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Investigating Heat-Treated Bagasse-Based Kraft Black Liquor for Physicochemical and Rheological Properties

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ABSTRACT: *Heat treatment is a promising approach to reducing the viscosity and improving the combustion behavior of black liquor. The bagasse-based kraft black liquor was heated in a series digester at a constant temperature of 180˚C in three batches for 15, 20, and 25 min to investigate its physicochemical and rheological properties before and after heat treatment. Black liquor heated for 25 min showed the highest residual active alkali consumption of 28.37%. The optimum heat treatment time was 20 min, and the heat-treated black liquor at this condition exhibited residual active alkali 5.02% as* Na_2O *and an increase in swelling volume ratio from 12 ml/g to 18 ml/g. Rheological studies of original and heat-treated black liquors were carried out in a rotational rheometer at 90˚C and 105˚C in the shear rate range of 1-100* s^{-1}*. 20 min heat-treated black liquor showed 74.09% and 71.56% reduction in viscosity at 90˚C and 105˚C, respectively, for 65% solids concentration. The effect of temperature and solids content on the rheological properties of black liquor was discussed. The results showed that black liquors obtained after heat treatment were non-Newtonian (pseudoplastic) in nature with a power law index less than unity* ($n<1$)*. The power law (Ostwald de Waele) model best fits the obtained viscosity data of heat-treated bagasse black liquor. The work presented here gives an insight into the importance of the heat treatment process for the viscosity reduction of bagasse black liquor. It may help better understand various Physicochemical properties and the flow behavior of heat-treated bagasse black liquor for chemical recovery.*

KEYWORDS: *Sugarcane Bagasse; Heat treatment; Viscosity; Power law; Chemical recovery; Pulp and paper.*

INTRODUCTION

Using agro residues for pulp and paper production has reduced dependence on forest resources. However, effectively utilizing agro-black liquor (BL) as fuel for chemical recovery is still a rigorous task. Sugarcane bagasse has emerged as the most suitable raw material for pulp and papermaking among various agro-raw materials used by paper mills [1]. Sugarcane bagasse is one of the significant agro-fibrous raw materials widely used in chemical and

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mechanical pulping processes with the added advantage of less bleaching chemicals requirement [2,3]. Bagasse is suitable for producing writing, tissue, and newsprint paper [4]. Due to the increasing cost of energy and cooking chemicals, kraft mills are adopting every possible way of efficient and optimal use of power because the economic progress of kraft mills entirely depends on chemical recovery facilities [5]. Evaporation and burning of BL are primary operations in chemical recovery, but the higher viscosity of BL directly affects these operations. The composition of BL depends on pulping conditions, which directly affects its viscosity. BL is a complex mixture of polysaccharides, lignin, resinous compounds, and soluble salt ions [6]. In BL, the concentration, molar mass, and molecular confrontation of lignin and polysaccharides are mainly responsible for the viscosity of black liquor [7]. BL is concentrated to increase the heat efficiency of the furnace, and a reasonable viscosity range is considered at 90 °C because this temperature is similar to the exit temperature from an evaporator for an actual chemical recovery operation [8]. Dynamic viscosity is a function of lignin molecular weight, concentration, and other organic/inorganic compounds [9]. The literature knows that firing BL at higher solids improves recovery boiler operations with added operational advantages of higher reduction efficiency, higher thermal efficiency, and lower NO_x/SO_x emissions [10,11]. The higher viscosity of BL leads to increased electrical energy for pumping, increased evaporator scaling, large droplet formation of BL in the recovery boiler, and plugging of firing nozzles, evaporators, and pipelines [12-14]. The higher viscosity of BL is also one possible reason for lower steam generation and lower thermal efficiency in recovery boilers because the heat transfer or evaporation rate of BL decreases with an increase in BL viscosity & at higher viscosity, evaporator capacity is highly affected [15]. Hence, any method for BL viscosity reduction is inevitable for the cost-effective operation of chemical recovery in terms of steam and energy generation.

Methods reported by various researchers for viscosity reduction are oxidation, salting-in, additives, and liquor heat treatment. Among these, liquor heat treatment is the most promising as it results in an irreversible reduction of the viscosity of BL [14,16]. Liquor Heat Treatment (LHT) is heating BL at a temperature higher than the pulping temperature for a specified time. In this process, residual active alkali reacts with higher molecular weight polymeric compounds such as polysaccharides linked with lignin molecules or Lignin- Carbohydrate Complex (LCC) [16]. This depolymerization process of LCC results in irreversible viscosity reduction of BL and makes it possible to achieve higher solid concentration in multiple-effect evaporators. The LHT process also improves BL's swelling volume ratio (SVR) as a higher amount of high molecular weight lignin and hemicellulose residue results in less swelling of BL droplets [17]. One of the benefits of LHT is a reduction in sulfur compounds and SO_2 emission, as there will be no need for a direct contact evaporator. According to the literature, semi-concentrated black liquor (SCBL) shows higher viscosity reduction than weak black liquor after heat treatment, as it is assumed that black liquor with higher solids has higher total hydroxides, which is necessary to achieve higher heat treatment efficiency [18]. Some authors have studied the effect of LHT on the physicochemical properties of agro and wood-based BL.

Nassar et al. [5] studied the viscosity of thermally treated bagasse-based black liquors at different temperatures (80 – 110 °C) and different solids (40 - 75%). They reported that the effect of heat treatment on black liquor is more prominent in higher solid content of black liquor. The reduction in viscosity at 40% and 70% concentration was around 25.8% and 84.1%, respectively, at 80 °C. *Tarun et al.* [12] carried out heat treatment of wheat straw-based black liquor in different ranges of temperature (175 – 185 °C), time (10 – 20 min), and solids (55 – 65%). They found that with 5.5 % residual active alkali (as NaOH) at 180 °C and 15 min, a 78% reduction in viscosity and 55% increase in swelling volume ratio can be achieved during heat treatment of black liquor. *Jain et al.* [16] studied the thermal treatment of bagasse-based black liquor in an indigenously designed heat treatment pilot plant to get an insight into viscosity reduction and combustion behavior in the temperature range 180 – 190 °C within different periods. They found that the combustion behavior of heat-treated black liquor improved with a 3.9% decrease in ignition temperature for untreated bagasse black liquor. Not only this, but heat treatment also led to a 52.94 % increment in swelling volume ratio, a 10 % improvement in the energy efficiency of the chemical recovery system, and 0.35 tons of additional steam generation per ton of black liquor solids. *Alabi et al.* [30] studied the effect of heat treatment on the viscosity of a softwood (*radiata pine*) based black liquor at 190 °C for 15 min. They found that heat treatment permanently reduced black liquor viscosity by ~ 17% for untreated fresh black liquor samples. *Klarin–Henricson* [34] explored the effect of kraft black liquor heat treatment on the diminution of total organic sulfur, the release of foul-smelling gases, and the reduction in viscosity. Though these authors investigated the black liquor heat treatment process from the abovementioned aspects, none explored the rheological behavior of heat-treated black liquor using any empirical models. Hence, a novel endeavor has been made in this study to explore the suitability of the Ostwald de Waele Model in describing the rheological parameters of heat-treated bagasse-based black liquor.

In India, agro residues hold a meager contribution to total paper production, even though India is an agricultural-rich country. The use is limited due to drawbacks associated with agro residues, which restrict chemical recovery operations. Such drawbacks are high viscosity and non-process elements in agro-black liquors. This work is also an attempt to promote the use of LHT for the viscosity reduction of bagasse BL. It will help integrate the LHT process into the existing chemical recovery facility for bagasse BL. Most bagasse black liquors with more than 40% solid content usually behave like non-Newtonian fluids [19]. Viscosity is an exponential function of solids concentration as at lower solids concentration, BL shows Newtonian behavior, but at higher concentration, viscosity increases exponentially, and BL shows non-Newtonian behavior [20]. BL's viscosity data helps decide the usable viscosity limit for pumps [21]. Hence, it is necessary to study the rheological behavior of BL after heat treatment, which will help design suitable capacity pumps and pipes for the transportation of heat-treated BL and which will be helpful in the optimization of energy requirements for economic chemical recovery operations. The objectives of this work are manifold, i.e., the evaluation of physicochemical properties of heat-treated BL, the study of combustion behavior of heat-treated BL, and the analysis of rheological behavior through obtained power law parameters at different solids concentrations.

EXPERIMENTAL SECTIONS

Sample collection and analysis

A Semi-Concentrated Black Liquor (SCBL) of bagasse was collected from an agro-based paper mill in northern India. The mill has acquired a kraft procedure for pulping bagasse. The SCBL was collected according to a standardized sampling method. In addition, bagasse used by the mill to produce this BL was also collected for investigating its physicochemical analysis because the properties of BL depend on the nature of the raw material. All parameters were performed in duplicate, and average values were reported. Samples for BL analysis were prepared by appropriate dilution.

Physico-chemical analysis of bagasse

100 g of bagasse was powdered in a Wiley mill (Thomas Scientific, USA). Bagasse was characterized for its chemical properties where parameters studied are ash content (TAPPI T 211 om-93), cold and hot water solubility (TAPPI T 207 cm-99), alcohol-benzene solubility (TAPPI T 204 cm-97), pentosans (TAPPI T 223 cm-01), acid insoluble lignin (TAPPI T 222 om-02), holocellulose (*Wise et al*. 1946) and alpha-cellulose (TAPPI T 203 om-88).

Analysis of black liquor

The kraft bagasse SCBL was evaluated for its physicochemical properties, i.e., total solids (TAPPI T 650 cm-99), pH, residual active alkali (TAPPI T 625 cm-85), swelling volume ratio (CPPRI TM III A12), inorganics/organics (TAPPI T 625 cm-85), silica content (TAPPI T 625 cm-85) and sugar content (UV method). The elemental analysis was performed using a CHNS analyzer (Elementar, model Vario EL cube, Germany).

Black liquor heat treatment

The heat treatment of kraft bagasse SCBL was performed in a series digester, as shown in Fig. 1. The digester consisted of a rotary assembly to hold the different bombs. Heat treatment of SCBL was conducted in three batches for different retention times, i.e., 15 min, 20 min, and 25 min. Three bombs filled with 1000 g (wt. basis) SCBL were kept one after the other at 180˚C in an electrically heated polyethylene glycol bath of digester for 15 min, 20 min, and 25 min, respectively. After completion of the process, all three bombs were quenched in a water bath, and treated liquors were taken for further evaluation of physicochemical properties and rheological behavior. The black liquors heat treated for 15 min, 20 min, and 25 min are referred to as BL_{15}, BL_{20}, and BL_{25}, respectively, in this paper.

Fig. 1: (a) Series Digester used for LHT of bagasse BL (b) Bomb inside digester filled with SCBL

Black liquor sample preparation and rheology measurement

A rotary vacuum evaporator (Hahnvapor, Korea) was used to obtain the BL at different solids concentrations, i.e., 50%, 55%, 60%, and 65% within the error range of ± 1.0%. The solid concentrations of BL were determined using an infrared moisture balance (Sartorius, Germany). The rheology measurement of BL was carried out in a rotational rheometer (Anton Paar, model MCR 102, Austria) at 90˚C and 105˚C. Cup and Bob assembly were used for the rheology study, and the sample was filled up to the index line in the cup. The rheological data of non-treated and heat-treated bagasse BL were obtained for the solid concentrations mentioned above. A thermostatic water bath controlled the temperature of the rheometer. The apparent viscosity values were obtained at 20 points by varying the shear rate linearly from 1 – 100 s^{-1}.

Power law model for rheological behavior

The rheological behavior of kraft BL can be quantified by the Power law or Ostwald de Waele Model, which represents the mathematical expression for the power law region of the Log Viscosity and Log Shear Rate curve. The obtained rheological data were fitted to the power law model as follows:

$$\sigma = k\,\gamma^{n} \quad (1)$$

$$\eta = k\gamma^{n-1} \text{ or } \ln\eta = (n-1)\ln\gamma + \ln k \quad (2)$$

here, σ = shear stress, k =consistency index, n = power law index, η = apparent viscosity (cP), and γ = shear rate (s^{-1}), for shear thinning behavior power law index (n) varies from 0 to 1, n > 1 for shear thickening, and n=1 for Newtonian fluids. Eq. (2) gives a linear plot between shear rate and apparent viscosity to obtain the power law and consistency indexes.

RESULTS AND DISCUSSION

Proximate chemical properties of bagasse

A proximate chemical analysis of bagasse was carried out to investigate the inherent properties responsible for the abnormally high viscosity of bagasse BL. Table 1 shows the proximate chemical analysis of bagasse and its comparison with literature values. Bagasse exhibited ash content of 2.8%, cold water solubility of 3.5%, hot water solubility of 5.7%, alcohol benzene solubility of 3.4%, and lignin of 23.2%. The obtained results are apparent and similar to the values shown in the literature. Bagasse is very suitable for papermaking as it contains a good amount of holocellulose (72.3%) and alpha-cellulose (42.16%). The 25.5% of pentosan content in bagasse is relatively higher than rice straw (16.4%), wheat straw (19.8%), and eucalyptus (11.07%) [22]. The higher pentosan content in bagasse results in higher sugar pentose in bagasse BL after pulping. Lignin and sugar pentose in bagasse BL cause the formation of a high molecular weight polymer, namely, the Lignin Carbohydrate Complex (LCC) [24]. This LCC is mainly responsible for the abnormally high viscosity of bagasse black liquor at higher solids concentrations.

Physico-chemical properties of kraft bagasse SCBL

Table 2 shows the physicochemical properties of kraft bagasse SCBL. The non-treated SCBL exhibited 29.86% total solids content. The solids content is one of the critical parameters used to control the BL evaporation process, and it estimates chemical recovery efficiency [25]. The BL was alkaline with a pH of 11.93. Residual Active Alkali (RAA) is one of the essential parameters that directly affect the viscosity of BL, as low RAA level results in precipitation of BL even at lower solids concentration during

Table 1: Proximate chemical properties of bagasse and its comparison with literature values

Parameters	Values obtained in the study	Literature value [22]
Ash content, %w/w	2.9	2.4
Cold water solubility, %w/w	3.5	2.9
Hot water solubility, %w/w	5.7	4.8
Alcohol benzene solubility, %w/w	3.4	2.9
Pentosan, %w/w	25.5	24.7
Holocellulose, %w/w	72.3	77.9
Lignin, %w/w	23.2	21.2
Alpha Cellulose, %w/w	42.16	41.0

Table 2: Comparison of kraft bagasse SCBL analysis before and after heat treatment

Parameter	Non-treated black liquor	Heat-treated black liquor		
		15 min	20 min	25 min
Total Solids, %w/w	29.86	30.35	31.12	34.61
pH	11.93	11.74	11.70	11.68
Residual Active Alkali as Na_2O, %w/w	6.52	5.66	5.02	4.67
Swelling Volume Ratio, ml/g	12	17	18	17
Inorganics as NaOH, %w/w	37.62	36.12	36.09	36.07
Organics, %w/w	62.38	63.88	63.91	63.93
Silica as SiO_2, %w/w	0.88	0.90	0.88	0.89
Carbon as C, %w/w	32.28	31.72	31.75	31.98
Hydrogen as H, %w/w	3.62	3.56	3.63	3.58
Nitrogen as N, %w/w	0.22	0.27	0.29	0.28
Sulfur as S, %w/w	3.45	4.09	3.90	3.58
Sugar content, %w/w	23.8	-	-	-

evaporation [26]. Higher pH and certain levels of RAA prevent the slow condensation of alkali lignin during evaporation, which causes the precipitation of BL. Also, a suitable initial level of RAA is required in BL as it reacts with LCC polymer during heat treatment of BL. The kraft bagasse SCBL showed a 6.52 % RAA level as Na_2O. Poor swelling was observed in SCBL as this BL could not create a porous homogenous film for combustion due to high molecular weight LCC. SVR is a crucial parameter to describe the burning characteristics of BL. Higher SVR indicates a homogenous film with free-air passages, which results in complete incineration of BL droplet. Organics and inorganics show BL's sulfated ash and give ideas about the total sodium that can be recovered from BL. The bagasse BL contained 0.88% silica. Silica also directly affects the chemical recovery operation, as higher silica content, increases BL viscosity and scaling in evaporators [10, 27]. Straw black liquors usually contain higher silica, but silica content also depends on soil and geographical region [28]. Carbon, hydrogen, nitrogen, and sulfur content help evaluate the combustion properties of BL, as the higher the carbon content in BL, the higher its heating value. Higher sugar content in bagasse BL is expected due to higher pentosan content [29].

Effect of heat treatment on Physico-chemical analysis of kraft bagasse SCBL

Table 2 shows the results of SCBL analysis before and after heat treatment. It can be seen that, except for RAA and SVR, no drastic changes were observed in other BL properties after heat treatment. The increase in total solid contents with treatment time can be attributed to some evaporation of black liquors during heat treatment; however, the change in solid content was not very significant in BL_{15} and BL_{20}. A slight reduction in pH was observed, which can be explained by the degradation of

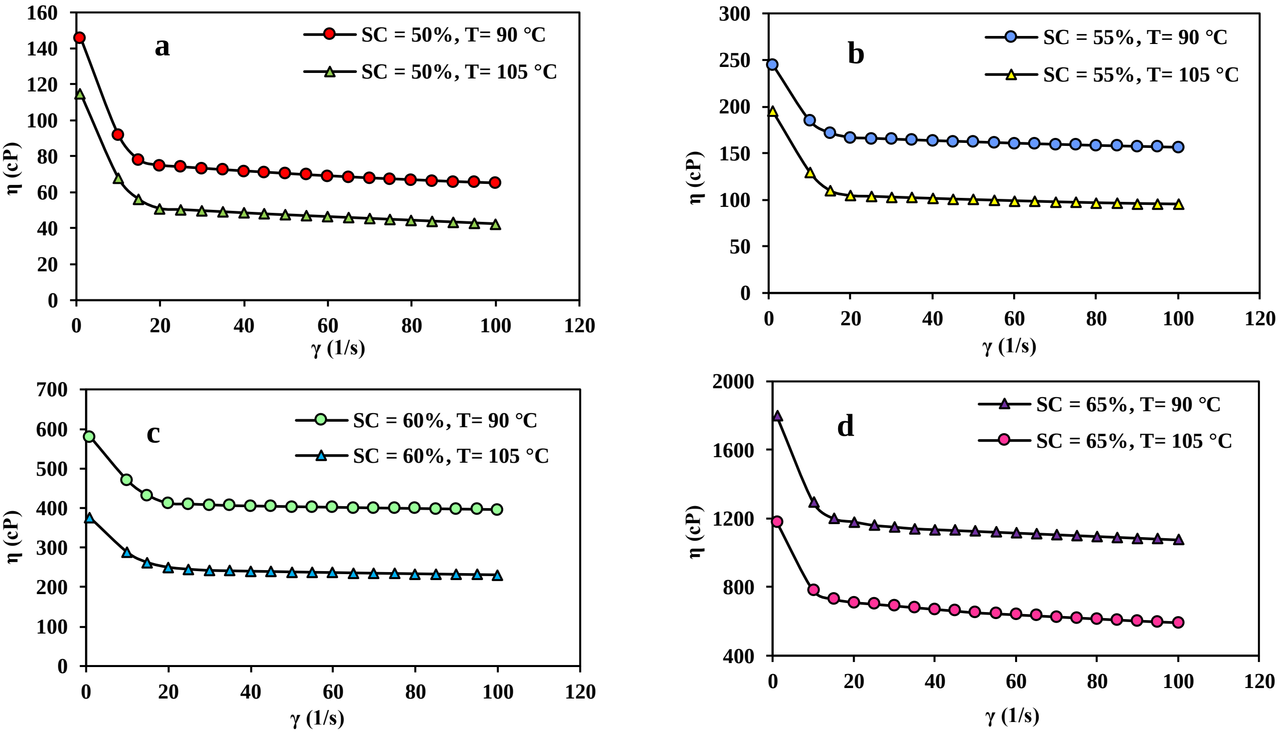

Fig. 2: Apparent viscosity vs. Shear rate at different solids concentration (SC) for non-treated kraft SCBL (a) 50%, (b) 55%, (c) 60 %, (d) 65% at temperature (T) 90 ^{0}C and 105 ^{0}C

lignin and hemicellulose to acidic compounds like acetic acid, formic acid, and another organic acid after the treatment of liquor heat [21]. The RAA was found to be in decreasing trend, which is the requirement of heat treatment of BL. During the heat treatment, polysaccharides and lignin content consumed some amount of RAA in BL [30]. The consumptions of RAA were 13.19%, 23.00%, and 28.37% in BL_{15}, BL_{20}, and BL_{25}, respectively. A suitable level of RAA keeps the BL colloidally stable. Still, no precipitation was observed during the concentration of heat-treated BL to higher solids content, so the remaining level of RAA was found to be sufficient in heat-treated black liquors. With liquor heat treatment, a long chain of lignin-pentosan polymeric molecules, or LCC, loses its degree of polymerization and breaks down into smaller fragments.

The reduced length of the polymeric chain thus allows better swelling during combustion of BL as lower molecular weight fractions of lignin swell better than high molecular weight fractions [31]. An increase in SVR can be attributed to polysaccharide and low molecular weight lignin content change in BL after liquor heat treatment [12]. Consumption of RAA also results in a slight reduction of inorganics after heat treatment, which is favorable for an increase in SVR. Kraft lignin and sugar acids in BL are mainly responsible for the swelling of BL, and higher inorganics decrease the SVR [31]. A maximum 50% increment was observed in the SVR of heat-treated black liquors. It was concluded that the improved Swelling Volume Ratio (SVR) of kraft bagasse BL indicates better combustion in the recovery boiler. No significant change was observed in silica content and elemental analysis of BL after liquor heat treatment.

Rheological behavior of kraft bagasse black liquor

Non-treated SCBL

Fig. 2 shows the apparent viscosity versus shear rate curves for non-treated BL at different solids content and temperatures. Results show that the apparent viscosity of kraft bagasse BL decreases with increased temperature and increases with increased solids content. The sharp increase in viscosity of BL at higher solids is due to the entanglement effect of polymeric lignin and polysaccharides present in BL [5]. Higher temperature increases the kinetic energy of molecules and decreases the friction between their layers. It leads to free space for the flow of molecules, which reduces BL's viscosity

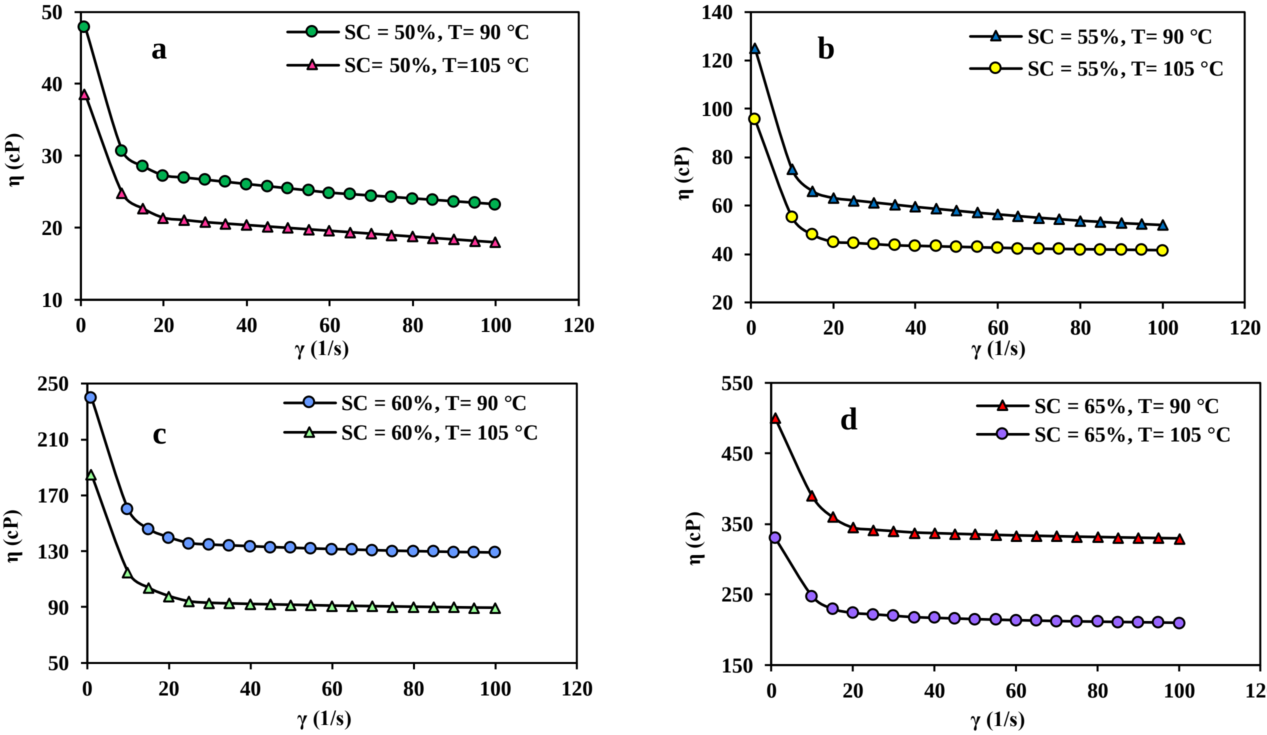

Fig. 3: Apparent viscosity vs. Shear rate at different solids concentrations for kraft SCBL thermally treated for 15 min. (a) 50%, (b) 55%, (c) 60%, (d) 65% at temperatures 90 ^{0}C and 105 ^{0}C.

at higher temperatures [10,32]. The non-treated bagasse BL at higher solids exhibited shear thinning behavior as apparent viscosity decreases exponentially with increased shear rate. This shear thinning (pseudoplastic) behavior appears due to the alignment of lignin macromolecules at a higher shear rate, which reduces their resistance to flow and ultimately reduces the apparent viscosity but at a lower shear rate, these macromolecules entangle easily and result in increased viscosity [7].

Shenglin Chen et al. explained BL's shear-thinning nature in their study. The entanglement of long linear chains of macromolecules present in BL leads to the formation of floccules, causing the disarrangement of molecular chains. Increasing the shear rate creates the consistent direction of these molecular chains; hence, BL ended up with reduced viscosity [33]. The viscosity curves shown in Fig. 2 indicate that the viscosity of non-treated bagasse BL is a direct function of solids concentration and an inverse function of shear rate and temperature.

Heat treated SCBL

From the apparent viscosity curves (Fig. 3, 4, and 5), it can be seen that there is a remarkable reduction in viscosity after heat treatment of BL because heat treatment of BL leads to depolymerization of high molecular weight Lignin Carbohydrate Complexes (LCC). The operability with non-treated BL was complex as it possessed exceptionally high viscosity at 65% solid concentration. The liquor heat treatment carried out in this study introduced scope for reduction in viscosity, which resulted in easy operability with bagasse BL at 65% solid concentration. At the industrial scale, reduction in viscosity favors better evaporation of BL by making it easier to achieve higher firing solids concentration in multiple-effect evaporators [16]. For 65% solids concentration, the mean apparent viscosities of non-treated BL are 1164.5 cP and 681.15 cP at 90˚C and 105˚C, respectively. The BL_{15}, BL_{20}, and BL_{25} showed 70.19%, 74.09%, and 76.12% reduction in viscosity, respectively, at 90˚C for 65% solid concentration; also 67.26%, 71.56%, and 59.17% reduction in viscosity respectively at 105˚C for 65% solid concentration. In this study, the viscosity data were obtained up to 65% solids concentration; however, % viscosity reduction would be more significant for BL with higher solids concentration (>65%) as it will possess higher original viscosity [34]. The mean apparent viscosities of heat-treated BL are given

Table 3: Mean apparent viscosity and Power law parameters for heat-treated kraft bagasse black liquor

Heat Treatment Time (min)	Solid content (%)	Temperature (^{0}C)	Mean Apparent Viscosity (mPa-s)	Standard Deviation (mPa-s)	Power Law Parameters			
					k (mPa-s^n)	n	SSE	R^2
15	50	90	26.71	5.34	39.77	0.8853	0.00397	0.9922
		105	20.98	4.45	35.30	0.8554	0.04985	0.9842
	55	90	61.61	15.91	100.28	0.8583	0.00450	0.9933
		105	46.35	11.99	52.25	0.9502	0.00158	0.9960
	60	90	139.7	24.70	153.09	0.9628	0.00049	0.9991
		105	98.11	21.33	104.69	0.9662	0.00120	0.9935
	65	90	347.17	38.54	372.41	0.9734	0.00122	0.9917
		105	223	26.69	251.64	0.9604	0.00156	0.9938
20	50	90	22.72	5.31	41.80	0.8275	0.01468	0.9941
		105	18.51	4.31	33.62	0.8312	0.02259	0.9854
	55	90	51.39	16.22	72.24	0.8908	0.00608	0.9908
		105	40.04	10.31	52.46	0.9134	0.00590	0.9863
	60	90	120.17	23.05	138.10	0.9510	0.00211	0.9905
		105	84.07	19.13	98.19	0.9442	0.00241	0.9904
	65	90	301.67	26.88	333.95	0.9679	0.00121	0.9882
		105	193.67	23.86	204.18	0.9776	0.00074	0.9957
25	50	90	21.14	4.88	32.52	0.8728	0.00529	0.9948
		105	18.26	4.55	38.21	0.7986	0.00706	0.9898
	55	90	48.93	13.82	64.07	0.9100	0.00336	0.9945
		105	37.27	9.91	57.11	0.8788	0.00626	0.9878
	60	90	109.68	21.52	123.35	0.9557	0.00246	0.9879
		105	79.05	18.48	88.68	0.9535	0.00239	0.9900
	65	90	278.13	29.55	309.82	0.9648	0.00138	0.9899
		105	182.94	25.51	194.42	0.9736	0.00102	0.9924

SSE= Sum of Squared Errors

in Table 3. Comparatively higher viscosity reduction was achieved in BL_{20}. Hence, 20 min was considered the optimum time for heat treatment of bagasse BL used in this study with a sufficient remaining RAA level of 5.02 % as Na_2O. However, such LHT conditions may not apply for all bagasse BL types as its viscosity depends on raw material composition, type of pulping, and BL composition [7]. The mean apparent viscosity of BL_{20} at 90°C and 65% solids concentration is 301.67 cP, which is under the pumping limit of the centrifugal pump for BL [35]. Such a level of viscosity is quite reasonable for bagasse BL for pumping. BL with low viscosity favors the higher heat transfer coefficient during evaporation and consumes less electrical energy during pumping. The results indicate that LHT can be applied as viscosity reduction technology in agro-based pulp and paper industries.

The statistical analysis was carried out using Minitab 18 software. The mean, standard deviation, and power law parameters by regression analysis were obtained for heat-treated bagasse BLs. Figures 3, 4, and 5 show the viscosity curves for heat-treated black liquors at different solids concentrations and treatment times. It can be seen that the viscosity of BL_{15}, $BL_{20,}$ and BL_{25} showed a decreasing trend with an increase in shear rate; this indicates that heat treatment has reduced the viscosity but has not affected the shear thinning (non-Newtonian) behavior of bagasse BL. Therefore, it was assumed that breaking LCC in BL by heat treatment only reduced viscosity but did not change the pseudoplastic nature of bagasse BL used in this study at higher solids concentration. At a lower shear rate, there is a sharp decrease in apparent viscosity for all heat-treated BLs. However, a slight decrease in apparent viscosity

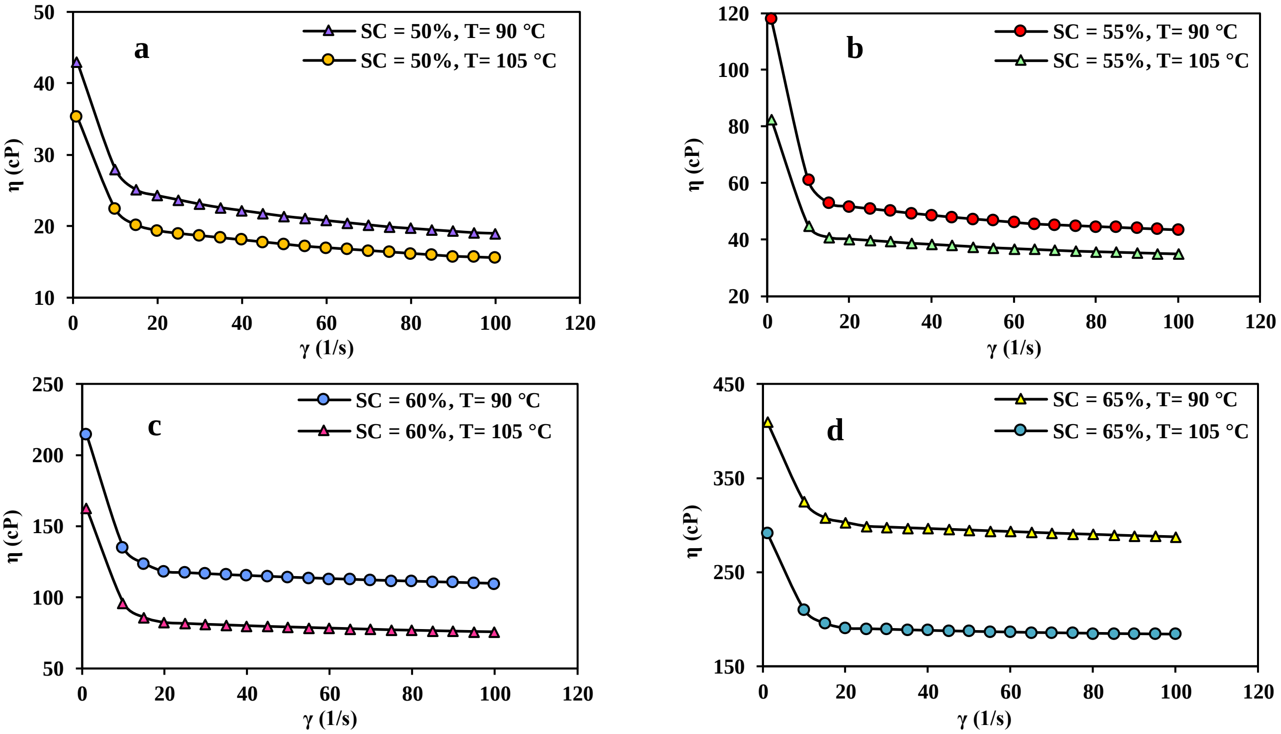

Fig. 4: Apparent viscosity vs. Shear rate at different solids concentrations for kraft SCBL thermally treated for 20 min. (a) 50%, (b) 55%, (c) 60%, (d) 65% at temperature 90 ^{0}C and 105 ^{0}C.

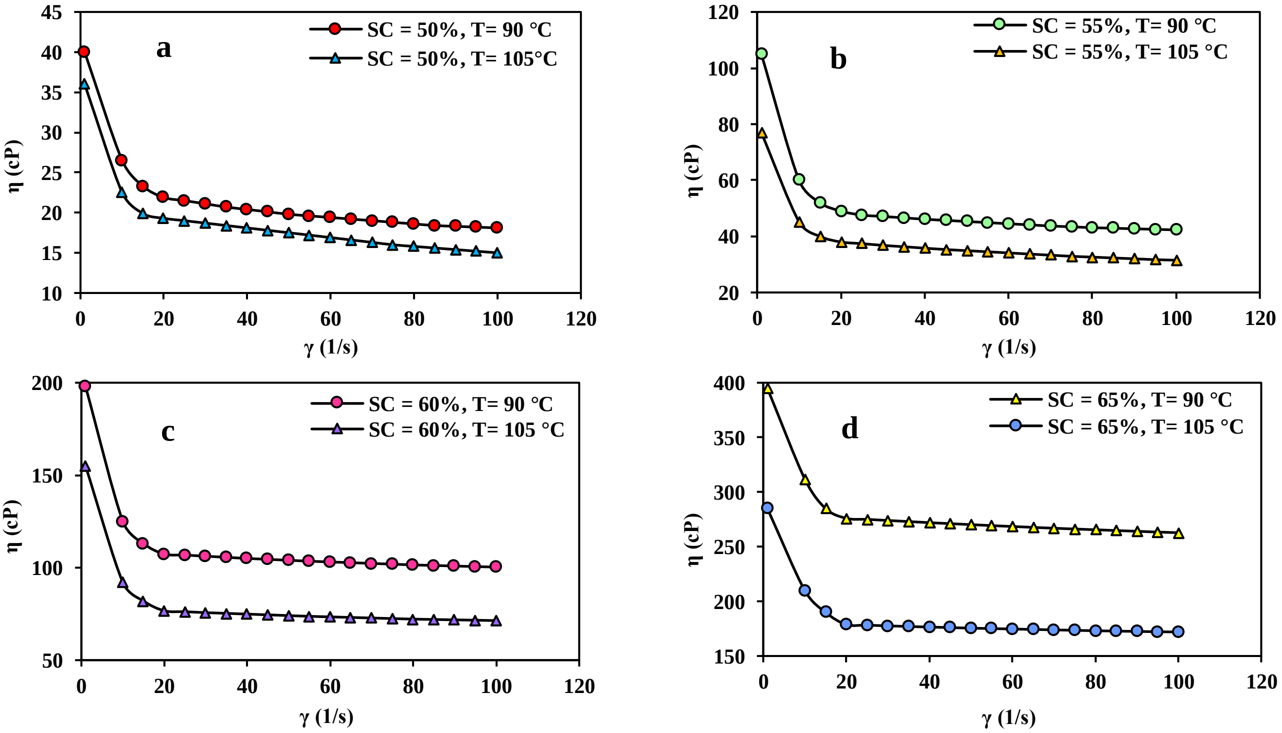

Fig. 5: Apparent viscosity vs. Shear rate at different solids concentrations for kraft SCBL thermally treated for 25 min. (a) 50%, (b) 55%, (c) 60%, (d) 65% at temperature 90 ^{0}C and 105 ^{0}C.

was observed after a specific shear rate, and apparent viscosity vs. shear rate curves followed a regular trend. This more considerable viscosity reduction at a lower shear rate was due to a higher temperature and shear thinning behavior of BL, which becomes slow at the higher shear rate [19].

The regular trend data (apparent viscosity and shear rate) of thermally treated BL were fitted into the power law model, and parameters were obtained by linear regression analysis shown in Table 3. Consistency index (k) indicates the viscous behavior and, as expected, was found to increase with solids concentration and decrease with temperature. For BL_{20}, the consistency index was in the range of 41.80 - 333.95 and 33.62 - 204.18 at 90 °C and 105 °C, respectively. For all BLs, the values of the power law index (n) were found to be lower than unity ($n<1$), which indicates the pseudoplastic nature of bagasse BL after heat treatment. For BL_{20}, the power law index (n) was in the range of 0.8275 – 0.9679 and 0.8312 – 0.9776 at 90 °C and 105 °C, respectively. However, the effect of temperature and solids concentration on the power law index (n) was not evident, as no regular change was observed concerning temperature and solids concentration [36]. The values of SSE (0.00049 - 0.04986) and correlation coefficients R^2 (0.9842 - 0.9991) indicated the best fit of obtained rheological data in the power law model. It was found that bagasse BL, after heat treatment, remains non-Newtonian (pseudoplastic) in nature at higher solids concentrations. Obtained rheological data could be used to predict the rheological behavior during pumping, evaporation, and burning of heat-treated bagasse BL.

CONCLUSIONS

The importance of heat treatment on kraft bagasse BL was studied in this work. High pentosans (25.5%) and lignin (23.2%) content in bagasse contain high molecular weight LCC in bagasse BL. Comparatively, BL_{20} showed the highest increment (50%) in SVR; thus, the RAA level in BL_{20} was considered optimum. Increased SVR indicates better combustion of bagasse BL in the recovery boiler furnace, which could eventually increase the steam generation and thermal efficiency in the recovery boiler. The results obtained in this study have shown that after thermal treatment of bagasse BL, more than 70% and 60% reduction in viscosity can be achieved against 65% solids concentration at 90˚C and 105˚C, respectively. Decreasing viscosity with shear rate denoted the shear thinning behavior of treated and non-treated bagasse black liquors. For BL_{20} of 65% solids concentration, the power law index (n) was 0.9679 and 0.9776 at 90˚C and 105˚C, respectively. Heat-treated bagasse BL's rheological data perfectly fit the power law model, as evidenced by lower SSE and higher correlation coefficient (R^2) values. The parameters obtained may help envisage the flow behavior and design recovery operations for kraft bagasse BL. Though the results obtained are promising, this study needs further exploration. The current study was based on kraft bagasse black liquor and the power law model. Furthermore, the study can be expanded with mixed (Bagasse and Wheat straw) kraft/ soda black liquor, and validation of rheological data can be studied by other available models.

Nomenclatures

Liquor heat treatment	LHT
Black liquor	BL
Black liquor heat treated for 15 min	BL_{15}
Black liquor heat treated for 20 min	BL_{20}
Black liquor heat treated for 25 min	BL_{25}
Total solids	TS
Oxides of nitrogen and sulfur	NO_x/So_x
Lignin carbohydrate complex	LCC
Swelling volume ratio	SVR
Semi-concentrated black liquor	SCBL
Residual active alkali	RAA
centipoise	cP
Temperature	T
Solids concentration	SC

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