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RHEOLOGY OF EUCALYPTUS AND PINE KRAFT BLACK LIQUOR

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ABSTRACT

Black liquor is a by-product of pulp mill and is the 5th most used fuel in the world. More than 1.3 billion tons of weak black liquor are processed each year and about 200 million tons of dry solids are burned in recovery boilers The objective of this work is to study the chemical, rheological, and behavioral differences between liquors produced from pine and eucalyptus wood, which directly influence transfer work, their use as fuel, and the production of cellulose pulp. The results show that the black liquor of eucalyptus has a higher concentration of lignin and a lower lignin molar mass than the pine liquor. This is because, in the pulping process, the weaker bonds of the lignin contained in eucalyptus wood mean that it has a much higher concentration and becomes more fragmented when it enters the liquor.

Keywords: Black Liquor. Cellulose. Eucalyptus. Pine. Rheology.

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INTRODUCTION

The Kraft process is the main chemical process, alkaline, to produce chemical pulps in the pulp industry. In this process, the cellulose fibers are dissociated from the lignin by chemical reactions. These reactions occur in a digester, a pressurized environment where wood chips or fibers are heated and cooked with the cooking liquor which is basically composed of NaOH (sodium hydroxide) and sodium sulfide (Na_2S), the latter added to the liquor to improve the dissociation of lignin from cellulose fibers, accelerating the wood cooking operation and increasing the mechanical resistance of pulp (Mäkelä et al. 2018). The products resulting from digester reactions are cellulose pulp and black liquor. In the chemical recovery process, there are three important points to observe. The first is the efficient production of electrical energy through the efficient generation of steam, which, in turn, is related to chemical recovery and pulping. The second point is the efficient use of black liquor, improving its calorific value. The sustainable destination of dissolved wood substances is the third point to note (Bajpai 2018).

In the Kraft recovery unit, the black liquor passes first through a set of multi-effect evaporators, where it is fed at 15% and generates about 70-82% solids that become a suitable fuel. Before entering the recovery boiler, this liquor is usually mixed with sodium sulfate to adjust the content of inorganic compounds in the liquor. The Kraft recovery boiler acts as a chemical reactor (producing Na_2S and Na_2CO_3), as a steam generator (using heat from organic material combustion to produce steam), and also as a waste incinerator. The molten inorganic salts produced (Na_2S and Na_2CO_3) melt flow (lower region of the boiler) into the dissolving tank, where they are mixed with the weak white liquor to generate the green liquor. This green liquor is clarified and causticized to recycle calcium carbonate and regenerate white liquor, which returns to the process (Vakkilainen 2018).

According to Tran and Vakkilainen, approximately 130 million tons of kraft pulp are produced per year, representing two thirds of the production of virgin cellulose and more than 90% of the world’s chemical pulp. Globally, more than 1.3 billion tons of weak black liquor are processed per year are processed; about 200 million tons per year of dry solids of black liquor are burned in recovery boilers. The makes black liquor the fifth used fuel in the world, alongside coal, oil, natural gas, and gasoline (Tran and Vakkilainnen 2012). In 2018, Brazil was responsible for approximately 12% of total global pulp production. About 96% of the fibers used are of arboreal origin, while the remaining 4% are bagasse, sisal, and bamboo. Brazilian short fiber cellulose comes from eucalyptus (representing 85% of

Brazilian production), while long fiber cellulose comes from pine (which represents 15% of national production and is concentrated in the southern region of the country). Another issue in evidence is the management of forest liabilities from eucalyptus and pine plantations, which must be consistent with environmental sustainability. Although the environmental issue is not the target of this work, it is important to mention this concern in industrial production (Souza and Gonçalves 2024).

Wood is basically an organic substance composed for the most part of carbon, hydrogen, and oxygen. Typical compositions can be found in the tab. 4. However, the grouping of these elements produces a very complex chemical structure consisting of at least 5000 substances (Bardak, Nemli, and Tiryaki 2017). The main chemical constituent of wood is organic polymeric, which are called structural substances: cellulose, hemicellulose, and lignin. The cellulose molecules are completely linear and impregnated in a matrix composed of hemicellulose and lignin. Hemicelluloses are composed of several sugars and acids interconnected by various types of chemical bonds that form branched and amorphous structures. Lignin is basically an aromatic polymer made up of a heterogeneous branched system with phenylpropane as the main repeating unit. In addition to these macromolecules, there are several other substances without structural function, among them the so-called wood extractives.

There are basically two main types of wood used in the manufacture of cellulose pulp by the Kraft process: hardwood and softwood. The main characteristic of hardwoods, for example eucalyptus, is that it produces short fiber cellulose pulp (0.7 to 1.5 mm in length) that is suitable for the production of printing papers or absorbents (Hsing, de Paula, and de Paula 2016; Martinez, Sermyagina, and Vakkilainen 2021; Nagar et al. n.d.). Softwoods such as conifer-type pine are suitable for producing high-strength papers, because cellulose pulp fibers are long, 2 to 6 mm in length. Lignins isolated from coniferous and hardwoods have very different basic structures (Sermyagina et al. 2021).

The objective of this work is to study the chemical and rheological differences between the liquors produced by pine and eucalyptus wood. Understanding these differences directly influences industrial processing, pulp transfer, and production operations.

REVIEW OF THE LITERATURE

The purpose of the wood pulping process is to break the bonds in the lignin structure to reduce its size to such an extent that the fragments can be dissolved and removed with the cooking liquor while maintaining minimal carbohydrate degradation. Of the wood components, only the lignin structures react with the sulfide, forming thiolignins, which are soluble in the cooking liquor.

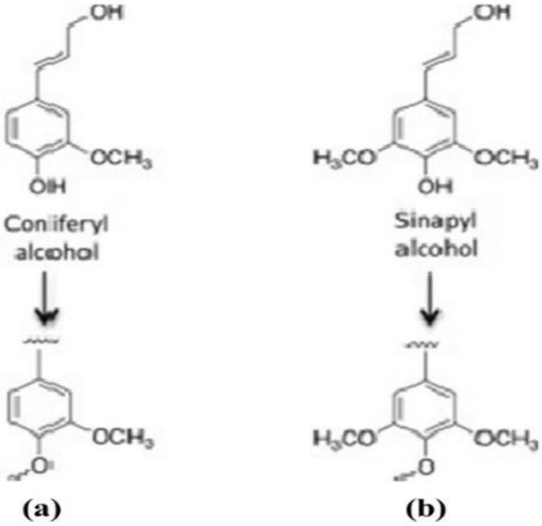
WOOD PULPING

The penetration of the cooking liquor in the wood structure occurs basically through two mechanisms: penetration of the reactants; and diffusion of ions (Na^+, S_2^-, HS^-, OH^-) into the cooking liquor inside the chips. One striking feature in the atomic structure of hardwoods is the presence of open vessels. The rapid growth of hardwood which often take place, is caused by these vessels which are responsible for the high circulation of sap. When processed in the pulp mills, the vessels in the chips enable the impregnation of the cooking liquor, facilitating the breakdown and the removal of the lignin. In coniferous woods, which do not have vessels, penetration occurs only through the diffusion process of ions.

The Kappa number represents the degree of pulp delignification through a test that measures the consumption of potassium permanganate per gram of cellulose. The Kappa number is a traditional way to check the quality of the pulp obtained at the end of the chip-cooking process (José et al. 2022).

In the chemical structure of coniferous lignin, the basic phenylpropane monomer has a methoxyl group in carbon C_3 (guaiacyl unit, G), while in hardwoods the predominant syringyl unit (S) has methoxyl groups in carbon C_3 and C_5. The syringil/guaiacyl (S) ratio significantly affects the degradation and solubilization of lignin of hardwoods. A recent study with eucalyptus woods showed that the increase in the S/G ratio favors delignification, allowing the use of lower alkali charge in Kraft pulping with a consequent increase in yield (Hinchee, Gabriela, and Bassa n.d.) (Fig. 1).

Fig. 1- Chemical structure of lignin, (a) guaiacyl and (b) syringyl.



Source: (Hinchee, Gabriela, and Bassa n.d.).

The extent of the impact of hydroxylation and methylation of p-coumaricotin acid on the lignin structure determines whether it will be guaiacyl- or guaiacyl-syringil-like type. The softwoods have a guaiacylas structure, having stronger connections than the hardwoods that have a guaiacyl-syringil structure with much weaker connections.

Some factors, such as the characteristics of wood, can influence the pulping of wood, affecting the Kappa number. Remember that the kappa number is an indirect method for determining the remaining lignin in cellulose pulps (Hinchee, Gabriela, and Bassa n.d.). It was observed that the high extractive content, in addition to the lack of open vessels in Pinus wood, requires a higher active alkali content to reach the desired Kappa, as it consumes alkali and prevents better delignification between the fibers. The authors also observed that the high content of lignin, in addition to the phenylpropane groups that make up pine wood compared to Eucalyptus, causes a higher chemical and thermal energy consumption for fiber individualization for a proposed Kappa (usually between 22 and 30).). Therefore, the pulping process of pine wood is quite different from eucalyptus wood (Kappa number, usually between 15 and 18). Generate liquors with very distinct characteristics (Hinchee, Gabriela, and Bassa n.d.).

In kraft pulping, lignin and extractives are separated from cellulose. Hemicelluloses follow celluloses to the extent possible and desirable. Unbleached cooked pulp contains 2 to 10 % lignin. After bleaching, the pulp typically has very little lignin left in the fiber. The overall yield obtained for fully bleached market pulps depends mainly on the type of wood and, especially, the content of lignin and hemicellulose. More of the glucomannan is retained than of glucuronoxylan. Due to their lower lignin content and different types of lignin, hardwoods can be cooked under milder conditions compared to softwood, thus also contributing to better selectivity and higher yield for hardwoods (De Jesus et al. 2019).

In general, BLs with high concentrations of lignin tend to have high viscosity because lignin can cluster into amorphous and voluminous molecules of high molar mass. On the contrary, BLs with a low lignin content exhibit a lower viscosity because lignin agglomerates in a compact and spherical molecular structure (Cardoso et al. 2009 [2]). From an alkalinity point of view, lignin becomes soluble above 12.5 pH due to ionized phenol groups. As alkalinity decreases (pH < 12.5), a shapeless and voluminous conformation of the lignin structure is observed due to its partial dissolution (Adams et al. 1997). From this, it is expected that softwood BLs will show a viscosity higher than that of hardwood BLs. However (Cardoso et al. 2009 [2]) reported average values of lignin concentration and molar mass for Brazilian EBL of 41.5 % and 1357, respectively; and for Scandinavian PBL of 39.0 % and 2728, respectively. Hardwood BLs generally contain less organics, tall oil and soap, and have a lower heating value (about 5 % lower) compared to softwood BLs (Tran and Vakkilainnen 2012). The Tab. 1 shows the general composition for *Pinus sp.* (softwood) and (hardwood) Birch BLs obtained from the Kraft process. This fact can change the connotation of the characteristics of liqueurs.

Tab. 1 - Typical composition (%) of the total dry matter of Pinus sp. (Softwood) and Birch (Hardwood) BLs from Kraft pulping

Constituent	Pinus sp. (Softwood)	Birch (Hardwood)
Lignin	43.2	31.8
Aliphatic carboxylic acids	30.7	35.2
Other Organics	3.0	5.3
Sodium Content	17.3	16.4

Source: (Reyes et al. 2020).

It follows that wood consumption as a ton of wood / ton of wood produced (dry yield) differs depending on the wood raw material, cellulose grade, and process conditions applied. Typical global yields for bleached Nordic softwood market pulp are in the range of 44 to 46%, birch around 47 to 49%, and for eucalyptus (eucalyptus globulus) 51 to 54%. The amount of black liquor generated depends mainly on the yield during cooking. Tab. 2 shows the typical amounts of black liquor generated using typical wood species and pulping conditions. The amount of wood used to produce a pulp differs, and especially the amount of black liquor produced differs greatly (Nuncira et al. 2024).

Tab. 2 - Example of differences in specific wood consumption and black liquor generation due to wood species and pulping conditions

Wood	Pulp	Wood Consumption/ Adt pulp (excl. wood / fiber loss)		Black liquor	Wood density	Bleached pulp yield estimation	EA charge, estimate
		BDt wood	m^3_{sub}	kgDS/Adt pulp	kg/m^3_{sub}	BDt base %	% in BDt wood
Scots pine	BSKP	2.1	5.0	1750	410	44	20
Norway spruce	BSKP	2.0	4.8	1700	410	46	20
Birch	BHKP	1.9	3.8	1580	500	48	18
E. globulus	BEKP	1.7	3.1	1365	550	53	18
E. urograndis	BEKP	1.9	3.6	1470	527	48	18

Source: own authorship (2024).

CHARACTERISTICS OF BLACK LIQUOR

The results show that the black liquor of eucalyptus from Brazilian plants has a higher concentration of lignin and a lower molar mass of lignin than the liquor of pine, whereas in general, pine wood is widely used in the northern hemisphere (Cardoso, de Oliveira, and Passos 2009). This is because, in the pulping process, the weaker bonds of the lignin contained in the eucalyptus wood mean that it has a much higher concentration and becomes more fragmented when it enters the liquor. This fact gives this liquor very specific rheological properties, giving it its own behavior in the evaporator and industrial recovery boiler, different from the behavior of black pine liquor (Cardoso, de Oliveira, and Passos 2009).

Differences between the chemical compositions between eucalyptus liquors from Brazil and pine liquors from countries in the northern hemisphere, and their molar masses, were reported in Tab. 3. The tab. shows the chemical composition of various liquors in relation to chemical structures and in relation to elemental composition (Cardoso, de Oliveira, and Passos 2009).

Tab. 3 - Molar mass of liquors of different origins

Liquor (type/material processed)	Mill location	O/I (-)	C_{lig} (%) (mass per mass dry solids)	MM_{lig} (Da)
Hardwood/Eucalyptus grandis[a]	Brazil/mill A (Kraft process)	1.81	42.3	820
Hardwood/E. grandis[a]	Brazil/mill B (Kraft process)	2.2	40.2	1641
Hardwood/E. grandis[a]	Brazil/mill C (Kraft process)	1.94	41.8	1401
Hardwood/E. grandis[a]	Brazil/Mill D (Kraft process)	2.1	42.3	1050

Hardwood/E. grandis[a]	Brazil/mill E (Kraft process)	1.86 ± 0.09	39.7 ± 2.2	1871 ± 221
Fibrous plant/Bambosa vulgaris[a]	Brazil/mill F (soda process)	2.30	45.3	3282
Softwood/Pinus Caribaea[b]	Scandinavia (Kraft process)	1.33	39.0	2728

Source: adapted from (Cardoso, de Oliveira, and Passos 2009).

The results of the elementary analysis for the black liquors of eucalyptus and bamboo are shown in Tab. 4.

Tab. 4 - Chemical composition of various wood species (% dry weight of wood)

Liquor (type of processed wood)	Mill location	Elementary composition (% mass per dry solid)							
		C	H	N	Na	K	S	Cl	Si
Hardwood/Eucalyptus grandis[a]	Brazil/mill A (Kraft process)	30.8	3.6	0.01	21.8	1.8	3.7	4.5	0.1
Hardwood/E. grandis[a]	Brazil/mill B (Kraft process)	35.2	3.7	–	21.2	2.1	3.0	4.3	–
Hardwood/E. grandis[a]	Brazil/mill C (Kraft process)	29.6	3.6	–	18.7	2.2	4.4	2.6	–
Hardwood/E. grandis[a]	Brazil/mill D (Kraft process)	34.8	3.4	0.04	18.3	2.1	3.6	3.2	–
Hardwood/E. grandis[a]	Brazil/mill E (Kraft process)	32.3 ± 0.3	3.1 ± 0.1	0.04 ± 0.01	23.5 ± 3.2	1.8 ± 0.3	4.9 ± 0.5	2.2 ± 0.3	–
Fibrous plant/Bambasa vulgaris[a]	Brazil/mill F (soda process)	35.4	3.6	0.30	19.3	3.3	0.2	1.3	3.8
Softwood/Pinus sylvestris and Pinus caribaea[b]	Scandinavia and North America (Kraft Process)	33.9 to 35.8	3.3 to 3.6	0.06 to 0.07	17.2 to 19.8	1.4 to 2.2	4.6 to 5.7	0.3 to 0.9	–
Hardwood[b]	Scandinavia (Kraft process)	33.2	3.3	0.08	20.8	2.6	5.2	0.3	–
Hardwood/Eucalyptus[b]	North America (Kraft process)	37.3	3.6	0.09	17.3	1.8	3.4	1.6	–
Fibrous plant/Straw[c]	South America (soda process)	39.1	4.5	1.0	8.8	4.1	0.8	3.5	0.23

Source: adapted from (Cardoso, de Oliveira, and Passos 2009).

The black liquor generated is a complex mixture of water, dissolved inorganic salts, and organic matter. Black liquor is considered a polymeric solution because polymeric lignin constitutes more than 50% of the organic components of black liquor (Zaman and Fricke 1995). The organic matter present in black liquor consists of fragments of alkaline lignin, polysaccharides, and resinous materials. It is also combustible organic material, as it is burned in a recovery boiler. The inorganic fraction of the liquor consists of dissolved salts containing sodium.

Almost everything that does not come out as pulp is added to the black liquor. The most typical way to treat side currents in kraft pulping is to add them to the black liquor. It is common practice to add side streams such as recycled bleaching effluent, chemical manufacturing by-products, electrostatic precipitator ash, and wastewater treatment sludge.

The rheological behavior of the liquor affects the heat transfer in the evaporation units, the pump capacity, and the liquor spray characteristics in the recovery boiler. Low viscosity can aid in spraying the liquor, forming very small drops, and consequently increasing the drag on the recovery boiler superheater region, causing clogging problems. High viscosity may lead to the formation of very large liquor droplets that are very heavy and may impair the furnace reduction efficiency (Karlsson 2020; Mccabe et al. n.d.; Moosavifar, Sedin, and Theliander 2006).

Generally, the factors that affect the viscosity of black liquor can be grouped into four main classes: temperature, solid concentration, shear rate, and chemical composition of the liquor. The complex rheological behavior of black liquor is in line with these properties and with the pulping process (Alabi 2010; Martinez et al. 2016). Black liquor will also be modified by, e.g. continuing cooking reactions. This is experienced in the over 70% dry solids liquor tanks and evaporator effects where significant NCG can be generated (Ek, Gellerstedt, and Henriksson 2009). If enough alkali is present, e.g. polysaccharide chain structure is broken and glycosic bonds start to break, resulting in peeling-type reaction. Removal of polysaccharides will decrease the viscosity of the black liquor (Pola et al. 2022).

AA striking feature in the atomic structure of hardwoods is the presence of open vessels. The rapid growth of hardwood,hardwood, which often takestakes place, is caused by these vessels which are responsible for the high circulation of sap. When processed inin pulp mills, the vessels in the chips enable the impregnation of the cooking liquor, facilitating the breakdown andand removal of the lignin.

The extent of the impact of the hydroxylation and methylation of p-coumaricotin acid on the lignin structure determines whether it will be of guaiacila or of guaiacila-syringilike type. The coniferous woods have a guaiacilas structure, having stronger connections than the hardwoods which have a guaiacila-syringila structure with much weaker connections. Determined the lignin syringyl/guaiacyl (S/G) ratio in wood and black liquor, according to the Tappi T222 om-97 standard procedure (Gomes et al. 2015).

This work verified that the deconstruction of wood from four eucalyptus clones with alkaline kraft processes at different levels of the kappa number. An increase in the S/G ratio indicates that S lignin units, which predominantly form _O-4 alkyl-aryl ether structures, are preferentially removed from the wood (eucalyptus - S / G ratio of 2.6 to 2.9) during pulping and are enriched in black liquors (S/G ratio of 6.0 to 6.2) (Gomes et al. 2015).

These differences in structure impact the properties of the liquor. As the Heating Value of lignin extracted from hardwood is 25.110 kJ/kg and lower than the Heating Value (26.900 kJ/kg) of lignin extracted from softwood, a similar behavior would be expected for the value of heating of short fiber and long fiber liquors. This suggests that the greater presence of these weaker connections gives the liquor very specific and unique rheological properties (Marcelo Cardoso, Laura Passos, and chave Lieor Negro Analise Elementar Lignina Eucalyp tus gran n.d.; Martinez et al. 2016).

At lower concentrations below 50% solids, the viscosity of black liquor is relatively low and behaves like Newtonian fluid; however, at higher solids concentrations above 60%, the viscosity increases significantly and exponentially with respect to solids concentration (Cardoso, Oliveira, and Passos 2006). On the other hand, the results show that at any fixed solid concentration, viscosity is a strong function of the temperature exponential decay, and this degree of exponential dependence on temperature increases proportionally with the concentration of solids.

EXPERIMENTAL METHODOLOGY

The experimental part of this work consists of the preliminary evaluation of two samples composed of an average of several batches of liquor samples, with the aim of presenting test results that elucidate the previous explanations. The strategy of using batches of samples in a single composition is a way of concatenating the sampling variation, making it more representative of the industrial process.

Black liquor samples collected from two different industrial units were used. The first produces bleached eucalyptus Kraft pulp for export and is located in southeastern Brazil and will be called BLE in this work. The second comes from a factory located in the south of the country, using a mixture of wood, eucalyptus, and pine. The samples were taken directly from the first effect of the evaporation system, corresponding to the concentrated liquor. The second sample has a composition of 50% pine and 50% eucalyptus and will be called BLEP in this work.

To characterize the black liquors, originating from the Kraft process, samples were taken from each industrial plant, from April to September 2019, and stored at 40 ° C. The methods used in the physical characterization of black liquor are shown in the Tab. 5. The concentration of solids (Css) is obtained using the oven drying method at controlled temperatures and the heating value (HV) is evaluated using the standard test om-90 of TAPPI - T684. Shear stress vs. shear rate was determined as a function of liquor temperature with controlled variation of the shear rate, at 45 ° C. The rotational test for complex rheology was performed as follows: Oscillation with a speed of 6.28 rad/s (constant) for 120s, followed by simple rotation with a constant torque of 2.3 x 10^5 (Nm for 120s, followed by oscillatory movement with a speed of 30.5 rad/s for a time of 400s (Mendoza Martinez et al. 2019).

Tab. 5 - Techniques used in the physical characterization of the mixture of eucalyptus, BLE, and eucalyptus-pine, Sample 2

Analysis	Parameters Measured	Technique and equipment used	References
Solids Content	Solids concentration (Css)	Dry a known mass of liquor in an oven at controlled temperature until mass constant - digital Metler balance AB204 (±10-4 g)	TAPPI test T650 om-89
Calorific Heating value	Heating Value (HV)	Heating of a complete oxidizing liquor in an adiabatic bomb calorimeter (Shimadzu model C-03)	TAPPI test T684 om-90
Viscosity	Liquor (mPas)	Viscosity measurements at different shear stresses and temperatures – Calibrated rotational Anton-Parr rheometer, MCR 502 model with 8mm parallel plates, adapters, control unit temperature	

Source: own authorship (2024).

RESULTS AND DISCUSSION

Solid concentrations (Css) and heating values (HV) for eucalyptus liquors (BLE) and eucalyptus-pine mixture (BLEP) are presented in Tab.5. It is important to note that the HV presented are kJ per kg of dry solids. The higher HV values found for the mixture were expected, since the lignin present in long fiber liquor has stronger bonds in its structure than those found in short fiber liquors. This corroborates literature data, since the lignin extracted from hardwood is 25110 kJ/kg and lower than the HV (26900 kJ/kg) of lignin extracted from softwood, The HV data in Tab. 6 are within the typical range of eucalyptus liquor and HV pine liquor, which is 13400 to 15500 kJ/kg. (Adams et al. 1997).

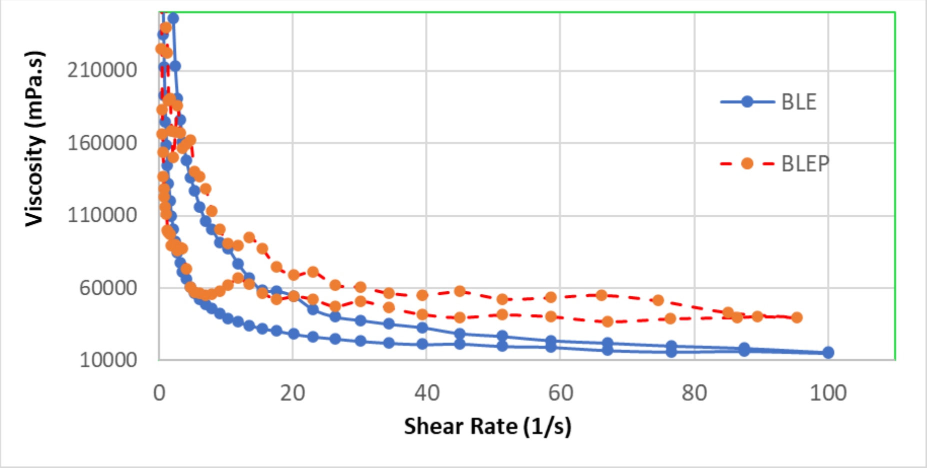
Tab. 6 - Mean heating value (HV) of black liquors from eucalyptus and eucalyptus-pine mixture from Brazilian mills

Samples	Solids Concentration – Css (%)	Heating Value (kJ/kg ss)
BLE	70.5 (±0.3)	14473 (±246)
BLEP	69.3 (±0.2)	15087 (±217)

Source: own authorship (2024).

Remember that BLE and BLEP differ mainly in chemical composition, since BLE is derived purely from eucalyptus, while BLEP has 50% wood of Pine origin in its composition. The pseudoplastic behavior can be observed in both samples, characterized by a reduction in viscosity with increasing shear rate, illustrated in Fig. 2.

Fig. 2: Viscosity of BLE (eucalyptus) and BLEP (mixture of 50% pine and 50% eucalyptus) at 45 ° C.

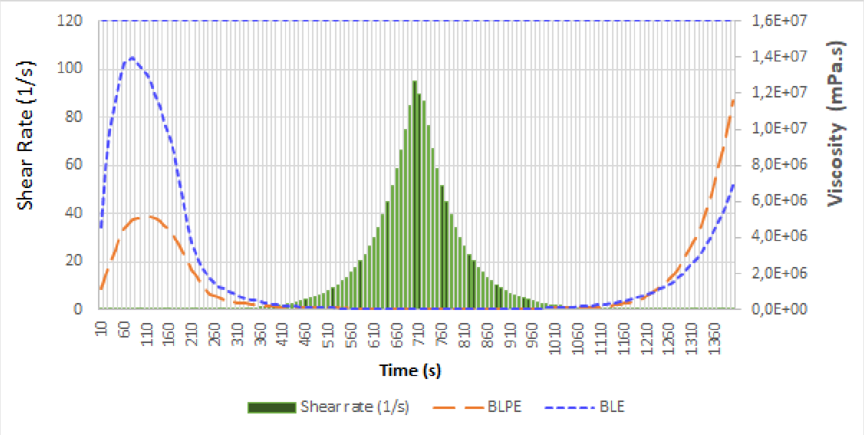


Source: own authorship (2024).

Hysteresis is one of the characteristics that may be present in samples with pseudoplastic behavior. The lower viscosity of BLE in relation to BLEP (shown in Fig. 2), primarily at high shear rates, can be attributed to the chemical composition of the sample, since liquors from Pinus have higher viscosity than liquors from Eucalyptus. The effect on the shear rate on the samples can be observed by attribution of the orientation or alignment of the particles in the flow direction. As the shear rate increases over time, the viscosity increases the organization of sample particles in the direction of flow by the shear effect, to a certain extent, changing the physical structure of the sample.

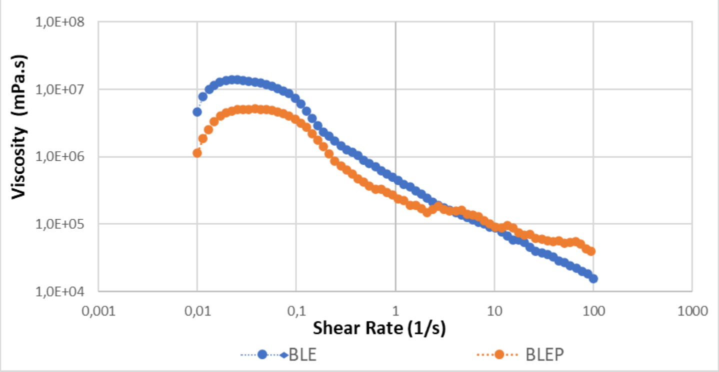
Eucalyptus liquors have smaller molecules than pine liquors (Brodin, Sjöholm, and Gellerstedt 2009). They also exhibit a greater orientation and a greater reduction in their viscosity. Pseudoplasticity is also evidenced by a three-dimensional structure characteristic of a behavior (referred to as Gel), which is supported by ionic bonds and hydrogen bonds and is responsible for the increase in viscosity in pseudoplastic fluids (Nuncira et al. 2024; Sahade De Souza, Luporini, and Rigoli n.d.). The effect of hysteresis observed in Figures 2 appears when the Gel structure and particle orientation break. When at rest, the pseudoplastic samples can return to their original structures forming a Sol state, recovering their fluidity. The Sol and Gel structures, under favorable thermodynamic conditions, are reversible. When this occurs, a phenomenon called thixotropy can result, which is characterized by a reduction in viscosity over time. Figure 3 shows a reduction in viscosity with a change in the shear rate over time. The two-axis graph shows that at low shear, the viscosity is higher than at higher rates. This suggests a change in Sol and Gel structure, reversible as a function of the shear rate (highlighted in the center of a time variation from 410 to 960 s). As the rate increases, the orientation of the particles also increases, thereby producing this effect, followed by the accommodation of the particles while the consequent increase in viscosity occurs at a lower shear rate. In this case, a change in the liquor viscosity scale can be observed. For lower shear rates, the viscosity of eucalyptus liquor is higher due to the higher solid content. The shear rate was gradually increased over time, and the liquor molecules correspondingly reorganized. Pine liquor, whose molecules are stronger and have larger bonds, suffered a smaller reduction in viscosity compared to eucalyptus liquor. This illustrates the differences between the two liquors in relation to the structures and sizes of the lignin molecules and the resulting effects. These characteristics can be seen in the graphs of Figs. 3 and 4.

Fig. 3 - Reduction in viscosity with a change in shear rate over time



Source: own authorship (2024).

Fig. 4: Variation of the viscosity of BLE and BLEP with the log scale shear rate



Source: own authorship (2024).

In some cases, the shear rate viscosity curve appears to be one of viscosity increases at low rates, which is beyond common sense. This unusual fact may occur in some dense systems, where shear thickening shares first-order transition analogies, arising from a nonmonotonic equation of state. This curvature, similar to an inverted 'S', was reported in the work of Wyart and Cates (Gonçalves et al. 2024; Mari et al. 2015). The attribute of the existence of two states, one with friction and the other without friction, restricted to mechanical and hydrodynamic considerations and not thermodynamic considerations. Although this variation occurs more frequently in micellar systems with a low volume fraction, in black liquor we also observe this fact at low shear rates. In some granular flows, a nonmonotonic relationship similar to a phase transition also appears. This issue in some polymeric systems includes this transition with the origin and dynamics of elasto-inertial instabilities. Although this work will not discuss these nuances in depth, it is worth highlighting this fact as a motivator for new studies on these occurrences. We recommend reading the literature cited for this question (Castillo Sánchez et al. 2022).

Another point of attention, reports on Walther's empirical equation from 1931 modified and standardized by ASTM D341- 2009 and described according to equation 1, which is also widely used in petroleum engineering and derivatives (Moosavifar, Sedin, and Theliander 2006; Stratiev et al. 2023). According to Farah, viscosity varies with the size of the molecule expressed by the number of carbon atoms or molar mass, the boiling temperature, and not with the nature of the oil fractions. The higher these parameters, the greater the influence on the absolute and kinematic viscosities. Although liquors are not petroleum-derived products, but considering that liquors are also used as fuels, with their complex organic composition, and that fuels are also evaluated in mass balance during burning, the empirical evaluation using the Walther equation is an attempt to verify the effects of molecule size and number of carbon atoms in liquors (Moosavifar et al. 2006; Stratiev et al. 2023).

$$\log\log z = A + B \log T \quad (1)$$

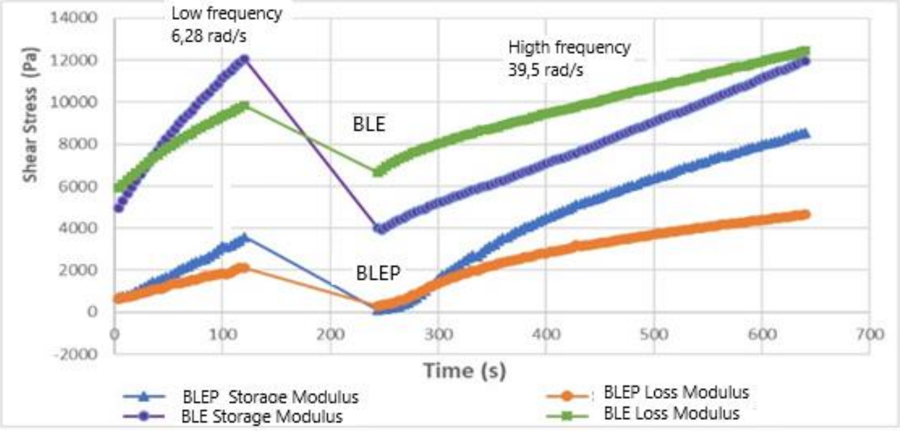
The factors "A" and "B" are derived from measuring the viscosity of the product (z factor) at two different temperatures (T kelvin). These parameters are characteristic of each particular sample.

Parameter A in the equation represents the variation in viscosity with the number of carbon atoms and the size of the molecule. Parameter B indicates the sensitivity of viscosity to temperature, the lower the value, the smaller the viscosity variation (Moosavifar, Sedin, and Theliander 2006; Stratiev et al. 2023).

Comparing the values of factor A and B, from the measurement of viscosity at two temperatures, reveals a value about 45% higher in BLEP than in BLE. This fact corroborates two ideas derived from this work. The first in relation to factor A is that the size of the molecules and the quantity of carbon atoms in BLEP is greater than that of BLE. Calculating the value of factor A, this factor does not reveal the proportion between the molecules, but it gives us an idea of the dimension of the size of the molecules in the chemical composition when compared, since they are similar, which suggests the higher viscosity of BLEP compared to BLE, this also corroborates the molar mass data presented in Tab.2.

The second idea, based on parameter B, corroborates the influence of temperature on viscosity, which also suggests that the higher the temperature, the greater the influence on BLEP, in relation to BLE. The graph in Figure 5 was projected with oscillatory tests performed at speeds of 6.28 rad/s and 39.5 rad/s, with 50 mm cone plate geometry at a constant temperature of 45 ° C. The complex rheological response for BLEP has a higher viscous response than the high-frequency elastic response (39.5 rad/s). This also corroborates the greater influence of parameter B of the Walther/ASTM equation. A small inversion of response occurs at low frequencies and low torque, as shown in Fig. 5. The BLE behaves in an inverse way, where the elastic response predominates at both low and high frequencies. These behaviors are related to the intrinsic nature of the samples and the Sol and Gel conformations they present.

Fig. 5: Complex rotational viscosity of BLE and BLEP rheological responses



Source: own authorship (2024).

FINAL CONSIDERATIONS

In this comparative study between liquors, in addition to evaluating the rheological behavior, it allows us to identify important parameters to understand liquor processing in the industry. In relation to chemical composition, the variation of the eucalyptus liquor in relation to the pine liquor becomes clear, mainly in relation to lignin. The rheological data indicate that pine liquors have lower viscosity than eucalyptus liquors and corroborate the observations in relation to molar mass, in relation to the structure of lignin, in relation to the amount of carbon atoms, and its chemical structure, resulting in the difference in the heating value (HV).). The rheological approach allowed us to justify the observations already made in relation to the chemical parameters and to understand the relationship between the composition structures. Although the higher lignin content is suggested to be predominant for a higher viscosity of the liquors, this fact cannot be seen in isolation, which suggests that all structures should be considered in determining the rheological behavior. This study also corroborates the pseudoplastic characteristic of cellulose black liquors.

Influences of the solid content can alter this configuration. The work carried out in black liquor recovery units must be aware of these differences that can result in variations in the processing and pumping procedures.

The correlation to predict the viscosity of hardwood and softwood black liquor, under normal industrial processing conditions, has been tested by carrying out several successful comparisons with data available in the literature. Finally, the wood from which the liquor originates is decisive for both its chemical composition and its rheological behavior.

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