Eucalyptus black liquor properties in a lignin extraction process: density, dry solids, viscosity, inorganic, and organic content

VITOR MACHADO VIANA CRUZ AND JOSÉ VICENTE HALLAK DANGELO

ABSTRACT: Extracting lignin from black liquor is becoming more common, although only a few research papers discuss the impact of the process on the liquor's primary properties. This work aims to determine the changes in black liquor properties as it undergoes a lignin extraction process using carbon dioxide (CO_2).

A diluted eucalyptus black liquor sample (DBL) was acidified with CO_2 to a final pH of 8.5. After filtration, the kraft lignin was removed, and the filtrated lignin lean black liquor (LLBL) was collected. Five acidified black liquors (ABL) samples were collected during acidification at pH 10.5; 10.0; 9.5; 9.0; and 8.5. The samples were analyzed regarding lignin content in solution, sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), density, dry solids content, and viscosity. While Na_2SO_4 remained almost constant, Na_2CO_3 presented an enormous increase in its concentration when comparing DBL with LLBL. As pH decreased, the lignin content in the solution was also reduced due to lignin precipitation. The results showed similar behavior for dry solids, density, and viscosity of the supernatant, but an increase in density was observed around pH 9.00. In light of this, the density of LLBL turns out to be closer to the one in the initial DBL. The significant increase in carbonate content could explain this behavior during acidification with CO_2 once the inorganic content significantly influences the property. The viscosity was determined from 10 s^{-1} to 2000 s^{-1}. We observed a Newtonian behavior for all samples. The increase in carbonate content in the sample is crucial information to the recovery cycle, especially for calculating the mass and energy balance when targeting the use of the LLBL.

Application: Eucalyptus black liquor properties are presented to help pulp mills better understand how the liquor behaves in a lignin extraction process and evaluate the potential correlations for these properties that are hard to measure, especially viscosity.

The physical behavior of black liquor, which is the raw material of the lignin extraction process, depends on its primary components, which are lignin, sodium sulfate (Na_2SO_4), and sodium carbonate (Na_2CO_3) [1]. Other authors [2-4] reported that black liquor's physical and chemical properties command unit operations in the chemical recovery cycle of kraft pulping, but are also the leading cause of mill operational problems.

Despite the operational differences between the lignin extraction process and the recovery cycle, studying black liquor's behavior in the lignin extraction plant is equally important from an operational point of view. Regardless of the method, extracting lignin from the liquor causes a significant impact on chemical and physical properties, whether by the removal of lignin itself or the formation of new chemicals, thus impacting the liquor's viscosity, density, and dry solids.

Pump operation in an extraction plant depends on fluid characterization, so the operation is suitable for its physical properties. Also, the filtration process depends on the physical and chemical behavior to calculate washing water and operating pressure, thus ensuring filtration efficiency and avoiding operational problems [5,6].

Among the physical properties, viscosity is the most important for fluid transportation, so it is vital to be aware of the rheological state of the liquor and its variation throughout the process [7-9]. As lignin structure varies with wood species, black liquor rheological behavior is also dependent on the wood source, varying wildly between tropical hardwoods (eucalyptus) and softwoods (pinus) [10].

The influence of black liquor's chemical composition on its physical properties is fundamental for the design and operation of lignin extraction plants. Some works [1-13] have studied the influence of these physical properties on the operation of industrial plants and on the final quality of the product. Most of these studies pointed out that the filtration resistance and the increase in carbohydrate contaminations is more significant when using hardwood than when using softwood.

Therefore, it is essential to promote impactful studies on black liquor feed stream properties. In other words, these properties are critical to the process because of the lignin and sodium salts in black liquor. In addition, the lignin lean black liquor can be reinstated to the liquor's chemical recovery process.

The characterization of black liquor streams from lignin extraction plants is scarce in the literature. Most papers [11-14] focus primarily on the process extraction efficiency or the application of the final product. Studies [7,15,16] that seek to characterize these streams' properties focus on analyzing streams from plants that used black liquors from softwoods. Moosavifar [7] analyzed a series of liquors, including hardwood, considering only two different samples for each liquor studied. One sample was the diluted black liquor, before acidification, and the other was lignin lean black liquor at the end of the acidification process. No intermediate samples, at different pHs, in between these two were analyzed, and then the author used linear interpolation to predict the behavior of intermediate samples as pH decreases. Besides this, no model for hardwood black liquor properties was proposed from his experimental data.

Although eucalyptus black liquor has been characterized in some previous papers as mentioned earlier, there is still a gap in studying eucalyptus black liquor properties throughout acid precipitation for the lignin extraction process, in order to identify the impacts of decreasing pH on its properties. Therefore, the main objective of our work is to characterize the eucalyptus black liquor properties not only before and after the acid precipitation process in an industrial plant, but also during the process as pH decreases, allowing us to understand how these liquor properties behave, especially the rheological behavior. Thus, these data can be used to understand the differences in the behavior of softwood and hardwood liquors. Definitive knowledge about the acid precipitation process is crucial for its improvement, leading to improved performance, competitiveness, and efficiency gains.

EXPERIMENTAL

Each black liquor sample underwent chemical and physical characterization in our work, and the following sections describe the materials and methods that were used. The details of the lignin extraction process using acid precipitation with carbon dioxide (CO_2) is not the focus of the study but rather how the industrial removal of lignin from eucalyptus black liquor impacts its main properties.

Samples

A pulp mill in São Paulo, Brazil, provided a diluted eucalyptus black liquor (DBL) sample. The DBL sample was acidified using CO_2. Samples of acidified black liquor (ABL) were collected at five different pHs during the acidification in an industrial lignin extraction plant. After the precipitation, the filtrate sample was collected and designated lignin lean black liquor (LLBL).

We analyzed the following samples: DBL, five ABL samples at given collected pHs (10.5, 10, 9.5, 9, and 8.5) and LLBL obtained from the first filtrate after acidification at pH 8.5. The designated streams are illustrated in **Fig. 1**. The DBL is the initial sample of the process before acid precipitation, and the LLBL is the final sample when all precipitated lignin is separated from the liquid phase.

The DBL sample was collected by an operator in the evaporation plant on August 20, 2018. We stored the sample in containers with double sealing and kept it in a refrigerated environment until analysis. The ABL samples, intermediate process samples that lost lignin in solution as it began to precipitate gradually, and LLBL were stored using the same procedure as for DBL.

The chemical and physical characterization included the determination of lignin concentration, carbonate concentration (CO_3^{2-}), sulfate concentration (SO_4^{2-}), density (25°C, 50°C, and 80°C), dry solids, pH (25°C, 50°C, and 80°C), viscosity (25°C, 50°C, and 80°C). Components such as carbohydrates, residual alkali (OH^-), and sodium (Na^+) concentration were measured. The physical and chemical analysis standard methods are presented as follows.

Chemical characterization

We determined black liquors' organic and inorganic composition using techniques described in a previous work [17]. The complexity of black liquor as fluid makes it hard to measure some components and is mainly caused by interference from other components. Therefore, different tech-

1. Illustrated schematic of samples of analyzed streams (DBL = diluted eucalyptus black liquor; ABL = acidified black liquor; LLBL = lignin lean black liquor).

Analysis	Methodology
Sodium sulfate and sodium	TAPPIT 625 cm-8 "Analysis of soda and sulfate black liquor"
Sodium carbonate	SCAN-N 32:98 "Carbonate content – TIC procedure"
Residual alkali	SCAN-N 38:10 "Acid-soluble metals"
Lignin UV_{280}	Alén, R. and Hartus, T., "UV spectrophotometric determination of lignin from alkaline pulping liquors" [18]
Lignin (soluble and insoluble)	TAPPIT 222 om-02 "Acid-insoluble lignin in wood and pulp" TAPPIT 250 um-83 "Acid-soluble lignin in wood and pulp"
Carbohydrates	SCAN-CM 71:09 "Pulps – carbohydrate content"

I. Analysis and methods used in chemical characterization.

niques were used to determine the components. **Table I** [18] shows the methods used in chemical analysis.

The concentration of carbohydrates and lignin in DBLs and LLBLs was determined using TAPPI T 222 om-02 "Acid-insoluble lignin in wood and pulp" and TAPPI T 250 um-83 "Acid-soluble lignin in wood and pulp." The latter standard method uses a UV spectrophotometer to determine the acid-soluble lignin, hence the need to use the appropriate extinction coefficient for lignin. We combined the TAPPI T 250 um-83 with Alén and Hartus [18] methodology, where the insoluble lignin yielded from TAPPI T 222 om-02 analysis was used to calculate the extinction coefficient and later the lignin concentration in a solution. The lignin concentration in solution in acidulate black liquor samples was measured only with the combined acid-soluble lignin method. The carbohydrate concentration was then calculated using a balance between the initial concentration (DBL sample) and the final (LBLL sample).

Physical characterization

We also measured the physical properties of black liquors using different methods presented in the previous work [17]. Black liquor viscosity analysis was the most important, since no recent works were found in the literature regarding eucalyptus liquor rheological behavior. **Table II** [19] lists the methods adopted in the physical analysis.

We visualized the heterogenous nature of acidulated black liquor samples after some time, with the precipitated lignin decanted. However, during the precipitation process, both phases exist. Rather than only analyzing the impact of lignin removal from the solution on physical properties, we have chosen to study the process impact when the precipitated lignin is considered in dry solids and density analyses.

The first scenario evaluated the influence of lignin yield in the process (only the supernatant/solution phase), while the second scenario accounted for the precipitated lignin in the solution. The second scenario was used as a comparative, since acid precipitation with CO_2 could lead to the formation of carbonate compounds, thus affecting the inorganic fraction of the liquor. The rheological analysis considered only the supernatant. The evaluated scenarios in the measurement of density and dry solids are illustrated in **Fig. 2**.

RESULTS AND DISCUSSION

After the measurements, we could obtain a complete characterization of the main physical and chemical properties of eucalyptus black liquor samples throughout the lignin extraction process. The seven analyzed samples represent

Analysis	Methodology
pH	pHmeter Manual (BEL-W3B)*
Density	Costa, H.F., Egas, A.P.V., Ferreira, A.G.M., et al., "Rheology of eucalyptus globulus kraft black liquor" [19]
Dry solids	TAPPIT 650 cm-99 "Solids content of black liquor"
Viscosity	Haake Mars III Manual**
* pH meter model BEL-W3B (Bel Equipamentos Analíticos Ltda; Piracicaba, SP, Brazil) ** Haake Mars III rheometer (Thermo Fisher Scientific; Waltham, MA, USA)	

II. Analysis and methods used in physical characterization.

2. Illustrated schematic of two analyzed scenarios of acidulated black liquor (ABL).

the three stages of the extraction process, in which the input (initial/feed), precipitation (middle), and output (final) stages are represented by DBL, ABL, and LLBL samples, respectively.

The acid precipitation process used CO_2 over time until a pH around 8.5 was achieved. Thus, with a variation in acidification time, based on a process need, we decided to present the results by classifying the samples as a function of lignin concentration and the pH at which the sample was collected in the process. Therefore, it was possible to discuss how the concentration of the main constituents in DBL, ABL, and LLBL influenced the density, dry solids, and especially viscosity.

Lignin and carbohydrates

The results obtained are presented in **Table III**. Since we have used acid precipitation, we analyzed the lignin and carbohydrate content for different pHs (13.6; 10.94; 10.34; 9.77; 9.42; 9.12; and 9.10 at 25°C) throughout the process. From Table III, we notice a considerable decrease in lignin concentration in the solution of LBL samples (pH 13.6 at 25°C) compared to DBL samples (pH 9.12 at 25°C). These results demonstrate the pH impact on lignin solubility also found elsewhere in [7,20]; therefore, the lignin concentration in solution decreases as pH decreases.

Samples	Lignin	Carbohydrates
	($g.kg^{-1}$ of dry solids)	
DBL	374.92	10.97
ABL 10.5	364.57	12.12
ABL 10	323.67	13.28
ABL 9.5	232.15	14.44
ABL 9	203.38	15.59
ABL 8.5	147.40	16.75
LLBL	144.56	17.90

DBL = diluted eucalyptus black liquor; ABL = acidified black liquor; LLBL = lignin lean black liquor.

III. Organic characterization of the samples.

Despite the error in lignin concentration determined only by the combined acid-soluble lignin, the estimate is sufficient to determine the decrease in the lignin concentration's nominal value in the solution. The difference between lignin concentration in the DBL (initial) and LLBL (final) samples allowed the calculation of precipitation efficiency, thus indicating that 61.4% of the lignin was extracted from the liquor. The extraction percentage is in agreement with the yield normally obtained by the acid precipitation process [15].

Sodium sulfate, sodium carbonate, and other inorganic components

The concentration of inorganic components, in their corresponding ionic form, for the analyzed samples is presented in **Table IV**.

The use of CO_2 increased CO_3^{2-} ions in the solution. In addition to being a primary agent in the lignin extraction process, it contributes to the mass transfer between CO_2 and the liquid phase. We observed an increase of carbonate in the LLBL compared to the liquor feed stream (DBL). The same behavior was noticed by Moosavifar [7] in the study of LignoBoost samples using coniferous liquors. The increase in carbonate was also mentioned elsewhere [15] as an essential parameter to consider when LLBL returns to the recovery cycle. The increase in sodium salt concentration is not desired due to the possible precipitation of these salts in the evaporation line. This phenomenon was partly attributed to the mass balance, because a lignin loss affects the calculation of dry solids.

The increase in CO_3^{2-} could also affect the dry solids and density. The impact on these properties is discussed in the appropriate section. We found that as the CO_3^{2-} concentration increases and pH decreases in solution, the hydroxide ion concentration (OH^-) decreases. Due to the technique used, we were not able to correctly detect the ion at a pH

Samples	Sodium Sulfate (SO_4^{2+})	Sodium Carbonate (CO_3^{2-})	Sodium (Na^+)	Potassium (K^+)	Residual Alkali (OH^-)
	(g.kg^{-1} of dry solids)				
DBL	22.52	71.84	222.80	20.36	22.56
ABL 10.5	22.24	92.07	230.38	21.04	8.24
ABL 10	23.17	138.00	230.32	22.90	n.d.
ABL 9.5	25.03	164.10	280.89	25.83	n.d.
ABL 9	25.32	173.62	246.15	25.37	n.d.
ABL 8.5	24.93	174.93	256.59	24.23	n.d.
LLBL	24.58	165.90	219.29	23.15	n.d.

DBL = diluted eucalyptus black liquor; ABL = acidified black liquor; LLBL = lignin lean black liquor; n.d. = not detected.

IV. Inorganic characterization of the samples.

below 10.5. Sodium ions (Na^+) also increased, as acidification caused a breakdown of lignin bonds with inorganic salts, especially sodium.

The concentration of the sulfate ion SO_4^{2-} had a slight increase throughout the process, primarily due to decreased lignin concentration during the precipitation process and possibly due to the oxidation of the remaining sulfide into sulfate. The rise in sulfate concentration indicates that its corresponding form in salt (sodium sulfate) was not impregnated in the extracted lignin, which benefits the final product. In contrast to CO_3^{2-}, SO_4^{2-} concentration does not significantly differ from the original black liquor, thus indicating that the sulfate ions would not be a considerable concern if LLBL were reinstated to the recovery cycle, especially in the evaporator.

Potassium (K^+) is an essential parameter to be controlled during the burning of black liquor [21], despite being an adjunct in the lignin extraction process, and remained stable.

Samples	pH		
	25°C	50°C	80°C
DBL	13.6	11.6	10.22
ABL 10.5	10.94	10.87	9.08
ABL 10	10.34	9.47	8.98
ABL 9.5	9.77	9.41	8.78
ABL 9	9.42	9.34	8.72
ABL 8.5	9.10	9.05	8.63
LLBL	9.12	9.06	8.65

DBL = diluted eucalyptus black liquor; ABL = acidified black liquor; LLBL = lignin lean black liquor.

V. The pH of samples at different temperatures.

pH

Considering that pH is a direct function of temperature, it is essential to understand that its value at room temperature changes as temperature increases or decreases. The pH value used to identify ABL samples corresponds to the pH of the sample collected in the plant. Therefore, the pH used to identify ABL does not necessarily reflect the pH of the sample at room temperature, which is used as a reference in the process analysis. **Table V** presents pH measurements at 25°C, 50°C, and 80°C

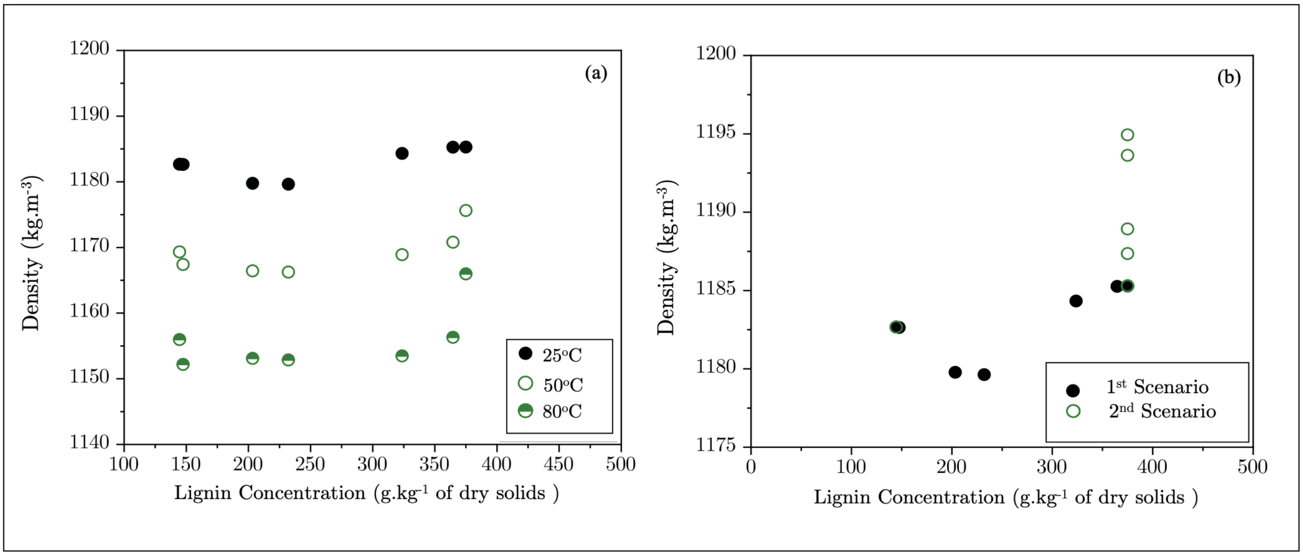
The dependence of pH on temperature is evident as acidification occurs. It is crucial to reinforce the relationship between the nominal values of the pH measured in the laboratory and the pH value used to designate the name of ABL samples in the preceding tables.

There is also a difference in pH as temperature increases. However, 80°C is not necessarily the temperature of the precipitation process of the lignin, and we used it only as a reference range that covers the temperatures of the studied process.

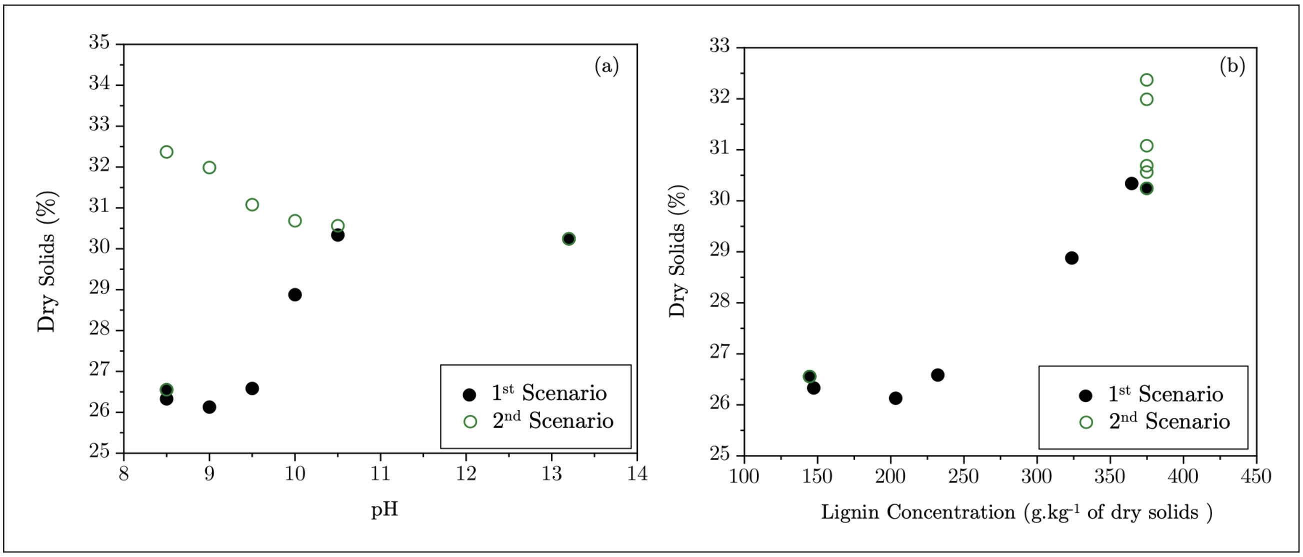
Density

Density values as a function of lignin concentration, obtained at 25°C, 50°C, and 80°C, are presented in **Fig. 3a**. The results of density (at 25°C) according to lignin concentration, considering the analyzed scenarios (Fig. 2), are presented in Fig. 3b.

We have identified a robust linear behavior between the increase of the inorganic fraction (CO_3^{2-} concentration) and the rise in density. The inorganic components significantly impacted this property and proved that the nonlinearity in decreasing density throughout the process was caused by the acid precipitation method. In other words, the loss of lignin in the solution does not cause a significant impact on the property due to the simultaneous increase in carbonate ions, because the inorganic compound affects the



3. Density variation with temperature regarding lignin concentration: (a) first scenario and (b) between the two scenarios.



4. Dry solids variation for the two scenarios with (a) pH and (b) lignin concentration.

property more than the organic compounds [1,22,23].

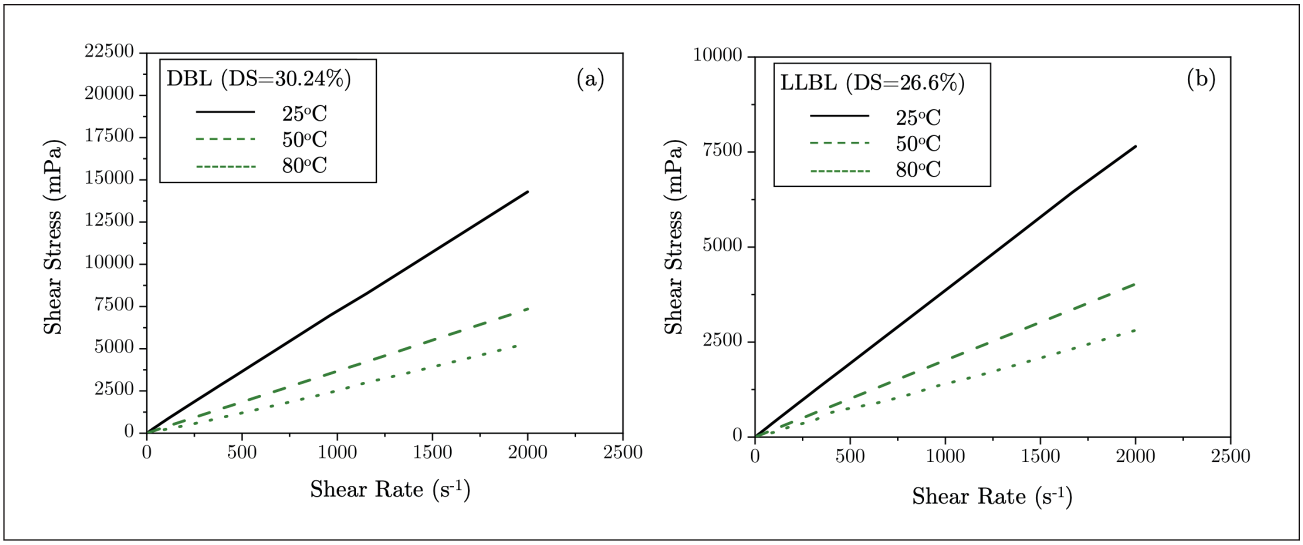
The variation of the liquor density with the increase in temperature followed an expected decreasing pattern and was reported by other authors [1,24]. Still, in contrast to the analysis presented by the authors, the property variation considers black liquors with different concentrations of lignin and pHs. However, the pattern of variation follows the same trend. With the increase in temperature, there is a decrease in density.

Dry solids

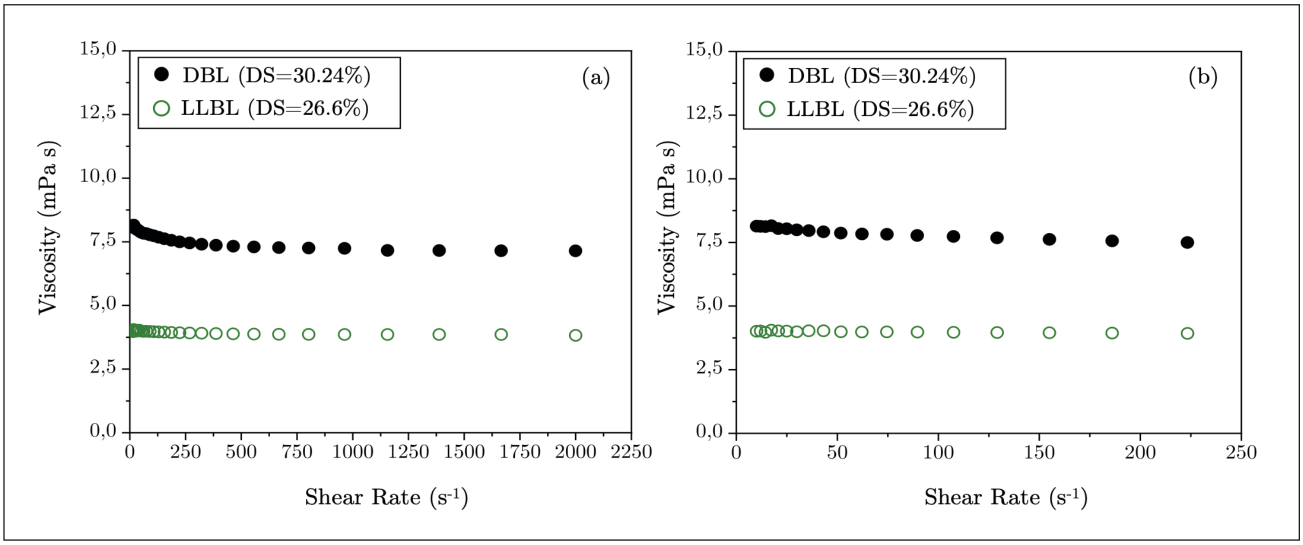
The comparative results of dry solids as a function of pH and lignin concentration, considering the two scenarios (Fig. 2), are presented in **Fig. 4a–b**. Unlike the density, we found dry solids more of a mass balance function than a direct influence of a specific component. The loss of lignin throughout the process caused a noticeable decrease in dry solids. Even though it had a lower molecular weight than inorganic salts, some authors pointed out that the organic material dissolved in black liquor corresponds to 60% of the total dry solids [2,12]. However, the magnitude of this decrease does not reach 20% of the initial value. When considering precipitated lignin mass (second scenario in Fig. 2) in dry solids, it was also possible to observe the increase in the inorganic load proportional to the property, thus indicating the impact of the rise in CO_3^{2-} concentration in the solution.

Viscosity

Although the flow curve analyzes viscosity variation by shear rate, the fluid rheological behavior is determined by a graphical analysis of shear stress vs. the shear rate. The



5. Rheological behavior (shear rate vs. shear stress) with temperature for (a) DBL and (b) LLBL (DS = dry solids).



6. Viscosity variation with a shear rate between (a) 10 s^{-1} and 2000 s^{-1} and (b) 10 s^{-1} and 250 s^{-1}.

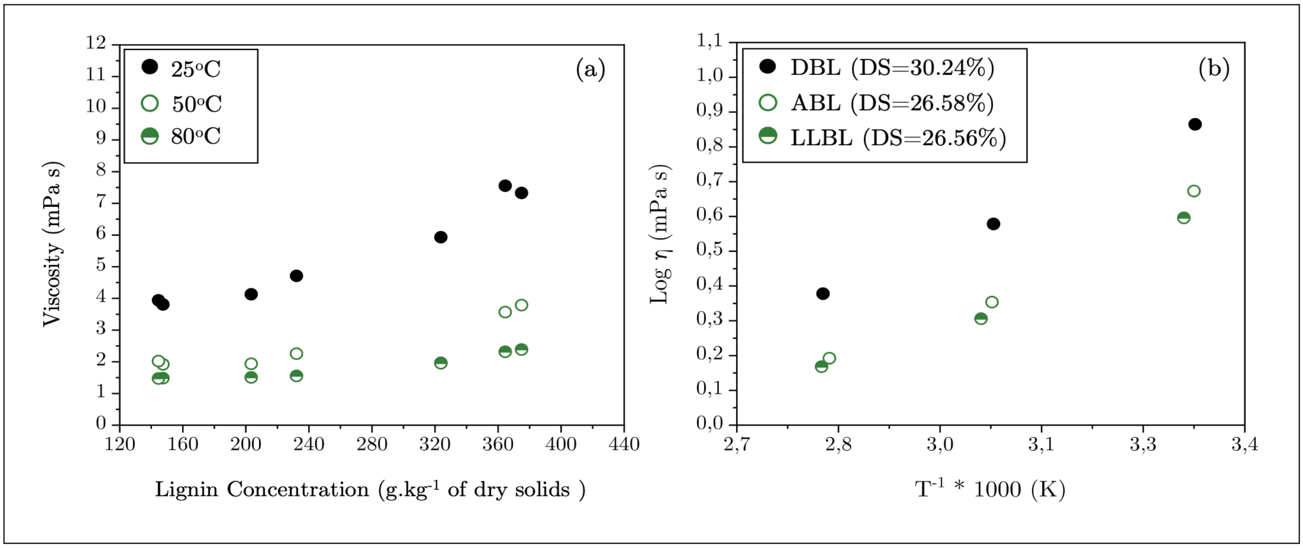
results for the study of fluid behavior, using the relationship between the shear rate and shear stress for DBL and LLBL samples, are presented in **Fig. 5a** and Fig. 5b, respectively.

We observed DBL's rheological behavior to be primarily Newtonian for the samples analyzed at 25°C, 50°C, and 80°C and shear rate between 10 s^{-1} and 2000 s^{-1}. Although lignin is predominantly responsible for non-Newtonian behavior, the results are supported by the fact that the black liquors analyzed are in a range of dry solids of less than 50%. Black liquors from the recovery cycle with a percentage of solids less than or equal to 50% do not deviate from Newtonian behavior [1,2]. When the behavior was evaluated for higher temperatures (50°C and 80°C), a lower slope was evident, reinforcing the influence of temperature on viscosity. A lower viscosity nominal value is implied in a less pronounced slope.

Since LLBL has less dissolved lignin, not only was a decrease in the slope expected, but also a pronounced Newtonian behavior. Another factor contributing to the standard behavior of LLBL samples is the removal of higher molecular weight lignin, because the low molecular weight lignin, in solution, causes a lower impact on the property [7,25].

The rheological behavior analysis was crucial for discussion of the flow curves to obtain a viscosity trend and the variation of the shear rate. The dynamic viscosity was evaluated with the shear rate using a graphical analysis of the flow curves. The dynamic viscosity in a shear rate range between 10 s^{-1} and 2000 s^{-1} at 25°C is presented in **Fig. 6a–b**.

We observed that the DBL samples presented a slight dependence between the viscosity value and the shear rate applied in the measurement. The sample showed the highest lignin concentration in solution and a higher percentage of solids. The data showed that although there was a variation in the viscosity value of DBL, the change was insig-



7. Lignin and temperature influence on (a) viscosity and (b) the interdependence between log viscosity (logµ) and temperature.

nificant. This result is an essential factor for dimensioning fluid pumping systems for the extraction plant, further evidencing the importance of comprehending the fluid behavior at higher shear rates. We also found that in contrast to the feed stream (DBL) results, the influence of the dynamic viscosity value was not evident in the LLBL sample, even at high fluid shear rates.

Therefore, lignin is not only one of the leading causes of deviation from Newtonian behavior, but lignin of higher molecular weight (extracted lignin) had a more significant impact on the property, as mentioned in other literature [2,9,20]. The literature also stated that the inorganic portion of black liquor does not significantly affect this property. Thus, the increase in carbonate ions did not cause a perturbation in the liquor rheological behavior. Once the concentration of carbohydrates is marginal in the samples, its influence could not be determined.

There was a stabilization of the value from 250 s^{-1}, so it is crucial to analyze the variation in the points preceding this rate. The dynamic viscosity of the samples in a shear rate range between 10 s^{-1} and 250 s^{-1} is presented in the graph in Fig. 6b.

We could confirm a marginal reduction in viscosity values in a reduced range (from 10 s^{-1} to 250 s^{-1}). The variation occurs mainly due to the low shear of fluid and the polymeric nature of eucalyptus black liquor, even in low percentages of solids. This variation could be due to eucalyptus black liquor dependence on shear rate and was also observed in other studies [2,19] at solids concentrations between 30% and 35%. Based on the non-significant variation between the low- and high-rate values of shear, we decided to use an average of all 30 viscosity values points collected in the range from 10 s^{-1} to 2000 s^{-1} to compare the behavior of the property according to other parameters.

One research paper that evaluated the rheological behavior of softwood liquors used the viscosity value at 150 s^{-1} to guarantee the laminar flow at the referred shear rate [7]. However, the author used liquors with a higher percentage of solids that presented a pronounced decrease in initial viscosity values, a trend not observed in our study. For this, the mean viscosity values were used because of the laminar flow throughout the analysis, as observed in Fig. 6b.

We used the calculated mean value in a more in-depth analysis of the influence of lignin concentration and fluid temperature throughout the extraction process on the property. The proportionality between the log viscosity (logµ) and temperature is evidenced for the measured viscosity values and agrees with findings from Zaman and Fricke [25], as illustrated in **Fig. 7a–b**.

Although all samples were measured concerning temperature variation, only the results of the samples of DBL, ABL at pH 9.5, and LLBL are presented for better data analysis. The graphic scale indicates that the lower the temperature (i.e., the higher the x-axis value) is, the higher the sample log viscosity is.

The temperature increase enabled the viscosity reduction by up to two times the original value. These results demonstrated the strong influence of temperature; therefore, it should be considered a fundamental parameter in project calculations and for constructing predictive models.

The same behavior was observed by Moosavifar [7], in which the viscosity of black liquor had a high dependence on temperature, although the data presented were for softwood. Cardoso et al. [2] measured the viscosity of different black eucalyptus liquors in various Brazilian pulp mills and showed similar trends.

Other authors [22,23,25,26] used temperature and dry solids as parameters to predict the fluid rheological behavior under different physical conditions. Even though dry solids and temperature strongly influence the viscosity, the composition of these solids, the wood species (softwood and hardwood), and operational conditions are also crucial in drawing analyses and building correlation models. In light of this, more research is needed to access solids composition and operational conditions as parameters to propose predictive models for viscosity.

CONCLUSIONS

The aim of our work was part of a much larger universe of possibilities in the study of black liquor's physical and chemical properties. A correlation for eucalyptus black liquor properties, especially viscosity, would be of great assistance, thus optimizing operation in the extraction process. The present research was relevant to reinforce the importance of studying eucalyptus black liquor, mainly due to the arrival of lignin extraction plants in Brazil.

It is essential to notice that the liquor's chemical characterization led to understanding its interdependence with physical properties. Thus, their measurements and analyses were crucial in establishing the composition relationship between dry solids, density, and viscosity.

The lignin extraction process drastically affected the liquor's chemical composition, causing a decrease in lignin concentration and an increase in inorganic contents. Sodium carbonate presented the most significant increase. Despite the lignin loss, the carbonate content increased drastically, affecting the density. On the other hand, the dry solids were most affected by lignin loss.

We also observed that viscosity followed the same pattern as dry solids, in which lignin loss dramatically impacted the property. The inorganic content presented a minimum or no influence on viscosity. Lignin is responsible for the non-Newtonian viscosity behavior in liquors, and its loss made its rheological behavior less susceptible to shear rate effects, even at low rates.

Lignin stability is highly dependent on pH, being more stable at higher pHs. The measured lignin content considered the dissolved portion of the polymer, indicating that the pH of the sample could maintain the given solids dissolved in the solution.

The temperature also profoundly affected viscosity, an essential property in the evaporation cycle. Therefore, such an effect must be considered, especially if the liquor has undergone a thermal process. The primary physical properties are essential in determining black liquor operational parameters. Thus, the liquor behavior can aid in selecting the correct destination for the LLBL (filtrate) during the extraction process. Understanding lignin's impact on viscosity allows the proposition of operational improvements, leading to different possibilities for black liquor and the reuse of LLBL.

There is a long way to go in our future research applied to the national scenario, where, to a great extent, eucalyptus is the dominant species used in kraft pulping. Despite the predominance, very little work has been done in the past ten years in the area. It is a horizon that the pulping industry needs to change to continue the pursuit of biorefinery paths. **TJ**

ACKNOWLEDGMENTS

I, Vitor Machado Viana Cruz, sincerely thank my advisor and coauthor, Professor Dr. José Vicente H. Dangelo, for the trust and partnership he has shown. I also wish to thank Dr. Vinicius Lobosco for his support; this project could not have reached its goal without his aid.

ABOUT THE AUTHORS

I (Machado Viana Cruz) have always been interested in the liquor recovery cycle, so the opportunity to research a new process within the cycle was exciting. This work contributes information about eucalyptus black liquor (within a lignin extraction plant) characterization techniques and how the data aid process operations.

The most difficult aspect of this study was acquiring and validating the rheology data, and presenting the data to industrial partners and fellow researchers was essential in overcoming this challenge. Through this study, I saw how high molecular mass lignin dominates eucalyptus black liquor rheological behavior. A particularly interesting finding was that lignin concentration can contribute to a more reliable and accurate black liquor viscosity correlation as opposed to using dry solids as a parameter.

For mills, understanding lignin's impact on viscosity allows the proposition of operational improvements and the reuse of lignin lean black liquor in evaporation plants. The next steps would be to develop a correlation for eucalyptus black liquor properties to optimize the extraction process, as well as to study the potential to reuse lignin lean black liquor in evaporation plants.

Machado Viana Cruz is a Ph.D. candidate in Chemical Engineering and Dangelo is associate professor at the University of Campinas (UNICAMP) in Campinas, SP, Brazil. Email Machado Viana Cruz at vitormachadovianac@gmail.com.

Machado Viana Cruz

Dangelo

LITERATURE CITED

1. Empie, H.J., *Fundamentals of the Kraft Recovery Process*, TAPPI Press, Atlanta, 2009.
2. Cardoso, M., Domingos de Oliveira, É., and Passos, M.L., *Fuel* 88(4): 756(2009). https://doi.org/10.1016/j.fuel.2008.10.016.
3. Andreuccetti, M.T., Leite, B.S., and D'Angelo, J.V.H., *O Papel* 72(12): 52(2011).
4. Oehman, F., Theliander, H., Tomani, P., et al., U.S. pat. 2010/0325947 A1 (Dec. 30, 2010).
5. Durruty, J., "On the local filtration properties of LignoBoost lignin: Studies of the influence of xylan and ionic strength," Ph.D. thesis, Chalmers University of Technology, Gothenburg, 2017.
6. Durruty, J., "On the local filtration properties during cake filtration: Studies on LignoBoost lignin and the influence of ionic strength," Lic. thesis, Chalmers University of Technology, Gothenburg, 2014.
7. Moosavifar, A., "Lignin extraction from black liquor: Properties of the liquors and sulphur content in the lignin," Ph.D. thesis, Chalmers University of Technology, Gothenburg, 2008.
8. Cardoso, M., de Oliveira, K.D., Costa, G.A.A., et al., *Appl. Energy* 86(1): 45(2009). https://doi.org/10.1016/j.apenergy.2008.03.021.
9. Patel, J.C., *TAPPI Kraft Recovery Course*, TAPPI Press, Atlanta, 2007.
10. Krotscheck, A.W. and Sixta, H., "Recovery," in *Handbook of Pulp* (H. Sixta, Ed.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006, pp. 967-996.
11. Zhu, W. and Theliander, H., *BioResources* 10(1): 1696(2015). https://doi.org/10.15376/biores.10.1.1696-1715.
12. Fang, W., Alekhina, M., Ershova, O., et al., *Holzforschung* 69(8): 943(2015). https://doi.org/10.1515/hf-2014-0200.
13. Lindgren, K., Samuelsson, Å., and Kulander, I., "Techno economic evaluation of lignin extraction in a dissolving pulp biorefinery," *7th Nord. Wood Biorefinery Conf.*, Innventia/VTT, Gothenburg/Espoo, Finland, 2017.
14. Jardim, J.M., Hart, P.W., Lucia, L., et al., *Polymers* 12(8): 1795(2020). https://doi.org/10.3390/polym12081795.
15. Tomani, P.E.R., Axegård, P., Berglin, N., et al., *Cellul. Chem. Technol.* 2(5): 533(2011).
16. Björk, M., Rinne, J., Nikunen, K., et al., *6th Nord. Wood Biorefinery Conf.*, Innventia/VTT, Gothenburg/Espoo, Finland, 2015, p. 185.

ABOUT THIS PAPER

Cite this article as:
Cruz, V.M.V. and Dangelo, J., *TAPPI J.* 22(3): 152(2023). https://doi.org/10.32964/TJ22.3.151

DOI: https://doi.org/10.32964/TJ22.3.151

ISSN: 0734-1415

Publisher: TAPPI Press

About this journal

17. Cruz, V.M.V., "Estudo do comportamento químico e físico do licor negro de eucalipto no processo de extração da lignina," Master's thesis, University of Campinas, Campinas, SP, Brazil, 2019.
18. Alén, R. and Hartus, T., *Cellul. Chem. Technol.* 22: 613(1988).
19. Costa, H.F., Egas, A.P.V., Ferreira, A.G.M., et al., *Appl. Rheol.* 21(4): 42533(2011). https://doi.org/10.3933/applrheol-21-42533.
20. Jardim, J.M., Hart, P.W., Lucia, L.A., et al., *Fibers* 10(2): 16(2022). https://doi.org/10.3390/fib10020016.
21. Tran, H., "Upper furnace deposition and plugging," in *Kraft Recovery Boilers* (T.N. Adams, Ed.), TAPPI Press, Atlanta, 1997, pp. 247-282.
22. Frederick, W.J., "Black liquor properties," in *Kraft Recovery Boilers* (T.N. Adams, Ed.), TAPPI Press, Atlanta, 1997, pp. 97-107.
23. Venkatesh, V. and Nguyen, X.N., "Evaporation and concentration of black liquor," in *Chemical Recovery in the Alkaline Pulping Process* (R.P. Green and G. Hough, Eds.), 3rd edn., TAPPI Press, Atlanta, 1992, pp. 5-12.
24. Cardoso, M., "Análise da unidade de recuperação do licor negro de eucalipto no processo 'kraft', avaliando alternativas de processamento," Ph.D. thesis, University of Campinas, Campinas, SP, Brazil, 1998.
25. Zaman, A.A. and Fricke, A.L., *J. Pulp Pap. Sci.* 21(4): J119(1994).
26. Tikka, P., Ed., *Papermaking Science and Technology: Chemical Pulping. Part 2: Recovery of Chemicals and Energy*, Paperi ja Puu Oy, Helsinki, 2008.