC/MS

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Polycarbonate (PC) is often the polymer of choice in many commercial and household products, due to its durability, clarity and temperature stability. Crossing-linking agents such as 1,1,1-Tris(*p*-hydroxyphenyl)ethane (THPE) are often used to increase the melt viscosity and average molecular weight of the polymer. Because of its impact on the characteristics of the polymer, it is important to know the final concentration of THPE incorporated into the polymer. This analysis normally involves hydrolysis of the PC followed by solvent extraction. The extract is then analyzed chromatographically. This methodology is cumbersome and often results in poor data quality.

The work presents a new approach for analyzing THPE in cross-linked PC. It is based upon reactive pyrolysis – GC [1]. Preparation of the sample is simple and straightforward – a known amount of PC is dissolved in a known volume of a solvent, such as methylene chloride to obtain a 20mg (PC) / mL (CH₂Cl₂) solution. Five microliters of this solution containing *ca.* 0.1mg (PC) along with 10μL of tetramethyl ammonium hydroxide (TMAH) [25% in methanol] are placed in a small sample cup. The sample is ready for analysis.

Analysis is performed using a multi-functional pyrolyzer (model 2020iD, Frontier Laboratories, Japan) interfaced to a GC/MS. The sample cup is dropped into the furnace, which is at 400°C. The heat initiates the hydrolysis of the cross-linked PC which is immediately followed by methylation of the hydrolyzates.

During the development of this method, both evolved gas analysis (EGA) and flash pyrolysis (Py) were evaluated. The results from these studies will be presented; however, both methods proved to be inadequate for the quantitative determination of “bound” THPE in polycarbonate. The ester linkages in cross-linked PC are amenable to thermal hydrolysis followed by *in-situ* derivatization, that is, reactive pyrolysis. Precision and accuracy data obtained by the developed method clearly illustrates that this method is easily implemented and applicable to the quantitative analysis of the cross-linking agent in PC.

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Thermal behaviour of PVC and a polyhydroxybutyrate -valerate copolymer

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PVC is (with polyethylene and polypropylene) one of the most employed polymers. PVC properties can be easily modified by the presence of different additives, as plasticizers, thermal stabilizers, fillers, antioxidants, etc... Among all the additives, it is worth mentioning plasticizers, that are usually employed in order to impart flexibility to PVC. Thus, although PVC is a rigid polymer, flexible PVC is commonly employed in toys, door gaskets, etc.

Apart from all these additives, PVC formulations may also include other polymers that could also be added for different purposes. In this sense, polyhydroxybutyrates (or in general terms polyhydroxyalkanoates) can be successfully employed in PVC formulations. They are renewable materials directly produced by different type of microorganism. Once the polymer has been synthesized, it is only necessary its purification and isolation.

In the present work, blends of flexible PVC and a commercial polyhydroxybutyrate -valerate copolymer (PHBV) have been prepared in concentrations up to 50 phr (part per hundred of PVC resin) and their thermal decompositions, in air and inert atmosphere, have been analyzed.

Degradation of blends occurs in two different and separated steps. The first occurs between 250-300°C, while the second process at temperatures above 400°C. Thermal degradation of pure PHBV begins at the same time that first stages of the weight loss attributed to PVC (plasticizer loss and PVC dehydrochlorination), but once it has started, it takes place rapidly and has concluded when PVC degradation is still occurring. The blends apparent thermal behavior is in general terms the addition of the contribution of the degradation of both polymers, and depending on the PHBV concentration, it appears as a shoulder or as a maximum. It is worth mentioning that PHBV degradation occurs in a similar way in both kinds of atmospheres (i.e. nitrogen and synthetic air), and in fact, its corresponding thermogravimetric curves are almost coincident. In good agreement with results Thermal degradation of PVC is more sensitive to the type of atmosphere employed than that of PHBV. It causes slight differences in the first degradation step (250-300°C) processes, while relevant differences in the second degradation step (above 400°C).

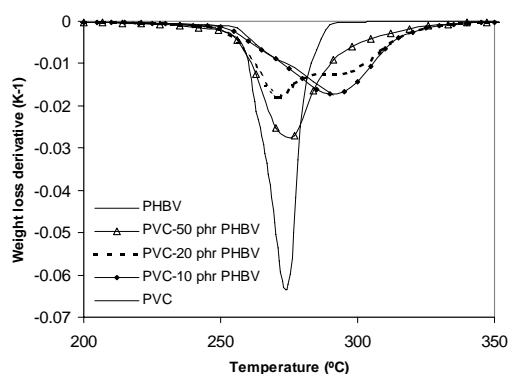


Figure 1. Weight loss derivative curves for pyrolysis experiments in the temperatures range 200-350°C.

Catalytic Cracking of Polyethylene over Zeolite Mordenite with Enhanced Textural Properties

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The worldwide polymer production has continuously grown in the last decades. Although being the worst strategy, plastics waste often ends-up in landfill, which implies in many countries the progressive depletion of the available space. Moreover, a used polymer is still a valuable raw material. Energy recovery and mechanical or feedstock recycling, are preferred options for the management of plastic wastes. Every choice possesses advantages and disadvantages, and the use of a mix of all recovery methods may be necessary in order to divert the disposal of used polymers from land-filling. Among the number of alternatives existing in the field of feedstock recycling, catalytic cracking over different solid catalysts has attracted special attention in the last years [1]. Particularly, zeolites have demonstrated to be efficient catalysts in the degradation of polyolefins into products with higher commercial value. Additionally, it has been pointed out the importance of the proportion of external acid sites, fully accessible for the polymer macromolecules, over the catalyst activity [2]. In this work, zeolite Mordenite has been chosen as catalyst in the pyrolysis of polyethylene. By means of a new synthesis method [3], different Mordenite samples with enhanced textural properties have been prepared, testing and comparing their activity on the catalytic cracking of low density polyethylene (LDPE) with a traditional Mordenite.

Cracking reactions of LDPE were carried out in a stainless steel batch reactor provided with a screw stirrer, operating at 420°C and atmospheric pressure for 2 hours under a continuous nitrogen flow. A mixture of 7.5 g of plastic and 0.15 g of catalyst (P/C = 50) were loaded into the reactor. Liquid and gaseous products leaving the reactor were separated in a condenser at 0°C and collected for GC analysis.

A number of Mordenite samples were synthesized, with BET and external surface areas from 385 and 9 m²/g, respectively, for the reference material, to 485 and 57 m²/g, for zeolites with enhanced textural properties. Thermal cracking of LDPE leads to plastic conversion lower than 30%, while values of 40% are reached when traditional Mordenite is used as catalyst. If Mordenite with enhanced textural properties is employed, a plastic conversion of 60% is attained, while turnover frequency (TOF) is twice higher than the value achieved on the reference sample (from 0.04 to 0.08 s⁻¹). In regards to the product distribution, both gas (C₁-C₅) and diesel (C₁₃-C₂₄) are formed as majority fractions when thermal and catalytic cracking over the reference mordenite is carried out. If modified Mordenite samples are used, both gas (C₁-C₅) and gasoline (C₆-C₁₂) fractions are obtained.

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Characterization of Styrene-Butadiene copolymers by catalytic pyrolysis over Al-MCM-41

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In this work, the Al-MCM-41 catalytic pyrolysis of styrene-butadiene copolymers carried out in a thermobalance has been studied. The degree of contact between the catalyst and the copolymer has been analysed and different particle size copolymer particles have been mixed with the catalyst. In addition, samples have been prepared by solution of the copolymer and mixing with the catalyst, thus assuring an intimate contact. Different decomposition steps which can be related to the degradation of the different domains of the copolymer (polystyrene (PS) and polybutadiene (PB)) have been observed. The application of a single pseudokinetic model would be exploited for the evaluation of the relative amount of material which evolves through each step. Therefore, the combination of both criteria, i.e., the assignment of each decomposition step and the application of the pseudokinetic model can be used for the characterization of the composition of commercial copolymers or mixtures of PB and PS, thus suggesting that the catalytic pyrolysis of polymers could be a valuable tool in order to provide a fast and simple method for the determination of the PB content of copolymers composed by styrene and butadiene units.

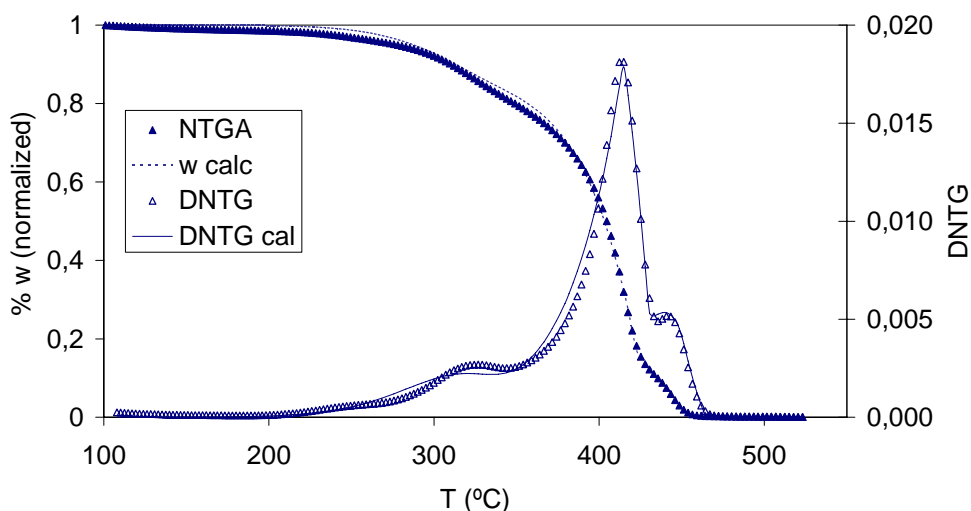


Figure 1. Comparison between the experimental and calculated TGA and DTG curves for HIPS.

Dechlorination of polychloroprene during thermal degradation

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Polychloroprene (PCP) is an elastomeric material used in combination with other rubbers for tubes, foams, and other applications where flexibility, resistance against cold and chemicals are required. In opposite to polyvinylchloride (PVC), the stability of the chlorine is much greater, due to the neighboring double bond. However, the removal of chlorine is required during recycling in order to protect facilities from corrosion, avoid the production of toxic products and maintain limits for the chlorine content.

The degradation of PCP was investigated by thermogravimetry (TGA), coupled with mass spectroscopy (TG-MS). Additional, PCP was decomposed in a quartz glass reactor. The products were analysed by GC-MS and ion chromatography (IC) in order to determine HCl.

PCP degrades in four steps. The apparent activation energies are 70~90 (weight loss: 0-8 wt%, temperature: 150-290 °C), 120~180 (8-44 wt%, 290-380 °C), 250~340 (44-52 wt%, 380-420 °C), and 290~300 kJ mol⁻¹ (52-64 wt%, 420-480 °C) in the first, second, third, and fourth stages, respectively, determined after the Ozawa method.

The first step is characterised by the evolution of HCl. Aliphatic products as chloroprene and its dimer are characteristic for the second step, while aromatics are mainly formed during the fourth step. HCl is produced over the whole degradation range, different to PVC where the dechlorination is mainly terminated below 260 °C [1].

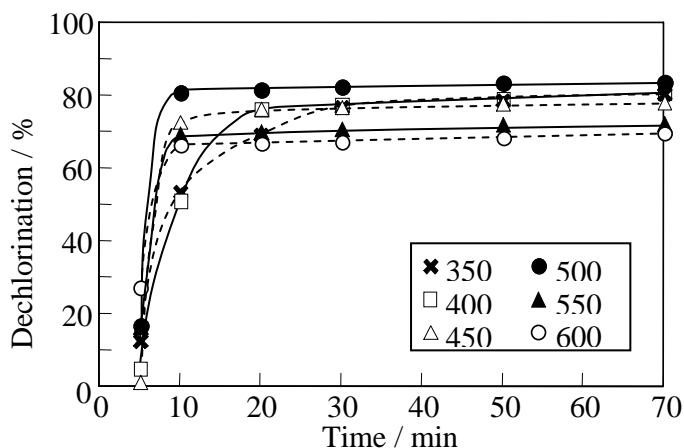


Figure 1. Variation in the dechlorination degree with the time during isothermal degradation of PCP at 350 ~ 600 °C.

Therefore, the dechlorination of PCP has to take place at higher temperatures. The best results are obtained at 500 °C. A dechlorination degree of more than 80% is achieved after 10 min (Fig.). At lower temperatures, the dechlorination velocity is reduced and also a lower dechlorination degree is obtained. However, also the rise of the temperature above 500 °C leads to a reduction of the dechlorination degree and velocity. Responsible might be the formation of chlorinated char making a further dechlorination difficult.

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Using waste FCC catalysts to de-brominate the pyrolysis products of flame retarded plastics

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Waste electrical and electronic equipment (WEEE) plastics are particularly problematic to recycle because they contain a variety of brominated flame retardants, some of which are extremely toxic. Pyrolysis has been proposed as a viable processing route for toxic WEEE plastics, but it has been found that the volatile pyrolysis products contain toxic brominated compounds. In this work, we have built on previous work where we reported that zeolite catalysts were capable of destroying toxic organobromines during pyrolysis.

We have investigated the pyrolysis of brominated high impact polystyrene and acrylonitrile – butadiene – styrene in the presence of a waste fluidised catalytic cracker (FCC) catalyst. The samples were pyrolysed in a fixed bed reactor with a final temperature of 410°C or 520°C. The waste FCC catalyst was mixed with the plastics in the reactor crucible. The pyrolysis oils were collected by a series of condensers and characterized by GC-MS and FT-IR and analysed for their bromine content. The pyrolysis gases were collected and characterized.

It is reported that, unlike Y-zeolite, the FCC catalyst did not completely destroy the organobromine compounds. However, the catalyst did lower the yield of bromine found in the volatile pyrolysis products by a mechanism that is as yet unclear. The waste FCC catalyst did not greatly alter the composition of the non-brominated pyrolysis products and valuable single ring aromatics were present in the pyrolysis oil.

Thermal and Catalytic Upgrading of Pyrolytic Oil from Pyrolysis of Municipal Plastic Wastes

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Recently, the generation amount of plastic wastes in Korea is about 4 million tones per year. For the recycling of plastic wastes, the pyrolysis technology is becoming a promising alternative, in order to recover fuel oil. The advantage of this method can treat all thermoplastic mixtures without using the separation treatment for plastic type in the mixture. Also, this can lower the environment resistance for air pollutant and soil contamination. However, the oil quality produced by pyrolysis of plastic wastes like wax material as low grade product was not good to use as alternative fuel oils. The upgrading of low grade oil that needs the change of chemical structure is required thermal and catalytic upgrading technology.

In this study, the low-grade pyrolytic oil supplied from a commercial rotary kiln pyrolysis plant for municipal plastic waste was upgraded on a stirred tank reactor with bench scale using fluid catalytic cracking (FCC) catalysts. The experiments were conducted by temperature programming with 10°C/min of heating rate up to 420°C and then holding time of 5 hrs. During this programming, the sampling of product oil was conducted at a constant lapse time. The characteristics of pyrolytic oil as raw material were examined. Then, the catalytic degradation of pyrolytic oil using fresh and spent FCC catalysts on the characteristic of products with different degradation temperature was also examined. These results were compared with that of thermal degradation. The thermal and catalytic upgrading effect the product distribution. The thermal upgrading without catalyst produced more residues instead of liquid product and also less gas product. The catalytic upgrading was more produced in oil and gas products as light hydrocarbons, in a comparison with those of thermal upgrading.

Table 1. Product yield obtained from thermal and catalytic degradation of pyrolytic oil at 420°C

Items	Oil	Residue	Gas
Pyrolysis	74.94	18.82	6.24
Catalytic degradation (spent FCC)	78.13	13.14	8.73
Catalytic degradation (fresh FCC)	79.08	13.05	7.87

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Feedstock recycling from oils/waxes of individual and mixed polyalkenes cracking products by copyrolysis with petroleum fraction

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Protection of our environment is now a global priority. One of many serious problems is the recycling of plastic wastes. They are not naturally decomposed. Their amount is increasing by year. Several petrochemical companies are looking for the possibility how to recycle plastic wastes in existing refinery facilities. There are two approaches how to treat plastic waste in refinery units: the plastic waste is either added into the feedstock during the process or the plastic waste is first of all thermally (catalytic) decomposed and then it is added into the feedstock [1]. Oils/waxes derived from thermal degradation of polyalkenes are aliphatic, they contain small amount of aromatics and are well soluble in liquid hydrocarbons [2].

The possibility of addition of oils/waxes to the petroleum fraction of virgin heavy naphtha was studied. The subject of our experiments was investigation of gaseous (mainly ethene and propene) and liquid products produced in copyrolysis. To be able to determine the influence of oils/waxes on product distribution, we made experiments with the individual virgin heavy naphtha at the same condition.

The preparation of solutions (LLDPE; HDPE/LDPE/LLDPE/PP (1:1:1:1) and LLDPE/LDPE/PP/HDPE/PVC/PET/PS (1:1:2:2:0.05:0.05:0.156 mass)) consists of two steps. In the first step polymers were thermally degraded in a batch reactor in the presence of nitrogen as inert gas at 450°C. The obtained oils/waxes were added to the virgin heavy naphtha in 10 mass %. The solutions were heated up to 60°C with goal to create homogenous solutions. In the second step they were copyrolysed in a laboratory flow reactor in the presence of steam at 780°C or at 820°C. The residence time varied from 0.08 to 0.51 s. The feedstock/steam ratio was 2:1 (mass). Detailed gas-chromatographic analyses of gaseous and liquid products were made.

Very interesting and promising results were achieved. The results of the investigation show that ethene and propene yields under the same conditions are higher or comparable with yields from virgin heavy naphtha. The finding proving that the solution of LLDPE/LDPE/PP/HDPE/PVC/PET/PS is able to provide maximum yields of propene and similar or higher yields of ethene in comparison with virgin heavy naphtha, at both temperature levels is rather positive. We have confirmed that even if the solution contains PET, PVC and PS is suitable for copyrolysis. The presence of PET, PVC and PS do not worsen the quality of oil/wax.

These results confirm that oils/waxes from polymers are suitable for preparation of feedstock for copyrolysis. Adding 10 mass % of waste polymers to virgin heavy naphtha can spare a substantial amount of this valuable liquid raw material.

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Pyrolysis of fire retardant anhydride-cured epoxy resins

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Introduction

Brominated epoxy resins (BER) make part of widely employed hardening plastics wherein bromine atoms play the role of active fire-retardant additives responsible for the self-extinguishing performance. From among numerous slow-burning epoxy resins, the practical outlets could be found predominantly for those obtained from diglycidylether of tetrabromobisphenol A (DGETBBA) and a number of hardeners amongst which the most popular are amines -aliphatic and aromatic- and anhydrides. In comparison to amines, anhydride cured epoxies in general provides longer pot lives, lower viscosity at the processing temperatures and curing with very slight exotherm; as a consequence they are preferred in epoxy sealants and putties as encapsulation materials for integrated circuits and semiconductor-based electronic systems. It has been reported that the presence of TBBA derivatives in amine cured BER strongly impairs their thermal resistance in comparison to that of non brominated epoxy resins (ER) [1]. Thermal stability is of relevance on the set up of temperature and residence time of pyrolytic thermal recycling which is an attractive economical revenue for end of life electric and electronic equipments. The purpose of the present study is to highlight some aspects of the thermal degradation processes anhydride cured brominated epoxy resins

Summary of the work performed, and the main conclusions.

Epoxies have been prepared on purposes by mixing phthalic anhydride (PHT) with diglycidylether of Bisphenol A (DGEBA) for ER and with a mixture 1/1 DGEBA/DGETBBA for BER. Curing was carried out at 120°C for 3 h. On curing increasing amount of -OH (3450 cm⁻¹), C=O (1724 cm⁻¹), 1264 cm⁻¹ (Ar-O(C=O) in DGETBBA) 1230 cm⁻¹ (Ar-O(C=O) in DGEBA) and decreasing amount of oxirane ring (3046 and 910 cm⁻¹) takes place. In parallel to what observed in amine hardened epoxies, the presence of bromine reduces here too the thermal stability: main weight loss in the TGA occurs at 383°C in BER and at 418 °C in ER; Evaporation of simple DGEBA and DGETBBA is located around 337°C, an additional stage at 378°C occurs in TGA of DGTEBBA in which brominated aliphatic are evolved.

Fast pyrolysis of the epoxies have been carried out at 423, 500, and 590 in Curie point Py-GC/MS equipment: PHT and epoxy monomers formed by a concerted mechanism of ester pyrolysis evaporate at 423°C. At 500°C acrolein is evolved from degradation of glycidyl groups, in addition DGETBBA run into debromination resulting in evolution of brominated aliphatic and brominated and unbrominated phenols/bisphenols. HBr is formed only in pyrolysis at T> 590°C.

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Converting of waste plastics into lighter hydrocarbons: the effect of the size increasing of process to the Pyrolysis

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Abstract

The reduction of the large amount of the waste polymers is more and more important not only from environmental but also energetic aspects, because these materials have reusable energy content. The chemical recycling or pyrolysis of polymer wastes is one perspective possibility of the industrial utilizations. In this paper different type of cracking processes has been presented for the waste polymers in particular the effect of the size increasing of the process to the yields and characteristic of products. Commercial real waste polyethylene and polypropylene were thermally decomposed by the use of tube reactors with different sizes: feed rate of 0,5kg/h with electric heating system and 7kg/h gas heating system using ~500°C temperature. Products were separated into fractions of gases, gasoline, middle distillates and heavy oil. It was found that plastic wastes could be converted into gasoline and middle distillates with yields of 20-37% and 30-41% depending on the applied reactor construction. Yields of hydrocarbons were affected by the construction, while their structure was mainly depending on the raw materials. The gas and liquid products had significant content of unsaturated hydrocarbons, principally olefins. Properties of products are advantageous for fuel-like applications, and productivity of refinery could be increased.

Keywords: waste polymers, recycling, pyrolysis, size increasing, octane number, cetane number.

Catalytic cracking of polyolefins over hierarchical HZSM-5 prepared from silanized seeds

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The world production of plastics continuously rises and so the management of plastic wastes has turned into worldwide problem. Feedstock recycling which involves a group of technologies aimed to transform the plastic waste into fuels or chemical raw materials has been proposed as one of the possible solutions. At present, the share of feedstock recycling in Western Europe is just 2% [1], mostly due to the high investment costs, the market uncertainty and the need of technological advances. Feedstock recycling of plastics by catalytic cracking towards fuels constitutes a feasible route to remove these wastes obtaining profitable products [2]. The bulky nature and high viscosity of plastics which leads to mass transfer constraints requires to use catalysts with high accessible surface area via mesopores or nanocrystalline materials in order to obtain high activities. In this way, the microporous zeolites such as ZSM-5 are to be attained either as nanosized crystals or as hierarchical zeolites (bimodal micro-mesoporous structure) to lead towards increased conversions with regards to conventional micrometer zeolites. Recently, a new procedure for the preparation of hierarchical zeolites by crystallization of silanized seeds was published [3] and successfully tested in the PP cracking. The present work is aimed at studying the cracking performance of hierarchical HZSM-5 samples prepared by silanized seeds with different polyolefins (LDPE, HDPE, PP), comparing them with conventional nanocrystalline HZSM-5 samples.

Hierarchical ZSM-5 samples with different surface area were prepared using as seed silanization agents 3-aminopropyltrimethoxysilane (APTMS), isobutyltriethoxysilane (IBTES), phenylaminopropyltrimethoxysilane (PHAPTMS). Conventional nanocrystalline HZSM-5 samples were synthesized by a low temperature and atmospheric pressure crystallization method. The crystallinity of the samples was checked by XRD, N₂ adsorption, TPD, FTIR, TEM. The cracking tests were carried out in a batch reactor at 340 – 360°C using plastic / catalyst mass ratio within 50 – 200. Depending on the chosen seed silanization agent, the external surface area of the hierarchical HZSM-5 zeolites varies from 166 to 314 m² g⁻¹. The activity per site of the hierarchical zeolites depends on the type of polymer and its value was higher than the conventional nanocrystalline ZSM-5 samples of similar external surface area. Thus, activities per site up to 1.4 s⁻¹ were obtained with hierarchical zeolites while for conventional nanocrystalline ZSM-5 reached at best only 0.6 s⁻¹. This indicates that the seed silanization method allows to prepare samples of not only higher external surface area but also increased crystallinity. The activity per site decreased according to the following trend LDPE > HDPE > PP.

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Compositional analysis of fluorinated and unfluorinated acrylic copolymers

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Polymers based on (meth)acrylic esters have found important applications since the forties in the formulation of varnishes, paints and adhesives for different substrates. Among the many different commercially available resins for such purposes, copolymers and polymer mixtures, either as solvent- or water-borne systems, often with undisclosed chemical structure and compositions, are the most commonly employed [1]. As many application-related properties strongly depend on the structural units of the polymer molecules, the chemical characterization of acrylic resins is therefore an important step of investigation, which permits to correlate performance with composition.

Within a comprehensive investigation on the durability of a series of acrylic products potentially usable for the protection and consolidation of monuments and stone surfaces, both commercial products and newly synthesized polymers [2], we have carried out preliminary compositional analyses. The monomeric components of a series of acrylic lattices containing fluorinated and unfluorinated monomeric units of different nature were determined by high temperature pyrolysis with direct analysis of volatile products of thermal degradation through a coupled system (pyrolysis-gas chromatography/mass spectrometry, Py-GC/MS), taking into account the pathways of thermal decomposition of acrylic and/or methacrylic homo- and copolymers [3]. The decomposition of (meth)acrylic polymers mainly yields to the constituent monomers, and both the methacrylic ester parent to the acrylic units and the acrylic ester corresponding to the methacrylic units, as secondary products. In addition, significant amounts of parent olefins, alcohols and alkanes, are formed from higher esters. In the case of dispersions with fluoro-containing acrylic monomers the component identification was possible by a direct comparison with the degradation behavior at high temperatures of a series of appositely prepared partially fluorinated acrylic copolymers. Finally, quantitative compositions were determined by ^1H NMR.

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Flash pyrolysis of heavy metal contaminated biomass from phytoremediation: Distribution of heavy metals in pyrolysis product streams

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Phytoremediation is a modern environmentally sound method for cleaning up metal contaminated soils. During phytoremediation, selected high biomass plants or trees are planted on the contaminated site; for transfer of the heavy metals from the soil into the plant biomass. Widespread application of this technique is inhibited due to the production of large amounts of metal contaminated waste, for which no suitable treatment process has been found yet [1]. Flash pyrolysis offers a valuable processing method for metal contaminated biomass: the rather low pyrolysis temperature – unlike combustion – prevents metals from volatilisation and valuable bio-oil is produced [2]. Knowledge of the metal distribution is of prime importance concerning the valorisation opportunities of the product streams.

Willow species (*salix spp.*) are grown as short rotation coppice on a testing site at a metal contaminated site in Balen (Belgium). Both plant stems and leaves are pyrolysed in a lab-scale semi-continuous reactor [3]. Biomass and pyrolysis products as oil and char are extensively analysed using elemental analysis and chromatographic methods with the focus on the metal distribution. For biomass, a standard microwave digestion method is applied, for bio-oil and bio-char a microwave digestion method is developed. Measurements are performed using ICP-AES; target elements include Zn, Cd, Pb and Cu.

Parameters under investigation are pyrolysis temperature, the use of hot-gas filtration and the co-pyrolysis of willow stems and leaves in their natural weight ratio.

Preliminary results indicated a product stream similar to the product stream of uncontaminated willow. The bio-oil yield, char yield and bio-oil water content are comparable to uncontaminated willows product streams. ICP-AES measurements confirm very low levels of metals occurring in bio-oil (Cu and Zn < 5 ppm; Cd and Pb < 1 ppm) and almost all of the metals accumulated in the char, thus releasing minimal or no heavy metals to the environment.

Flash pyrolysis can likely offer a valuable processing method for heavy metal contaminated biomass from phytoremediation, thus limiting the waste disposal problem associated with phytoremediation.

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Chlorine fixation by metal oxide in pyrolysis of Cl-containing polymers

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The emission control of volatile halogenated substances (VHSs) is a very important issue for thermochemical treatment of waste polymers. We have so far carried out fundamental studies on pyrolysis of various synthetic polymers and metal oxides in order to establish a simultaneous treatment of waste polymers and oxide wastes such as metallurgical dusts. One of the advantages of this treatment is that a proper selection of oxide leads to the considerable suppression of the emission of VHSs partly due to the chlorination of the oxide. In the present paper we discuss the chlorine fixation ability of various metal oxides in pyrolysis of chlorinated polymers.

We have examined poly(vinyl chloride), PVC, and poly(vinylidene chloride – co vinyl chloride), PVDC, with the nominal unit composition of C_2H_3Cl and $C_4H_5Cl_3$, respectively. Pyrolysis sample was prepared by mechanical mixing of polymer and reagent grade metal oxide powders. Pyrolysis experiment at constant temperature and thermogravimetric analysis (TGA) have been carried out, of which details have been described in our previous report [1], in which the pyrolysis of PVC with some metal oxides have been examined mainly in regard to the organic products.

It is well known that the pyrolysis of PVC and PVDC causes the emission of hydrogen chloride gas. Table 1 shows the analytical results of the amount of Cl anion collected at water trap in the pyrolysis at 800 °C. The table shows that the addition of oxide leads to the suppression of HCl, and that the apparent ability is clearly different among oxides examined. Our previous study showed that the addition of La_2O_3 in thermal degradation of PVC resulted in the considerable suppression of HCl with the chlorine fixation of >95% as oxychloride, $LaOCl$ [1]. In this case the high fixation ability can be achieved by the composition of $[Cl]:[La]=1:1$ for the initial sample. We have, therefore, examined the chlorine fixation ability of La_2O_3 by varying its composition in thermal degradation of PVDC. The fixation of ~78% was observed for the composition of $[Cl]:[La]=1:1$, and ~92 % for $[Cl]:[La]= 3:4$. The slight difference in the ability between PVDC and PVC can be related to both the different physical properties, such as particle size, and the difference in degradation behavior of PVC and PVDC.

Table 1. Ratio of Cl captured at water trap and the initial chlorine for the pyrolysis of PVC and PVDC -oxide mixtures at 800 °C. The composition of the mixture is [polymer] : [oxide] = 2:3 for PVDC – ZnO system and 2:1 for other systems in molar ratio

Oxide	None	ZnO	Fe_2O_3	La_2O_3	Nd_2O_3
PVC	92	36	69	3	25
PVDC	~100	16	75	71	65

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HDPE Chemical Recycling Promoted by Phenol Solvent

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Feedstock recycling includes a wide range of technologies designed to convert plastic wastes into chemical intermediates applied to the production of polymers, chemicals, lubricants or fuels. Thermal cracking is one such technology and involves plastic degradation at temperatures between 400 and 800 °C under inert atmospheric conditions. In the case of polyolefins, this process involves a random scission mechanism that generates a mixture of n-paraffins, α -olefins and α,ω -dienes over a wide range of molecular weights [1]. Degradation of polymers in the presence of a solvent has been proposed to reduce the polymer viscosity and therefore remedy the problems of low heat and mass transfer rates commonly encountered in polymer recycling by thermal cracking [2]. Nonetheless, the effect of some solvents is even more significant during the thermal decomposition of polymers. In particular, solvents with a hydrogen donor capability may participate in the degradation mechanism affecting the hydrocarbon yield and distribution [3]. In the current study, we have investigated the thermal cracking of HDPE using a hydrogen donor solvent (phenol). The work is focused on the effect of the solvent/plastic ratio in the product yield and composition. The experiments were performed in a stainless steel autoclave reactor under a nitrogen atmosphere.

As shown Figure 1, the yield of the gaseous hydrocarbons (C_1 - C_4) rose with the amount of solvent. Olefins were the main products in this fraction. The yields of the C_5 - C_{20} and C_{21} - C_{32}

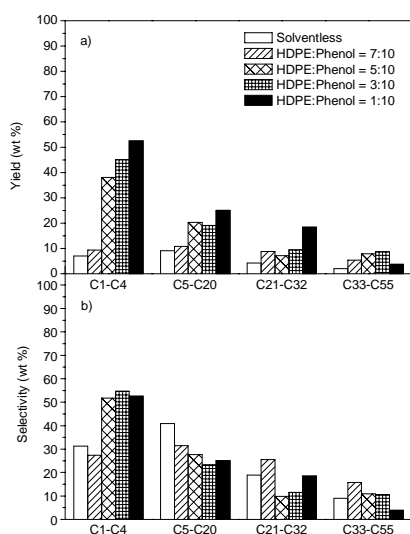


Figure 1. Effect of the plastic:solvent ratio on the a) yields and b) selectivities for hydrocarbon groups, based on the number of carbon atoms. Temperature = 400 °C. Time = 5 hours. Initial pressure = 20 bars.

hydrocarbon fractions also enhanced with the amount of phenol. In all reactions, the main products of these fractions were linear hydrocarbons such as n-paraffins and α -olefins. The yields of both hydrocarbons increased in line with the amount of phenol. However, the increase was more significant in the case of α -olefins. Conversely, the selectivities towards gaseous hydrocarbons kept nearly constant from the reaction free of solvent to the corresponding degradation at a 7:10 HDPE/Phenol ratio and increased significantly at a 5:10 HDPE/Phenol ratio. This selectivity, however, kept constant at 1:10 plastic/phenol ratio. As a consequence, a decrease in the selectivity to the C_5 - C_{20} fraction was observed with a larger amount of solvent. All these results indicate that the phenol promotes the plastic degradation from an HDPE:solvent ratio of 5:10 onwards. The production of gaseous olefins was particularly significant in the presence of these amounts of phenol. A reaction mechanism has been proposed to explain these

results. Random scissions and chain reactions are favored by the presence of this solvent during the HDPE thermal degradation.

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**Rapid determination of trace organophosphonates
used as ionic surfactants in an aqueous system
by reactive pyrolysis - GC/MS**

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Organophosphonates such as 1-hydroxyethylidene-1,1-diphosphonic acid [HEDP] and bis (hexamethylene) triaminopenta (methylene-phosphonic acid) [BHMT] are used in a number of diverse applications such as industrial water treatment, household and industrial surfactants, pulp and paper processing, oil recovery, etc. Determination of trace organophosphonates in a water system usually involves extraction and/or preconcentration of the target components. The extracts then are often subjected to chromatographic or spectroscopic methods. This conventional methodology is not only cumbersome but often results in poor data quality.

This work presents a novel approach for the rapid and precise determination of trace amounts of organophosphonates in aqueous solution. It is based upon reactive pyrolysis–GC/MS in the presence of tetramethyl ammonium hydroxide (TMAH) [1] using the multi-functional micro-furnace pyrolyzer (PY-2020iD, Frontier-Lab, Japan). A 10µL aliquot of water sample containing the trace organophosphonate was injected into the sample cup that is used with the pyrolyzer; 1 µL of 25% of TMAH methanol solution was then added to the cup. Analysis was performed by introducing the sample cup into the furnace which was at 350°C. The heat initiated the hydrolysis followed by methylation of the organophosphonate, and the resulting products were detected by GC/MS to yield the pyrogram.

The reactive pyrolysis of an aqueous solution of HEDP yielded various phosphonate related products. Methyl dimethyl phosphonate and trimethyl phosphonate were clearly observed on the resulting pyrogram. Using a calibration based on an external standard, it was possible to make a rapid and precise determination of the ppm level organophosphate in water system. Precision and accuracy data clearly illustrate the advantages of the reactive pyrolysis method over the conventional methodology currently in use.

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Structural Aspects of High Temperature Thermosets – Bismaleimide / Propargyl Terminated Resin System

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Epoxy resins are the most commonly used resins for the fabrication of composite structures for aerospace applications and have limited thermal stability. Among the most wide spread cross-linking functions currently used (maleimide, nadimide, acetylene, etc.) [1], maleimide functions have undergone the most rapid development and are intermediate between epoxy and nadimide resin systems in thermal stability.

The easy synthetic route to aromatic bispropargyl ethers and curing leads to void free materials without high pressure and the excellent properties of the cured thermosets such as good thermal stability, low moisture absorption and low dielectric constant made them to a potent competitor to acetylene terminated resin systems. Although several bismaleimide blends are reported in the literature [2], studies on bismaleimide-bispropargyl ether blends are scarce. N,N-bismaleimido-4,4'-diphenyl ether (BMIE), bispropargyl ether of bisphenol A (BPEBPA) and 40:60 blend of BMIE and BPEBPA are made and are thermally polymerized. The curing behaviour of these materials is studied using differential scanning calorimetry. The thermal properties are investigated using thermogravimetry. Isothermal (400 °C) degradation of the cured materials was effected in nitrogen atmosphere for a constant time interval (10 min). The volatile products are collected in a frozen acetone matrix and are separated in a gas chromatograph and are identified using quadrupole mass spectrometer. From the products identified, a detailed degradation mechanism is proposed and discussed.

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Development of an additive mass spectral library for the qualitative analysis in polymeric materials by pyrolysis-GC/MS

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Pyrolysis-GC/MS (Py-GC/MS) is applied to both the characterization of polymeric materials and the determination of additives in polymeric materials. While the degradation products for a large number of polymers have been cataloged, there are not so much data on the degradation products of versatile additives used in polymer formulations. Conventional mass spectrum (MS) libraries such as Wiley and NIST are not always applicable to the pyrolysis data; consequently, there exists a strong demand upon a pyrolysis-based library containing spectral data for the associated pyrolyzates of additives used for polymeric materials.

In this work, a new mass spectral library (ADD-MS06) containing the spectra of the main pyrolyzates obtained from the pyrolysis (at 600°C) of about 400 different additives together with their pyrograms. In the pyrograms, the pyrolyzates usually contains a variety of fragmented compounds relating to its original additives which are very useful for the identification of unknown additives in the polymeric materials. For a given unknown polymeric material, conventional evolved gas analysis (EGA) is first tried by temperature programming at 20°C/min from 100 to 700°C in order to find the volatile additive zone on the resulting thermogram and then the thermal desorption (TD)-capillary GC/MS run is carried out for the method for the selected zone to obtain its detailed compositional information.

The search algorithm and the trial search results for several additives present in a variety of polymeric materials will also be discussed using the new ADD-MS06, conventional Wiley and NIST libraries for comparison.

Prediction of Useful Lifetime of Rubber Component by Accelerated Tests

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Rubber products have very wide use in many different economic sectors - transport, machine manufacturing, water supply, construction, electrical engineering etc. During use they are exposed to whole spectrum of mechanical loads, affected by temperature, radiation and aggressive substances. The impact of all these factors causes physical and chemical changes in rubber which results in the deterioration of mechanical characteristics. This process is called the ageing of rubber. In order to solve specific engineering and technical tasks, it is necessary to determine mechanical properties of the rubber and forecast how will they change during ageing as well as predict the lifespan of the rubber product. In this paper, the heat ageing effects on the material properties and useful lifetime prediction of rubber materials for rubber component were experimentally investigated. The accelerated test was carried out to the useful life of NBR and EPDM, which is used in rubber component. Compression set results changes as the threshold are used for assessment of useful life and time to threshold value were plotted against reciprocal of absolute temperature to give the Arrhenius plot. The useful life at variable temperatures and activation energy are obtained in Arrhenius relationship. Also, we considered the effect of antioxidant agents. Useful life prediction procedure employed in this study could be used approximately for the design of rubber components at early design state.

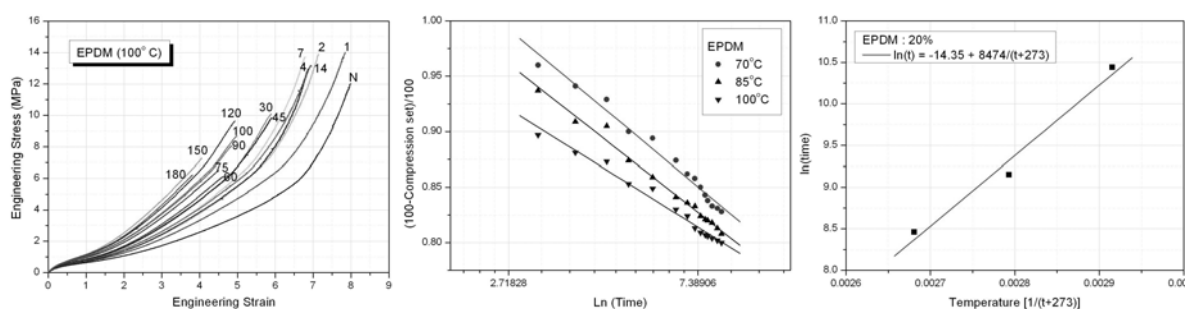


Figure 1. Heat ageing test and Arrhenius plot of rubber material

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The Effects of Calcium-type Catalysts on the Pyrolysis Reaction of LDPE and EVA Resin into Fuel-oil

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In Korea, the generation of waste vinyl film has increased to 238,000 tons in the year 2003 and 264,000 tons in the year 2006. Recycled the waste film to raw material is very ideal method but this method require very large amount of cleaning water. Therefore to convert fuel oil by pyrolysis in the low temperature is an economical method from a point of view of the environment and energy. Agricultural film is made to add the different additive to the base resins of low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and ethylene vinyl acetate (EVA) in Korea. And many researchers [1-3] have studied about silica alumina type catalyst for pyrolysis of these materials. So, in this study, the effects of resin additives and calcium type catalysts addition on the thermal decomposition of low density polyethylene (LDPE) and ethylene vinyl acetate(EVA) resin have been studied in a thermal analyzer (TGA, DSC) and a small batch reactor. The calcium type catalysts tested were calcinated dolomite, lime, and calcinated oyster shell. The resin additives were antifogging-agent and longevity-agent. Granular form LDPE resin (average molecular weight=24,000, density=0.92 g/cm³) was obtained from Hyudai Petrochemical Co., and Granular form EVA resin (contents of VA=12%, average molecular weight=29,000, density=0.93 g/cm³) was obtained from LG Petrochemical Co.. LDPE resin contained the antifogging-agent (nonionic surfactant), and LDPE resin contained the longevity-agent (light stabilizer) was offered from KMC Co..

As the results of TGA experiments, the addition of antifogging-agent increased the LDPE pyrolysis reaction rate, but addition of longevity-agent decreased the rate. Pyrolysis starting temperature for LDPE varied in the range of 330~360 according to the heating rate, but EVA resin had the 1st pyrolysis temperature range of 300~400 and the 2nd pyrolysis temperature range of 425~525 . The calcinated dolomite enhanced the pyrolysis rate in LDPE pyrolysis reaction, while the calcium type catalysts reduced the pyrolysis rate in EVA pyrolysis reaction. In the DSC experiments, addition of antifogging-agent decreased the heat of fusion and the heat of pyrolysis reaction. Also addition of calcium type catalysts reduced the melting point, but did not affect to the heat of fusion. Calcinated dolomite reduced 20% of the heat of pyrolysis reaction. In the batch system experiments, mixing of antifogging-agent and longevity-agent produced the fuel oil having lower carbon number. The mixing of calcinated dolomite and lime enhanced the yield of fuel oil, but did not affect to the distribution of carbon numbers.

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SESSION 6 PYROLYSIS TREATMENTS:
Pulp & Paper, Fossil Fuels & other Industrial Applications

Effects of potassium distributions in carbonizations of bituminous coal

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Activated carbon is the most widely used adsorbent due to its relatively large pore volume and high surface area. The carbon precursor or the carbonization conditions are chosen to achieve a unique set of desirable properties [1-3]. Coal provides about 28% of the precursors (4). Its carbonization is complex – depending on factors such as its compositions, guest-host interaction among the coal components, heating rate, carbonization temperature and the amount of its native inorganic compounds (5). In this presentation recent results on the carbonizations profiles of several samples of coal and coal/KOH will be discussed. The carbonized products were characterized using TGA, BET, TEM and adsorption of Lead from its aqueous solutions (10 – 100 ppm). The coal sample exhibited three major regions of weight losses corresponding to water losses (110 °C), onset of pyrolysis (350 – 500 °C) and gradual char decomposition above 700 °C. Less significant weight loss due to tar formation was observed at 250 °C. The carbonized coal residual weight was 65 % at 1,000 °C. This profile was changed in the presence of potassium. The weight losses associated with the onset of pyrolysis was lowered by about 200 °C. Depending on the degree of potassium distribution and intercalation in the samples, the residual weights range from 18 to 38 %. For the coal/KOH samples, no significant changes were observed at 400 – 700 °C. However, for the activated carbon obtained in this range (at 600 °C), the potassium distribution affected both the BET surface areas (661 – 1,994 m²/g) and the meso and micropore volumes ratios (0.48 – 0.91). There were also evolutions of nanostructures of both spherical and tubular morphologies as evidenced by TEM micrograph. The samples exhibited different adsorptive capacities. The amount of Lead adsorbed from its aqueous solutions ranges from 4.3 to 47.3 mg/g. Thus, different degrees of potassium effects led to activated carbons with different surface and adsorptive properties.

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Structural characterization of kraft *Pinus pinaster* pulps by analytical pyrolysis

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This study is focused on the residual lignin structure of *Pinus pinaster* kraft pulps. This species is the only softwood used in Portuguese pulp industry and its unbleached kraft pulp has a darker colour when compared with others softwood pulps.

In the present work several laboratorial kraft pulps were obtained and compared using analytical pyrolysis. Two sets of experiments were performed:

- 1) pulps were obtained by conventional kraft process with different delignification degrees (kappa numbers between 22 and 107)
- 2) pulps were obtained with the same kappa number (35) by different kraft processes (conventional batch, flow-through and modified batch using surfactants as cooking additives).

These pulps were compared with an industrial Portuguese pine kraft pulp and a *Pinus sylvestris* pulp obtained in the laboratorial kraft digester with the same conditions.

Pyrolysis results showed that the residual lignin of Maritime pine pulps with Kappa number ranging from 23 to 107 had an h/g ratio ranging from 0.11 to 0.37, approximately two to six times higher than the average h/g ratio of Maritime pine wood lignin (0.06). Pyrolysis results also show that Py lignin is very well correlated with kappa number ($r^2=0.93$). The reflectance factor is moderately correlated with Py lignin ($r^2=0.4$) and it is not correlated with lignin quality (h/g ratio) ($r^2=0.03$). Py lignin is moderately negatively correlated with h/g ratio ($r^2=0.40$).

Characterization of Primary Tars Produced from Coal Blends with Different Coking Pressure Characteristics

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The carbonization of coal to produce metallurgical coke for use in a blast furnace is carried out in horizontal slot-like ovens which are indirectly heated through the side walls. A moderate pressure within the oven is convenient for the development of coke structure. However, when some high-rank coals, commonly referred to as dangerous, are carbonized, the generation of excessive coking pressure may cause the bricks in the side walls of the oven to deteriorate, thereby shortening the life span of the oven [1-2]. Therefore, the coke industry and coal producers need to be able to forecast and assess the danger of a coal and to keep the coking pressure below certain limits in order to prolong the coke oven life. In a previous research work [3] ten coals were subjected to pyrolysis and their tars characterized. Tar composition was related to the coking pressure generation characteristics of the parent coals. In the present work the aim is to study the interaction of coals in blends in relation to coking pressure.

Four bituminous coals of different rank (VM content between 18.0 and 33.1 wt% db) were chosen for blending. Seven binary and three ternary blends were prepared. Gray-King pyrolysis (G-K) at 550 °C was carried out following the standard procedure (ISO 502). Primary tars were characterized using a gas capillary chromatograph fitted with a flame ionization detector (GC-FID). An HPLC analysis of the aromatic compounds present in the primary tar from the blends was carried out using a Hewlett-Packard HP1100 system incorporating two PLGel columns (300 mm length x 7.5 mm i.d.) packed with poly(styrene/divinylbenzene) of different nominal pore size (500 and 100 Å, respectively) and connected in series. For a better correlation of the coking pressure and tar composition, the GC chromatogram was divided into three regions depending on the boiling point of the compounds. Four major regions were defined in the HPLC chromatogram. The first three regions corresponded to *cata*-condensed PACs, while the last one corresponds to *peri*-condensed PACs. Coking pressure was measured in a movable wall oven of 15 kg capacity. In addition contraction/expansion was assessed by means of the Koppers-Incar test (KI).

The degree of additivity was studied in relation to the pyrolysis yields, tar composition, coking pressure and semicoke contraction/expansion.

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Application of TGA Parameters in Coke Quality Prediction Models for Coal Blends

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Coke is used together with iron ore and lime in the blast furnace to produce pig iron. Blast furnaces of a much larger capacity have come into use in the last few decades. These large furnaces and the injection of alternative types of fuels and sources of carbon like coal or plastic have led to the demand for coke of better quality. Nowadays the control of coke quality is assessed by means of the CSR index, which is the one most commonly used in the cokemaking industry. Coke reactivity to CO₂ depends on various factors [1, 2] such as coal rank, thermoplastic properties, ash and maceral composition, which are mainly related to the characteristics of the raw material. In a previous research work [3] TGA parameters were successfully used to predict coke quality. Our present aim is to find a way to predict the quality of coke produced from blends of coals on the basis of the coals characteristics. In the present work we investigate the possibility of introducing parameters derived from the thermogravimetric analysis of the coals into models designed to predict the quality of the blast furnace coke produced from blends of these coals.

Twenty one coal blends with a volatile matter (VM) content of between 20.8 and 28.9 wt% db were tested. The blends were composed of two, three or four coals of different rank (twenty five coals with a VM content of between 17.7 and 32.8 wt% db). A thermogravimetric analysis of the coals and the blends was carried out in a TA Instruments SDT 2960 thermoanalyser. For this test, a sample of 15-20 mg was heated up to 1000 °C at a heating rate of 10 °C/min. A nitrogen flow of 100 ml/min was maintained during the experiment to avoid oxidation and to sweep out the pyrolysis products. Carbonization tests of the coal and blends were carried out in a movable wall oven of 300 kg capacity. Coke reactivity towards CO₂ (CRI index) and coke strength after reaction (CSR index) were assessed by the CRI/CSR test developed by the Nippon Steel Corporation and standardized afterwards by ASTM (procedure D5341).

Various models were developed taking into account the different coal characteristics and the TGA parameters. The results obtained with our models were compared with those from in the literature. In both cases the correlation coefficients for the blends tested were similar.

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Thermal behavior and pyrolysis products of organo-layered silicate used on preparing *in situ* polyethylene nanocomposites

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A promising approach to effectively disperse organoclays into polyolefins matrices at nanometric scale is the *in situ* polymerization [1]. According to this method, the catalyst has to be immobilized into the filler layers and the subsequent clay dispersion degree into the polymer matrix depends on the concentration of the reactive sites formed between the silicate layers. Despite the number of papers appeared in the last years, the role of the different experimental procedures on final properties of the resultant nanocomposites is not well clear.

The present study is aimed at understanding the interactions between the clay and the cocatalyst during the pre-treatment step and their role in the *in situ* polymerization technique. The catalyst immobilization on clay plays a key role in achieving nanocomposites, so we have thoroughly investigated the effect of the pre-treatment of natural and ammonium-modified clays with iron catalysts. In particular, aluminosilicate was first allowed to react with organoclay to produce an evenly supported cocatalyst, then the iron pre-catalyst was added to supported cocatalyst suspension to pre-form *in situ* a layered silicate-immobilized catalyst.

The thermal behavior of organically modified layered silicates and intermediates is an important issue in the synthesis and processing of polymer nanocomposites [2]. Thus the determination of the onset degradation temperature as well as the identification of the decomposition products are crucial. We investigated the thermal degradation of pure clays and supported pretreated clays using TGA, TGA-FTIR and pyrolysis-GC/MS techniques.

Pyrolysis and thermogravimetric experiments allowed us to describe the evolution of the structure of the organoclay after the reactive pre-treatment with alkylaluminosilicate cocatalyst and to determine the influence of the experimental parameters (such as the nature of nano-filler, catalyst system and the synthesis strategy) on preparing polyethylene-layered silicate nanocomposites.

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Octanoic Acid Pyrolysis Coke in a stainless-steel tube: passivator, inhibitor or activator?

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Large amounts of used cooking oils are produced especially by the food industry as wastes. A good knowledge of the mechanism involved in the pyrolysis of used cooking oils is a prerequisite to predict reliably the optimal operating conditions of the process which would lead to the production of the target source of energy: (i) hydrogen for use in fuel cells, (ii) synthesis gas in favorable ratios to obtain either synthetic diesel by Fischer-Trosch catalysis or bio-methanol, (iii) hydrocarbons (high heating value gaseous fuel).

Since used cooking oils contain mainly triglycerides, diglycerides and free fatty acids, octanoic acid was selected in this work as first model molecule to analyze and modeling the behavior of the pyrolysis carboxylic acid chemical function. With the aim of an easier scaling-up of the developed pilot plant to a semi-industrial plant, octanoic acid pyrolysis was carried out in continuous flow stainless-steel tubular reactors. Nevertheless, the main drawback of using this kind of reactor materials is the coke formation that has obviously been observed in this work. Coke formation during thermal cracking is a complex phenomenon, which depends on many factors: operating conditions, feedstock, materials of construction and pretreatments of the inner walls of the pyrolysis tube [1]. Also, it is established that coke formation occurs in two main steps [2]. (i) First, coke is formed by an heterogeneous gas/solid catalytic mechanism by which the properties of the tube skin play an important role. (ii) Once the metal surface is lined with coke, an heterogeneous gas/solid non-catalytic mechanism dominates. Hence, coke quantitatively modifies the distribution of the pyrolysis products. Therefore, in this work, and as shown in previous literature exclusively focused on hydrocarbon thermal cracking [3], the dual nature of coke as accelerator or inhibitor was investigated in the particular case of octanoic acid as feedstock by on-line product analyses during the pyrolysis process (infrared spectrometry and gas chromatography analysis).

In order to analyze the effects of temperature, residence time, and reactor material composition, octanoic acid pyrolysis was conducted in reactors of various metal compositions and inner diameters (Incoloy 800 with i.d.: 14.3 mm ; Inconel Alloy 600 with i.d.: 21.1 mm). At all temperatures (873K – 1023K), higher octanoic acid conversion was observed at the smallest residence time obtained with the Incoloy 800 reactor. This result shows that, in addition of important effect of reactor surfaces, octanoic acid pyrolysis is catalyzed by Fe, Ni, and Cr metal content of the coke formed at the initial stage of the reaction (observed by Scanning Electron Microscopy analysis). Continuous CO, CO₂ and H₂ product analysis during octanoic acid pyrolysis confirmed this result and showed that the coke formed acts first as an activator and then as an inhibitor with regards to its two formation steps. This work definitely demonstrates that quartz reactors are prerequisite to generate kinetic data aimed at validating or extending homogeneous gas-phase kinetic model. The later may further be combined with models able to account for catalytic or non-catalytic surface reactions in order to obtain a realistic description of the full thermal cracking chemical process.

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Reductive Pyrolysis of Biodesulphurized Demineralized Coal

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The sulphur presence in coal is a serious obstacle for its utilization, since during combustion the sulphur is emitted into the atmosphere mainly as sulphur oxides. This high amount of sulphur needs to be removed before use from the coal by desulphurization processes and seems to be more effective in view of environmental aspects. Recently, biological approaches – biodesulphurization, as an environmental more friendly method for desulphurization becomes more popular.

The current study emphasis especially on the changes that occur in coal organic sulphur forms after biodesulphurization. An object of the biodesulphurization process are three high sulphur containing samples – Humovitrain Maritza East (Ro = 0.20 %), Beypazari lignite (Ro = 0.27%) and Pirin sub-bituminous coal (Ro = 0.34%). The white rot fungi “*Phanerochaeta Chrysosporium*” – ME446 is the microorganism used in the biodesulphurization process [1]. In order to concentrate our efforts on a deeper research on organic sulphur, samples were demineralized and depyritized before the biodesulphurization. Maximum effect of the biodesulphurization due to total sulphur decreasing (ΔSt) of 25% and organic sulphur decreasing (ΔS_{org}) of 24% for Pyrin was registered. On the contrary, minimum effect of the biodesulphurization due to ΔSt (11%) and ΔS_{org} (3%) for the Baypazari was determined.

Temperature programmed reduction at atmospheric pressure (AP-TPR) proves to be an effective technique for the specification of organic sulphur forms in coal [2]. To study what kind of S_{org} is removed during biodesulphurization AP-TPR coupled “on-line” with mass-spectrometry (AP-TPR-MS) in different gas media (H_2 and He), and by the “off-line” AP-TPR-GC/MS analysis were applied. Deuterated sulphur compounds as inner standards were spiked for quantitative GC/MS data interpretation.

Small amounts of volatiles organic sulphur compounds are neither reduced in the AP-TPR condition nor captured in the tar fraction. These volatiles were quantitatively determined by “off-line” GC/MS technique applying single ion monitoring (SIM). To have an idea of the organic sulphur compounds captured in the tar and char, oxygen bomb combustion followed by ion chromatography was used.

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Analysis of Lignosulphonates by Pyrolysis-Gas Chromatography/Mass Spectrometry

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Lignosulphonates are complex biopolymers which are recovered from the spent sulphite pulping liquids. In the production of wood pulp using a sulphite pulping process, the lignins are sulphonated so they become water soluble. Lignosulphonates are used as binders, dispersants, emulsifiers and sequestrants in a host of products such as gypsum board, animal feed pellets and micronutrient systems. The properties of lignosulphonates are strongly affected by their structure, and therefore whether they are produced from softwoods, hardwoods, or grasses.

In this work, we are using analytical pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) in order to get information on the structure of lignosulphonates. Analytical pyrolysis is a rapid and highly sensitive technique for characterizing the chemical structure of lignin, allowing the analysis of small amounts of sample without prior manipulation and/or isolation. Characteristic features of lignins, including their composition in terms of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units can be established based upon analytical pyrolysis.

Four different lignosulphonate samples (one from hardwood and three from softwoods) were selected for this study: #261 (hardwood calcium lignosulphonate); #264 (softwood lignosulphonic acid, ion-exchanged to H⁺); #265 (softwood lignosulphonic acid, ion-exchanged to H⁺); #266 (softwood lignosulphonic acid, ion-exchanged to H⁺). These samples were analyzed by Py-GC/MS in order to assess the suitability of this technique for their characterization.

All the lignosulphonate samples released, upon Py-GC/MS, high amounts of low molecular weight sulphur compounds (sulphur dioxide, dimethyl sulphide, propylene sulphide, dimethyl disulphide, dimethyl trisulphide and methanesulphonic acid methyl ester) arising from the sulphonate group. Lignin-derived compounds with both guaiacyl (G) and syringyl (S) structures, characteristic of a hardwood lignin, as well as some amounts of carbohydrate-derived compounds, were identified in lignosulphonate #261. However, only guaiacyl (G) lignin-derived compounds, characteristic of softwood lignins, were present in the rest of lignosulphonates (samples #264, #265, #266). The presence of only guaiacol and vanillic acid methyl ester in the pyrolysate of the lignosulphonate sample #266 seems to indicate that this sample is more oxidized than the rest.

Rapid Assessment of the Lignin Composition of Lignocellulosic Materials Commonly Used for Paper Pulp Manufacturing by Analytical Pyrolysis

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The production of cellulose pulp by chemical pulping involves the separation of the cellulosic fibers and the removal of lignin by using an alkali solution and high temperatures and pressures. The content and chemical structure of woody components, in particular the lignin content and its composition in terms of its *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) moieties are important parameters in pulp production in view of delignification rates, chemical consumption and pulp yields. The higher reactivity of the S lignin with respect to the G lignin in alkaline systems is known and in general, the efficiency of pulping is directly proportional to the amount of syringyl (S) units in lignin. This is because the S lignin is relatively unbranched and has a lower condensation degree and therefore is easier to delignify while the G units have a free C-5 position available for carbon-carbon inter-unit bonds, which make them fairly resistant to lignin depolymerization in pulping. Therefore, the lignin S/G ratio of the respective lignocellulosic raw materials strongly affects the pulping efficiency. Higher S/G ratios will therefore imply higher delignification rates, less alkali consumption and therefore higher pulp yield.

In this work, the lignin composition (in terms of their S/G ratios) of different lignocellulosic materials commonly used for pulp and papermaking, including woody (eucalypt woods) and nonwoody fibers (flax, hemp, kenaf, sisal, jute, abaca and curaua), were characterized “in situ” by Py-GC/MS. Analytical pyrolysis has been found to be useful for the characterization of complex macromolecules including lignocellulosic materials and is a rapid and highly sensitive technique for characterizing the chemical structure of lignin, allowing the analysis of very small amounts of sample without prior manipulation and/or isolation. Characteristic features of lignins, including their composition in terms of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, can be established based upon analytical pyrolysis.

The estimation of the lignin content of the different raw materials indicated that flax and hemp fibers present the lowest lignin content (less than 5% Klason lignin), while kenaf, sisal, jute, abaca and curaua ranged from 10-14% Klason lignin, and eucalypt wood present around 20% Klason lignin. The lignin composition (S/G ratios) estimated by Py-GC/MS indicated that kenaf, sisal, jute, curaua and abaca fibers, as well as eucalypt wood, present high S/G lignin ratios (S/G molar ratio up to 5). However, flax or hemp fibers have lower ratios (S/G < 0,5). The high S-lignin content observed in some fibers is advantageous for delignification during pulping because the S lignin is mainly linked by more labile ether bonds, is relatively unbranched and has lower condensation degree than the G lignin. Therefore, the lignocellulosic raw materials with high S/G lignin ratio will be easier to be delignified because of the lower condensation degree of the lignin, despite having higher lignin content than other fibers. On the other hand, flax and hemp fibers, with very low lignin content, present a very low S/G lignin ratio which will make them fairly resistant to chemical pulping and subsequent bleaching.

Influence of temperature on the formation of soot in the pyrolysis of ethanol

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The shortening of fossil fuels and the promotion of ethanol production from renewable resources (bioethanol) make this alcohol a very interesting alternative to conventional fuels. In this context is of great interest the study of ethanol pyrolysis, with emphasis on the formation of soot, regarded as one of the most important atmospheric pollutants.

The present work reports a laboratory study on soot formation from ethanol pyrolysis. The pyrolysis experiments have been carried out in a quartz flow reactor for a total concentration of ethanol of 50000 ppm, in the 800 – 1200°C temperature range and for a gas residence time dependent on the operation temperature: $t_r = 4550/T(K)$. The product gases have been analyzed by a Gas Chromatograph equipped with TCD and FID detectors. Soot produced during the reaction time has been collected and quantified. Experimental results have been simulated and interpreted in terms of a literature detailed gas phase mechanism. The mechanism used in this study was the one used by Borruy and cols. (2008), additional reactions were added from the ethanol oxidation mechanism of Alzueta and Hernandez (2002). Calculations have been performed using Senkin which runs in conjunction with the Chemkin library.

Under the studied conditions, the results show that temperature is a fundamental parameter affecting both gas and solid products coming from ethanol pyrolysis. The soot yield increases as temperature does, whereas gas yield decreases. The temperature threshold value found for soot formation is 1050°C, comparatively higher than the values found for other reactants such as acetylene and ethylene, Ruiz and cols. (2007) under similar conditions of the present study. Modeling results fit reasonably well with experimental data, however the kinetic model exclusively includes the gas phase reactions. This fact can explain the disagreement found between the experimental and modeling results obtained for the concentrations of hydrogen and acetylene, regarded the most important reactants involved on soot formation and growth, according to the HACA (H₂ Abstraction C₂H₂ Addition) mechanism.

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Formation of Cyclopentadienyl Radical from Pyrolysis of Hydroquinone, Catechol and Phenol

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The formation of radicals from the gas-phase pyrolysis of hydroquinone, catechol, and phenol is thought to contribute to the free radicals in cigarette smoke. In this work, pyrolysis experiments between 800-1000 °C were carried out using the precursors in combination with Low Temperature Matrix Isolation-Electron Paramagnetic Resonance (LTMI-EPR).[1] Each reactant was transported through the reactor using carbon dioxide carrier gas at atmospheric pressure. Pyrolysis products were continuously removed through a silica probe at low pressure (*ca.* 0.1 torr). A micro diameter orifice (~ 100 μ m) was used to sample the pyrolysis gases into the cold finger. For radical measurements, the reactor effluent was frozen on a cold finger at 77 K using liquid nitrogen.

The initially samples in the 77 K carbon dioxide matrix produced a poorly resolved EPR spectra. Gradual warming of the Dewar was employed to allow annealing of the matrix and annihilation of mobile or reactive radicals. [2] These annealing experiments yielded more resolved, identifiable spectra. Annealed spectra of all three samples resulted in the generation of EPR spectra above 800 °C with 6 lines, hyperfine splitting constant 6.0 G, $g = 2.0043$ and peak-to-peak width ~ 3 G that was readily assignable, based on the literature and theoretical calculations, as that of cyclopentadienyl radical. Using low pressure pyrolysis of phenol (0.1 torr) in a carrier gas of CO₂ (0.3 torr), it was possible to detect and identify phenoxyl radicals based on the differences in the magnetic susceptibility of phenoxyl and cyclopentadienyl radicals. Conclusive identifications of phenoxy radicals were based on comparison to spectra produced from pyrolysis or photolysis of known phenoxyl precursors. To our knowledge, this study represents the first measurement of radicals produced from the gas-phase pyrolysis of hydroquinone and catechol.

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Pyrolysis of various biomass residues and char utilization for the production of activated carbons

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It has been widely reported the feasibility of using agricultural by-products as renewable source of energy by means of pyrolysis and gasification processes. Most biomass residues are composed by cellulose, hemicellulose and lignin, and subjected to pyrolysis processes, they decompose into three phases whose distribution depends on the raw material, temperature, heating rate and flow of inert agent. These phases are a solid (char), liquid (known as tars or oils) and gas, being all them a potential energy source to be used in different applications. Because of its incipient porosity, the char can be used as a precursor for the production of activated carbons. In activation processes, the porosity of the carbon produced depends mainly on the raw material and on the experimental conditions used: activating agent (and flow), activation temperature and time, use of chemicals...etc, which can be controlled in order to achieve a certain adsorption capacity for a determinate application [1]. Most of the works found in the literature study the influence of the operating parameters on the activation process, but the research focussed on the influence of the lignocellulosic composition of the raw material on a concrete activation process is scarce.

In this work the pyrolysis process of various different biomass materials (almond shell, walnut shell, almond tree wood, olive stone) was studied in terms of the energy content of the phases generated (gas and liquid). Then, the feasibility of preparing effective adsorbents from the char generated was studied. With this aim the char was used to prepare activated carbons by steam gasification at concrete activation temperature and time, identical for the four chars. The differences found were related to the chemical composition of the parent material.

The raw materials were characterized in terms of their proximate analysis (following standard norms), ultimate analysis (LECO CHN 1000 elemental analyser), and HHV (Parr 1351 calorimeter bomb). The pyrolysis was studied in two systems: first, by thermogravimetric analysis using a SETARAM thermogravimetric system. Then, quantifying the phases generated in an experimental installation that has been described elsewhere [2] and was also used in the activation processes. The composition of the gas produced was analysed by a 4000 HRGC KONIK gas chromatograph and the HHV of the tar generated was determined. The textural characteristics of the activated carbons were measured by means of N₂ (at 77 K) and CO₂ (at 273 K) adsorption isotherms, Hg porosimetry and He stereopictometry.

The results obtained in this work confirm that the lignocellulosic composition of raw material influences the distribution of the phases generated during the pyrolysis process. Also, it is deciding factor on the porosity development of the activated carbon obtained from the char, when the same operating parameters are used.

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Pyrolysis as a method to separate and recover materials from scrap printed circuit boards

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Printed circuit boards are problematic to recycle because they contain a heterogeneous mixture of organic and metallic material and, in addition, they can contain toxic brominated flame retardants as well as other toxic metals. In this work, we have investigated using pyrolysis to decompose and recover the organic fraction of printed circuit boards while simultaneously making the boards friable so that the metallic material can be recovered.

Printed circuit boards from waste computers, televisions, and mobile phones were pyrolysed in a fixed bed reactor. A selection of printed circuit boards from each of the three waste classes was pyrolysed at 800°C and the pyrolysis products were analysed using GC-FID, GC-TCD, GC-MS, GC-ECD, ICP-MS, and SEM-EDX. The pyrolysis oils contained high concentrations of phenol, 4-(1-methylethyl)phenol, and p-hydroxyphenol, as well as bisphenol A, tetrabromobisphenol A, methyl phenols, and bromophenols. The pyrolysis oils also contained significant concentrations of organo – phosphate compounds and a number of tetrabromobisphenol A pyrolysis products were also identified.

The pyrolysis residues were very friable and the organic, glass fibre, and metallic fractions could easily be separated and the electrical components could easily be removed from the remains of the printed circuit boards. The ash in the residue mainly consisted of copper, calcium, iron, nickel, zinc, and aluminium, as well as lower concentrations of valuable metals such as gallium, bismuth, silver, and gold; silver was present in particularly high concentrations. Many other metals were also identified in the ash by ICP-MS and SEM EDX. The pyrolysis gases mainly consisted of CO₂ and CO but all of the C₁ – C₄ alkanes and alkenes were present, as were some inorganic halogens.

Pyrolysis of waste latex gloves in the presence of Y-Zeolite

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In recent decades, increased awareness about infectious diseases such as HIV and hepatitis and increased levels of personal protection required in scientific and technological industries has meant an increased demand for latex gloves. Rubber gloves (and medical waste in general) present several disposal problems because they are a biological hazard and therefore must be disposed of in a manner which does not endanger public health

In this study we have investigated the possibility of processing waste rubber gloves using pyrolysis. Y-zeolite catalyst was employed to upgrade the pyrolysis products to give higher yields of valuable aromatic compounds such as toluene and xylenes. The composition of the pyrolysis products was determined using GC-MS, GC-FID, GC-TCD, and FT-IR. It was found that when rubber gloves were pyrolysed in the absence of a catalyst, the pyrolysis oil consisted mainly of limonene and oligomers of polyisoprene. When Y-zeolite was added to the reaction system, the yields of toluene, xylene, methylbenzenes, ethylbenzenes, and naphthalenes increased dramatically. The Y-zeolite also catalysed the decomposition of limonene which was absent from the catalytic pyrolysis products. The presence of the Y-zeolite catalyst also increased the yield of hydrocarbon gases. The tests were carried out at both 380°C and 480°C and it was found that the higher reaction temperature led to increased yields of all the major compounds, both in the presence and absence of the Y-zeolite catalyst.

Carbon prepared from guava seed and removal optimization of acid orange 7 using the Taguchi method

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The preparation of carbon from waste materials of natural or industrial origin is an economic alternative for the removal of dyes from wastewater. For the adsorption of acid dyes such as acid blue 74, acid green 25, acid violet and acid blue 25 the avocado kernel seed [1]; the cassava peel [2] and the corn cob [3] have been used in the preparation of carbon. The results of adsorption were satisfactory; however controlling the principal adsorption conditions the efficiency could be higher. In this work four samples of carbon were obtained by thermal treatment at 1000 °C (CGU-P1, CGU-P2, CGU-P3 and CGU-P4) using as precursor the guava seed with different particle sizes. The morphological and textural characteristics of the carbon samples were determined by microscopy and nitrogen adsorption at 77 K. The adsorption of acid orange 7 was studied using the Taguchi statistical method to identify the optimal conditions and to select the parameters having the most deciding influence on the removal of the dye. A lineal relationship was observed between the particle size of the precursor and the average pore diameter of the carbon samples. The exception was CGU-P3 due to a particular morphological property. A total removal of acid orange 7 was reached when the conditions of adsorption were the following: pH: 2, temperature: 15 °C, mass to volume ratio of 0.03 g ml⁻¹ using as adsorbent CGU-P1 (material with a specific surface of 598 m² g⁻¹). Moreover, the most influential factor in the adsorption process was the specific surface of the carbon samples.

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Pyrolysis and combustion of electronic wastes

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The decreasing costs and increasing availability of electronic products of all kinds, including mobile phones, audio and video equipment, and personal computers and their accessories, coupled with advances in technology that rapidly make these products obsolete, foretell a growing disposal problem [1]. Brominated flame retardants are widely used in electronic products, and the thermal decomposition of these wastes can produce high amounts of brominated compounds.

The materials employed in the present work were a mobile phone (printed circuit board + casing) and printed circuit boards alone. Bromine content of these samples was around 5 % wt. The thermogravimetric behavior of these electronic wastes both in nitrogen and nitrogen:oxygen atmospheres using different heating rates were presented. Some TG-MS experiments were carried out in order to know better the decomposition of electronic wastes and identify some compounds emitted during the controlled heating of this material. Furthermore, pyrolysis and combustion runs at 500 °C in a horizontal laboratory furnace have been performed, and the analysis of the gas and semivolatile fractions (mainly dioxins and furans and “dioxin-like” PCBs) are showed. Mobile phone and printed circuit boards have been analyzed for PCDD/F and “dioxin-like” PCB content in order to establish the level of pollutant in the samples themselves.

More than 130 compounds have been identified and quantified, including carbon oxides, light hydrocarbons, PAHs and brominated compounds as bromophenol, bromobisphenol A, dibromobisphenol A and tribromobisphenol A. The main semivolatile compounds detected were phenol and bisphenol A. In Table 1 are showed PCDD/Fs obtained for the materials and runs.

Table 1. PCDD/F content in electronic wastes and pyrolysis and combustion runs

Mobile phone (pg I-TEQ/g sample)			Printed circuit board (pg I-TEQ/g sample)		
Material	Pyrolysis 500	Combustion 500	Material	Pyrolysis 500	Combustion 500
2.5	29.1	7.3	0.57	28.2	3.4

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Characterization of the composition of the main stream of smoke obtained by smoking different tobacco samples

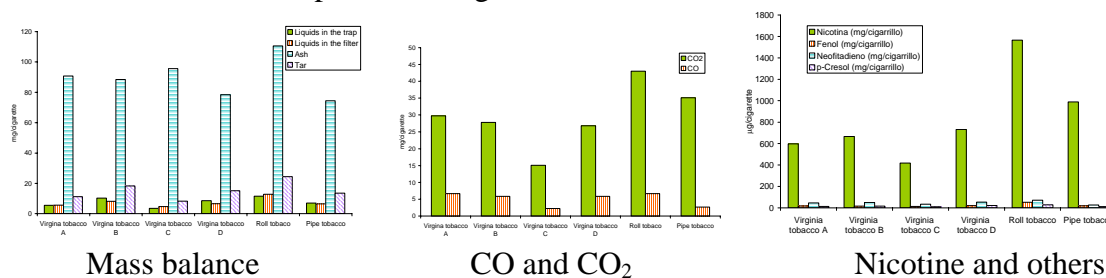
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Smoking habit represents a serious problem for the nowadays society with negative consequences on the health of the human beings and a great impact on the public health department budgets. The smoke generated from the pyrolysis and combustion of tobacco has a series of toxic and carcinogenic compounds that are inhaled by both active and passive smokers, and turns the tobacco consumption in one of the main death causes on a global scale. Many different compounds belonging to all the organic compounds families have been detected in tobacco smoke [1] with concentrations in the range of the micro and picograms. Moreover, the tobacco smoke is a complex, dynamic and reactive system, and due to its physical and chemical properties, the study of its composition is very difficult. In addition, its composition is strongly affected by different variables [2]. Different methods and additives have been suggested and studied with the purpose of reducing the toxicity of the tobacco smoke. These studies require the use of a smoking machine in order to simulate the smoking process and to generate the streams of smoke and the condensed fraction which are inhaled by the smokers, as well as the use of the analytical techniques for the chemical analysis of such as fractions. In this way, the comparison with the behaviour of the original tobacco always is need, and the study of the characteristics, similarities and differences among the different forms of presentation of tobacco, as well as among the different commercial types of tobacco would be an useful support.

In this work, several tobacco types (a commercial Virginia tobacco from a commercial cigarettes trademark, three original Virginia tobaccos supplied by an industrial provider, and commercial pipe and roll tobaccos) have been tested in a smoking machine, and the respective amounts of gases, liquids and gases generated in each case have been compared. As an example, the following figure shows the comparison among the values of some variables in the different tobacco samples, showing the existence of noticeable differences.



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Comparison the formation of selected tobacco pyrolysis products under different conditions

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The goal of this work was to monitor the quantitative changes of a few selected smoke compounds at varied pyrolysis conditions. The effect of temperature, atmosphere, sample size and sample particle size was examined. Two different types of tobacco (Virginia and Burley) and some possible precursor compounds (cellulose, quercetin dihydrate, chlorogenic acid hemihydrate) were examined. The formation of 1,3-butadiene, isoprene, phenol, hydroquinone, catechol, benzene and naphthalene was studied at 450, 600 and 900°C temperatures.

On-line fast pyrolysis experiments were carried out in a Py-GC/MS system under helium and the sample size was about 0.8mg. Pyrolysis products from as-received and cryo-milled tobacco powder were compared. In order to examine the effect of sample size, bigger samples (about 80mg) of tobacco and cellulose were pyrolysed in a tube reactor in nitrogen atmosphere and the pyrolysis products were analyzed off-line by GC/MS. To study the effect of oxygen, the off-line pyrolysis experiments were carried out in 2% oxygen-98% nitrogen atmosphere. In general, butadiene, benzene and naphthalene formation was promoted while phenol formation was hindered when the atmosphere contains of 2% oxygen.

The results confirmed that cellulose and polyphenols are source compounds of butadiene, benzene and naphthalene at 900°C. The polyphenols may be considered as precursors of catechol, and chlorogenic acid could be a precursor of hydroquinone at lower temperatures (<600°C).

The changes of selected compounds as a function of pyrolysis temperature showed similar trend independent of the sample size. It was found that the particle size did not modify either significantly the formation of selected pyrolysis products. This does not mean, however, that the sample size and the particle size do not affect the thermal decomposition processes. To clarify this, thermogravimetric studies (TGA) were carried out at low sample masses (0.4 - 2 mg) in inert ambient as well as in the presence of 2 - 9% oxygen. Small, but significant and characteristic differences were found when the samples were pulverized in a cryo-mill. The sample mass also had effects on the TGA results, especially in the presence of oxygen, at temperatures where the combustion reactions dominated.

Conversion of the Estonian Fossil and Renewable Feedstocks in the Medium of Supercritical Water

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For decreasing the dependence on imported oil products and gas it is essential to Estonia to find alternative opportunities for obtaining fuels and chemicals from local feedstocks. Oil shales and biomass in their multitude and variety represent an available natural organic feedstock for production of both liquid and gas by using thermochemical conversion methods. Conversion with supercritical water is one of the prospective methods enabling effective conversion of high-molecular organic matter [1, 2].

In this work Kukersite (W^a 0.6, $(CO_2)^d$ 12.8, A^d 37.2, OM^d 50.5%) and Dictyonema (W^a 1.4, A^d 81.2, OM^d 16.0%) oil shales and willow (W^a 7.1, A^d 1.6, OM^d 98.4%) biomass were submitted to supercritical water conversion with the aim to compare liquefaction and gasification potential of those feedstocks and to investigate the chemical composition of conversion products. Common and specific features of lignocellulosic and kerogeneous organic matter were described. Isothermal processing was performed at 380 °C during 4 hours in a 500 cm³ stainless steel autoclave. Volatile gaseous, liquid as solubles and solid insoluble conversion products separated after cooling the autoclave were submitted to quantitative and qualitative analysis. Individual and group composition of conversion products was investigated by using chromatographic and spectroscopic methods.

The maximum and the minimum total yield of solubles differed from 62% in Kukersite conversion to 17% in Dictyonema shale conversion. Gas yields as high as 47 and 52% were registered in Dictyonema shale and willow biomass conversion, respectively, surpassing that from Kukersite considerably. The solubility of liquids despite originating from oil shales or biomass increases with solvents used in the row: dimethyl ketone < water < benzene. Investigation group composition of the benzene-soluble compounds demonstrated that various oxygen compounds dominate over hydrocarbons in all cases. The majority of hydrocarbons are represented by polycyclic aromatic ones. The content of aliphatic hydrocarbons varied from 6 to 11% obtained from Kukersite and willow, respectively. Abundant carbon dioxide formation in feedstocks conversion processing was occurred. Among gaseous hydrocarbons from both fossil and renewable feedstocks prevailed CH₄.

As a conclusion, oil shale and biomass can be alternatively to semicoking effectively converted and co-converted in the medium of supercritical water to obtain liquids characterised as non-conventional oil and valuable gaseous compounds.

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Peat Semicoking and Hydrocracking

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Peat represents one of the types of natural high-molecular organic matter what can be converted to liquid fuel, gas and chemicals. Various thermochemical methods and different conversion conditions can be used for peat liquefaction and gasification.. In [1] peat was subjected to the flash pyrolysis at 500 and 800 °C in a fluidized-bed reactor. The maximum yield of liquid and that of gas amounted to 40 and 60%, respectively. Peat refining and hydrogenolysis in the medium of reducing agents at 290-400 °C has been carried out in an autoclave and intermediate products of improved qualities were obtained [2, 3].

In this work moderately decomposed peat (organic matter content - 93.2 wt.%, degree of decomposition - H5) was submitted to thermochemical conversion processing with the aim to investigate yield and chemical composition of both liquid and gaseous conversion products obtained. Semicoking in a Fischer assay in standard conditions (ISO 764-74: heating 50 g of sample up to 520 °C during 90 min) as a method of slow pyrolysis was performed. Hydrocracking was carried out at 380 °C during 4 hours in a batch autoclave charged with initial peat sample, hydrogen and Co-Mo/Al₂O₃ (AkzoNobel 848) catalyst. The initial pressure of hydrogen was 5 MPa and 60 g of the sample was weighted for each run. Liquid, gaseous and solid conversion products were collected and their yield was calculated. Chemical group and individual composition of products was investigated by chromatographic and infrared spectroscopic methods.

As a result of semicoking and hydrocracking 54 and 60% of peat organic matter was transformed to liquid and gas composition. In semicoking gas yield surpassed that of liquid up to four times while hydrocracking resulted in equal liquid and gas yields. 48-75% of the oily liquid was characterized as benzene-soluble. Compared with slow pyrolysis, catalytic hydrocracking considerably increased content of non-aromatic hydrocarbons and decreased that of oxygen compounds in liquid composition. *n*-Alkanes up to C₃₃ in hydrogenate were identified. In gas composition hydrocarbons C₁-C₄, H₂S and carbon oxides were identified the relative concentration of CO₂ being particularly high.

It was concluded that semicoking and hydrocracking represent alternative methods of peat liquefaction and gasification accompanied with obtaining a wide spectrum of hydrocarbons.

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Evolved Gas Analyses in Modeling Studies of Pre-Sintering Step in Fabrication of Ceramic Alumina Specimens

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High grade engineering alumina (corundum, α -Al₂O₃) is a widely used polycrystalline ceramic substance due to its excellent mechanical, optical properties and resistance to chemical corrosion, in various industrial fields [1]. In the shaping and compaction step of ceramic sintering, usually organic dispersant and adhesives (binders) are applied [2], which are finally eliminated, i.e. burned out in a pre-sintering step carried out in air atmosphere [3]. Complete removal of residues of organic origin, even at low temperature, is essential for the final quality of polycrystalline ceramics, especially used as envelopes of light sources. On the other hand the released volatile gaseous products are subject of environmental concerns.

In order to study the pyrolytic processes taking place in pre-sintering procedures, alumina-binder mixtures with various composition have been subjected to evolved gas analyses by simultaneous thermogravimetry and differential thermal analysis coupled online with mass spectrometry (TG/DTA-EGA-MS) and with FTIR spectroscopic gas cell (TG-EGA-FTIR) up to 700°C in flowing air.

Especially, elimination of organic vapors and formation CO₂ have been monitored and compared with the overall weight loss dynamics (indicated by the DTG curves) at constant heating rates. Below 280°C elimination of organic vapors are dominated, while above 280°C evolution of CO₂ has been found responsible for the mass losses, indicating that additional measures are to be taken to complete burning of organic vapors released at relatively low temperature in considerable amount in the pre-sintering process, meanwhile relatively high temperature and long durations are needed to obtain ceramics free from the residues of the useful additives.

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Pyrolysis of glycerine: influence of the purity grade and the presence of catalysts on the products obtained

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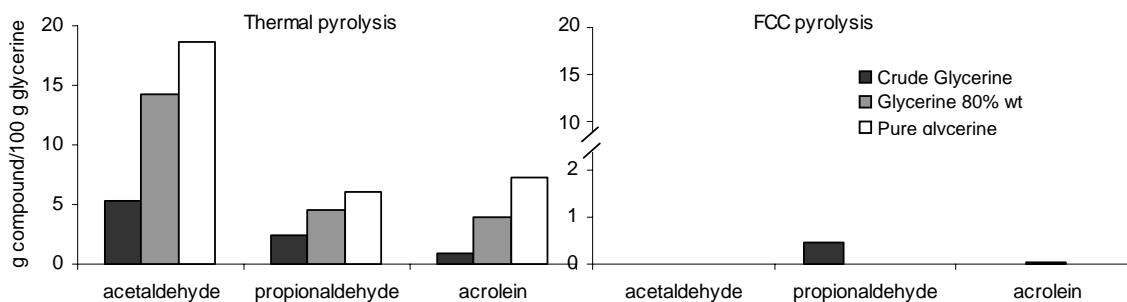
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In the last years, the increasing interest in the biocombustibles has caused a significant increase in biodiesel production. In converting vegetable oils into their methyl esters, about 10 wt % of glycerine is produced as a byproduct [1]. Although glycerol presents a lot of applications such as medicines, cosmetics, etc. [2] its world demand is limited. Glycerine has suffered a devaluation process and it is necessary to find new markets for this product.

A possible alternative for the revalorization of glycerol is its incineration. However, the generation of acrolein, toxic product, during the process is a significant disadvantage of this method.

In this work, thermal and catalytic pyrolysis of glycerine has been evaluated as a new alternative of its revalorization. Three glycerine samples with different purity grade have been degraded: crude glycerine obtained from the biodiesel production process, purified glycerine with 80 % wt of glycerol and pure commercial glycerine. The reactor employed has been a laboratory scale fixed bed reactor (14.8 x 1.58 cm) and the catalyst evaluated has been a FCC equilibrium catalyst.

The results showed that the presence of the catalyst modifies the product distribution obtained. The presence of a FCC equilibrium catalyst during the pyrolysis of glycerine increases the yield of methane, ethylene and benzene and reduces significantly the yield of oxygenated compounds such as acetaldehyde, propionaldehyde or acrolein. Thus, independently of the purity grade of the glycerine evaluated, acrolein yield was lower than 0.5 g/100 g glycerine. CO and H₂O are increased under catalytic conditions.



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Carbon-based adsorbents from de-inking paper sludges

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In recent years, the recycling of paper is increasing significantly due to their important environmental and economical benefits [1]. Paper recycling reduces the use of virgin fibre, the water and the energy consumption [1]. However, removing the ink, clay, coatings and contaminants from waste paper in order to produce recycled paper creates large amounts of waste materials such as de-inking paper sludges (DPS). The main components of DPS are cellulose fibres, calcite and kaolinite [2]. Due to their high organic matter content, DPS could be used as amendment to improve or restore soil fertility and biological functioning [3]. Other possible alternative is composting mixed with other organic materials in order to reduce their high C/N ratio. Finally, cement industry could incorporate DPS due to their high calcite content [2]. Previous works carried out by our research group have shown that pyrolysis of different waste paper industry leads to carbon-based adsorbents with interesting properties for the Cu removal from water. The main objective of the present work is to study the behavior of carbon-based adsorbents prepared from pyrolysis of DPS in the removal of Cu, Ni, Zn and Cd at different pHs and metal concentrations (10-200mgL⁻¹). Carbon-based adsorbents were prepared by pyrolysis at 650°C during 2 hours. At this temperature, pyrolysis of cellulose and dehydration of kaolinite was finished. Characterization of carbon-based adsorbents (cation exchange capacity, pH, carbon content, BET, FTIR and SEM) was performed. The maximum adsorption according Langmuir equation at pH=3 and pH=5 follows the sequence: Zn>Cd>Ni>Cu.

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Pyrolysis behaviour of different paper industry waste materials

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Paper pulp manufacturing separates cellulose fibres using both, mechanical and chemical process and generates important amount of waste materials with high organic matter content, especially cellulose fibres. In recent years, the recycling of paper is increasing significantly due to their important economical and environmental benefits [1]. However, the removal of the ink, clay and coatings from creates large amounts of waste materials. Previous works carried out by our research group have showed as pyrolysis of paper industry waste leads to carbon-based adsorbents with elevated metal and organic matter removal [2,3]. The main objective of the present work is to study the similarities and differences on the pyrolysis behavior of paper industry waste materials. In order to achieve that, 10 paper industry waste materials were selected from different industries and widely characterized according to their pH, CIC, organic matter and CaCO₃ content. Representative SEM micrographs of waste materials were achieved. Finally, FTIR of samples and thermogravimetry analysis in air and nitrogen atmosphere were made.

In general, waste materials from recycling paper showed elevated CaCO₃ content leading to basic materials (pH from 7.7 to 9.2). The appearance of cellulose fibres was more broken as the recycled cycle's increases and more deteriorate cellulose fibres correspond to de-inking sludges from press paper. The presence of more functional groups observed by FTIR corresponds to de-inking paper sludges. Finally, TG, DTG and DTA analysis show main differences in the composition and pyrolysis behavior of different paper industry waste materials. In general, three different zones were observed, at temperatures lower than 450°C weight loss mainly corresponds to cellulose fibres decomposition, greatly influenced by their origin, and other organic compounds; the second area (<550°C) was related to dehydration of kaolinite present in waste materials from recycled paper and finally, at elevated temperatures, carbonate decomposition was produced.

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Influence of temperature in the reaction of an activated carbon with NO in the presence of CO

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Reburning using biomass is gaining attention during the last years as one of the technologies for the reduction of NO emissions from stationary fossil-fuel combustion sources. Specially important is the NO reduction through heterogeneous reactions involving the biomass char, as in some cases they can contribute to a higher NO reduction than the corresponding gas-phase NO reactions [1]. The efficiency of this heterogeneous reaction depends on different variables, the origin and preparation history of the char, the temperature, the presence of oxidants (O_2 and CO_2) and of a reducing agent such as CO. The effect of these variables on NO reduction has been the object of different studies [2] although few of them deal with the influence of the CO presence in the biomass char-NO reaction at reburning temperatures. Therefore, this work is focused on analyzing the effect of the temperature on the NO reduction by the biomass char when CO is present at relatively high temperatures.

To accomplish this objective, a commercial activated carbon similar to some of the biomass chars has been selected as a model material. An experimental study of the temperature influence in the activated carbon-NO reaction has been performed with CO presence and also without CO, for comparison. Temperatures were varied in the range 700-1000 °C. The NO and CO concentrations were fixed in 1500 and 800 ppmv, respectively. The experimental setup and methodology used in this study have been previously described [3]. The activated carbon employed in this work was manufactured by MERCK. It was characterized by means of different techniques, such as ultimate and proximate analysis, main ash components, determination of surface area, SEM and XRD.

Compared to the case without CO, there is an increase in NO reduction when CO is present in the activated carbon-NO reaction. For the activated carbon studied, this increase in NO reduction seems to decrease as temperature rises. The apparent activation energy of the activated carbon reaction with NO and CO was calculated and resulted 23.27 kcal/mol. This value is lower than the value obtained in similar conditions without CO (39.07 kcal/mol) and similar to the values reported by other authors in similar reaction conditions.

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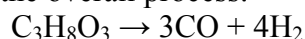
Syngas production from microwave pyrolysis of glycerol using a carbonaceous catalyst

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Glycerol, a by-product from the production of biodiesel, is expected to grow in importance in the future due to an increased demand for environmentally acceptable processes. Glycerol markets are limited, so novel techniques must be developed. There are many possible ways of turning glycerol into value added products [1,2]. One of them consists in converting glycerol to synthesis gas which can be achieved by various processes [1,2]. The following stoichiometric equation represents the overall process:



In this work, we report the pyrolysis of glycerol in a fixed-bed reactor at atmospheric pressure, over a temperature range of 500-900 °C using different heating methods: (i) electrical furnace (EF) and (ii) microwave oven (MW). Unlike the metal-based catalysts used until now, two commercial activated carbons were used as catalysts. The reforming of glycerol with CO₂ was also carried out by both heating methods.

The production of synthesis gas from the conventional pyrolysis of glycerol was higher over activated carbons (up to 76% in the EF at 800 °C) than over inert material (quartz particles), possibly due to the catalytic effect of the activated carbon. Moreover, the activated carbon with the highest specific surface area and ash content presented the best results from the point of view of H₂+CO content.

Due to the ability of activated carbon to absorb microwaves, the pyrolysis of glycerol was also carried out in the MW using this carbonaceous material as a receptor in order to reach the required operation temperature. It was observed that the amount of H₂+CO was even greater (up to 82% at 800 °C), than that obtained in the EF for the same experimental conditions.

From the experiments carried out, it can be inferred that syngas production is favoured at elevated temperatures and it is higher in the MW at all pyrolysis temperatures. The low levels of CO₂ should also be noted. Furthermore, at 500 °C the MW is more effective in CO₂ reduction. The greater efficiency of the MW at low temperatures has already been proved with other kinds of waste [3].

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Sulfur Removal of Leaching Waste for the Recovery of Precious Metals by Pyrolysis process

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The mining industry has developed processes to leach copper from chalcopyrite using bacteria and autoclave reactors where copper, iron and zinc are dissolved and lead, gold and silver are reported in the lead-silver residues. Sulfur can be produced in the residues as elemental sulfur or as sulfuric acid depending on the oxidizing conditions during copper leaching. This is an important issue due to the next process after copper leaching because gold and silver are recovered by cyanidation. Elemental sulfur reacts preferentially with sodium cyanide than gold and silver, this implies high cyanide consumptions to recover precious metals. This work shows an alternative to reduce the sodium cyanide consumption in gold and silver leaching removing the elemental sulfur from Lead-Silver residues. The separation and recovery of sulfur is made through the pyrolysis process, in an N₂ atmosphere [1].

In the experimentation two samples of Lead-Silver residues were treated by pyrolysis, the first one was from a bioleaching process and the second one from an autoclave reactor. During the pyrolysis process performed at 450 °C, the elemental sulfur was released in the form of steam and then captured in the condensation train [2,3]. The results showed, for the bioleaching residue, that 59 wt.% of the sulfur content in the initial sample was released, 36 wt.% was recovered as elemental sulfur and 23 wt.% as non-condensable gas. For the autoclave sample, 52.5 wt.% of the initial sulfur was released, 42 wt. % was recovered as elemental sulfur and 10.5 wt.% as non-condensable gas. The consumption of cyanide in the leach ore before pyrolysis was of 11.54 kg/ton and after the pyrolysis process was 2.5 kg/ ton, reducing the consumption of cyanide to 78 wt.%.

Keywords: mining industry, Lead-Silver residues, Sulfur.

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Modeling and Evolutionary Computation Strategy for Multi-objective Optimization of Propane Thermal Cracking Reactor

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There are several reports on the optimization of thermal cracking plants. Dynamic optimization of the production period of thermal cracking has been used with respect to coke formation in cracking coil and TLX. It was reported the simulation and optimization of naphtha thermal cracking in a pilot plant. In this work the elitist nondominated sorting genetic algorithm (NSGA-II) is used for optimization of thermal cracking of propane. Simultaneous maximization of two objective functions such as propane conversion and propylene selectivity are carried out using NSGA-II.

An industrial propane thermal cracking reactor was modeled assuming a molecular mechanism for the reaction kinetics coupled with material, energy, and momentum balances of the reactant-product flow along the reactor. Multi-objective optimization of two objectives such as feed conversion and propylene selectivity was carried out using an evolutionary algorithm. The Pareto optimum set was obtained successfully with elitist non-dominated sorting genetic algorithm and finally the effect of decision variable were discussed.

The study produced a wide gamut of optimal operational options for the reactor, revealing a qualitative as well as quantitative relation of the reaction process with the operation variables. It demonstrated both the individual and combined roles played by reactor temperature, reactor pressure, and residence time in achieving the objectives. In general a multiobjective optimization study is beneficial for understanding the performance tradeoff of conflicting objectives and decision variables and for producing a wide range of optimal solutions.

Keywords: optimization, evolutionary algorithm, genetic algorithm, cracking, propane.

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Effects on The Porosity of two Wood Charcoals by Carbonization and Thermal Treatments in Steam Atmosphere

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Adsorbent materials are necessary for numerous applications [1]. We have characterized wood charcoals manufactured in Extremadura (Spain) as far as their potential production of carbon adsorbents is concerned [2]. It was concluded that the characteristics of the charcoals depend not only on the starting wood, but also on the carbonization system. In particular, their pore structures are formed by pores in the range of micro- to macropores, with total porosity approximately in the range 0.500-1.000 cm³ g⁻¹.

As a continuation, we have studied the changes in the porosity of two very different wood charcoals by thermal treatments. The first charcoal was manufactured by partial combustion in a discontinuous furnace from holm-oak wood and the second charcoal in a continuous furnace from eucalyptus wood.

As-received wood charcoals were first crushed and sieved; the size fraction of 1-2 mm was used in the treatments. The holm-oak charcoal was demineralized with diluted hydrochloric acid. The thermal treatments were: carbonization in the atmosphere formed as the temperature increased from room temperature to 750, 850 and 950 °C, at a heating rate of 10 °C min⁻¹, carbonization-steam activation to 950 °C, and carbonization-steam activation to 950 °C-isothermal steam activation at 950 °C during 60, 90 and 120 min.

The samples were characterized by thermogravimetry, chemical analyses, densimetric measurements, mercury porosimetry and scanning electron microscopy. The total pore volume accessible to helium at room temperature (V_p) was obtained by the expression $V_p = 1/\rho_{Hg} - 1/\rho_{He}$; ρ_{Hg} is the density measured by mercury displacement and ρ_{He} is the density measured by helium displacement.

The porosity in the chars is the result of two effects: devolatilization and shrinkage of the carbon structures. The porosity in the activated carbons is the result of these effects and of steam activation. The initial porosity is developed by devolatilization and activation, while mentioned shrinkage causes an opposite effect. The three effects depend on the starting charcoal; the demineralization of the holm-oak charcoal favors the porosity development.

Acknowledgements

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Behaviour of heavy metals during flash-pyrolysis of sewage sludge

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Municipal and especially industrial wastewaters often contain significant concentrations of heavy metals which are removed during biological stage and effluent of the process is heavy metals free. However heavy metals are accumulated in the sewage sludge. The common metals found in raw wastewater and sludge are Cd, Cr, Cu, Ni, Mn, Pb and Zn [1]. Land application or the use of sewage sludge as a fertilizer can result in the accumulation of heavy metals in the soil. Thermal treatments as pyrolysis at low temperature (400-500°C) are an alternative way to solve sludge disposal problem and use energy potential of sewage sludge. Heavy metals present in sludge are fixed inside the carbonaceous matrix of produced solid residuum, resulting in a rather heavy metals free bio-oil. Metals incorporated into the solid residuum are relatively resistant to natural lixiviation [2].

3 types of sludges from the wastewater treatment plants (WWTP) in Prague and Pardubice, namely thickened excess activated sludge (secondary sludge), digested and special treated dried secondary sludge (WWTP Pardubice) were investigated. The flash pyrolysis was performed in a semi-continuous lab scale reactor. The operating temperature was 500°C. Low concentration of heavy metals or their absence in liquid pyrolytical products was confirmed by ICP-OES. Presence of heavy metals in char and sludge was determined by XRF analysis and ICP-OES after decomposition of the matrix. The mobility of heavy metals present in the carbonaceous matrix of solid residuum to natural lixiviation was evaluated by complementary leaching tests.

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Investigation of Pitch Stabilisation Using Pyrolysis-Gas Chromatography-Mass Spectrometry

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Oxidative stabilisation of mesophase pitch is an essential step in its processing to form graphitisable carbon products. However, this step is diffusion-controlled and therefore severely limits the dimensions of these products. Stabilisation of such products whose dimensions are larger than a few tens of microns is time-consuming and costly or even impossible [1]. Control and understanding of this step is of very great interest in the production of highly oriented graphitisable material as it could lead to a dramatic reduction in production costs. The mechanism of such stabilisation is thought to involve oxygen cross-linking but its exact nature is still not fully understood [2]. Py-GC-MS is well suited to identification of structural changes occurring in the pitch during oxidative stabilisation. In addition, the use of reactive gas Py-GC-MS offers a method for performing oxidative stabilisation on an analytical scale.

Oxygen-treatment of mesophase pitch under various conditions generated a set of samples with differing potentials to become stabilized following further heat treatment (as demonstrated by softening point behaviour). These samples have been characterized using Py-GC-MS to identify and quantify volatile species evolved both upon pyrolysis and reactive pyrolysis in oxygen. Identification of the fragments has shed light on the nature of the functionalities within the oxygen-treated pitch and therefore helped to elucidate the mechanism of the stabilisation process.

A correlation was observed between the evolution of oxygenated fragments and the degree of stabilisation potential in the pitch. Py-GC-MS in reactive mode using oxygen enables stabilisation to be performed on an analytical scale, producing further evidence for the proposed stabilisation mechanism. The methods which have been developed in this work are capable of screening pitch samples, investigating stabilisation reaction pathways and optimising the conditions for oxidative treatment.

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CFD Flow and Heat Transfer Simulation for Empty and Packed Fixed Bed Reactor in Thermal Cracking of Hydrocarbons

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Light olefins such as ethylene, propylene, and butanes are usually produced by the steam pyrolysis of naphtha or light alkanes. Also steam cracking reactions are always accompanied with the formation of coke which deposits on the walls of the tubular reactors. This work aims to test the application of computational fluid dynamics (CFD) modeling to thermal cracking reactors. Studies of CFD with an empty and fixed bed design commonly use a regular packing with define bed geometry. CFD allows us to obtain a more accurate view of the fluid flow and heat transfer mechanisms present in fixed bed equipment. Light hydrocarbons such as ethane and LPG were used as feedstock and the reactor length was 80cm. It is divided in three sections that ceramic inert packed bed in the middle section of the reactor. The reaction scheme was involved one primary reaction and secondary reactions. Because of high CPU times in these simulations, parallel processing have been used. In this study the product yields and coke formation process in empty and fixed ceramic bed reactor was simulated and compared. In addition, the effect of steam ratio and feed flow rate on product yields and coke formation was investigated.

Keywords: Product yields, Coke Formation, CFD Simulation, Fixed Bed & empty reactor

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Determination of residual lignin in unbleached Kraft pulps. Comparison of analytical pyrolysis with kappa number and Klason lignin content

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The amount of undissolved lignin in pulp, the so-called residual lignin, which is traditionally expressed by the kappa number, is an important parameter for process control in both pulping and bleaching. The kappa number method is a tedious procedure that requires a not always available amount of sample, and is additionally affected by the presence of hexenuronic acid groups [1].

Analytical pyrolysis was already used for the quantification of the lignin content (Py-lignin) of Maritime pine, spruce and larch wood samples directly from the pyrograms [2, 3]. The main advantages of analytical pyrolysis are the easy sample preparation (drying and milling), short analysis times, rapid analysis times, and the small amount of sample required (micrograms range) [3].

In this work thirty samples of unbleached Kraft pulps of Maritime pine (*Pinus pinaster* Aiton) obtained in the laboratory with kappa numbers in the range from 58 to 100 were assessed by analytical pyrolysis. A good correlation was obtained between Py-lignin and kappa number with a high coefficient of determination ($R^2=0.91$). The Klason lignin content determined in six selected pulp samples gave a better correlation with Py-lignin with a higher coefficient of determination ($R^2=0.95$). The results obtained show that analytical pyrolysis is a suitable method to determine the residual lignin in pulps that additionally allows the estimation of kappa number and Klason lignin content.

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A technical application for the production of activated carbon from waste biomass

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As a result of environmental requirements in many countries and new areas of application the demand on activated carbon is still growing. Due to the unavailability of the main basic materials like hard coal, wood or coconut shells in many countries other biomass matters are tested for their appropriateness for activated carbon production.

First the feedstock has to be pyrolysed to obtain primary char. In a second treatment step called activation the specific surface of the char is enhanced by steam reforming at temperatures of more than 900 °C. These investigations were run in lab-scale pyrolysis and activation facilities to generate the operating parameters like residence time, steam flux and temperature for more than 12 different biomass matters [1]. Some of the results are shown in Fig. 1. Here the active surface of the carbon matters is given as function of the conversion rate, i.e. the loss of char mass due to partial oxidation in the steam atmosphere.

The lab-scale experiments are scaled up to a continuous production process. The biomass is pyrolysed in the technical scale rotary kiln reactor called HALOCLEAN[®] [2], the activation reactor is adapted to the HALOCLEAN[®] principle with an inner screw to regulate the char residence time. The activation reactor can be heated to 1000 °C and it operates with steam atmosphere. The char input amounts to 500 g / h and is build up as pilot scale reactor, Fig. 2. First experiments show, that the lab-scale experiments can be transferred into the pilot scale reactor. The same product qualities can be achieved.

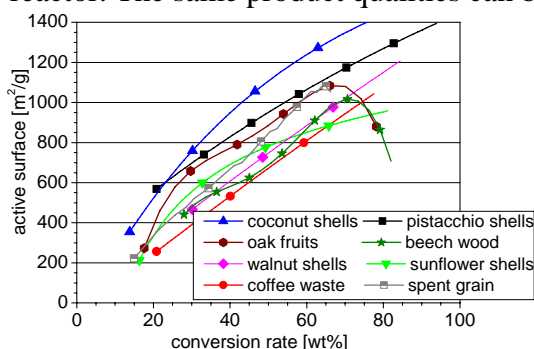


Figure 1. Active surface as function of the conversion rate in the activation step.

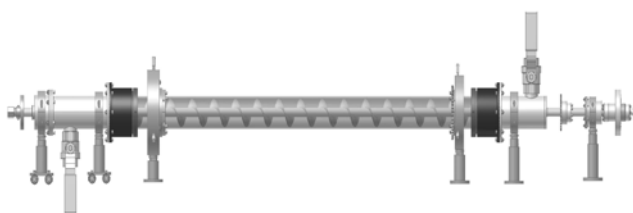


Figure 2. High temperature activation reactor.

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Pyrolysis of Hydrocarbon Fuel ZH-100 Under Different Pressures

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Abstract

The endothermic hydrocarbon fuel can work as a coolant to disperse the heat generated by the surface and engine of a hypersonic aircraft, due to its endothermic pyrolysis reaction under a supercritical condition. Herein the cracking of the hydrocarbon fuel ZH-100 in a continuous tubular reactor under four pressures of 0.1MPa, 1.5MPa, 2.5MPa and 3.5MPa are studied. It is found that the conversion and the yield of gas product are lowest at the lowest pressure of 0.1MPa, the maximum value appears at 1.5MPa, and the values at 2.5MPa and 3.5MPa are middle and in different order under different conditions. Methane and hydrogen are the most abundant components when under the atmospheric pressure and low temperatures. The light components in liquid product systems consist of many small alkenes, and the content of the light components can be promoted by increased temperature and pressure.

Keywords: Pyrolysis; Endothermic hydrocarbon fuel; Supercritical condition.

Electrochemical characteristics of Sn/SnO₂ composite anode for Lithium ion battery

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SnO₂ and Sn-based composite oxide electrodes have been considered as alternative electrodes for lithium rechargeable batteries. Anodes derived from oxides of Sn have been of considerable recent interest because, in principle, they can store over twice as much Li⁺ as graphite. However, large volume changes occur when Li⁺ is inserted and removed from these Sn-based materials, and this causes internal damage to the electrode resulting in loss of capacity and rechargeability. So we have investigated Sn/ SnO₂ compound in order to complete these defects. Use of Sn/SnO₂ composites could be a solution, as this could increase the Sn :Li₂O ratio in the anode matrix. SnO₂ powder were synthesized by aerosol flame deposition (AFD) technique. After that, SnO₂ powder heated at 150 °C for 3 h, and then treated for 3 h at 600 °C in Ar + H₂ mixed gas atmosphere, reduction reaction, in which SnO₂ is reduced and Sn is formed. It was composed of the Sn/SnO₂ compound at the rate of 1 :2 and 2 :1. Sn/SnO₂ compound was investigated in detail by X-ray diffraction(XRD), Scanning electron microscope(SEM), X-ray photoelectron spectroscopy(XPS), cyclic voltammograms and galvanostatic charge-discharge measurements. The SnO₂-rich compound exhibited a higher specific capacity and a lower irreversible capacity than SnO₂ and Sn-rich compound.

Thermal Dissolution of Estonian Oil Shale

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The formation of oil from fossil fuels can be realized by pyrolysis in an open system (retorting and fast pyrolysis) or in a closed system (autoclave). At retorting oil is evaporated when its vapor pressure is sufficient for evacuation, and the higher molecular thermobitumen (TB) remains in the solid residue. In the closed system both oil and TB (TBO) remain in the autoclave. The review and recent experimental results concerning formation of TBO and TB from Estonian oil shale (kukersite) in autoclaves and retorts has been described in the papers [1, 2]. When kukersite is decomposed to TB stage, 80-90% of its organic matter (OM) is transformed into soluble in organic solvents phase, besides gases and solid residue. The last consists of mineral part and insoluble in the solvents organic matter (not yet decomposed OM and coke formed).

The pyrolysis in autoclaves allows alteration of pyrolysis conditions by addition of solvents (and/or hydrogen) which can change the yield and composition of the products. It is known that solvents have the most destructive ability under their supercritical conditions.

The thermal dissolution of kukersite in time in the presence of benzene, ethanol, water and oil shale petrol in autoclave at nominal temperatures 360-380 °C was studied. TBO was extracted exhaustively with boiling benzene in a Soxhlet's extractor. The percentage of OM in the initial kukersite and solid residues was estimated by the mass burning out at 825 °C from the acid-treated and dried residues.

The results show that the total yield of benzene-soluble products, TBO, has a maximum at an optimum residence time and thereafter decreases due to coke formation. It is shown that, formation of TBO from kukersite at thermal dissolution in benzene, supercritical water, ethanol and oil shale petrol is accelerated in comparison with pyrolysis of kukersite without any solvent. The quantity of coke depends on residence time and increases with used solvents in the row: ethanol < benzene \approx without solvents < oil shale petrol < water. The coke formation continuous at secondary thermal dissolution of TBO obtained at corresponding to the solvent optimum conditions and thereafter extracted from mineral part with benzene. About 80% of the TBO obtained both by primary and secondary dissolution stage consists of polar and non-polar high-molecular heteroatoms. For production of liquid fuels the TBO obtained at thermal dissolution should be upgraded by cracking hydrogenation.

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Sulfur Release from Bituminous Coal in O₂/CO₂ Mixture

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Abstract: O₂/CO₂ recycle coal combustion technology is considered as economically promising and technically feasible to facilitate CO₂ sequestration and to achieve emission reduction. It is significant to study the sulfur release mechanism of coal in O₂/CO₂ mixture for optimizing combustion and controlling sulfur emission. In the work reported here, the X-ray photoelectron spectroscopy (XPS) was used to study sulfur functionality in the bituminous coal and a thermogravimetric analyzer (TGA) was used to evaluate its combustion behavior under O₂/N₂ and O₂/CO₂ atmospheres by changing O₂ fraction in the mixture. The Fourier Transform Infrared (FTIR) spectrometer was employed to track the gas released from bituminous coal combustion on-line. The results show that in O₂/CO₂ atmosphere, no other gaseous sulfur except SO₂ was detected with FTIR spectrometer. In 21%O₂/79%N₂ mixture, there are two SO₂ absorbance peaks, first of which is originated from organic sulfur and the second from pyrite. In 21%O₂/79%CO₂ and 30%O₂/70%CO₂ mixture, a third peak appears due to the reducing effect of high concentration CO₂ on sulfate. When O₂ concentration is over 40%, there is only one peak left. The reason is that O₂ enrichment promotes the pyrite release from coal ahead to the first emission peak and prevents the sulfate from decomposing. However, increasing O₂ concentration has no obvious influence on the time corresponding to the first peak, which indicates O₂ enrichment can not make the organic sulfur release earlier. The integrals of the SO₂ releasing curves also show that total SO₂ released from coal goes up first and then declines as the O₂ concentration increases. SO₂ emission exhibits the highest at 30%O₂/70% CO₂. By comparing the sulfur release from the bituminous coal and its char in 30%O₂/70%CO₂ atmosphere, it can be found that the first SO₂ absorbance peak of char disappears, arguing that the sulfur contributing to the first peak is completely from the volatile matter of the coal. The results demonstrate that there is not a simple relationship between SO₂ emission from coal and O₂ concentration, and further work considering different coal species should be carried on.

Keywords: O₂/CO₂ recycle coal combustion, X-ray photoelectron spectroscopy (XPS), S release, Thermogravimetric; Fourier Transform Infrared (FTIR).

Pyrolytic synthesis of porous biomorphic SiC ceramics

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Today's nature has increasingly become a model for innovation in structural design. Recently, a new class of structural materials, biomorphic ceramics, has attracted a lot of attention. These materials were prepared by the biotemplating technique, where natural grown structures are used as bulk templates for fast high-temperature conversion into ceramics. Bioorganic substances like wood are characterized as a strongly anisotropic structure, where the basic units are elongated channels, assembled parallel to the growth direction. The advantage of wood as a structural material is the durability of the structure combined with a low bulk density. The introduction of silicon in wood opens up the possibility to obtain porous silicon carbide ceramics during high-temperature treatment in an inert atmosphere.

Pine tree (*Pinus silvestris*) wood with shaped sample dimensions of 20 x 20 x 5 mm (axial) was selected as the raw material. Samples were dried, and, for some of the samples, resin extraction from the sample was applied. SiO₂ sol was prepared, and samples were impregnated under different vacuum/pressure conditions. The impregnation and drying procedures were repeated up to three times to increase the SiO₂ amount introduced in the sample. Impregnated samples were pyrolysed at 500°C under oxygen-free atmosphere with the subsequent high-temperature treatment at 1600°C in an Ar atmosphere - the obtained ceramic materials retained a tubular pore structure of pinewood. It has been observed that such SiO₂ gel affects the sample dimension changes during pyrolysis - does not create cracks in cell walls, which could mean that no reasonable internal stress appears. Generally, wood starts to thermally degrade at about 250°C. The SiO₂ gel/wood composite begins to degrade earlier at 220°C because of residual ethyl groups in the SiO₂ gel.

Biomorphic SiC ceramics and its precursors were investigated using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). An experimental result shows that the optimized vacuum/pressure impregnation technique is highly effective for introduction of SiO₂ in the wood. Staged pyrolysis treatment decreases the amount of vapours in the high-temperature oven, although the first pyrolysis step cannot exceed 600°C, by the resulting template cooling gives some quantities of hard melting SiO₂ crystalline modification.

**SESSION 7 ADVANCES IN PYROLYSIS METHODS &
INSTRUMENTATION**

A real time quantitative measurement for fuel pyrolysis using FTIR

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SCRAMJET (Supersonic Combustion RAMJET) fly uses fuels as liquid cooler. This technology presents problems for measuring some parameters such as the fuel composition and flow rate before injection and its temporal evolution. This composition is important to provide information in order to control the combustion in the engine. One solution is to use an on-line optical technique to measure it [1]. In the COMPARER project (Control and Measure of PArameters in a REactive stReam), a new experimental setup using Fourier transform infrared spectrometry (FTIR) has been implemented. A spectrometer NICOLET 6700 has been added on-line to the pre-existing COMPARER bench and this tool allows us measuring in real time the fuel composition generated during pyrolysis of n-dodecane. The purpose of this paper is to present and validate the new configuration of COMPARER bench for the measurement of the composition of pyrolysis products of the n-dodecane with two analysis techniques: gas chromatography/mass spectrometry (GC/MS) and FTIR [2].

The calibration of the FTIR instrument was performed with five products of pyrolysis which have already been analysed in former works (methane, ethene, ethane, propene and propane) [3]. The spectrometer is equipped with a DTGS detector, a KBr beamsplitter and a cell with a pathlength of 10 cm. It is employed to obtain the absorption spectrum all 15 seconds with 4 scans and with a resolution of 0.5 cm⁻¹. OMNICTM software is used to acquire data and to control the instrument, and TQ AnalystTM software to calibrate the FTIR instrument. A classical least squares (CLS) method is applied to measure reference levels of these gas and the IR bands have been selected to minimize the interferences between absorptions (for methane : 1304-1308cm⁻¹, for ethene : 2043-2049 cm⁻¹ and 1886-1890 cm⁻¹, for ethane : 821-823 cm⁻¹ and 1529-1532 cm⁻¹, for propene : 1647-1652 cm⁻¹ and 2963-2971 cm⁻¹, for propane : 2883-2889 cm⁻¹). The *Series* application (real time acquisition) of OMNICTM software is used to obtain the evolution of the concentration of these gases during an experiment with COMPARER bench. A mass flow of 0.1 g.s⁻¹ or 0.05 g.s⁻¹ of n-dodecane is pyrolysed in a titanium reactor heated from 550°C to 900°C with two working pressure of 1 MPa and 6 MPa. The products of pyrolysis are cooled down and the two resulting (liquid and gas) are separated at ambient temperature and atmospheric pressure. The composition of the gaseous phase is then analysed using the two instruments (GC/MS and FTIR).

This study shows the efficiency of the *Series* analysis of FTIR (in comparison of other “static” Infrared spectroscopy of this phase). Four concentration of the five compounds studied with FTIR under many temperature of pyrolysis are consistent with results obtained with GC/MS (with a certain tolerance : 13.4% for methane, 5.2% for ethene, 9.3% for ethane, 9.2% for propene, 26.8% for propane). For the concentration of propene, the value is higher due to interferences of IR absorption band of other alkenes and PAH in the gaseous phase.

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Developments of analytical methods to quantify pyrolysis gas on a short sampling time

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It is of important interest to quantify pyrolysis gas and tar on a short sampling time and if possible with on-line analysis systems: (1) to investigate fast pyrolysis mechanisms and (2) to monitor pyrolysis processes.

New analytical systems have been investigated for these purposes first for a pyrolysis tubular reactor. This type of reactor allows an easily investigation of the pyrolysis experimental conditions, the mass balances and of the analytical methods recovery.

Permanent gas (N₂, H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆) were quantified by a chromatographic system specifically developed for quantification on a short sampling time. This system couples a 16 loops multi-port valve, 3 capillary columns (CP Mol Sieve 5 A, Poraplot Q, SIL 5) according to an “inject/backflush” and “serial/by-pass” setting-up and thermal conductivity and flame ionization detectors in serial (GC/TCD-FID). The accuracy of this system has been compared with Fourier transformed infra red (FTIR) quantification (for CO, CO₂, CH₄) on the whole gas flow rate, without sampling. This GC/TCD-FID system allows an accurate pyrolysis gas quantification with a short sampling time (up to 2 seconds).

10 aromatic tar (benzene, toluene, o-xylene, phenol, o-cresol, indene, naphthalene, 1,2-methylnaphthalene, acenaphthylene, phenanthrene) were quantified with a new analytical method based on solid phase adsorption (SPA) followed by Thermal Desorption/GC/Mass Spectrometry analysis [1]. This method has been quantitatively compared with the conventional cold-trapping technique in solvent-filled impingers followed by liquid injection [2]. SPA tubes has been coupled to a multi-port valve thus providing an accurate analytical methods for tar analysis with a sampling time in the range of 2 seconds and with a low limit of detection in the range of the ppb (of tar in gas).

Mass balances (considering gas, tar, water and char) from 92 to 102% as a function of the reactor temperature (700-1000°C) were determined for wood (spruce) chips experiments thanks to this complete analytical system and thus evidenced the satisfying recovery of the developed analytical methods.

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Linear moving reactor for thermal reaction studies

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One of the main problems in the design of laboratory reactors for solid combustion studies is the calculation of the bulk air ratio λ ($\lambda = (m_{\text{air}}/m_{\text{fuel}})_{\text{actual}} / (m_{\text{air}}/m_{\text{fuel}})_{\text{stoichiometric}}$). Since it is very difficult to generate a constant continuous feeding m_{fuel} , there is also difficulty in calculating the bulk air ratio.

In a previous work [1], it was proved that it is possible to produce a continuous feeding using a moving boat. If the boat is moving into the reactor at enough speed we can assume that the burning rate is the same as the sample feeding rate. The main problem of this boat system used in previous works is that the total time of continuous feeding is shorter than one minute. With this time it is difficult to generate steady state conditions. Furthermore, some of the compounds usually studied are present in very low concentrations and longer sampling times are in this case required in order to increase the detection limit.

A laboratory reactor able to produce a continuous feeding for a longer time has been designed. In this system, it is not a moving boat but the reactor quartz tube which moves using a linear actuator. This robotic actuator system can be programmed to move between 0.1 mm/s and 100 mm/s. The maximum movement is 50 cm long which allows experiments longer than 1 hour. At the exit of the system a module for pollutant retention in a XAD-2 resin is disposed. Figure 1 shows a schematic draw of the designed system.

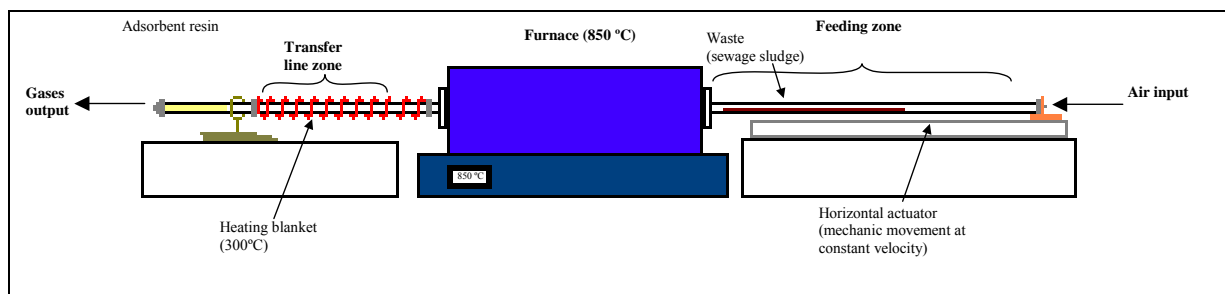


Figure 1. Schematic configuration of the laboratory solid combustion system.

Experiments using sewage sludge have been performed in order to prove if the system reaches a steady state condition and if experimental results agree with the calculated bulk air ratio λ . In order to ensure that all the semivolatile compounds reach the XAD-2 resin, the transport capability of the system has also been tested using a mixture of aromatic compounds.

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Development of a new device to investigate the fast pyrolysis of wood particles at high temperature

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Fluidized-bed reactor (FB) is a promising gasification technology for converting biomass into a syngas upgradable to liquid fuel. The temperature in such a reactor ranges between 700 and 1000°C and the biomass particles undergo heating rates of several hundred of degrees per second. Since pyrolysis is one of the key processes involved during this conversion, it has to be properly understood. Since the biomass particles fed into a FB are typically one to several millimeters in diameter, the pyrolysis kinetics is both chemically and heat transfer controlled¹. A lab-scale apparatus has been conceived to simulate the thermal history undergone by wood particles in a FB and to investigate the coupling of the thermal processes with the chemical reactions involved during the pyrolysis of millimetric particles.

Various types of devices have been used to study the fast pyrolysis of biomass particles. Dupont² gives a brief overview of the different disposals used for that purpose: entrained flow reactor (free-fall reactor), tubular reactor, filament pyrolyzer, image furnace... Here, a new lab-scale equipment is presented, the core of which being a 12kW induction furnace. This apparatus is dedicated to the investigation of biomass fast pyrolysis at temperature ranging between 700 and 1000°C, with a solid residence time varying from a few tens seconds to several minutes and a gas residence time of a few seconds. The particles can be as large as 10mm in diameter. In parallel, a numerical model aimed at describing these processes is being developed, to compare the experimental data with the numerical results.

A major attention is paid to the closure of the mass balance of the experiment. Under the thermal conditions (temperature and heating rate) set in these experiments, the wood particle decomposes into gases, tars and a solid residue. Hence the gas produced is collected and measured for its major constituents (H₂, CO, CO₂, CH₄, C₂H₂ and C₂H₄), with a micro gas-chromatograph analyzer. A tracer method is used to determine the volume of gas produced during the reaction. The mass of tars condensed on the cool parts of the disposal is weighted, as well as the mass loss of the wood sample during the reaction. In addition, the temperature history of the biomass sample is monitored, firstly with a pyrometer focused on its surface, and secondly with a thermocouple introduced into the wood sample. The whole apparatus and the first results collected with this device will be exposed.

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Unraveling reactions during RockEval pyrolysis: Application of a hyphenated RockEval6-MS technique

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During the past five years several approaches have been published attempting to maximize the information gained from standard [1] RockEval pyrolysis measurements. Some researchers have interpreted the S2 and TOC values of groups of samples in addition to the HI value to discriminate between samples from distinct sequence stratigraphic system tracts or to assess the amount of “inert” organic carbon within sedimentary samples.

Others have correlated the peak form of the S2 peak or the relative proportion of two relative S2 peak maxima with the composition and degradation state of the bulk organic matter in the sample [2]. Sebag et al. [3] have extended this concept to the interpretation of organic matter in soil samples from different horizons. They used a deconvolution technique to fit four different components with Gaussian peak shapes to the S2 peak. The interpretation used the RockEval pyrolysis data for a number of biopolymers to quantify the percentage of labile and resistant biological macromolecules – and to address the degradation state of the soil organic matter [3].

To investigate the reactions during routine RockEval pyrolysis measurements, a split of the sample effluent directed towards the detector within the RockEval6 instrument was fed through a heated interface to a GC-MSD system (HP5890GC-5971MSD) operated in full scan mode. The electron impact spectra were acquired for the m/z range 10-570 with a cycle time of 3s.

The results being presented for a variety of biopolymers and sedimentary samples of maturity series with type II or type III kerogen shed new light on individual reaction products and the processes during the RockEval pyrolysis run and hence help to understand the different S2 peak shapes.

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A Practical Method to derive Sample temperature during Nonisothermal TG-DSC Experiments

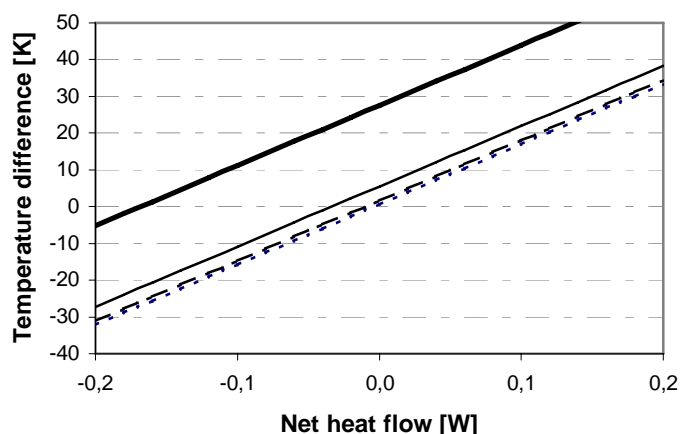
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Nonisothermal TG-DSC (ThermoGravimetry – Differential Scanning Calorimetry) mountings is intensively used for the determination of kinetic parameters and reaction heat, along the chemical transformation of a solid. Nevertheless, when tests are performed with heating rates as high as those encountered in industrial processes - e.g. several tens of $\text{K}\cdot\text{min}^{-1}$ – there is a great uncertainty in the knowledge of the exact sample temperature.

In this work, a method to derive a simple mathematical expression is proposed and fully described in order to calculate the real sample temperature throughout a temperature-ramped test on a commercial apparatus. The furnace temperature and the heat flow signals were used, together with the crucible specific heat and the heating rate. Using this method, the kinetic parameters for a reference first order reaction are reconciled over a large range of heating rates from 3 to 50 $\text{K}\cdot\text{min}^{-1}$. A number of alternative validation tests were performed.

The temperature difference between the sample actual temperature and the furnace temperature indicated by the apparatus is shown to be largely significant, and can be characterized as illustrated in the above figure for (--) 1, (-.) 3, (-)10 and (-)50 $\text{K}\cdot\text{min}^{-1}$ heating rates.



Yttria Stabilized Zirconia films deposited by Electro-Spray Deposition for Solid Oxide Fuel Cells

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Solid Oxide Fuel Cells (SOFCs) are interested as an energy conversion system of future with high efficiency and environmental cleanness. To fabricate the micro fuel cell for mobile application, it is essential to develop a process for the deposition of dense electrolyte films. In this study, for the micro-SOFC application, YSZ electrolyte films were prepared by Electro-Spray Deposition (ESD) method. The studied deposition parameters were deposition temperature, distance between nozzle and substrate, solution concentration and DC voltage. Depending on these parameters, the surfaces were remarkably changed from cracked or rough surface to smooth and dense film. Dense films was prepared from the conditions of the nozzle-substrate distance of 4 cm, the deposition temperature of 150 °C, the deposition time during 4 minutes, and voltage power of 16 kV.

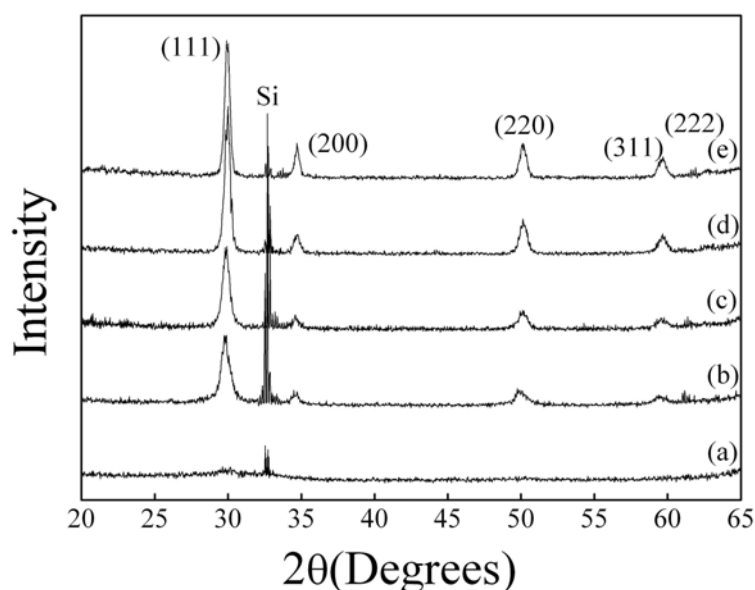


Figure 1. X-ray diffraction patterns of YSZ films, prepared from the conditions of the nozzle-substrate distance of 4 cm, the deposition temperature of 150 °C, the deposition time during 4 minutes, and voltage power of 16 kV, sintered in (a) 400, (b) 600, (c) 800, (d) 1000 and (e) 1200 °C.

**SESSION 8 ANALYTICAL PYROLYSIS APPLICATIONS I:
Soil, Geochemistry and Environmental Sciences**

Do molecular assemblages released at progressive pyrolysis temperatures reflect different organizational levels in the structure of soil humic acid?

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Analytical pyrolysis is a classical tool for the structural research of humic substances, invoked as a technique superior to wet chemical degradation because its outstanding potential for the breakdown of the C–C bonds even in the most recalcitrant structural domains. Also, it enables the release of a large variety of products in a wide range of polarity and derived from lipid, carbohydrate, lignin or protein. Nevertheless, the potential of analytical pyrolysis for unbiased structural analysis is the subject of controversy. In extreme cases, it is considered that pyrolysis is only valid for fingerprinting purposes in samples analyzed with the same device under exactly the same analytical conditions.

Due to the above limitations, the structural information inferred from pyrolytical analysis of strongly heterogeneous macromolecular material such as humic substances requires comparison between results from destructive and non-destructive techniques in a set of widely differing, well characterized samples, where pyrolysis under more or less drastic conditions e.g. at different temperatures, is carried out.

Pyrolysis was carried out in a Pyrojector (SGE instruments) connected to a GC/MS system Finnigan Trace GC Ultra with a Trace DSQ mass spectrometer. The chromatograph had an HP-1 capillary column (30m × 250 µm), and the helium flow was adjusted to 1 ml min⁻¹. Oven temperature was 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 320 °C.

Comparison of the pyrolytic patterns showed dramatic differences in terms of temperatures, the most remarkable being: a) the lack of methoxyphenols in pyrograms at 700 °C as regards to those at 500 °C and b) the release of a conspicuous alkyl series mainly in samples at 700 °C. The latter series consisted of fatty acids (mainly C₁₂ to C₁₈ with strong even-to-odd C-number preference) and hydrocarbons (alkanes and olefins in the C₇ – C₂₁ range and no C number preference).

The preliminary results are interpreted as: a) most of the alkyl products (C₇–C₁₇) are not thermoevaporation products but pyrolytic fragments, b) most of the information concerning lignin and other methoxyphenol-releasing structures are lost after pyrolysis at high (700 °C) temperature and c) it is postulated that mainly high pyrolysis temperature (700 °C) provides data on the condensed alkyl domain in humic substances (in some cases referred to as unhydrolyzable residue or protokerogen-like material).

The role of agricultural practices on humification patterns in virgin and cultivated soils from South Africa, Tanzania and Zimbabwe

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Cultivation of Southern African soils often led to considerable depletion of soil organic matter, the qualitative and quantitative effects of which were studied by standard agronomical analyses, isolation and quantification of the different amounts of soil humic fractions, and analytical pyrolysis of whole soil material.

Pyrolysis was performed using a 2020 Frontier Laboratories unit directly connected to a GC/MS system Agilent 6890 with a 30-m fused silica column HP 5MS. Oven temperature was at 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 300 °C for 10 min at a heating rate of 20 °C min⁻¹. The carrier gas used was helium with a flow of 1 ml min⁻¹.

In six experimental farms from three Southern African countries a regular trend attributable to the effects of cultivation consisting of a relative increase of organic fractions tightly bonded to the mineral fraction (i.e., humic acid and insolubilized humin) was often observed. In some cases (e.g. Domboshawa and Guquka fields), a significant decrease of the humic acid-to-fulvic acid ratio as a result of cultivation was also observed, indicating enhanced oxidative processes leading to the breakdown of humic acid molecules into oligomer fractions, whereas in other soils the relative depletion of the humic acid fraction could point out to enhanced leaching processes in cultivated soils. The results obtained by analytical pyrolysis showed that under tropical conditions no large changes were observed in pyrolytic descriptors of the alteration degree of plant lignins, as reflected on changes in the methoxyphenolic patterns, whereas the most significant changes were observed in the structures derived from the alkyl domain. In fact, in Chiqwaka and Domboshawa soils a cultivation-induced “alkyl depletion” was observed. In Guquka, Hertzog and Mafiga soils there were small changes and lower amounts of aromatic products whereas in Mkindo soils a cultivation-induced “alkyl enhancement” was observed. These differences are being interpreted as regards to the extent to which plant-derived organic matter is substituted by microbial products.

Preliminary conclusions, supported by the distribution of the major C-forms in soil humic acids studied by ¹³C-NMR suggested: a) alkyl pyrolysis compounds (except fatty acids) are important indicators of different biogeochemical trends in the sites studied, b) mainly α,ω -alkanedienes and alkanes were found to be responsive for microbial metabolism and selective preservation of alkyl biomacromolecules (cutans, suberans, etc.), c) due to the intense lignin degradation in the sites studied, the methoxyphenolic patterns had a limited value to illustrate the extent to which lignin is transformed into humic acid-like macromolecules, d) as a difference to cultivation effects often described in soils from countries under wet and/or temperate climate, a possibility observed in the South African experimental farms studied is that strongly aromatic and condensed organic matter in some uncultivated ecosystems may turn into less transformed, comparatively aliphatic, young organic matter upon cultivation, as a possible result of the interaction of herbaceous crop wastes and intense microbial reworking in wet sites with fallowed soils.

Thermogravimetric and Pyrolysis methods to characterize organic matter at the molecular level: application to a bio-urban waste compost

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To prevent soil erosion and desertification, amendments of organic wastes are evaluated. Different amendments such as compost, sewage sludge, ovine manure or humic acids solutions have been studied [1]. The pathways of transformation of these organic substances at the molecular level are however still far from being understood. The purpose of this work consists in studying the bio-urban waste compost components by different thermal techniques for compost characterization and latter to better understand the Carbon dynamics during compost organic matter incorporation in soil.

The organic amendment is a bio urban waste compost (composting plant of La Villedieu du Clain, France). The compost, its granulometric fractions and its humic substances were characterized by Infrared Spectroscopy (FTIR), Thermogravimetry and Differential Scanning Calorimetry (ATD-ATG) and thermochemiolysis (TMAH or TEAAc/Py-GCMS) on inert or oxidative conditions.

Different organic matter (OM) constituents have different thermal stabilities and, therefore, the formation of a peak in ATD spectra in a certain temperature range can be related to the decomposition of specific OM structures [2]. Compost ATD showed two major distinct exothermic peaks in the temperatures ranges: 200–350 °C (peak 1), 350–450 °C (peak 2). In literature, peak 1 is generally assigned to the decomposition of aliphatic organic matter whereas peak 2 is associated to aromatic ones [3]. Thermochemiolysis of the compost at temperatures of 200°C, 385°C and 650°C were performed so that the origin of organic matter of each peak is determined. Major components obtained by thermochemiolysis are of vegetal and bacterial origin (lignin monomers and fatty acid methyl esters). Even though more aromatic compounds are detected at the highest temperature, alkanes and fatty acids are identified at each temperature. Peak1 is then more representative of a labile structure and relatively simple organic matter components compared to peak 2 assigned to more humified organic substances.

The studied compost will be then be added on a reference soil and the incorporation of its organic matter followed by the two thermal methods.

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Pyrolytic descriptors of the effect of parent material, climate conditions and vegetation type on soil biogeochemical quality in Mediterranean soils from Sierra de Cazorla-Segura-Las Villas Natural Park

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A study was carried out on structural characteristics of the soil humic acid in surface horizons of soils from different geological (mainly calcareous rocks) and ecophysiological characteristics in a Natural Park of great environmental interest under Mediterranean climate in Southeast Spain. The mean annual temperature is 11 °C, the mean annual rainfall is about 866 mm, the altitude in sites sampled ranged between 700 to over 1780 m.a.s.l., and the slope between 4 and 57%. The vegetation consisted of sclerophyllic (oak) forest, pine forests or dense shrubs (coverage of 75% or more). Analytical pyrolysis was carried out in a Pyrojector (SGE instruments) connected to a GC/MS system Finnigan Trace GC Ultra with a Trace DSQ mass spectrometer and HP-1 capillary column (30 m × 250 µm).

Humic acid samples from scrubland showed comparatively simple pyrograms, in some cases comparable to those from sclerophyllic oak forest, which is interpreted as an efficient biogeochemical transformation probably responsible for the prevalence of a stable aromatic domain with frequent C–C intermolecular bonding. Conversely, conifer forests showed large yields and diversity of lignin-derived methoxyphenols accompanied by well-preserved alkyl series suggesting low biodegradation of the humic aliphatic domain. In the case of sclerophyllic forest (evergreen oak and other *Quercus* species) the comparatively simple pyrograms with dominance of guaiacol and phenol suggest condensed residual lignin (guaiacyl-type) where the low methoxyl content, which is originally associated to lignin evolutionary chemotaxonomic features (guaiacyl lignin in gymnosperms and syringyl lignin in angiosperms) is strongly constrained by their further evolution in soil, where condensed lignins (guaiacyl-type) behaves as comparatively more recalcitrant in soils than lignins with comparatively lower degree of intramolecular cross-linking (syringyl-type). The corresponding ratio, when properly interpreted, may be used as a soil organic matter quality index.

The conclusions inferred after application of multivariate data treatments (mainly multidimensional scaling), suggest that the vegetation results a key factor in determining the humification mechanisms, followed by the geological substrate. A series of valuable surrogate descriptors of the factors influencing the humification processes were obtained from the relative abundance of pyrolysis compounds: a) the alteration of the original lignin methoxyphenolic signature (ratio between methoxyl-lacking to methoxyphenol compounds), b) the extent and C-range of the alkyl domain, c) the degree of demethoxylation of the aromatic moiety (syringyl/guaiacyl ratio) which simultaneously inform on the vegetation type (gymnosperms vs. angiosperms) and on the maturity degree of the soil organic matter and, d) the biodiversity indices of the molecular assemblages after analytical pyrolysis, which tend to decrease in comparatively resilient humus formations.

Double-shot pyrolysis of humic fractions from subtropical humic Latosols under different land use (Atlantic Forest, Minas Gerais – Brazil)

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The structural transformations underwent by humic acids (HA) and fulvic acids (FA) isolated from the arable layer (0-10 cm) of a subtropical humic Latosol (Oxisol) under various vegetation covers (natural Atlantic forest, pasture (*Melinis minutiflora*.) and coffee (*Coffea Arabica*)) were investigated using double-shot pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). The humic fractions were extracted and purified following conventional methods [1], and successively analyzed by thermal desorption (280 °C) and true pyrolysis (610 °C).

The main results obtained are summarized in Table 1. The pattern of thermal desorption products revealed clear structural differences between the HA extracted from the soil under forest and pasture. In the latter a recent input of lignin compounds is evidenced by the presence of higher proportion of methoxyphenols. Polysaccharide derived compounds were the major volatile fragment liberated by thermal desorption of HA and FA from the cultivated soil, whereas the structure of both fractions in the soil under forest seems to contain important contributions of N bearing compounds. In general, thermal desorption at 280 °C seems to be a sensible technique for diagnostic land use influence in humic fractions structural modifications. On the other hand, the patterns of pyrolysis compounds released at 610 °C show that the stabilization mechanisms for humic fractions in the studied soil probably involve the accumulation of aromatic and N compounds preferentially into HA, and aromatic compounds (phenols) into FA.

Table 1. Relative percentages ^(**) of the main families of pyrolysis compounds released from HA and FA by thermal desorption and pyrolysis

Humic and Fulvic Acids: thermal desorption and pyrolysis						
Compounds	Coffee		Pasture		Forest	
	Humic Acids					
	Desorption	Pyrolysis	Desorption	Pyrolysis	Desorption	Pyrolysis
Aliphatic	3.34	1.76	7.46	3.99	22.49	2.10
Aromatics	nd	38.11	14.26	42.5	19.52	42.94
Fatty acids	nd	0.26	15.88	0.66	1.69	0.43
Lignin	5.63	2.73	16.73	5.97	nd	6.10
N compounds	nd	26.43	10.95	20.75	42.71	16.95
Phenols	nd	22.51	1.23	19.07	nd	10.76
Polysaccharides	91.02	2.97	32.36	1.84	11.81	1.33
Other Compounds	0.01	5.23	1.13	5.22	1.78	19.39
	Fulvic Acids					
	Desorption	Pyrolysis	Desorption	Pyrolysis	Desorption	Pyrolysis
Aliphatic	1.71	2.01	1.77	0.72	0.71	2.23
Aromatics	8.20	17.90	16.28	31.38	4.88	28.81
Fatty acids		1.09	1.04	0.64	3.76	3.09
Lignin		6.42	3.18	5.26	5.34	4.80
N compounds	7.28	7.99	2.44	9.94	52.23	12.10
Phenols	1.72	17.19		28.99	2.07	27.60
Polysaccharides	39.06	6.28	69.26	8.24	31.02	2.13
Other Compounds	42.03	41.12	6.03	14.83	0.01	19.24

^(**) % relative to the total ion chromatogram (TIC) area; nd: no detected.

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Disclosure of structure patterns relationships of humic fractions in solution

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Historically, traditional researchers in the humic substances (HS) world had been carried out a fractionation of humic acid into two different fractions: gray humic acid (GHA) and brown humic acid (BHA). This fractionation can be made in presence of high concentration of electrolyte and this fact is owed to a different physicochemical behavior of these two fractions [1]. A number of studies have shown the presence of different molecular patterns in the main fractions of HS: gray humic acids (GHA. Macromolecular pattern), brown humic acids (BHA. Supramolecular and macromolecular patterns) and fulvic acids (FA. Supramolecular pattern). However, little information is available about the main structural domains in these humic fractions, principally in GHA and BHA, which could explain the different molecular patterns [2].

In this study, we investigate the principal structural moieties present in the different HS fractions using Pyrolysis GC/MS and Thermogravimetry, and complemented with typical analytical characterization including Kumada's UV-Visible characterization.

The results obtained indicate that GHA present a dominant aliphatic character and a relatively low functionality, whereas BHA are principally aromatic and more functionalized than GHA, with FA presenting a more polar character and aromatic functionalized structures. These results also could suggest that the formation of stable aggregates in BHA and FA could be related to inter-molecular interactions, possibly dispersive forces (π - π and van der Waals forces) [3], involving functionalized polar structures.

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Sequence of pyrolytical geochemical proxies in a Southern Africa slackwater flood deposits record

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Slackwater palaeoflood sediments (SWD) are deposited in flow marginal areas of bedrock canyons during high flood stages, reflecting long term flood magnitude and frequencies of large floods over decades to millennia. A major advantage of individual event based stratigraphy (e.g. SWD) is that units represent a “snapshot” of flood dynamics, suspended load and even catchment environmental conditions. This study aims to provide insight into the palaeoenvironmental changes of the Buffels river (Namaqualand Province, NW South Africa), through the analysis of a proxy sequence of pyrolytical geochemical components.

The stratigraphic profile is *ca.* 2 m in thickness and provided evidence of at least 10 floods deposited over the last 500 years (radiocarbon dated 1-sigma AD 1444–1641). The flood units are composed by fine sand and silt, with thickness between 10–50 cm. In this sequence (numbered from bottom to top), three flood units contain couplets of fine sand and organic enriched layers of 5 to 13 cm in thickness. The rapid sedimentation of successive flood sand units on top of the organic enriched units provides a record of organic compound development which can be interpreted in terms of environmental conditions associated to these riparian environments. Pyrolysis of these organic matter enriched sediment samples was performed in a 2020, Frontier Laboratories unit connected to a GC/MS system Agilent 6890 with a 30-m HP 5MS column.

The results indicated low yields of methoxyl-containing compounds, suggesting moderate terrestrial inputs and predominantly autochthonous origin of the organic sediment, or its transformation in hydromorphic conditions. The major peaks correspond to alkyl-substituted benzenes (major peaks of styrene, toluene and xylene) and naphthalenes. Nitrogen compounds were represented by pyridines. In the intermediate layer (K9/8), radiocarbon dated as AD 1475–1610, it was observed the largest biodiversity in the molecular assemblages with dominant aromatic series but significant peaks for carbohydrate-derived compounds (furans), and N-compounds (benzonitriles). This layer includes conspicuous series of naphthalenes, fluorenes, anthracenes and phenanthrenes, indicating diagenetic transformation and complex trophic system during the formation of the sediment. The patterns was similar but less complex in the uppermost layer (K9-6), which present the best-defined alkyl series consisting of α,ω -alkanedienes and alkanes indicating biomass under prevailing aquatic conditions. In the lowest (K9-10) layer the pyrolytic signature was relatively poor as could correspond to organic matter of high transformation degree presumably formed under comparatively oxic conditions.

In general the results show that organic matter is derived from progressively terrestrial to aquatic inputs, which is accompanied by enhanced diversity in the molecular assemblages in the materials accumulated in the most recent sedimentary events. These results can be interpreted as due to an increase in water availability in the depositional environment which can be related to increasing stream flow and wetter climate conditions.

Organic matter characteristics in connection with the physical quality in the different orders of cultivated semiarid soils in Central Spain

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One natural soil and eight agricultural soils developed under xeric conditions and classified as Entisols, Inceptisols and Alfisols, were studied. The study area (Castilla-La Mancha, Central Spain) show an average altitude of 700 m.a.s.l., with a geological substrate consisting of a Paleozoic basement of quartzites and shales and Miocene deposits of continental origin. The temperature regime is Warm Temperate, and the hydric regime is Dry Mediterranean. All soils have similar apparent characteristics but differ in lithology and development. The aim of this work was to compare soil physical properties with the characteristics of the soil organic matter, which is known to be a key factor in soil quality of semiarid soils.

Apart from standard agrochemical characteristics, a series of soil physical properties were studied in field and laboratory conditions (soil infiltration curves, water holding capacity, aggregate stability, bulk densities, textural analyses...). The soil humic acid was isolated and analysed by spectroscopic techniques and analytical pyrolysis carried out at 500 °C in a Pyrojector (SGE instruments) connected to a GC/MS system Finnigan Trace GC Ultra with a Trace DSQ mass spectrometer. The chromatograph was provided with an HP-1 column (30m × 250 µm), and the helium was adjusted to 1 ml min⁻¹. The oven temperature was 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 320 °C.

In general the humic acids yielded characteristic pyrolytic compound assemblages ranging along extreme patterns: from relatively simple pyrograms with alkylbenzenes and alkylphenols as major pyrolysis products, to pyrograms with large amounts of methoxyphenols (guaiacol, syringol and their methyl-, ethyl-, vinyl-, propenyl- and acetyl-derivatives) accompanied by more or less defined homologous series of alkanes, alkanedienes and, to lesser extent, fatty acids.

The results were analyzed using data matrices with soil-dependent characteristics managed both as raw variables or as ratios as regards the total soil organic matter content. Then, a series of simple and multiple regression analyses as well as multidimensional scaling were applied in the joint processing of soil physical characteristics and yields of the major pyrolysis compounds in an attempt to identify valid descriptors or to postulate functional relationships between soil organic matter characteristics and their bearing on the soil physical status.

The results suggest the limited forecasting potential of simple pyrolytic compounds. In the sample set studied, some valuable hydrophysical and structural properties appeared to be correlated to humic structural factors suggesting a weakly-condensed humic structure with a substantial aliphatic domain. This is tentatively interpreted (assuming some cause-to-effect relationship) such as moderate hydrophobicity conferred to the humic acid by the alky domain in addition to comparatively low condensed, flexible aromatic skeletal structures are associated to active role in improving soil physical properties. To some extent, this contrasted with classical concepts suggesting that the substantial aromaticity of resilient soil organic matter of long average residence time is directly related to their positive environmental role.

Monitoring by analytical pyrolysis the post-mining soil rehabilitation with urban compost in Southern Spain (Almería)

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In general, gypsic soils from the study area (Southeast Spain) have low organic matter content. The organic matter concentrations range between 1 and 2% in the topsoil and from 0.25 to 1% in the underlying horizons. Under these conditions, the post-mining soil rehabilitation is hampered because the original source of soil has been removed and replaced by alternative “soil-forming materials” which are intended to represent suitable substrate for plant growth. An important limitation of these materials is their inherent poor structure, mainly because of their low content of organic matter. In these cases, the development of soil structure can be accelerated through the use of organic amendments. However, not all organic amendments are equally beneficial and there is classical controversy on their suitability as starting materials for the formation of humic substances. The experimental design included pyrolytic analyses of whole soil samples taken at different depths (10–30 cm) in order to monitor the effect of burial and lixiviation in soil organic matter dynamics as well as to compare control and compost-amended sites after compost application (50 Mg/ha of composted urban wastes) and after 4 years transformation in soil. Pyrolysis was carried out using a 2020, Frontier Laboratories unit directly connected to a GC/MS system Agilent 6890 with a 30-m fused silica column HP 5MS. Oven temperature was at 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 300 °C for 10 min at a heating rate of 20 °C min⁻¹. The carrier gas used was helium with a flow of 1 ml min⁻¹.

The results indicated poor methoxyphenolic yields in amended soils, indicating urban compost not suitable to be transformed into resilient humic acid fractions. The major pyrolysis compounds were alkylbenzenes (major peaks of styrene, toluene and xylene) furans and naphthalenes. The most significant qualitative effect of urban compost application was the accumulation of alkyl compounds where fatty acids were practically lacking but well-defined series of α,ω -alkanediene and alkanes accumulated irrespectively to soil depth. After 4 years of transformation in soil, both control as well as amended plots showed preserved series of alkyl compounds and no additional fatty acids (suggesting weak microbial activity) but major series of low-range (< C₂₀) alkanes pointing to stabilization in soil of alkyl compounds from the added compost. Further concentration of alkyl compounds in deep horizons (>30 cm) could be interpreted as low oxidative biodegradation in addition to leaching of aliphatic (e.g. fulvic acid-like) substances throughout the soil profile to reach horizons with higher moisture and less efficient oxidative processes. The overall results suggest that the major changes in soil organic matter in the course of the post-mining soil rehabilitation are not due to rapid formation of humic substances similar to that in control soil, but to accumulation of recalcitrant aliphatic compounds which could act as a source of descriptors of the selective biodegradation and translocation of compost constituents.

Influence of Ion Exchanged Metals in Humates of Sieniawa Brown Coal Humic Acids on Composition of Liquid Pyrolysis Products

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The Sieniawa brown coal (Poland) was demineralised with HCl to remove cations bounded to acidic oxygenated functional groups. Humic acids were obtained from the demineralised brown coal by sodium hydroxide extraction and conversion of sodium humates solution to their acidic form by HCl treatment and further washing out of Cl^- . Metal complexes of the humic acids with cations: Ca(II), Ba(II), Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Ga(III), Pb(II), and $\text{UO}_2(\text{II})$ were obtained by ion exchange from the respective acetates. The amount of cations uptake was: for gallium 0.58 mmol/g, for calcium 2.98 mmol/g, while for the other cations it oscillated around 1 mmol/g. The cation unexchanged humic acids and respective humates were pyrolysed under flow of argon in electrically heated quartz tube to final temperature 800 °C at rate of 30 °C/min. The solutions of liquid volatile pyrolysis products were trapped at a furnace outlet into chloroform and were then subjected to GC-MS analyses.

The investigated metal cations revealed rather small effect on the summary amount of *n*-alkanes and *n*-alk-1-enes released. They have effect on the relative abundance of *n*-alkane/*n*-alk-1-ene pairs of the respective homologs. The alkaline earth cations and Ga(III) as well as d-electron cations except Cd(II) cause little increase of total concentration of the *n*-alk-1-enes on expense of concentration of the *n*-alkanes. Highly pronounced opposite effect was caused by Cd(II), where very big decrease in total concentrations of the *n*-alk-1-enes and increase in total concentration of *n*-alkanes is observed. Similar effect as Cd(II), but less pronounced, give Pb(II) and $\text{UO}_2(\text{II})$. It indicates different thermal decomposition pathway of humic acids catalysed by Cd(II), Pb(II) and $\text{UO}_2(\text{II})$ as compared to the other cations. The total concentrations of released FAMES in pyrolysates from humic acid metal complexes are lower than released from uncomplexed humic acids except for Ba(II) and $\text{UO}_2(\text{II})$ complexes, where they are higher. All cations cause pronounced lowering effect in release of total amount of free, lower molecular weight ($\text{C}_6 - \text{C}_{14}$) alkanolic acids; in Cd(II) pyrolysis products they are absent. Amounts of alkylbenzenes released from metal humates are lower for most complexes, however, for Ni(II) and particularly Cu(II) and Ga(III) complexes they are respectively more than twice and 1.3 times higher. This indicates some selectivity in Cu(II) and Ga(II) catalytic effect on formation of alkylbenzenes during humic acids thermal decomposition.

The investigated cations cause a decrease in the amounts of phenol and disappearance of o-dihydroquinone in the pyrolysis products. Some amount of o-dihydroquinone is present only in pyrolysates obtained from uncomplexed humic acids as well as from their Cu(II) and Ga(II) complexes. These metals appeared the most active catalyst in formation of biphenyl, 9H-fluorene, dibenzofuran, tetranaphthalenes. The Ca(II), Mn(II), Ni(II), Cu(II), Ga(II) and in far bigger extend $\text{UO}_2(\text{II})$ caused increase of the PAHs concentration i.e. phenanthrene, anthracene, fluoranthene and perylene in respective pyrolysates, as compared to their concentration in pyrolysate from uncomplexed humic acids.

Pyrolytic assessment of the changes in the chemical composition of humic fractions from organic wastes associated to their composting processes

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Composting has turned out to be a suitable waste management method to reduce the amount of organic wastes that is accumulated in landfills. However, these composts from organic residues must have been adequately treated and stabilized with the aim of reducing the initial toxicity of the wastes in order to avoid negative effects on soil. Among the different techniques that can be used to characterize the humification degree of organic materials, analytical pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC/MS) has been proposed as a reproducible technique that allows the characterization of humic matter from various origins, including composted materials [1].

In this context, the purpose of this study is to determine the changes in chemical composition occurred during composting processes of total humic-like extracts (THE) obtained from composted materials of diverse origin (solid wastes of wineries, solid mill olive wastes, domestic wastes, ovine manures plus straw, and a mixture of animal manures) and from their corresponding initial raw fresh organic mixtures were analysed. Pyrolytic behaviour of several humic and fulvic acids from soils, including reference acids purchased from the International Humic Substances Society, was also evaluated.

The results indicated that the pyrolysates of the THE from composted samples were enriched in aromatic and nitrogenated structures, whereas polysaccharide-derived compounds diminished during the composting process. The main pyrolytic products yielded by soil humic acids were alkylbenzenes and alkylphenols, whereas fulvic acids showed higher contents in aromatic and polysaccharide-derived compounds. When comparing THE with reference humic substances, the former showed the highest levels of N-containing structures, whereas the increase in the aromaticity as the result of composting is in all cases below the degree of aromaticity obtained for reference humic substances. Notwithstanding pyrolysis results only account for 50-70 % of the total sample, they correlated well with previous studies by nuclear magnetic resonance techniques [2], supporting the suitability of Py-GC/MS for estimating the humification degree of organic materials.

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Molecular features of dissolved HA fractions at different extraction times

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Humic substances (HS), found in all terrestrial and aquatic environments, represent an important and active fraction of the refractory organic matter [1]. Humic substances are operationally defined in terms of their solubility in aqueous media as a function of pH. Humic acid (HA) is the fraction of HS that is soluble at high pH values.

The HA was originally extracted and purified from a soil with andic characteristics according to the procedures recommended by the IHSS (elemental composition: N 4.86%, C 52.57%, H 5.06%, O 37.18%, S 0.33%). For detailed information about this HA and dissolution kinetics see Brigante *et al.* (2007) [2]. Double-Shot Py-GC/MS was used to investigate the molecular features of HA that enters in solution in aqueous media (pH 8.5) at different extraction times. Total desorption (280° C) and pyrolysis (500° C) products (Fig. 1) were analysed in the original HA and in six fractions obtained after re-precipitation of the dissolved HA (pH 1.5). Alkyl (alkane/alkene pairs), aromatic (methyl naphthalenes), other polyaromatics (PAHs) and lignin markers (methoxyphenols) were also investigated.

Differences were found in the products released by desorption and pyrolysis from the six fractions. It is found that lignin markers are typical desorption products and that the sequential technique used (Double-Shot Py-GC/MS) provide complementary windows of information to elucidate molecular features of complex organic matrices such are HAs.

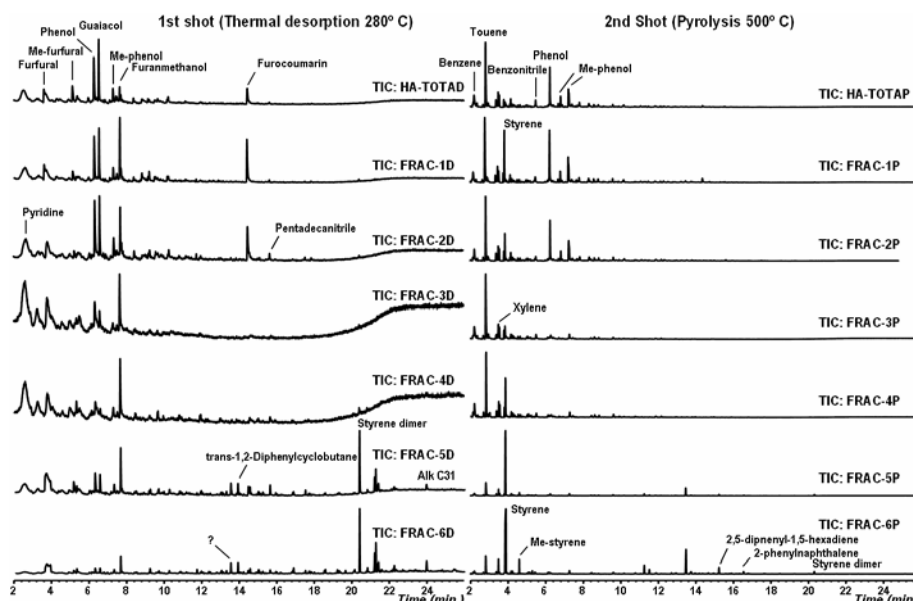


Figure 1. Original HA (TOTAL) and six re-precipitated HA fractions (1-6) TICs.

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Analysis of DOM from an agricultural soil as seen by pyrolytic techniques

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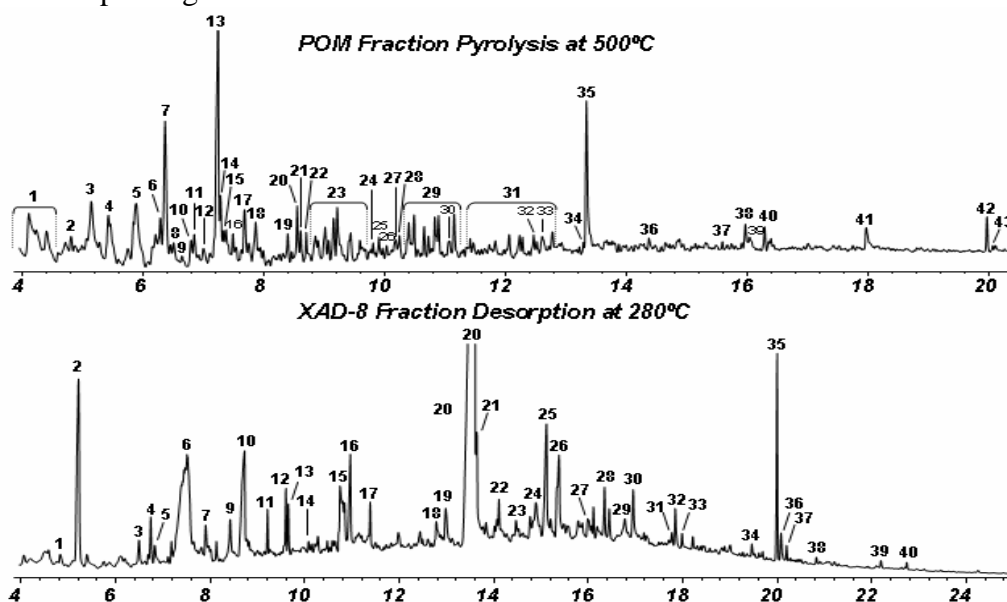
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Humic substances (HS), found in all terrestrial and aquatic environments, represent an important and active fraction of the refractory organic matter [1]. Dissolved Organic Matter (DOM) in drainage waters, although a minor component of HS, can represent significant losses of soil organic matter over a long period of time. This depends on various factors i.e. the amount of water that pass to the drains, the composition and properties of the soils, and the time of the year [2]. In this work, a first approach was done to the study of the molecular features of particulate filtered fraction (POM) and in the XAD-8 resin humic fraction isolated from the DOM by means of Double Shoot Py-GC/MS. The samples were collected in lysimeters from an agricultural soil at the long-term observatory for environmental research in Poitiers, France.

Best pyrolysis/desorption conditions were estimated in preliminary experiments. A desorption at 280° C was found appropriate for XAD-8 fraction whereas a pyrolysis temperature of 500° C was needed for investigating the molecular composition in the POM fraction.

Higher abundance of marker compounds with a biota origin was found in the XAD-8 humic fraction that could derive from polysaccharides, protein, lignin (methoxyphenols), lipids and waxes. In this fraction it was also possible to detect common contaminants from plastics, but also others from agrochemicals.

The information provided by the POM fraction was more difficult to interpret. Some biota markers were detected including a well defined lignin signature, and contaminants. However many of the pyrolysis compounds released from the POM fraction were unspecific, unknown or have a multiple origin.



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Molecular characterization of potentially interfering materials when studying “Black Carbon” forms. The combined use of Analytical Pyrolysis, Solid state- ^{13}C Nuclear Magnetic Resonance and thermogravimetric techniques

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Due to geochemical and environmental implications, there is an increased interest in the study of the different forms of refractory organic matter (ROM) widely widespread in soils, water and sediments. Included in the refractory OM pool are kerogens, humic-like materials as well as the so-called “black carbon”(BC). These materials might remain sequestered in soils and sediments (slow geological C cycle) from thousand to million of years, being considered as an important sink for atmospheric CO₂ (fast C cycle) and part of the “missing C” in the global C budget. As pointed out by many authors [1] there is therefore a need to develop accurate and comparable analytical protocols to determine the amount of BC stored in different environmental matrices. However, despite the significant improvements achieved in the analytical techniques and a considerable effort devoted recently to characterise sedimentary organic carbon, a large fraction of it remains bio-chemically uncharacterised [2].

Black carbon (BC), the product of incomplete combustion of fossil fuels and biomass, is considered the most stable form of C within the ROM. In this work we present a comprehensive study of 4 samples of different materials potentially interfering in the analysis of BC. Those materials consist of melanoidin, shale, lignite coal and bituminous coal. This study deals with the analytical characterization of those materials by using different analytical techniques including thermogravimetry (TG), TG coupled with differential scanning calorimetry (DSC), solid state ^{13}C CP-MAS nuclear magnetic resonance (NMR) spectroscopy and Pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC/MS).

Thermal analysis (TG, TG-DSC) provided mainly information about the proportions of labile, recalcitrant and refractory OM forms, whereas Py-GC/MS and ^{13}C NMR provided complementary windows of structural information on the bulk matrices and their OM fractions. Good agreement was observed between recalcitrant C as determined by TG analysis and the aromatic content measured by ^{13}C NMR. Results indicated a high BC content in the bituminous coal. Analytical Pyrolysis results showed an important presence of aromatic compounds in samples rich in BC like material. By using analytical pyrolysis (Py-GC/MS) it was also possible to directly identify, with no pretreatment, several specific compounds released which could allow a clear identification of potentially BC-interference reference material. Other markers were also identified which provide information about OM origin.

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Thermochemolysis in search for organics in extraterrestrial environments

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Many organic molecules are present in interstellar clouds and might have been carried to the early Earth by comets and meteorites during the heavy bombardment phase in the first few hundred million years of the solar system. It has been suggested that extraterrestrial organic material may represent a part of the organic material available for the origin of life. The analytical technique on such organics has to be robust, sensitive and non-specific due to the large scope of targeted molecules. For both *in situ* and laboratory analysis, automated techniques are required. Extractions followed by derivatization enable the analysis of molecules such as amino acids by GC-MS [1]. The main objective of this work is to present the capabilities of thermochemolysis for the analysis of linked organics in surface or sub-surface samples (Mars, comets) by evaluating this technique on a Mars-like soil sample.

We analyzed a soil sample from the dry Mars-like environment of the Atacama Desert in Chile [2]. The material was subjected to off-line pyrolysis by placing the air-dry sample in a ceramic reaction boat in presence of a 25% w/w methanol solution of tetramethylammonium hydroxide (TMAH). The material was heated at 400°C for 30 minutes before being analyzed by GC-MS.

Fatty acid methyl esters (FAMES) were the main products obtained after TMAH-thermochemolysis. The short-chain range (C₁₄–C₂₀) was dominated by the palmitic acid (as methyl ester) (C₁₆). Unsaturated fatty acids, including palmitoleic (C_{16:1}) and oleic (C_{18:1}) acids were also present. The C₂₀–C₂₈ range originating from higher plants was absent. Another family of long-chain compounds observed is a series of n-alk-1-enes from C₁₄ to C₂₈. Among other origins, the alkenes can arise here from the thermal degradation of alkanols. C₁₆ and C₁₈ 1-methoxyalkanes, corresponding to methylated n-alkanols were also identified. These compounds formed by thermochemolysis were mainly alkanols bound by ester groups in the organic structure [3]. Some of them can be possibly bound to the matrix by ether linkages.

Thermochemolysis enable to detect polar and apolar organics in the same time linked or not to the matrix. This technique tested on a Mars analogue has confirmed that the origin of the organic matter is mainly from bacterial sources, with no contribution from higher plants. However care must be taken in the interpretation as some compounds originate from the thermal degradation of more complex organics.

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TMAH-preparative thermochemolysis for the characterization of organic matter in densimetric fractions of a Mediterranean forest soil

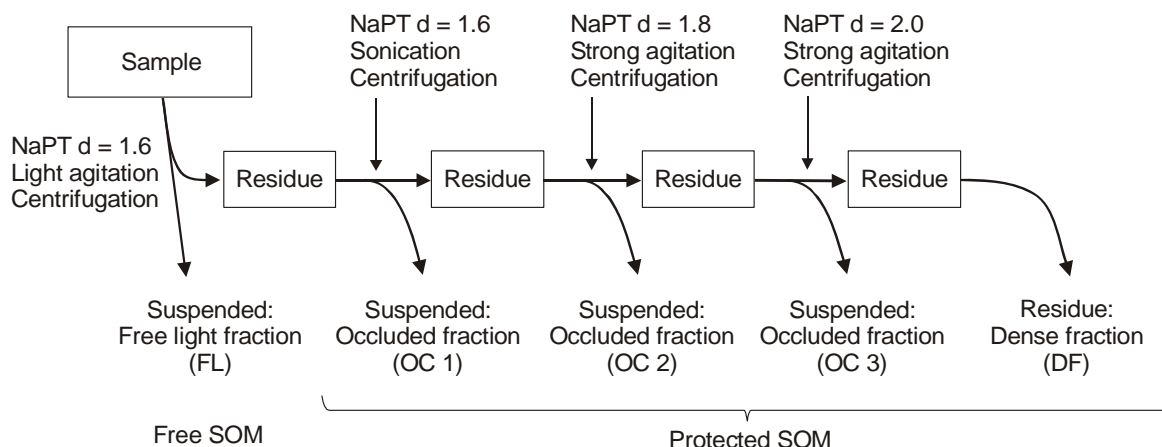
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Physical fractionation methods are used to isolate and/or quantify soil organic matter fractions of contrasting dynamics [1]. The fractions extracted with dense liquids are always heterogeneous mixtures, but a relationship has been observed between soil organic matter density and resistance to decomposition [2]. The significance at the molecular level of these differences is the aim of this study. We focused on the study of density fractions obtained with dense solutions of Sodium Polytungstate (NaPT) from a forest soil taken from horizons H to B2 over limestone and below holm oak stands (*Quercus rotundifolia*). To this end, thermochemolysis with tetramethylammonium hydroxide followed by gas chromatography-mass spectroscopy analysis was applied. This method is widely used to identify and quantify biomarkers released from complex organic matrices. With a preparative device [3], it is possible to carry out a rapid analysis on samples with small amounts of organic carbon.



We focused on molecular families able to give information about the degree of microbial transformation of the SOM, relative to its origin (mostly plant-derived): aliphatic fatty acids, α,ω -dicarboxylic acids, ω -hydroxy acids, alkanols and aromatics (lignin monomers). Results from the light fractions and the dense fractions suggest the dominance in these fractions of plant-derived lipids; in contrast, results from the occluded fractions ($1.6 < \text{density} < 2$) suggest a dominance of microbial-derived organic matter. However, this organic matter has undergone microbial transformation. The occluded fractions appear to be more transformed by the microbial activity than the free and the dense fractions, the composition of which being closer to the vegetal origin.

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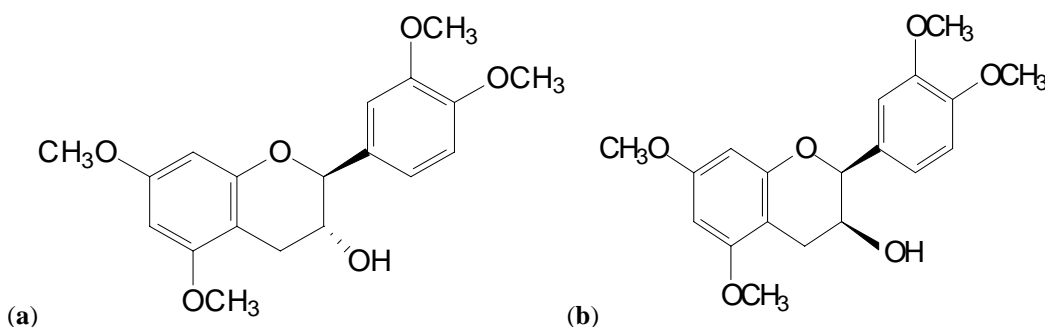
Analysis of Catechins and Condensed Tannins by Thermally-Assisted Hydrolysis/Methylation-GC/MS and by a Novel Two Step Methylation

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Catechins and condensed tannins are important for human health acting as antioxidants, and, for the health of plants which contain them, acting as phytoalexins. In previous studies, catechins and condensed tannins were subjected to thermally assisted hydrolysis and methylation (THM) using TMAH (tetramethylammonium hydroxide) [1-2]. However, the harsh conditions result in small methylated fragments of the original 3- flavanol. Also, in complex samples, one may not be able to differentiate them from other classes of biomolecules such as the lignins. The present study will show techniques for formation and identification of unique chemical markers of catechins using THM- GC/MS in the presence of trimethylsulfonium hydroxide (TMSH) ,and, of dimer condensed tannins using a novel two step methylation technique. The two step methylation procedure involves pre-methylation of the tannin with trimethylsilyl diazomethane (TMS-diazomethane) at room temperature followed by THM in the presence of TMSH. In contrast to other studies [1-2] in which markers were small methylated phenolics the markers from this study are high molecular weight compounds including partially methylated forms of catechin (**a**) and epicatechin (**b**) (3-Flavanol, 3',4',5,7-tetramethoxy, cis/trans; $m/z = 346$) and partially methylated forms of epigallocatechin and gallocatechin (3-Flavanol, 3',4',5,5',7-pentamethoxy, cis/trans; $m/z = 376$). By the two step methylation procedure we also identified an even higher molecular weight marker (> 490 amu) for B1 dimer condensed tannin. These techniques were further applied to the analysis of series of condensed tannins isolated from plant material, and, tannins present in (hot water) extracts of tea leaves.



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Appraisal of management types on agroecological quality in different vineyard soils developed on volcanic ash (Tenerife, Canary Islands)

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The influence of agricultural management in soil carbon cycle is not completely understood especially in soils developed on volcanic ash materials which are traditionally postulated to exert a significant enhancement in organo-mineral complexes. This interaction is reflected in the performance both in soil carbon sequestration and in soil agroecological quality. A total of 30 humic acids collected from undisturbed and cultured soils from Tenerife (Canary Islands) were studied. The sampling sites were representative for different types of vineyards on volcanic materials either consisting of pumites or soils with more or less marked allophanic character. The vineyard management types consisted of traditional, intensive and minimum tillage, including organic agriculture. In the former case, a series of anthrosols consisting of allochthonous volcanic materials (pumites or andic horizons) were also included. The sampling points were also arranged in an altitudinal catena from 100 to 1100 m.a.s.l.

The humic acids were characterized by derivative visible, infrared and nuclear magnetic resonance spectroscopies followed by analytical pyrolysis. This technique was carried out at 500 °C in a Pyrojector (SGE instruments) connected to a GC/MS system Finnigan Trace GC Ultra with a Trace DSQ mass spectrometer. The chromatograph was provided with an HP-1 capillary column (30m × 250 µm), and the helium was adjusted to 1ml min⁻¹. The oven temperature was 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 320 °C.

The results suggested significant interaction between mineralogical substrate (compositional gradient between allophanic materials and coarse pumite fractions) and management types (minimum tillage vs. conventional tillage, intensive or ecological management, plant vs. mineral cover) that was reflected in a series of spectroscopic features and pyrolytic patterns that could be interpreted in terms of soil complexity of the soil trophic system and the biogeochemical performance. A set of soils (mainly developed on pumites) showed humic acids with typical patterns of resistant plant biomacromolecules as well as a weakly condensed macromolecular structure (low optical density and comparatively small amounts of perylenequinone chromophors) also reflected by the substantial yields of lignin-derived methoxyphenolic units.

Other set of soils, where the allophanic substrate is frequently associated with traditional management, in general show humic acids with large condensation and aromaticity (high optical density), and pyrograms with comparatively infrequent methoxyl-substituted aromatic compounds, and higher yields of not especially diagnostic compounds (mainly styrene, benzene) and methylfurfural. This suggests complex organic matter forms with stable aromatic domain not amenable to analytical pyrolysis, but reflected in the ¹³C-NMR spectra.

The overall interpretation of the biogeochemical information suggest the possibility to control the humification processes by the farmer action, which—in the study zone—may exert a significant role on soil organic matter characteristics, with a stronger effect than that expected from the geological and topographical gradients.

Structural features of humic acids from a soil toposequence in Western Siberia

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Western Siberia occupies the middle part of Russia. This area extends more than 3000 km from the West to East and more than 1500 km from the North to the South and it is characterized by a diversity of natural conditions. In the Western Siberia the latitudinal and vertical zonality of soil and plant cover is more clearly pronounced. Soil-forming conditions, environmental situation and soil genesis have been studied rather completely where, to some degree, the changes of humus composition have been considered as a result of the prolonged soil use. The results of the above mentioned investigations have been described in some review monographs (Klenov, 1981, Dergacheva M.I., 1984). In this study analytical pyrolysis was performed using a 2020, Frontier Laboratories device and a GC/MS Agilent 6890 with an HP 5MS column. Oven temperature was held at 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 300 °C for 10 min using a rate of 20 °C min⁻¹. The gas used was helium with a flow of 1 ml min⁻¹.

Latitudinal gradient (North to South) is reflected by a classical sequence of soils and pyrolysis compounds from humic acid. The most striking feature of Podzol (Albeluvisol) soil (**a**) was the high yield of levoglucosan, suggesting preservation of carbohydrate-derived structures in Taiga soils. In Umbric Podzol (**b**) there was a well-defined methoxyphenol (lignin-derived) pattern but additional unspecific aromatics (alkylphenols and alkylbenzenes), N-compounds (pyridinone and lesser amounts of alkylpyrrols) and carbohydrate-derived products (furans). Compared to the former sample, this pattern suggest aromaticity in a medium where selective preservation of protein and carbohydrate is an efficient factor for soil carbon sequestration. In Gray Luvic Phaeozem (**c**) the N-compounds may represent major peaks in the pyrogram, whereas in Luvic Chernozem (**d**) large aromaticity and condensation (methoxyl-lacking aromatic fragments) is recognized, whereas furans and benzofurans point to condensation of aromatic and carbohydrate-derived units from herbaceous plants in a medium with substantial microbial reworking of lignin. In Southern chernozem (**e**) (Calci-Glossic Chernozem) the pyrolysis pattern included major peaks from S- and N-containing structures (mercaptoethanol and pyridine). Finally (**f**), in Cestnut soil (Haplic Calcisol,) the high aromaticity observed may probably result from the overlapping of humification processes leading to preservation of methoxyphenols in addition to condensed structures yielding alkylphenols and alkylbenzenes. The variety of pyrazoles, pyridines, pyridinones, and benzonitriles suggest stabilization of heterocyclic N forms and carbohydrate dehydration products and is compatible with thermal impact, as well as with conditions of contrasted temperature and moisture and a significant desiccation period.

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Lignin alteration patterns responsive for soil carbon sequestration mechanisms in undisturbed, reafforested and cultivated ecosystems (Almería, Spain)

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The Natural Park Sierra María-Los Vélez (Almería, Southeastern Spain) with a geologic substrate of limestones, marls and dolomies, is characterized by a Mediterranean-type climate, with strong continental features. The soil types are mainly Mollic-Petric Calcisols, Rendzic Leptosols, Hypocalcic Calcisols, Hypercalcic Calcisols, Luvic Calcisols and Petric Calcisols. The analysis of the soil humic acid fraction by spectroscopic and pyrolytic techniques (2020, Frontier Laboratories device and a GC/MS Agilent 6890 with an HP 5MS column; helium flow of 1 ml min⁻¹; oven temperature at 50 °C for 1 min, increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 300 °C for 10 min using a rate of 20 °C min⁻¹), suggested different structural features, interpreted as indicative of extreme situations in a gradient of humification mechanisms reflected in the quantitative balance of soil carbon sequestration.

From the qualitative viewpoint, a series of humic acids with featureless infrared spectra showed high optical density and polynuclear chromophors of fungal origin. The pyrolytic patterns showed major peaks for methoxyl-lacking aromatics (alkylbenzenes and alkylphenols) as well as poor yields of alkyl compounds indicative of efficient biodegradation of both microbial and plant-derived aliphatic constituents. This is interpreted as the consequence of biogeochemical mechanisms involving both microbial synthesis and condensation processes.

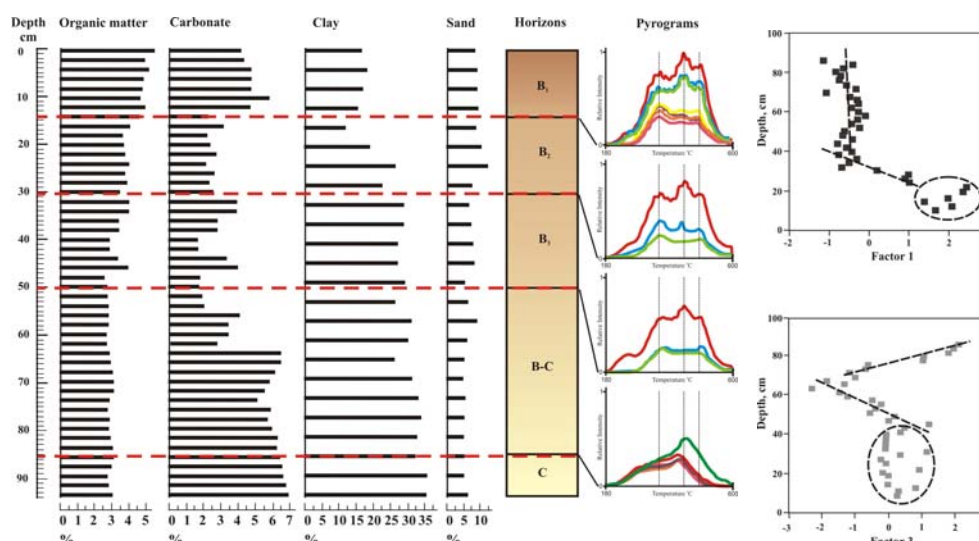
This pattern contrasts with that in soils with humic acids of marked aliphatic character and low molecular weight: intense 2920 cm⁻¹ infrared band, low optical density and high E₄₆₅/E₆₆₅ extinction ratio. The infrared spectra displayed typical lignin and amide bands, pointing to preservation of comparatively young organic matter. This is in agreement with the pyrolysis results, where conspicuous series of methoxyphenols (guaiacol, syringol and their methyl-, ethyl-, vinyl-, propenyl- and acetyl- derivatives) were the major peaks, in some cases accompanied by aromatic compounds of comparatively high molecular weight (e.g., biphenyls) and by well-defined alkyl homologues series (alkanes, α,ω -alkenedienes and fatty acids), indicating carbon sequestration mechanisms based on stabilization of plant biomacromolecules and aliphatic structures. In this latter group of samples, a systematic feature mainly of climatic pine forest is the release of polycyclic aromatic hydrocarbons mainly phenanthrenes and diterpene resin acids (e.g., dehydroabietic acid) suggesting incorporation of these conifer resin constituents to the soil humic acid. These polyaromatic compounds could represent additional biogeochemical proxies in the Natural Park under study, informing on the intensity of carbon stabilization mechanisms in ecosystems with comparatively low biogeochemical performance.

Characterization of a paleosol profile by Rock-Eval pyrolysis: new method in the paleosol pedological analysis

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Humification of biopolymers is determined by those environmental parameters (relief, climatic conditions), which define soil types too. The aim of our work was (i) to apply Rock-Eval (RE) pyrolysis for characterization of organic matter dynamics in a Quarter paleosol profile and (ii) reconstruction of the formation of the paleosol by statistical evaluation of classical (sedimentological, pedological, micromorphological) parameters and RE data. Previous studies used Gaussian curves for deconvolution of RE pyrograms [1, 2]. In this work we try to develop the method and to apply Lagrange curves for evolution of the major classes of soil organic matter with different thermal stability. We analyzed buried paleosol samples from an archeological site (NE Hungary), where the development of the soil was finished in the Neolithic Age.



We found, that the Rock-Eval pyrolysis is usable new method for determination paleosol type and supplements the routinish classical measurement methods. Pyrolysis of the known paleosol type provided new data in accordance with the classical data. Rock-Eval pyrolysis is capable for determination parameters, which help to define of unknown paleosol type and allow to identify minor occurrences within genetical horizons.

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Influence of Pyrolysis Temperature on Thermally Assisted Hydrolysis and Methylation of Neutral Sugars, Exuronic Acids and Plant Gums

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Plant gums are polysaccharides obtained from nature. At present they are used in a number of industrial applications and in the past they were largely employed as art materials thank to their solubility and swelling in water. These gums are well known adhesives and binding media for pictorial works, especially for cellulosic substrates.

Plant gum analysis requires preliminary polymer decomposition, a procedure that needs both time and material consumption. Moreover a large quantity of sample is necessary and this is often not consistent with the analysis requirements in the cultural heritage field.

In a preliminary work a thermally assisted hydrolysis and methylation method, in combination with analytical pyrolysis coupled to GC/MS, was developed and applied to the characterization of plant gums typically used as artworks. In the present contribution, in order to further improve the analytical method, the influence of the pyrolysis temperature on the analysis of sugar standards and gum arabic is studied. Tested pyrolysis temperatures vary from 300 to 700 °C, with steps of 100 °C.

The marker pyrolysis products considered in this study are permethylated aldonic acids [1] derived from neutral sugars and some permethylated aldaric acids, characteristic marker compounds of exuronic acids [2]. All these markers are easily identifiable through the fragment ion at 129 m/z, that appears in the mass spectra.

Data obtained from exuronic acids show that temperature affects the reaction yield, calculated as the peak area to sample weight ratio. The ratio decreases with increasing the pyrolysis temperature and partially rises again at 700°C.

For neutral sugars, in particular galactose, the pyrolysis temperature does not seem to affect the formation of permethylated aldonic acids. In addition, no differences were observed between the analysis of gum arabic at low and high pyrolysis temperature. It was not possible at any temperature to identify the uronic acid markers necessary for a precise characterization of the gum.

Therefore, it will be important to find and optimize other parameters that affect the thermally assisted hydrolysis and methylation yield of plant gum markers. This with the final aim to make exuronic acids detectable, as well as minor constituent sugars whose percentages are too low to allow their identification with the analytical methods currently in use.

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Pyrolytic characterisation of charcoal fractions sampled after slash burning

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Slash burning is practiced in many parts of the world. In particular, it is used as land preparation before cultivation in tropical regions. This practice produces charcoal, an aromatic organic matter compound, susceptible to remain in soil for long. Recently it has been shown that characteristic pyrolysis products can be obtained from fire affected material [1]. The objective of this study was to examine the degree of alteration of the molecular signature of charcoal fractions produced by slash burning in a tropical environment.

We studied charcoal sampled from a field and a forest site after slash burning. Particulate charred organic matter was hand picked randomly at six to seven different locations and separated in a fine fraction (FF < 2 cm) and a coarse fraction (CF > 2 cm). In addition, plant litter was sampled at the two sites. All material was subjected to Curie point pyrolysis coupled to gas chromatograph and mass spectrometry. The relative contributions of single molecules were obtained by integration of the total ion chromatogram.

The abundance of pyrolysis products released decreased in the charcoal fractions compared to plant litter sampled from the field and forest site. Lower amounts of pyrolysis products were detected in charcoal sampled from the field site compared to the forest site. Fire increased the amount of benzene and other aromatic compounds, such as phenanthrene and naphthalene. These aromatic hydrocarbons are typical fire markers. Other fire induced changes in the molecular composition included the reduction of the abundance of polysaccharide derived pyrolysis products, such as furfural and furanone. Guaiacol, syringol and other lignin-derived pyrolysis products were detectable in all samples except the fine fraction sampled from the field.

We suggest that the higher abundance of pyrolysis products derived from lignins and polysaccharides in charcoal sampled from the forest site suggest that the biomass was affected by less severe fire. This is consistent with field observations, which indicate that fire at the forest site occurs accidentally when slash on the field site is burned deliberately.

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Organic Matter Changes in Polderized Soils: Characterization by the Combined Use of Analytical Pyrolysis and ^{13}C NMR Spectroscopy

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The polderization of coastal areas has been a common practice along the Spanish coast. In this process, an estuarine area is reclaimed, drained and then used for farming, grazing or urban purposes, giving rise to important transformations on the affected soils.

The main aim of this work is to outline the potential of analytical pyrolysis and ^{13}C NMR spectroscopy to detect changes on soil organic matter (SOM) composition due to the polderization processes.

For this purpose surface sediment and soil samples (0-5 cm) were collected from the Urdaibai estuary (Bask Country, North Spain). Three different scenarios with different environmental characteristics were selected: i) a tidal channel (TC); ii) a salt marsh beside the channel, covered mainly by *Halimione portulacoides* (SM); iii) an adjacent polder, transformed to grassland (PA).

Analytical pyrolysis (Py-GC/MS) was performed using a double-shot pyrolyzer (Frontier Laboratories, model 2020) directly connected to a GC-MS system Agilent 6890. The detector consisted of an Agilent 5973 mass selective detector (EI at 70 eV). The GC-MS conditions were the same for all the experiments. The identification of individual compounds was achieved by single ion monitoring for different homologous series, low-resolution mass spectrometry and comparison with published and stored data (NIST and Wiley libraries).

In all the samples, pyrograms were dominated by series of alkanes/alkenes pairs and simple aromatic compounds derived from benzenes and phenols (figure not shown). However, significant differences among samples were also found. SM sample had the highest level of pyrolyzed material, which was in agreement with the elemental analysis results (it presented the highest organic carbon content). The presence of lignin derived compounds was observed in the SM and PA samples.

Pyrolytic results were compared to spectroscopic studies. VACP/MAS Solid-State ^{13}C -NMR spectroscopy analyses of demineralized samples were performed on a Bruker DSX 200 spectrometer, operating at a ^{13}C resonance frequency of 50.3 MHz. For quantification of the ^{13}C NMR spectra, the integration routine of the spectrometer was used to quantify the relative intensity of the following chemical shift regions defined previously by Knicker and Lüdemann (1995) [1]: 0-45 ppm (alkyl C); 45-60 ppm (N-alkyl/methoxyl C); 60-110 ppm (O-alkyl C); 110-160 ppm (aromatic/olefinic C); 160-185 ppm (carboxyl/amide C) and 185-245 ppm (ketone/aldehyde C). The ^{13}C NMR spectra confirmed most of the variations observed in the pyrolytic analysis, corroborating the abundance of aliphatic compounds in all the samples. Spectra of SM and PA samples were dominated by the 110-60 ppm signal, attributed to O-alkyl C compounds, mainly polysaccharides, while TC spectrum was dominated by an aromatic signal (160-110 ppm), which could be related to the existence of charred organic materials.

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Pyrolytic assessment of the recalcitrance of hydrothermal carbonization products from eucalypt sawdust as an index of its performance for atmospheric CO₂ sequestration

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The hydrothermal carbonization basically consists of a thermal treatment of biomass mixed with water, in a closed vessel at relatively low temperatures (< 250 °C). Under these conditions, the chemical structure of biomass is heavily transformed, via dehydration, condensation and aromatization processes. As a result, the obtained solid product (here denoted as hydrochar) exhibits higher percentages of carbon (C ~ 70%) in relation to the biomass (C ~ 50%) and abundant oxygen functional groups (typical O/C atomic ratio ~ 0.2–0.4) [1]. The carbon in the hydrochar product is believed to consisted mainly of aromatic ring structures [2]. Our hypothesis is that hydrothermal carbonization of biomass may constitute a way to transform the biodegradable biomass carbon into non-biodegradable carbon, thus representing an efficient way to sequester atmospheric CO₂.

For hydrothermal carbonization, eucalypt sawdust was dispersed in water (50 mL), stirred for 4 hours and autoclaved at 250 °C (38 bar) with stirring. The solid product (hydrochar) was dried at 120 °C for 4 hours. Following this scheme two hydrochar products were prepared under different conditions: a) SE-L sample (2 g of sawdust and 18 h of reaction time) and b) SE-C (8 g of sawdust and 2 h of reaction time). Pyrolysis was carried out at 500 °C in a Pyrojector (SGE instruments) connected to a GC/MS system with a Finnigan Trace DSQ mass spectrometer. The chromatograph had an HP-1 capillary column (30m × 250 µm), and the helium was adjusted to 1 ml min⁻¹. Oven temperature was 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 320 °C.

The pyrolysis data results from the untreated sawdust showed the expected patterns from lignocellulosic materials, with a large variety of peaks derived from carbohydrate and lignin, including the typical twelve methoxyphenols. The pyrolytic signature dramatically changed after hydrothermal carbonization, with no significant differences between samples SE-C and SE-L. The pyrograms from the hydrochars were dominated by dimethoxyphenol and trimethoxybenzene, as well as for minor peaks of furans and thiophenes. The new pattern is interpreted as due to demethoxylation and condensation of lignin, the transformation of native carbohydrate and the generation of a recalcitrant residue not readily amenable to analytical pyrolysis. The results were compared with those from natural black carbon samples collected from environments affected by wildfires or biomass combustion. The additional results confirm the high efficiency of the hydrothermal method, leading to a pyrolytic pattern similar to that from heavily carbonized materials, but with lower loss of weight and energy.

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The occurrence of unusual hopenes in hydropyrolysates generated from severely biodegraded oil seep asphaltenes

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Hydropyrolysis (pyrolysis assisted by high hydrogen gas pressures) is an emerging technique that possesses the unique ability to produce high yields of biomarkers from coals, petroleum source rocks and heavy oil fractions whilst minimising alteration to their isomeric [1]. In this study we show how hydropyrolysis can be used to generate reliable biomarker profiles from a West African oil seep which had been subjected to such severe biodegradation that it contained no recognisable biomarkers. Asphaltenes isolated from the seep oil were pyrolysed under slow heating conditions (250°C to 520°C at 8°C min.⁻¹), a hydrogen pressure of 15 Mpa in the presence of a sulphided molybdenum catalyst. The *m/z* 191 mass chromatogram of the product oil is presented in Fig. 1, and shows a full suite of hopenes including excellent preservation of the longer chained homologues. The higher abundance of C₂₉ αβ norhopane relative to the C₃₀ αβ hopane is typical of hydropyrolysis products, as is the absence of Ts, which as a rearrangement product should always be absent from the bound phase. Hydropyrolysis enables a more complete characterisation of this oil seep in terms of both its maturity and important source information, such as the occurrence of gammacerane, than would be possible with traditional pyrolysis techniques.

In addition to the expected suite of hopenes the hydropyrolysates also contained a number of abundant hopenes. Peak X on Fig. 1 was identified as 22,29,30-trisnorhop-17(21)-ene and is very common in hydropyrolysis oils. Peaks Y and Z are more unusual, and after fractionation by HPLC the hopene rich fractions were subjected to mild hydrogenation (PtO₂ and pentane at room temperature for 30 min.) and acid catalysed isomerisation (0.1M perchloric acid in glacial acetic acid at room temperature for 30 min.). The hydrogenation products and the very rapid isomerisation to hop-17(21)-ene together with the spectra and relative retention positions of these two compounds (Fig. 1) allowed them to be identified as: Y - C₃₀ 17α(H)-hop-20(21)-ene, and Z - C₃₀ 17β(H)-hop-20(21)-ene. Such compounds are very rare in nature although the 17α(H) compound has been previously reported by Bisseret and Rohmer (1993), and was obtained from the heating of hop-17(21)-ene in molten sulphur. Whether these compounds were original constituents of the bound asphaltene structure, and were simply released by hydropyrolysis, or generated from other hopenes during the hydropyrolysis procedure is not currently understood. However, occurrence appears to be related to the presence of sulphur, as demonstrated by the experiments of Bisseret and Rohmer (1993) [2].

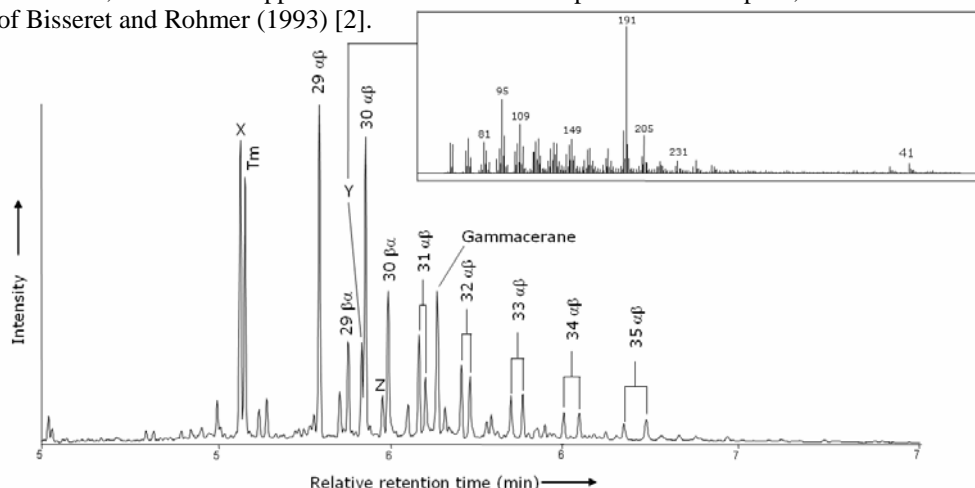


Figure 1. *m/z* 191 mass chromatogram of the aliphatic fraction of the asphaltene hydropyrolysate from a heavily biodegraded West African oil seep. The inset shows the spectra for peak Y, C₃₀ 17α(H)-hop-20(21)-ene.

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Application of analytical pyrolysis in monitoring the reliability of vermicomposting residual biomass from hemiparasitic epiphyte *Tillandsia recurvata* (San Luis Potosí, México)

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Different species of *Tillandsia* (Bromeliaceae) are well-adapted to wet, warm forest formations in South America countries and in most Mexican States. In San Luis Potosí it represents a natural resource for local communities (animal feed, bulking agent in packaging, manufacture of ropes or cushions). More recently, some emerging research is focusing on the assessment of the potential of the biomass from this species in compost production. In this preliminary research two important features for the economical feasibility and final quality of compost are analyzed by analytical pyrolysis, i.e. the performance of the whole process by conventional composting or vermicomposting with *Eisenia foetida* (red earthworm) and the assessment of the optimum composting time determined from samples periodically collected from piles transformed up to 7 months.

Pyrolysis was carried out at 500 °C in a Pyrojector (SGE instruments) connected to a GC/MS system Finnigan Trace GC Ultra with a Trace DSQ mass spectrometer. The chromatograph was provided with an HP-1 capillary column (30m × 250 µm), and the helium was adjusted to 1ml min⁻¹. The oven temperature was 50 °C for 1 min, then increased up to 100 °C at 30 °C min⁻¹, from 100 to 300 °C at 10 °C min⁻¹ and isothermal at 320 °C.

The pyrolysis results showed that: i) *Tillandsia recurvata* is suitable material for compost production, their pyrograms showing a systematic, well defined methoxyphenolic pattern with dominance of vinylguaiacol, guaiacol and lower amounts of syringols. The presence of vinylphenol and other phenols suggested HGS-type lignin which is observed to be relatively resistant to selective biodegradation both in piles composted with or without the earthworm, ii) a series of diagnostic humification (maturity) indices for this material consisted of ratios between carbohydrate-derived (mainly alkylfurfurals and cyclic ketones) and aromatic compounds, which decreased with compost maturity reflecting selective preservation and concentration of altered lignins, iii) the changes in alkyl compounds were not a source of maturity indicators suitable to monitor compost quality or its degree of transformation (minor pyrolysis compounds) whereas changes in the syringyl/guaiacyl ratio could be used for the assessment of the transformation extent of the lignin.

**SESSION 9 ANALYTICAL PYROLYSIS APPLICATIONS II:
*Art, Forensics and Natural Products***

Gas chromatographic and mass spectrometric characterisation of European provenance ambers

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The availability and unique physical properties of amber have made it one of the materials of choice since antiquity for the production of jewels, tools, ornaments and works of art. Amber belongs to the class of fossil resins formed by the evaporation of volatile components and polymerization reactions over geological timescale. In Europe, this kind of fossil resins are particularly present in the Baltic area and they are generally called Baltic ambers. Nevertheless, deposits of ambers of different geological eras can be found all over Europe: Italy, Spain, Germany and Romania.

This paper presents the most significant results of a systematic study aimed at the chemical characterization of ambers of different European provenance. Samples of succinite, simetite, zigburnite, glessite, gedanite and ambers from Italian Apennine have been selected for this research. The aim was to improve knowledge of these materials, and of their chemical characteristics and composition so that they may be effectively used as references in provenance studies both of geological and archaeological findings.

Because of the chemical complexity of these organic substances, an analytical approach based on the use of gas chromatographic and mass spectrometric techniques has been chosen. In particular, direct exposure-(electron ionization)mass spectrometry (DE-MS, a direct in-source Py-mass spectrometric technique), pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) using N,O-bis(trimethyl)silyltrifluoroacetamide (BSTFA) for the in-situ thermally assisted derivatisation of pyrolysis products and gas chromatography/mass spectrometry (GC/MS) have been used in this study. DE-MS analysis gives an excellent fingerprint of the sample as well as information on the main constituents present, while py-GC/MS and GC/MS give detailed compositional information at a molecular level on polymerised and on solvent soluble components, respectively. The use of this analytical approach on the same amber sample provided complementary information and enabled the chemical composition of ambers to be reliably studied.

Study on the Microbiodeterioration of Polyvinyl Resins used as Binding Media of Painting by Pyrolysis-Silylation-Gas Chromatography-Mass Spectrometry

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Evaluation of the alteration produced by microbiological attack on vinyl resin-based binders from canvas paintings has been carried out using Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC-MS). The proposed methods include the on-line derivatisation of vinyl resins using hexamethyldisilazane during pyrolysis. Specimens consisting of a vinyl medium have been used as reference materials. Analyses performed on a series of specimens on which different genus of bacteria and fungi were inoculated and lead to grow, indicate that no specific mechanism, commonly found in enzymatic attack of biodegraders, has been found in the studied polyvinyl resins. A decrease in the content of the main products of pyrolysis formed from the polyvinyl polymer specimens inoculated with fungi suggests that metabolic processes in these microorganisms are more significant than those from bacteria.

Py-GC/MS Analysis of Black Crust from Historic Buildings of San Francisco de Campeche and Seville Cities: a Comparative Study

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In this study, we analyzed the organic composition of black crust formed on the walls of two representative historic buildings in the cities of San Francisco de Campeche, México (Bastion of San Carlos) and Seville, Spain (The Cathedral).

For the analysis, a protocol based on analytical pyrolysis-simultaneous methylation coupled with gas chromatography/mass spectrometry (Py-GC/MS) was tested. The analysis of the samples indicates that the black crusts formed on the buildings are related with the particular conditions of each city.

The samples from the Cathedral of Seville presented the predominant presence of *n*-fatty acids, *n*-alkanes with a bimodal distribution, α,ω -dicarboxylic acids and benzenecarboxylic acids and their methoxy derivatives. Most of them are typically produced by automotive emissions in urban environments.

In the case of the Bastion of San Carlos, we found that the major compounds were *n*-alkanes, *n*-alkenes, *n*-fatty acids and *n*-alkenoic fatty acids. These compounds and their distribution can be related with biogenic sources like cell walls of microorganisms which are present forming characteristic colonies upon the walls of the Bastion. On the other hand, no compounds produced during fossil fuel combustion were identified in the samples.

The Nature of the Polar Fraction from Diesel Soot

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Analysis of urban and rural aerosols have demonstrated that besides the presence of inorganic salts, the particles can be fractionated into water-soluble and solvent-soluble organic compounds. Water-soluble organic species may represent between 20 and 50 % of the bulk organic aerosol mass. Decesari et al. (2000) [1] divided this fraction into three main classes of compounds: i) neutral species, ii) mono- and di-carboxylic acids, and iii) polycarboxylic acids. This last class of compounds was also related to macromolecular compounds recently evidenced in aerosol samples for which a similarity was suggested with naturally occurring humic substances. In this paper we show the analysis of a polar fraction extracted from diesel soot, a major contributor to aerosols in urban environments, involving methylation with TMAH and pyrolysis-gas chromatography-mass spectrometry.

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Characterization of microalgae species through TGA/FTIR analysis. Application to *nannochloropsis gaditana*

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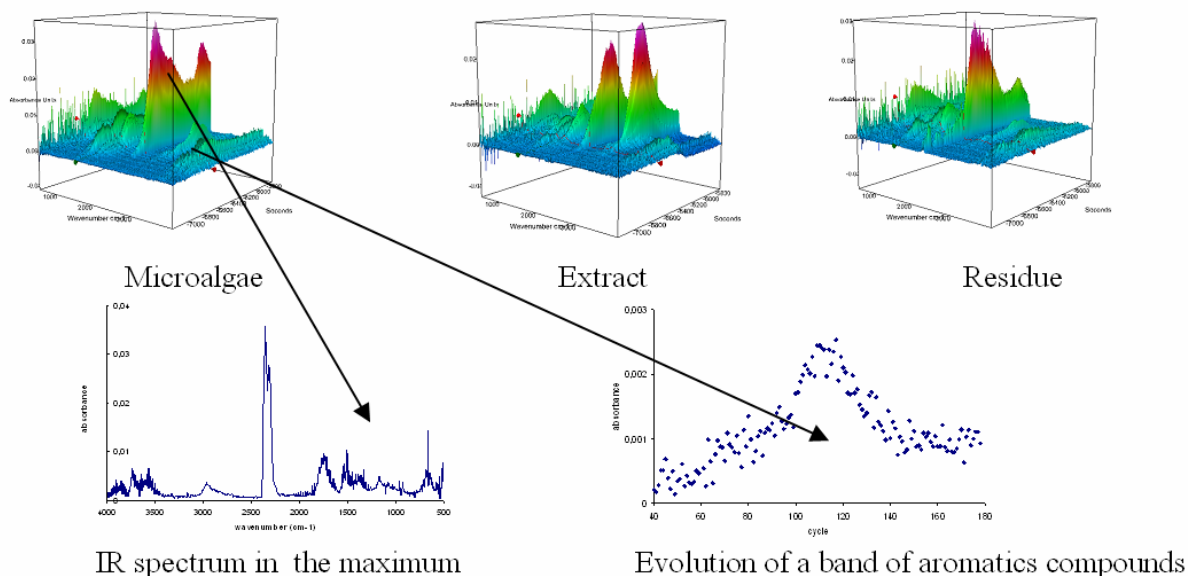
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The on-line combination of Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectrometry (FTIR) has been successfully applied for the study of the evolution with the time of the volatile products evolved in the thermal and catalytic pyrolysis of polymers [1, 2]. On the other hand, TGA has been applied from years for the chemical characterization of different materials, including microalgae species [3]. In this work, TGA/FTIR analysis has been applied in order to characterize the different decomposition steps observed in the thermal pyrolysis of *nannochloropsis gaditana*. In this way, the microalgae has been treated in order to separate the lipidic fraction, by breaking the cells and extracting the fraction soluble in hexane, and both fractions, i.e., the extract and the solid residue, have been also analyzed by TGA/FTIR.

Despite the complexity of the chemical composition of the microalgae, the results obtained permit us to carry out a characterization of the products evolved at each temperature, through the corresponding evolution of the IR absorption bands, which can be exploited in order to characterize the fraction decomposed in each degradation step. As an example, the following figure shows the comparison between the 3D diagrams corresponding to the microalgae and to the residue and extract fraction. From such diagrams, the IR spectra corresponding to each decomposition step can be extracted, and the evolution of the absorbance of several representative absorption bands can be studied.



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A Py/GC/MS characterisation of medieval inks

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A set of inks were analyzed using the Py/GC/MS technique. They were prepared following some ancient recipes and then analyzed after drying in air to obtain solid samples. A simple analytical procedure was adopted which excludes any treatment of the samples and consists of introducing the solid sample directly into the injector of the furnace pyrolyzer. Inks were also spread on Whatman filter paper and analysis of inks on paper were carried out. Comparing the pyrograms it was possible to distinguish fragments derived from ink, from the ones formed by the decomposition of paper by influence of ink on paper. In order to understand the origin of the fragments formed during the pyrolysis of inks we also analyzed the standard compounds used to prepare them. Two more fresh inks were prepared in the laboratory using general recipes. The pyrograms were compared to the other inks prepared about one year before in order to determine if some differences occur with time.

Py-GC/MS analysis of paints for domestic use

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The purpose of the present study is to investigate on composition of some paints and varnishes (PV) for domestic use by an integrated approach using IR, TGA and the PY-GC/MS techniques. Market of constructions, buildings, do-it-yourself PV for domestic applications is somewhat different from that of industrial coatings. On one hand producers are mostly small firms often with a poor theoretical background, on the other PV for private consumers are not subjected to strictly capitulation and quality controls. For these reasons components of these PV frequently are only roughly known. Forensic and environment can be two of the main issues of the present study. Residual fragments of PV left on the crime scenario are to be identified and compared in forensic investigation. Despite their huge diffusion, PV are considered dangerous preparations and increasing concern about environment prompts European Commission to issue specific legislation. Directive 2004/42/CE, related to the solvent content of certain paints and varnishes and vehicle refinishing products (respraying, repairs), aims to reduce emissions of volatile organic compounds across the Europe. The objective of Directive 2006/8/CE, as an implementation of 1999/45/CE, aims to identify and control dangerous finished product formulations and communicate their safety properties by prescribing specific classification and labelling measures for preparations.

Six white domestic-use paints, for architectural, decorative and automotive applications have been subjected to TGA, IR and PY-GC/MS in order to elucidate their composition and the nature of the polymer binder in particular. Derivatization with tetramethyl ammonium hydroxide has been performed on selected samples. Table 1 reports experimental results compared to the labelling information.

Table 1

Product	Label	This work
A	Acrylic waterborne enamel for wood, metals and plastics	Thermosetting acrylic based on MMA, BA, EHA and AA
B	Acrylic solventborne enamel for wood, metals and plastics	Long oil Alkyd based on pentaerithrite, phtalic anhydride and linseed oil
C	respraying paint for car repair	Nitrocellulose and Styrene modified alkyd
D	Artist paint oil	Drying oil based on linseed oil
E	Acrylic for painting on canvas	Vinyl latex based on VAc and VVersatate
F	respraying nitro paint for car repair	Thermoplastic acrylic based on MMA and BMA

The drying process of drying oils and alkyd can be monitored through specific markers such as nonanedioc acid

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Comprehensive Evolved Gas Analysis of Amorphous Precursors for S-doped Titania by in situ TG-FTIR and TG/DTA-MS. Precursor from Thiourea and Titanium(IV)-n-Butoxide

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Titanium dioxide with anatase structure is a promising photocatalyst for photodegradation of organic pollutants in water using UV light. Preparation of specifically doped or modified titania showing photocatalytic activities already under visible light is of great importance [1]. Recently, S-(sulfur)-doped titania were also reported to absorb visible light [2]. Among others, applying Ti(IV)-alkoxide and thiourea chemicals, one can produce solid precursors, which form after annealing in temperature range 400-700°C S-doped TiO₂ [2, 3]. Evolved gas analytical (EGA) monitoring of thermal annealing can help to reveal and understand the chemical mechanism of such pyrolytical doping process.

Decomposition of such an amorphous precursor for S-doped titania (TiO₂) nanopowder, prepared by controlled sol-gel hydrolysis-condensation of titanium(IV) tetrabutoxide and 5 % thiourea in aqueous butanol, has been studied up to 800°C in flowing air by simultaneous thermogravimetric and differential thermal analysis coupled online with quadrupole mass spectrometer (TG/DTA-MS) and FTIR spectrometric gas cell (TG-FTIR) for analysis of gases and their evolution dynamics (EGA) in order to explore and model thermal annealing processes of fabrication techniques aimed S:TiO₂ photocatalysts with photocatalytic activities under visible light.

The studied S-doped precursor's decomposition course remembers to that of non-doped xerogel from Ti(IV) tetrabutoxide, which seems to retard a considerable amount of organics in the solid phase even at high temperature, probably in polymeric forms, proven by evolution of CO₂ in several temperature regions of decomposition stages. The incorporation form of thiourea in the original xerogel seems to be chemically bounded, resulting lower decomposition temperature than that of pure thiourea, and producing evolution of carbonyl sulfide (COS) already between 120 and 190°C. Nevertheless, evolution of SO₂, and that of CO₂ is also observed above 500°C by both EGA detection methods. The latter observation implies that the black samples obtained even at 750°C are simultaneously S and C doped ones, hopefully still showing photocatalytic activities under visible light.

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Thermally Evolved Gases from *trans*-Diammine-bis(Nitrito) Complex of Pd(II) and Pt(II) Analyzed *in situ* by Coupled TG/DTA-MS and TG-FTIR

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Aqueous ammonia solutions of $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ and $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ are used, after impregnations and heat treatments between 150 and 350°C, for a successful sensitization of SnO_2 layers for CO gas [1]. In order to identify the active sensing chemical species of residues from the Pd or Pt solutions, a detailed study on thermal decomposition of solid $\text{trans-Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ (**1**) and $\text{trans-Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ (**2**), crystallized from the used solutions, has been carried out. Compound **1** and **2** has been characterized by their FTIR spectra and XRD profiles. Their composition and trans configuration have also been identified by reference IR spectra [2] and XRD reference patterns (PDF 00-45-598 and PDF 00-54-155) [3]. The crystal and molecular structure of $\text{trans-Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ (**1**) has been determined by single crystal X-ray diffraction ($R = 0.0515$). The obtained crystallographic data of the triclinic crystals of **1** (space group $P-1$, $a = 5.003(1)\text{\AA}$, $b = 5.419(1)\text{\AA}$, $c = 6.317(1)\text{\AA}$, $\alpha = 91.34(2)^\circ$, $\beta = 111.890(10)^\circ$, $\gamma = 100.380(10)^\circ$) has been found close to that was reported earlier. A better understanding of mechanism and dynamics of the gas evolution from these solid complexes **1** and **2** probably sensitive to shock seems to be essential during a scaling up of sensor fabrication.

The pyrolytic mild explosion-like processes of **1** and **2** has been followed by simultaneous thermogravimetric and differential thermal analysis (TG/DTA), while the evolved gaseous species has been traced by *on-line* coupled TG/DTA-MS and TG-FTIR instruments in He and air, whilst the solid residues (collected in a sealed Al sample holder with a pinhole) are checked by XRD and FTIR analysis. Reference spectra from a public gas-FTIR and -MS library of NIST have been applied for the identification and tracing the various species of gases and vapors evolved.

In He purge gas at around 250°C in an exothermic decomposition step, beyond N_2 and H_2O [6], NH_3 , N_2O and NO could be identified with MS for both compound **1** and **2**. In air purge gas, H_2O , NH_3 , N_2O and NO could also be observed for compound **1**, meanwhile only evolution of N_2O and NO for compound **2** by FTIR. All the solid residues are identified as metallic Pd and Pt for compound **1** and **2**, respectively.

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Prasinophytes with and without Tricyclic Terpenoids

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Tasmanites (green algae) are generally believed to represent a biological source of tricyclic terpenoids [1, 2]. However, extremely well preserved *Tasmanites* which have been recovered from sedimentary rocks of the Fetlika-1 borehole (SE Turkey), and which have suffered low-temperature conditions only, do not show any tricyclic terpenoids in pyrolysates.

In order to avoid any misinterpretations, we have exclusively used handpicked, taxonomical well assigned palynomorphs after separation from the sediments by standard palynological methods and cleaning with dichloromethane. Then samples were subjected to Curie point pyrolysis-gas chromatography-mass spectrometry (Curie temperature=650°C). Results are supplemented by comparisons to pyrograms of predominantly Silurian to Devonian aged prasinophytes from other locations, e.g. Rheinisches Schiefergebirge (Famennian, Germany), Chattanooga Shale (Upper Devonian, Virginia, USA) and Arbuckle Mts. (Upper Devonian, Oklahoma, USA) and to micro-scale FTIR analyses.

The pyrolysates from both *Tasmanites* (thick-walled prasinophyte) and *Leiosphaeridia* (thin-walled prasinophyte) from SE Turkey are dominated by a series of *n*-C₆₋₂₂ alkene/alkane doublets which are typical of pyrolysis products of algaenan, the microbiological resistant algal biopolymer [3]. Aromatic hydrocarbons such as alkylbenzenes and alkylphenanthrenes occur in minor concentration.

No traces of tricyclic terpenoids have been detected from the pyrolysates of *Tasmanites* from SE-Turkey, but interestingly, the pyrolysates of *Leiosphaeridia* from the same stratigraphic horizon do show the presence of monounsaturated and diunsaturated tricyclic terpenes as well as monoaromatic tricyclic terpanes. Thus, it is concluded that an inherent relationship between *Tasmanites* and tricyclic terpenoids may not always exist and that these biomarkers also have other source(s) (i.e., *Leiosphaeridia*). The occurrence of tricyclic terpenoids is not limited to areas of high *Tasmanites* content. Further studies may clarify if the association of prasinophytes to tricyclic compounds represents a question of evolution, site or taxa.

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Did the Organic-Walled Microfossil Chitinozoa Ever Have Chitin?

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Chitinozoans represent a group of flask-like organic-walled microfossils with uncertain biological affinity, occurring in Early Ordovician to Late Devonian marine sediments [1]. Established as an individual group of palynomorphs [2], for the first time the name Chitinozoa was assigned because these fossils looked like chitinous remains of animals. Chitin was never identified, however, although its detection has been tried by enzymatic approaches [3]. Hence, the chemical nature of Chitinozoa has never been elucidated.

Extraordinarily well-preserved chitinozoans like *Bursachitina*, *Calpichitina*, *Cingulochitina*, *Pterochitina*, *Ancyrochitina*, *Angochitina*, *Urnochitina*, cf. *Conochitina* have been recovered from sedimentary rocks (Upper Silurian) in the Fetlika-1 borehole, SE Turkey, where they have suffered low-temperature conditions only within a locally restricted time window.

Rocks collected from three stratigraphic horizons were processed using standard palynological methods. By handpicking, samples of pure chitinozoans were prepared (300 individuals equivalent to about 300 µg), cleaned by dichloromethane and analysed by Curie point pyrolysis-gas chromatography-mass spectrometry (Curie temperature = 650°C). In addition, some specimens of Chitinozoa were analysed by micro-FTIR.

Major pyrolysates from Chitinozoa include both aromatic hydrocarbons such as alkyl-benzenes, alkyl-naphthalenes, alkylphenols and alkylphenanthrenes and aliphatic hydrocarbons including a homologous series of *n*-alkene/*n*-alkane doublets. Micro-FTIR spectra of Chitinozoa are characterised by aliphatic CH_x absorptions at 3000-2800 and 1460-1450 cm⁻¹. The absorption at 1375 cm⁻¹ is assigned to deformational vibration of CH₃. A strong absorption signal attributed to aromatic C=C stretching vibration (1610-1560 cm⁻¹) is peaking at 1603 cm⁻¹. Prominent absorption signals at 900-700 cm⁻¹ (peaking at 869 cm⁻¹, 816 cm⁻¹ and 760 cm⁻¹) are due to aromatic CH out of plane deformation.

Both pyrolytic and spectroscopic investigations suggest that biomacromolecules of Chitinozoa consist of both aliphatic and aromatic compounds. Although extraordinarily well-preserved Chitinozoa from sediments of relatively low thermal maturity have been analysed, no pyrolysate products diagnostic of chitin or protein have been detected.

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Influence of temperature on the yield of compounds obtained in the flash pyrolysis of microalgae

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One of the most important applications of biomass is its conversion to bio-fuel by pyrolysis. The main advantages of using this bio-fuel are its renewability, better quality exhaust gas emissions, its biodegradability and its zero contribution to a net rise in the level of CO₂ in the atmosphere [1].

Fuels obtained in the pyrolysis of biomass are energy rich, easier to handle, store and transport and show lower sulphur and nitrogen content than fossil fuels [2].

Microalgae have a high photosynthetic efficiency and present a faster growth compared to lignocellulosic materials. Due to this, microalgae are considered a very interesting biomass to produce fuels.

In the present work, the influence of the process temperature on the compounds obtained in the pyrolysis of two different species of *Nannochloropsis Gaditana* has been evaluated. Four different temperatures in the range 300-800 °C have been studied, analyzing all products generated in each case. The experiments have been carried out in a laboratory scale fluidized bed reactor (71 cm x 5.2 cm) with nitrogen as fluidizing gas and sand as inert bed.

The results obtained showed that temperature has not a significant influence on the yield of gas and liquid compounds generated in the pyrolysis of the species evaluated, in the range 400-800°C. Obviously, the highest gas production is obtained at 800 °C, although this increase is lower than could be expected. Thus, in the range 400-800°C, the gas yield only increases from 13 to 23% and from 10 to 27%, depending on the species studied. Three groups of compounds can be specially remarked: carbon oxides (the major compounds generated), light hydrocarbons (C₁-C₄) and ketones, aldehydes and aromatics.

In the case of liquid fraction, in the range 400-800°C, there are not significant differences in the yield values (around 40%) with temperature and an increase from 40 to 50%, depending on the species analyzed was observed. The major condensable compounds detected are carboxylic acids, neophytadiene, indol and triacetoneamine.

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Py-GC-MS and TGA Characterisation of *Miscanthus* Genotypes: Key Biomass Markers and Reaction Kinetics

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Due to the rise in demand for renewable energy, dedicated biomass energy crops such as *Miscanthus* are becoming more widely cultivated across Europe. At present the majority of *Miscanthus* planted commercially is of the *Miscanthus x giganteus* hybrid genotype, however, other *Miscanthus* genotypes have been shown to provide improved biomass yields and feedstock characteristics in terms of thermochemical conversion [1]. Major barriers to breeding *Miscanthus* varieties with improved energy conversion traits include: A lack of knowledge regarding the composition of the cell wall and the range of variation between genotypes; the lack of a high-throughput screening tool which can identify the origins of compositional variation and provide information which may be directly applied to rapid breeding techniques such as marker assisted selection.

In this study, fifteen genotypes of *Miscanthus* initially planted in the UK under the European Miscanthus Improvement (EMI) project [2], were screened for Klason lignin, cellulose and hemicellulose content at two intervals within the growing season. The objective was to identify the extent of genetically derived variation in their cell wall composition. Five genotypes of *Miscanthus* which best accounted for the range of observed variation were selected for further analysis: *M. x giganteus*; *M. sacchariflorus*; *M. sacchariflorus x sinensis* hybrid; two *M. sinensis*. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was used to identify key cellulose and lignin markers. In addition to Py-GC-MS characterisation, thermo-gravimetric analysis (TGA) was used to examine feedstock properties (moisture, volatiles, char, ash, and fixed carbon content) and apparent first order reaction kinetics.

In total, 58 key cellulose and lignin markers were identified in *Miscanthus* genotypes and significant variation in the relative yields of thermal degradation products was observed between genotypes ($P=0.05$). *Miscanthus* lignin was found to be predominantly composed of *P*-Hydroxyphenyl units (3-5%TIC) and significant differences in the relative proportions of H and S units were also identified between genotypes ($<P=0.01$).

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Evaluation of Acidic Paper Deterioration in Library Materials by Pyrolysis-Gas Chromatography

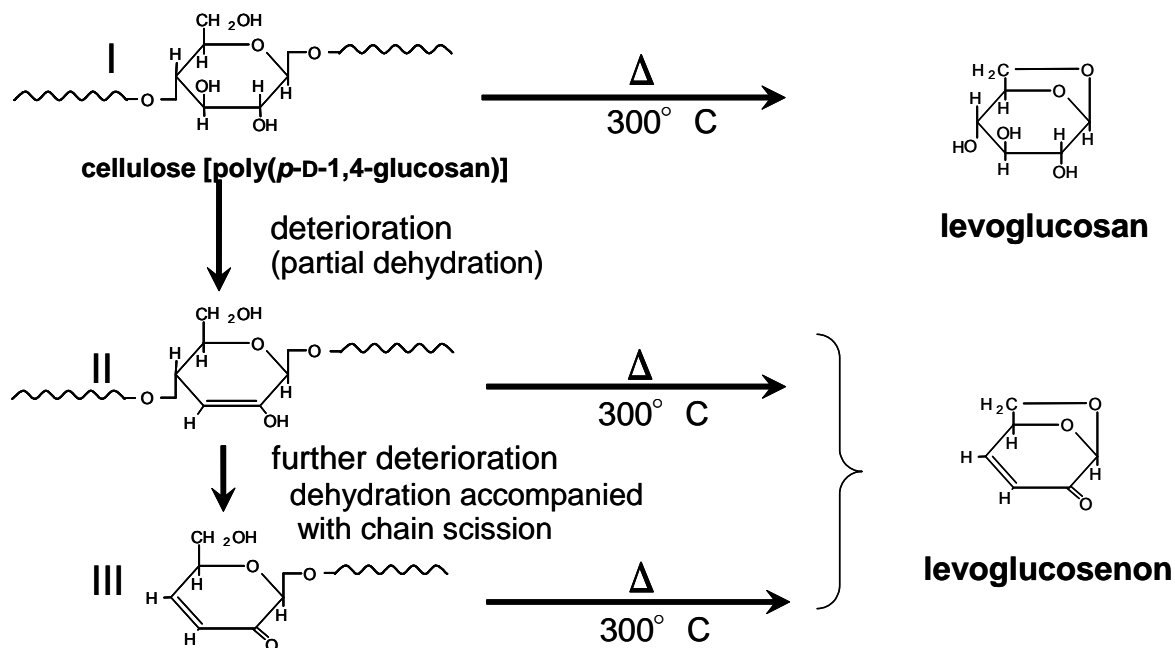
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It has been recognized worldwide as a severe problem that paper constructing old books and articles in library are gradually but inevitably deteriorated mainly due to the acidic nature of rosin-alum sizing agent. To preserve appropriately such degrading library materials, it is important to evaluate the degree of deterioration of the aged paper in the materials. In this work, pyrolysis-gas chromatography (Py-GC) was applied to the evaluation of the deteriorated paper in old books.

A tiny piece (ca. 0.25 mg) of severely deteriorated paper in an old book published in Mexico in 1932 was subjected to Py-GC measurement. The aged paper sample was rapidly and almost completely pyrolyzed even at 300°C where a normal paper sample was slowly and only partly decomposed. In the pyrograms of the deteriorated paper, levoglucosenone was characteristically observed, which was the dehydrated form of levoglucosan, typical pyrolysis product of cellulose. In addition, the relative yield of levoglucosenone was much higher for the paper sample taken at the heavily deteriorated marginal part than that in the center even for the same page of the old book. These results suggest that levoglucosenone can be used as a marker to evaluate the degree of the deterioration of the acidic paper. Moreover, the formation of levoglucosenone was attributed to the possible deterioration process of paper, in which dehydration reactions played important rolls accompanied by the chain scission of cellulose main chain as follows:



Determination of the Plasticizer Content in Poly (vynil acetate) Paint Media by Pyrolysis-Silylation-Gas Chromatography-Mass Spectrometry

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Polyvinyl acetate polymers (PVA), with the addition of plasticizers, achieve optimal mechanical properties, making them suitable as binding media for paints. The loss of these properties with ageing is often related to the slow migration and evaporation of these plasticizers, resulting in severe embrittlement and potential damage to the paint layer.

A new method is here proposed to quantify the plasticizer content of PVA samples with “on-line” silylation-pyrolysis using hexadimethyldisilazane (HMDS) as a derivatization agent in Py-GC-MS, using 1,4-dibromobenzene as an internal standard. For this purpose, a series of specimens of Mowilith 50 (a pure PVA resin) with the addition of two plasticizers, diethylphthalate (DEP) and dibutylphthalate (DBP), were prepared as thin films and submitted to a multi-step UV-light artificial ageing program. The plasticizer content was determined during the several ageing steps and the effects of the disappearance of these compounds on the mechanical properties of the resin films were determined by tensile strength tests.

Application of Pyrolysis-Gas Chromatography-Pattern Recognition to the Discrimination of the Chinese Traditional Medicine *Dendrobium*

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Dendrobium, known as 'ShiHu', is used in traditional Chinese medicine for antipyretic, eyes-benefiting and immunomodulatory effects. The chemical composition of *Dendrobium* which affects its clinical efficacy often varies to some extent depending on the species and the growing places. Therefore, it is needed to develop a method to discriminate the species and the origin of *Dendrobium*.

In this paper, pyrolysis-gas chromatography (Py-GC) was applied for construction and similarity analysis of Py-chromatographic fingerprint for *Dendrobium*. About 0.4 mg of crude drug powder was pyrolysed in a vertical microfurnace pyrolyzer at 450 °C, and the products were directly carried into a gas chromatograph equipped with a flame ionization detector (FID) and a capillary fused-silica column (30 m × 0.25 mm I.D.) coated with 50% diphenyl-50% dimethylpolysiloxane, (df 0.25 µm). The data for Py-GC fingerprint were analysed by pattern recognition using SPSS software. The results showed that *Dendrobium* samples could be classified into three categories: *Dendrobium candidum* Wall.ex Lindl., *Dendrobium devonianum* Paxt. and *Dendrobium crystallinum* Rchb. f. by means of the principal component analysis. Furthermore, discrimination of *Dendrobium candidum* Wall.ex Lindl. collected from the three different growing places was achieved by use of hierarchical cluster analysis.

Study of Ageing of Ketone Resins Used as Pictorial Varnishes by Pyrolysis-Silylation-Gas Chromatography-Mass Spectrometry

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This contribution presents a research aimed at the study of commercial products *Laropal K80*, *Keton N* and *MS2A* ascribed to ketone resins prepared as thin films, attempting to reproduce the pictorial layers and protective finishes, commonly present in contemporary paintings. For this purpose, a new method has been proposed based on the “on line” silylation-pyrolysis using hexamethyldisilazane as derivatisation reagent in pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS). This proposed procedure leads to the unambiguous identification of this type of binders and improves the conventional direct Py-GC-MS. Chemical changes due to the degradation effect of environmental agents have been specially considered. For this purpose, three different accelerated ageing processes were applied on a series of specimens prepared from the studied commercial products: thermal, UV light and ageing in SO₂ polluted chamber. Chemical changes due to UV light and thermal ageing are in good agreement with those previously reported in literature. Bleaching exhibited by the three commercial products after SO₂ saturated atmosphere exposition, and specially, MS2A resin has been related to the diffusion of SO₂-rich water vapour into the film. This stronger effect observed in this latter product is associated to the higher content in hydroxyl groups in this product.

INTERNATIONAL SYMPOSIA ON ANALYTICAL & APPLIED PYROLYSIS

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1	1965	Paris, France	G. Guiochon
2	1972	Paris, France	C.E.R. Jones
3	1976	Amsterdam, The Netherlands	J. Kistemaker
4	1979	Budapest, Hungary	T. Szekeley
5	1982	Vail, CO, USA	K.J. Voorhes
6	1984	Wiesbaden, Germany	I. Lüdewald & H.-R. Schulten
7	1986	Reading, UK	C. Gutteridge
8	1988	Lund, Sweden	I. Ericsson
9	1990	Noordwijkerhout, The Netherlands	J.J. Boon
10	1992	Hamburg, Germany	W. Kaminsky
11	1994	Nagoya, Japan	S. Tsuge
12	1996	Venice, Italy	G. Audisio
13	1998	Munich, Germany	A. Kettrup
14	2000	Seville, Spain	F.J. González-Vila
15	2002	Leoben, Austria	J. Fink
16	2004	Alicante, Spain	R. Font & A. Marcilla
17	2006	Budapest, Hungary	M. Blazsó
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