

ON THE IMPORTANCE OF RAW MATERIAL ASSESSMENT AND SELECTION FOR LOW COST EUCALYPT KRAFT PULP PRODUCTION

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ABSTRACT

Wood density and chemical composition (cellulose, hemicelluloses lignin and extractives) are important traits for commodity bleached kraft pulp production cost because they strongly affect specific wood (SWC) consumption and pulping yield. More recently, wood uronic acids content and lignin syringyl/guaiacyl ratio (S/G) have also become relevant and they are focused in this work. The two major costs in the production of bleached eucalyptus Kraft pulp derive from wood and chemicals, which can be minimized by increasing fiber line yield and decreasing bleaching chemical usage. An important alternative for increasing fiber line yield is the optimization of the kappa number at which cooking shall actually terminate before other means of delignification take over. The ideal kappa to terminate cooking is highly dependent on the wood type. It is our belief that cooking shall terminate at the point where pulp achieves maximum HexA/Lignin ratio, regardless of the kappa number. Hence, this study was aimed at determining the exact kappa number at which the HexA/Lignin ratio maximizes for three different eucalyptus woods (*E. globulus*, *E. urograndis* and *E. camaldulensis*) and how this affect pulp yield and bleachability. It was observed that maximum HexA/Lignin ratio occurs at kappa 14 for *Eucalyptus globulus* whereas this ratio maximizes at kappa 20 for *E. camaldulensis*. The maximum HexA/Lignin ratio at a given kappa also coincides with maximum pulp yield and bleachability. The kappa number where HexA/Lignin ratio maximizes depends upon wood lignin syringyl/guaiacyl ratio.

I. INTRODUCTION

Industrially, eucalyptus wood quality for kraft pulping is assessed by the following main traits: density and cellulose, hemicelluloses, lignin and extractive contents. These traits are relevant for commodity products because they strongly affect kraft pulp production costs by impacting specific wood consumption (SWC) and pulping yield. Wood uronic acids content and lignin syringyl/guaiacyl ratio (S/G) as well as other traits such as fiber morphology (coarseness, fiber population, microfibril angle, etc.), cellulose crystallinity, crystal structure, cellulose and xylan molecular weight distribution, non-process elements (minerals), acetyl group, and others have been recognized as important, but they have not been widely used for wood selection in most forest and pulp and paper companies. Altogether, the traits aforementioned affect not only pulp production costs but also its utilization since they impact pulp refinability, drainability and strength properties, which influence paper machine runnability and productivity [1].

The two major costs in the production of bleached eucalyptus Kraft pulp derive from wood and chemicals, with the first being more significant. Within the industrial domain, the most effective way of decreasing wood costs is by increasing overall fiber line yield and decreasing wastes in the wood preparation room. The decrease of chemical costs is more effectively done through optimization of the pulp bleaching operation where most of the unrecoverable chemicals are used.

Some studies have inferred that is always better to terminate the cook at a higher kappa number, within the limits of equipment runnability, and continue the delignification for example with an oxygen stage [2-4]. Recently, the extended impregnation technology has been developed to minimize the amount of rejects in high kappa pulping [5]. Of course, the ideal kappa to terminate cooking is highly dependent on the wood type [6]. For hardwoods, the approach of terminating the cook at the highest possible kappa number is likely not the right one because the defiberization point for such woods depends upon the syringyl/guaiacyl ratio of their lignins. Some studies have indicated that wood lignin S/G ratio may play a role in wood defiberization point during Kraft cooking [7, 8].

Instead of terminating the cook at the highest possible kappa number, this study proposes that the cook shall terminate at the point where the pulp achieves maximum HexA/Lignin ratio, regardless of the kappa number. Maximization of pulp HexA/Lignin ratio signifies maximization of hemicelluloses retention and as consequence maximization of yield. In spite of some controversies, it is mostly accepted that pulps containing maximum HexA/Lignin ratios at a given kappa number will present highest bleachabilities in ECF bleaching processes as well [9-12]. Therefore, this study aimed at determining the exact kappa number at which the HexA/Lignin ratio

maximizes for three different eucalyptus woods (*E. globulus*, *E. urograndis* and *E. camaldulensis*) and how this affect pulp yield and bleachability.

II. EXPERIMENTAL

Eucalyptus wood chips were prepared from 12 yr. old *E. globulus* and 7 yr. old *E. urograndis* and *E. camaldulensis*. The chips were cooked in an M&K digester to kappa number varying in the range from 10-26. Pulps of variable kappa number at fixed residual effective alkali of 6-7 g/L NaOH were prepared by varying process conditions, including three temperatures (160, 165 and 170°C), eight active alkali charges (12, 14, 16, 18, 20, 22, 24 and 26% as NaOH) and 8 times at temperature (30, 60, 90, 120, 150, 180, 210 and 240 min). The time to maximum temperature, liquor to wood ratio and sulphidity were kept constant and equal to 90 min, 4L/kg and 25%, respectively. Six pulp samples of each one of the three eucalypt species were bleached to ISO brightness 90% with the O-D_{HT}-(EPO)-D-P sequence. These samples were selected of the pool of different pulps on the basis of their kappa numbers (10-24 range) and residual effective alkali (6-7 g/L range). The alkali charge in the O-stage (10% consistency, 100 °C, 500 kPa, 75 min and 2.2% O₂) were varied in order to achieve 11-11.5 end pH. The charges of chlorine dioxide applied to the D_{HT} (10% consistency, pH 3, 90 °C, and 120 min) and D-stages (10% consistency, pH 5-5.5, 80 °C, and 120 min) were varied in order to achieve the target brightness for each one of the selected pulp samples. The ClO₂ charge in the D_{HT} stage was a function of incoming kappa number and established based on a fixed kappa factor of 0.14. Three different charges of ClO₂ were tested in the D₁ stage and the brightness values achieved with the three charges at the end of the bleaching (after the P-stage) were interpolated to 90% ISO brightness. The alkali charge in the (EPO)-stage (10% consistency, pH 10.5-11, 85°C, 120 min, 0.3% H₂O₂) and P-stage (10% consistency, pH 10.5-11, 80°C, 120 min, 0.3% H₂O₂) were varied to reach the end pH of 10-10.5. Wood and pulp analyses were performed as described elsewhere [11].

III. RESULTS AND DISCUSSION

Wood Chemical Characterization

Eucalyptus globulus and *Eucalyptus urograndis* presented much higher uronic acids content than *Eucalyptus camaldulensis* (Table 1). The total extractives and mineral contents were significantly higher for *E. camaldulensis* in relation to the other two species. A striking difference among the various eucalypts relates to the syringyl/guaiacyl ratio of their lignins, with *E. globulus* showing a much higher value than the other two eucalypt woods.

Table 1. Chemical composition of the three eucalypt wood species

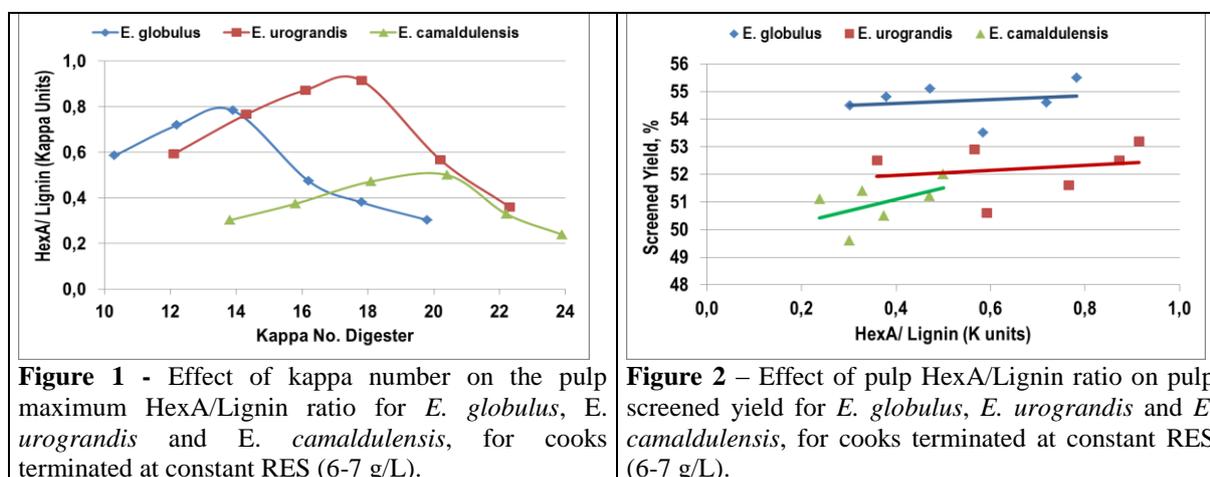
Chemical Trait	<i>E. globulus</i>	<i>E. urograndis</i>	<i>E. camaldulensis</i>
Acid insoluble lignin, %	20.6	25.3	26.7
Acid soluble lignin, %	4.5	3.4	3.1
Lignin S/G ratio	5.2	2.8	1.7
Glucans, %	46.9	46.5	46.8
Xylans, %	14.5	12.2	11.3
Mannans, %	1.6	1.1	0.9
Arabinans, %	0.3	0.2	0.3
Galactans, %	1.2	1.6	1.1
Total uronic acids, %	4.0	3.9	3.1
Acetyl groups, %	3.2	2.7	2.2
Total extractives, %	2.2	2.7	3.5
Ash, %	0.37	0.42	0.58

Maximizing the HexA/Lignin Ratio

Figure 1 shows that the maximum pulp HexA/Lignin is achieved at kappa numbers of approximately 14, 18 and 20 for *E. globulus*, *E. urograndis* and *E. camaldulensis*, respectively. It is apparent that the maximum HexA/Lignin ratio achievable in a given pulp is affected by the pulp degree of delignification. However, the exact kappa number at which the pulp HexA/Lignin ratio maximizes depends on the wood type. The reason for such behavior stems from differences in the cooking easiness of the various woods evaluated.

Maximizing Pulp Yield

The composition of the kappa number was proven very important to compare yield results. By splitting the kappa number into two fractions, hexenuronic acids and lignin, the important relationship HexA/Lignin was developed; this relationship allows for the comparison of yield and other pulping parameters at different kappa numbers as long as the residual effective alkali of the cooks are similar and only screened yield is taken into account. **Figure 2** show that maximum screened yield tend to occur at the maximum pulp HexA/Lignin ratios, regardless of wood species. The kappa numbers where maximum screened yields were attained for *E. globulus*, *E. urograndis* and *E. camaldulensis* were about 14, 18 and 20, respectively, and they coincided with the maximum HexA/Lignin ratios for these species. Increasing kappa number over these ranges resulted in increased rejects and decreased pulp xylan contents, which in turn penalized the screened yields. On the other hand, decreasing kappa number under this range resulted in decreased pulp xylan contents with negative consequences on yield. In principle, the kappa number where the ratio pulp HexA/Lignin maximizes for a given wood species should coincide with maximum pulping yield because of maximum xylan retention (**Figure 3**). The wood defiberization point is influenced by the wood density and chemical composition but the lignin syringyl/guaiacyl ratio (S/G) is likely the most important factor affecting this parameter. The higher the S/G ratio the lower is the kappa number at which wood will defiberize. Among the three wood species under investigation, the *E. globulus* showed the highest S/G (**Table 1**) and it defiberized at lower kappa numbers than the other three species.



Maximizing Pulp Bleachability

In this study bleachability was defined as the amount of kappa units removed per unit % of chlorine dioxide consumed across bleaching. **Figure 4** shows that pulp bleachability increases with increasing HexA/Lignin ratio. Hence, for minimum chlorine dioxide consumption the cook shall terminate at the kappa number where HexA/Lignin ratio maximizes. Of course, the value of this kappa number cannot be established as a set rule since different eucalypt woods produce maximum HexA/Lignin ratio at different kappa numbers. Thus, technically speaking there is no ideal kappa number for terminating the cook for eucalypt wood aiming at best pulp bleachability since it is species dependent.

IV. CONCLUSIONS

Maximization of pulp yield and bleachability is achieved at the pulp kappa number where pulp HexA/Lignin ratio maximizes. The HexA/Lignin ratio maximizes at different kappa numbers depending upon the eucalypt wood species. The kappa number where HexA/Lignin ratio maximizes is affected by the wood lignin syringyl/guaiacyl ratio (S/G).

V. ACKNOWLEDGEMENT

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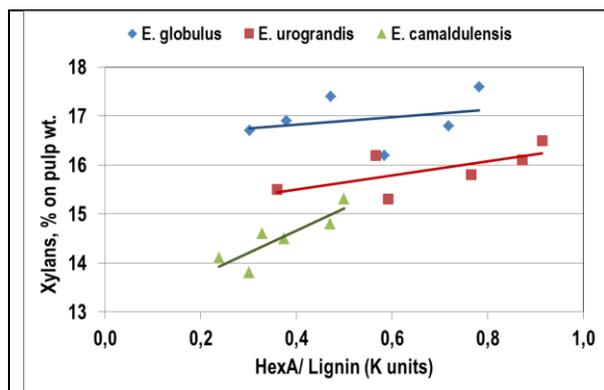


Figure 3. Effect of pulp HexA/Lignin ratio on pulp xylan content for *E. globulus*, *E. urograndis* and *E. camaldulensis*, for cooks terminated at constant RES (6-7 g/L).

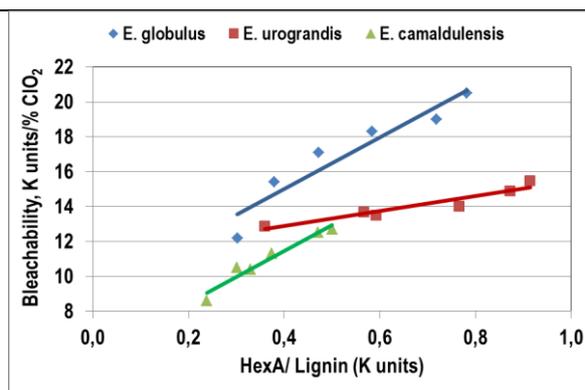


Figure 4. Effect of pulp HexA/Lignin ratio on the bleachability of *E. globulus*, *E. urograndis* and *E. camaldulensis* pulps to 90% ISO brightness (interpolated) with the O-D_{HT}-(EPO)-D-P sequence.

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PREDICTION OF REAL TIME KRAFT PULP YIELD: FROM SCIENCE TO PULP MILL TRIALS

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ABSTRACT

A new method was developed for the prediction of alkaline pulp yield. The full version of the equation allows predicting pulp yield from the cellulose content and the degree of polymerization of wood raw material used and the corresponding pulps. From the slope and intercept of this linear equation, the lignin-free pulp yield, Y_T' , of a pulp sample can be calculated when the cellulose content (G') and its degree of polymerization are determined by sugar analysis and viscosimetry, respectively. This equation was extensively tested and validated at laboratory/pilot scales for the effect of wood variability and process conditions on pulp yield. Then, industrial trials were successfully applied in two mills operating with different wood species (birch and softwoods) and process conditions (modified continuous and batch kraft cooking).

I. INTRODUCTION

As wood is the dominant cost factor for a pulp mill production, an increase in pulp yield has a major impact on its competitiveness. In order to optimize pulp yield, a pulp mill must be able to monitor the pulp yield accurately. Traditionally, the pulp yield is estimated based on wood usage and pulp sales data covering a period of 3-6 months. However, it is inconceivable to perform mill trials over long periods to compare pulp yield gains due to wood or process changes [1]. To overcome this difficulty, several indirect or direct methods for the prediction of the pulp yield have been proposed, but they are often based on empirical considerations and have to be adapted to different situations in a case-by-case approach [1,2,3,4].

Cellulose is a homopolymer subject to wellknown degradation kinetics during alkaline pulping. Therefore, the development of the cellulose mass fraction based on wood may be predicted theoretically. In an earlier work, a theoretical relationship between pulp yield and the cellulose mass fraction based on wood and the cellulose mass fraction of pulp was derived, validated for cotton, then tested for some wood species and process conditions [5,6]. The original form of the equation is the following [6]:

$$\frac{1}{Y_C} = \frac{1}{K_1} + \frac{1}{K_1} \frac{(\Delta DP)_S}{DP} \quad (1) \quad \text{where} \quad K_1 = \frac{[DP_0 + (\Delta DP)_S - (\Delta DP)_P]}{DP_0} Y_{C,W} \quad (2)$$

DP_0 = average degree of polymerization of cellulose chains in wood; DP = average degree of polymerization of cellulose chains in pulp; $(\Delta DP)_P$ = loss of degree of polymerization due to primary peeling; $(\Delta DP)_S$ = loss of degree of polymerization due to secondary peeling; $Y_{C,W}$ = cellulose mass fraction of the original wood and Y_C = cellulose mass fraction of pulp based on wood.

As DP_0 is more than one order of magnitude larger than $(\Delta DP)_S$ or $(\Delta DP)_P$, and because $(\Delta DP)_S$ and $(\Delta DP)_P$ are of the same order of magnitude and have an opposite sign in equation 1, one may simplify the equation by replacing K_1 in equation 1 by $Y_{C,W}$, resulting in a simplified pulp yield prediction equation which is obtained in the following form:

$$\frac{1}{Y_T' G'} = \frac{1}{Y_{C,W}} + \frac{(\Delta DP)_S}{Y_{C,W}} \cdot \frac{1}{DP} \quad (3)$$

This simplified equation, called henceforth PulpYield project equation, can be used to calculate the lignin-free pulp yield, Y_T' , of a pulp sample when G' (lignin-free cellulose content of the pulp) and the cellulose DP of the pulp [7] are determined by sugar analysis and viscosimetry respectively, and the values of $Y_{C,W}$ and $(\Delta DP)_S$ are determined by laboratory cooks or are known for the considered furnish.

II. EXPERIMENTAL

Laboratory cooking

Wood chips were received from pulp mills or produced from manually debarked logs then chipped with a pilot wood chipper. In most cases, the wood chips were air-dried, classified for fines and oversized chips removal and stored. Before cooking, the moisture content of the wood chips was carefully determined using a representative sample. A known weight of chips (usually 500 g o.d.) was cooked in a 3.5-liter rocking, oil-heated, multi batch digesters at a liquid to wood ratio of 4.0 l/kg. Alkali and sulfidity charges, cooking temperature plateau and H-factor values were dependent on the different cases. After cooking, the wood chips were disintegrated, washed and then screened. The total and screened yields were calculated based on the average dryness of the pulp, the total wet pulp weight, the dry weight of the rejects and the dry weight of the chips added to the cook.

Wood and pulp analyses

The intrinsic viscosity was measured according to ISO SCAN C15:62 standard using a RPV-1 automatic viscometer (Rheotek, England). The degree of polymerization of cellulose in the pulp was calculated according to the equation by da Silva Perez and van Heiningen [7]:

$$DP = \left(\frac{(1.65[\eta] - 116H)}{G} \right)^{1.111} \quad (4)$$

Chemical composition of wood and pulps were determined according to the standards and methods described in an earlier publication [6].

III. RESULTS AND DISCUSSION

Different pure wood species, both softwoods and hardwoods were cooked at different conditions, pure and in mixture. Some examples of the results applied to equation (3) are presented in **Table 1** commented in the subsections here below. R^2 , (Δ DPs), and $Y_{c,w}$ were obtained from the data plotted according to the equation (3), while $Y_{c,w}$ was measured from sugars analysis of the wood furnish.

Table 1 – Application of PulpYield project equation to different wood supply and process conditions

Wood species	Process conditions	R^2	(Δ DPs)	$Y_{c,w}$ (estimated)	$Y_{c,w}$ (measured)
Beech	Conventional Kraft	0.9203	1107	0.5119	0.5197
Birch	Conventional Kraft	0.9632	1039	0.5042	0.5111
Chestnut	Conventional Kraft	0.8375	229	0.4329	0.4107
Eucalyptus	Conventional Kraft	0.9262	471	0.4852	0.5124
Poplar	Conventional Kraft	0.9554	526	0.5057	0.5211
Chesnut/beech	Conventional Kraft	0.9588	614	0.4477	0.4652
Chestnut/beech	Conventional Kraft	0.9401	1000	0.4610	0.5161
Poplar/beech	Conventional Kraft	0.8919	748	0.5102	0.5204
Chestnut/beech/poplar	Conventional Kraft	0.9046	458	0.4525	0.4838
Eucalyptus clone A	Conventional Kraft	0.9541	782	0.5534	0.5452
Eucalyptus clones B/C	Conventional Kraft	0.9170	959	0.5860	0.6032
Birch	Kraft / AQ (0.1 %)	0.8970	1091	0.4807	0.5111
Eucalyptus	Kraft / AQ (0.1 %)	0.9926	455	0.4879	0.5124
Birch	Multi-stades	0.9702	1400	0.5013	0.5111
Eucalyptus	Multi-stades	0.9253	456	0.4940	0.5124

Effect of inter- and intra- wood species variability

Different pure wood species, both softwoods and hardwoods were cooked at different conditions. The graphical results of the results applied to equation (3) are presented in **Figure 1a** for different hardwoods to illustrate the inter-wood species variability. Results were also obtained for different softwoods, pure and in mixture (not shown here). Very good linearity was observed for all the wood species. Among hardwoods, a slightly weaker performance was observed for chestnut (R^2 around 0.84). The explanation for this particular behavior is the high content of extractives present in chestnut (sometimes up to 15 %) which disturbs the kraft cooking through an important consumption of alkali. Cooking of mixture of wood species both softwood or hardwoods was also performed. Although the results are not shown here due to lack of space, it was observed that mixtures of softwoods can be modeled as an average of the behavior of the individual wood species. For hardwoods, especially the mixtures containing chestnut, interactions occur during pulping of different wood species which

lead to overcooking or undercooking of one of the wood species and therefore affects the overall pulp yield. Therefore, the benefits of pulp yield gains due to one species (poplar for example) are lost due to overcooking. It is also clear that in these cases, chestnut is the wood species governing the behavior of the pulp yield. The intra-wood species effect was tested for eucalyptus clones (Figure 1b) and poplar clones (not shown). Three different clones were used for each wood species. For eucalyptus clones, it is clearly seen that clone A differs significantly from clones referred as B and C, which can be treated in a single straight line. These two clones presented similar cellulose content, much higher compared to clone A, which explains the behavior observed.

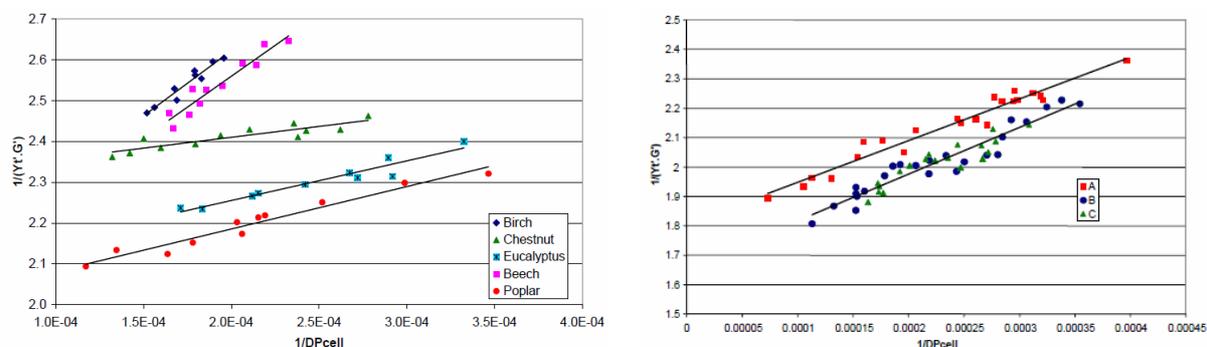


Figure 1 - Application of PulpYield project equation to: **a)** hardwoods (left) and **b)** eucalyptus clones (right).

Effect of process conditions

Different process conditions impacting the pulp yield such as the use of additives (anthraquinone, polysulfide and surfactants), the effect of scale-up (laboratory or pilot), conventional (1 stage) x modified (multi-stages) kraft cooking and the effect of uncooked chips were also studied.

The efforts were concentrated on AQ (0.1 %) as this was the only additive giving consistent and measurable pulp yield gains. Tests were carried out for 4 wood species: birch, eucalyptus, spruce, and pine. Only results obtained for hardwoods are presented here (Figure 2). For all wood species, the increase in pulp yield due to the action of AQ is detected by the equation in the form of a reduction in the ΔDP s. This is expected from the mechanism of anthraquinone protection and is observed for all the wood species. A significant impact is observed for birch as the slope is considerably reduced as well as the ΔDP s. However, the estimated $Y_{c,w}$ for AQ-containing cooks is always lower than those obtained for non-AQ and of the measured $Y_{c,w}$ values. AQ and high sulfidity black liquor prevent the primary peeling by stabilizing the original reducing groups in wood cellulose. This occurs at relatively low temperatures during the heat up phase. When secondary reducing groups are formed by alkaline hydrolysis at higher temperatures then the peeling reaction rate is so fast that AQ cannot stop it.

Modified multi-stage kraft cooking is claimed by the equipment suppliers to have a positive impact on pulp yield. In this part of the project, the pulp yield of conventional single stage kraft and a 3-stage kraft cooking (basis for EMCC or Lo-Solids cooking) was carried out for 4 wood species: birch, eucalyptus, spruce and pine. Results obtained for hardwoods are shown in Figure 2b. In the conventional cooking, the whole alkaline charge was applied at the beginning with a liquor/wood ratio equal to 4. The modified 3-stage cooking was performed with the same total alkaline/sulfidity charges, but in 3 stages. Black liquor was removed and replaced by fresh liquor at 1/3 and 2/3 of the targeted H-factor. Pulp yield increase was detected by equation (3) due to lower alkaline in modified cooking conditions as evidenced by higher DP and lower values of (ΔDP s).

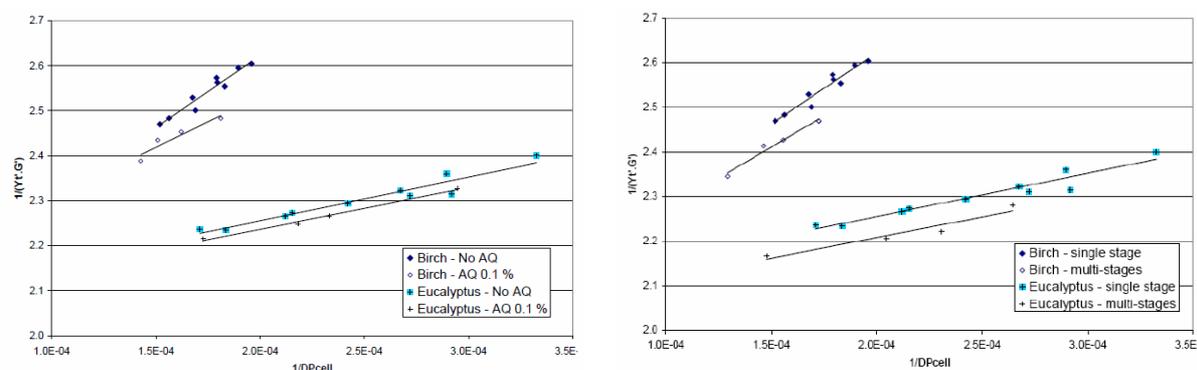


Figure 2 - Application of PulpYield project equation to: **a)** effect of AQ (left) and **b)** multi-stage cooking (right).

Industrial trials

After the work carried out in laboratory, the method for predicting pulp yield presented here was applied in two pulp mills (A = pulp mill operating a continuous modified Kraft cooking of birch and B = operating with softwoods, mainly pine, spruce and sawmill chips and batch cooking). Wood and pulps were sampled during a campaign of production and sent to FCBA laboratories, where they were analyzed individually. Wood samples were grouped into a single lot for birch and two for softwoods (SW1 = rich in spruce and SW2 = rich in pine), characterized and used for laboratory cooking in order to establish the PulpYield project equation parameters (**Figure 3a** for the mill A and **Figure 3b** for the mill B). Then, the acquired parameters were used to predict the yield of the industrial pulp samples based on their properties.

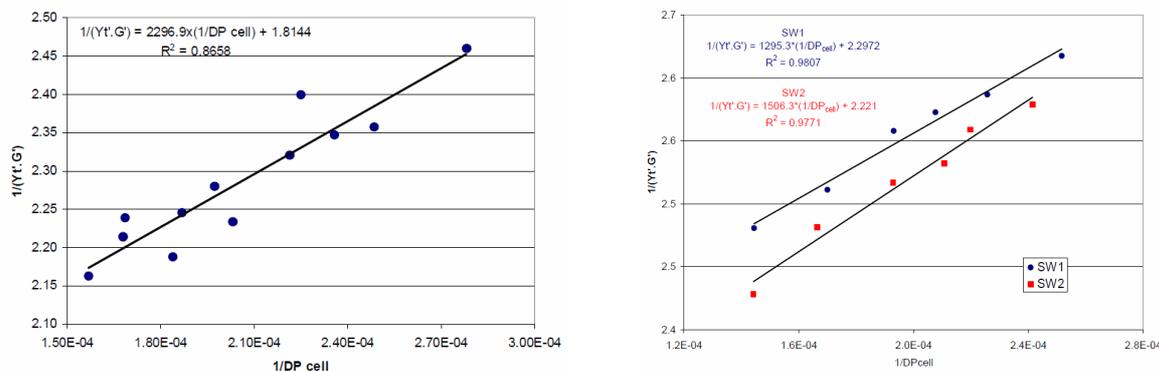


Figure 3 – Application of PulpYield project equation to mill A (birch) and mill B (softwoods).

Then, using the analytical data of the wood and pulps sampled in both mills and the parameters obtained from the equation 3 applied to the different situation, it was possible to predict their pulp yield of the industrial pulps. For the mill A operating with birch and continuous cooking, the average of pulp yield was 52.83 % with a standard deviation of 0.41 % for 8 samples taken along the 8-hour campaign trial. For the mill B, the average of pulp yield was 44.76 % for the spruce-rich wood supply with a standard deviation of 0.35 % for 3 samples obtained in the beginning, the middle and in the end of the batch digester. For the pine-rich pulps, the average value was 45.48 % with a standard deviation of 0.18 %.

IV. CONCLUSIONS

PulpYield project equation was successfully validated at both laboratory/pilot and industrial scales. The results of the project demonstrated that wood variability (both from inter- and intra-wood species) is a very important factor for pulp yield control. Most of the variability sources can be detected by PulpYield project equation but specific calibrations are needed. Process conditions are also important for pulp yield monitoring. Industrial trials were successfully applied in two mills operating with different wood species (birch and softwoods) and process conditions (modified continuous and batch kraft cooking). PulpYield project equation is nowadays ready for routine purposes and will be hopefully tested in other pulp mills in a near future.

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EFFECT OF RAW MATERIAL AND PULPING CONDITIONS ON THE PROPERTIES OF DISSOLVED KRAFT LIGNIN

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ABSTRACT

Composition, molecular weight and chemical structure of lignin affects its properties, reactivity and performance in various applications. It is thus of great importance to know how processes, in which lignin is dissolved from wood and other plants, affect the characteristics.

In the present study, we investigated the impact of raw material and cooking time on the structure of dissolved lignin. Kraft pulping was performed on wood chips of eucalyptus, pine and spruce. The black liquor was recovered after three different cooking times and the dissolved lignin was thoroughly characterized.

The results indicate that increased cooking time resulted in increased phenolic content and higher glass transition temperature of the dissolved lignin. The sulfur content was higher in the eucalyptus lignin compared to the softwood lignins.

I. INTRODUCTION

Lignin is a main chemical component of lignocellulosic materials, abundantly accessible and easily available. Various technical lignins are currently available in large quantities and viewed as low value by-products from the pulp and paper industry. However, structurally lignin possesses properties which make it a promising starting material for chemical modifications, leading to the preparation of valuable polymeric materials. Detailed characteristic of lignin samples coupled with information on the pulping conditions will help to adjust the pulping process not only with regards to pulp properties but also with respect to obtain lignin with desired characteristics.

Since the main object of the processes in which lignin is recovered is to obtain cellulosic fibres, few efforts have been made to alter process conditions in order to obtain lignin with more suitable characteristics. A number of studies have analyzed the structure of kraft lignin with regard to amount, functional groups, organically bound sulfur and molecular weight [1-3]. The objective of these studies was to get information of the delignification process. Other studies, more aimed at understanding the heating value of black liquor, mainly influenced by the lignin content, have also characterized kraft lignin to some extent [4-5]. As the interest in using lignin as a raw material for value added products has increased, many studies have been conducted to characterize different types of technical lignin [6-7]. These studies have looked into kraft lignin obtained after kraft cooks of different wood raw materials or in spent liquors after different pulping processes. However, there is still a lack of knowledge how pulping conditions influence the kraft lignin characteristics.

The aim of this study was to investigate the effect of raw material (eucalyptus, pine and spruce) and cooking time on the characteristics of dissolved lignin.

II. EXPERIMENTAL

Materials

Industrial wood chips of pine, spruce and eucalyptus wood chips were used in the study. They were dried to a dry solids content of 91-95%. The chips were sorted manually and a fraction of 2-8 mm thickness, without knots and bark, was used.

Kraft cooking

The kraft cooks were performed in steel autoclaves according to cooking parameters presented in **Table 1**. After terminating the cooks, the black liquor was separated from the chips. The black liquors were stored in a fridge until precipitation.

The dissolved lignin in the black liquors was precipitated by acidification according to [8]. The pH of the original black liquors was around 12 and before addition of sulphuric acid, the black liquors after the softwoods cooks were heated to 70°C and the eucalyptus black liquor to 60°C. Sulphuric acid was added during stirring

until a pH of 9 was reached. The beaker with precipitated lignin was cooled in an ice bath and then put into the fridge for 10-12 h. The lignin colloids deposited in the bottom of the beaker and the supernatant was filtered off. The lignin filter cake was then re-dispersed in distilled water and the pH lowered with sulphuric acid to pH 2 under rapid stirring. The lignin was filtered again and collected on a glass dish to dry in a ventilated oven at 65°C.

Table 1 - Pulping conditions

	NaSH [M]	NaOH [M]	Liquor-to-wood ratio, l/kg	Cooking temperature, °C	Cooking time, min
Pine	0,26	1,2	4	157°C	100, 200, 260
Spruce	0,26	1,2	4	157°C	100, 200, 260
Eucalyptus	0,26	1,0	4	157°C	30, 60, 100

Analysis

The phenolic content in lignin using an UV-vis method was determined according to a modified method proposed in [9] using a SHIMADZU UV – 2550 UV-vis spectrophotometer and fused quartz cuvettes.

Total solid content in black liquor was determined by placing 10 ml of each black liquor sample into an oven with a temperature of 105°C for 10-12 h. After gravimetrically determining the dry solids content, the ash content in the black liquor samples was subsequently determined by placing the samples for 6 h in an oven holding a temperature of 500°C. The ash content in precipitated samples was determined by drying 0,3 g of each precipitated lignin sample in the ash oven at 500°C for 6 h.

The chemical composition was determined using both acid hydrolysis in combination with Klason lignin, according to SCAN-CM 71:09, as well as by analytical pyrolysis, Py-GC/MS. The monosugars after acid hydrolysis were analyzed in a high-performance anion exchange chromatograph equipped with a pulsed amperometric detection (HPAEC-PAD) and CarboPac PA1 column (Dionex, Ca, USA). Analytical pyrolysis was performed on precipitated lignin samples at the Latvian State Institute of Wood Chemistry, Lignin Laboratory using a Frontier Lab (Japan) Micro Double-shot Pyrolyser Py-2020iD, with pyrolysis temperature of 500°C and a heating rate of 600°C/s. Directly coupled with the Shimadzu GC/MS-QP 2010 apparatus (Japan) with capillary column RTX-1701 (Restec, USA), 60 m × 0,25 mm × 0,25 µm film, with injection temperature of 250°C with EI of 70 eV, and MS scan range m/z 15-350 with gas helium at the flow rate of 1 ml/min and split ratio of 1:30. The sample size loaded was between 1,0-2,0 mg. The oven temperature program was 1 min isothermal at 60°C, then heating for 6°C/min to 270°C, and finally held at 270°C for 10 min. The identification of the peaks was performed on the basis of GC/MS chromatogram using Library MS NIST 147.LI13. The relative area of the peaks was calculated using the Shimadzu software and for some corrected or integrated manually where it was needed on the basis of the GC/MS data. The relevant peaks were averaged between the double samples.

Differential scanning chromatography (DSC) was performed in a Mettler Toledo DSC 1 STARe System. The samples were put into 40 µl aluminium standard cups and the sample weight noted. The samples were heated from 25°C to 150 °C at a rate of 10°C/min in nitrogen gas with a flow rate of 50 ml/min. The temperature stayed at 150°C for 3 min and then dynamically cooled to 25°C and reheated to 300°C. The glass transition temperature was recorded at the midpoint temperature of the heat capacity transition of the second heating run using the Mettler software. The results for each samples were reported as the average of two samples.

Elemental analysis was performed on all precipitated lignin samples at the Latvian State Institute of Wood Chemistry, Lignin Laboratory. About 30 mg homogenized sample is packed in tin foil, weighed and placed into carousel of the automatic sample feeder and analyzed with Elementar Analysen system GmbH, (Germany) Vario MACRO CHNS. Oxygen was calculated by subtracting the weight of N, C, H, and S from the total sample weight.

III. RESULTS AND DISCUSSION

The dissolved lignin in black liquors after kraft cooking of eucalyptus, pine and spruce was precipitated by acidification, filtered and dried before analysis, with the exception of phenolic content, which was determined spectrophotometrically. Filtration of precipitated lignin is quite troublesome, as the precipitate easily clogs the filter. An interesting observation is thus that lignin obtained after longer cooking was significantly easier to filter. For the kraft cooking of softwood, the amount of lignin dissolved into the pulping liquor increased up to 200 min of cooking time, **Figure 1A**, after which a decrease was observed. In the case of eucalyptus, although almost half of the lignin in the eucalyptus chips had been dissolved after 30 min of cooking time, **Figure 1B**, the

lignin particles apparently were too small and could not be recovered by filtration, **Figure 1A**. Surprisingly the eucalyptus lignin precipitate was much darker and distinctively green, whereas softwood lignin was light brown to yellowish in color.

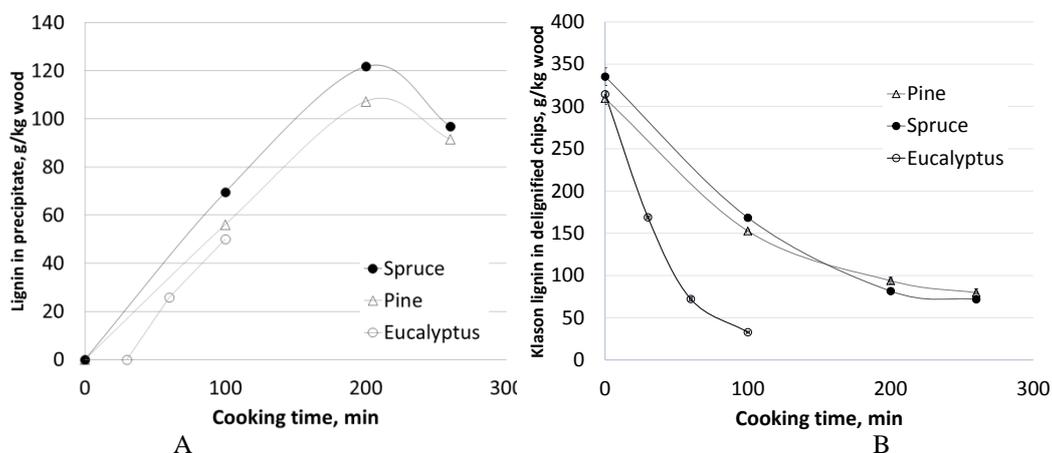


Figure 1. Amount of lignin in black liquor, A; and amount of lignin in chips, B, after different cooking times.

The chemical composition of the precipitates was determined both by acid hydrolysis, **Figure 2A**, and by analytical pyrolysis, Py-GC/MS, **Figure 2B**. There was a discrepancy between the results of the two methods. According to the acid hydrolysis, the precipitate from black liquor after cooking eucalyptus contained higher amount of lignin, whereas according to Py-GC/MS the lignin content was higher in the softwood precipitates.

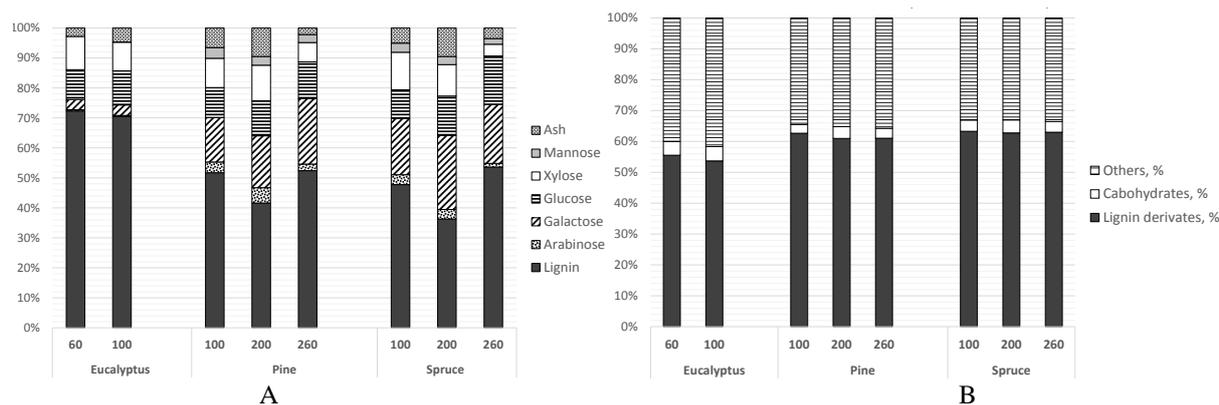


Figure 2. Chemical composition of samples precipitated from black liquor after kraft cooking of eucalyptus, pine and spruce determined by acid hydrolysis, A and by Py-GC/MS, B.

However, in the case of pyrolysis, the sulfur content of the precipitate ends up in the “Others” fraction, whereas in acid hydrolysis, the sulfur will precipitate with the lignin, as it to a large extent is bonded to lignin. As can be seen in **Figure 3**, the sulfur content was higher in the eucalyptus lignin compared to the softwood lignins, especially according to the Py-GC/MS results.

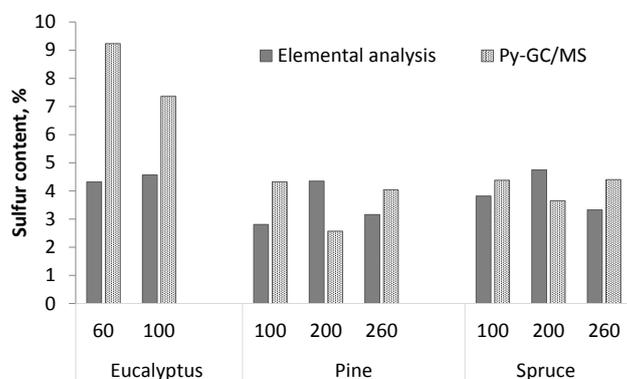


Figure 3. Sulphur content determined by elemental analysis and Py-GC/MS.

As can be expected, the lignin dissolved from eucalyptus was mainly composed of syringyl units, around 60%, whereas the softwood lignins almost entirely consisted of guaiacyl units. Cooking time didn't affect the ratio

between the different lignin units. The phenolic content in the lignin, however, increased with increased cooking time for all wood species as seen in **Figure 4a**. The glass transition temperature was highest for the softwood lignins obtained after the longest cooking time, **Figure 4b**.

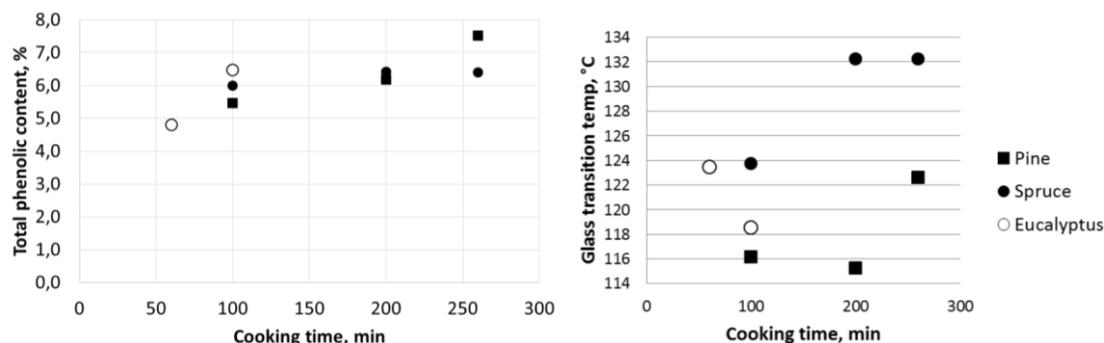


Figure 4. a) Total phenolic content and b) glass transition temperature of lignin.

IV. CONCLUSIONS

Increased cooking time during kraft pulping resulted in a more easily filterable lignin precipitate. The phenolic content of the dissolved lignin increased with cooking time. Eucalyptus lignin contained higher amount of sulfur compared to softwood lignin. The highest glass transition temperature, 132°C, was obtained for spruce lignin obtained after the longest cooking time.

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