Rheology and viscosity of bagasse black liquor

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Considering the increasing cost of petroleum oil, cooking chemicals and severe pollution problems, pulp mills should have suitable chemical recovery system. For design and development of economic process equipment and also for smooth monitoring of chemical recovery operation it is important to know the behavior of spent pulping liquors, particularly, during evaporation and combustion stages besides thermal properties. Though, some data is available for some of the properties but not much of the information relating to the rheological properties of bagasse black liquor and its boiling point. In the present study, viscosity of bagasse kraft black liquor as well as normal boiling point are measured at different conditions from concentration and temperature. Viscosity increases gradually up-to 20% concentration and shows a sharp rise above 20% Swollen Colloidal Lignin Molecules (SCLM) concentration. Black liquor behaves as Newtonian flow above 40, 50, 60, 70, and 80 °C for black liquor concentrations 20, 30, 40, 45, and 52% respectively as well as lower concentrations (less than 20%). Below mentioned temperatures corresponding to each concentration, it behaves as non-Newtonian flow (exhibiting Bingham plastic behavior). A new reliable correlation is obtained to correlate viscosity (μ), and Normal Boiling Point Rise ($NBPR$) as follow, $\mu = 10^{A}(\mu_{uater})^{B}$ where, $A = \sinh\left[2.981(TDS/100)^{0.67}\right]$ and $B = \cosh\left[1.462(TDS/100)^{0.38}\right]$ $NBPR = 8.0 * 10^{-5}(TDS^{3}) - 5.2 * 10^{-3}(TDS^{2}) + 0.2(TDS)$ where, $T_{sat}^{n} = 373.15 + NBPR$.

نظرا لارتفاع اسعار البترول والمواد الكيميائية وكذلك مشاكل التلوث الملحة فانه يتعين علي مصانع لب الورق أن تحتوي علي انظمة استرجاع للمواد الكيميائية. ولعمل تصميم اقتصادي لوحدات استرجاع وتشغيلها فمن المهم معرفة السلوك الانسيابى للسائل بجانب خواصه الحرارية لاسيما خلال عملية التبخير والحرق. ونظرا لندرة هذه المعلومات للسائل الاسود الناتج من مصاص القصب اثناء عملية الطبخ لانتاج لب الورق، فان هذا البحث يهدف لدراسة كل من السلوك الانسيابي واللزوجة ودرجة الغليان لهذا السائل عند ظروف مختلفة من درجة الحرارة وتركيز المواد الصلبة الذائبة. وقد تبين أن اللزوجة تزداد تدريجيا حتي تركيز ٢٠% وبعدها تزداد بشكل سريع مع التركيز. وقد وجد أنه عند درجة حرارة أعلي من ٤٠‘ ٥٠‘ ٦٠‘ ٧٠‘ ٨٠ مº يكون السريان طبقيا (Newtonian) وذلك لتركيزات ٢٠‘ ٣٠‘ ٤٠‘ ٥٠‘ ٥٢% علي الترتيب وكذلك لتركيز أقل من ٢٠% وغير ذلك فان السريان يكون غير طبقى (non-Newtonian). وقد تم صياغة النتائج في معادلات رياضية احداها للزوجة والاخري للارتفاع فى درجة الغليان العادية للسائل الاسود وكانت المعادلات كالتالى:

where, $\mu = 10^{A}(\mu_{uater})^{B}$

$A = \sinh\left[2.981(TDS/100)^{0.67}\right]$ and $B = \cosh\left[1.462(TDS/100)^{0.38}\right]$

where, $T_{sat}^{n} = 373.15 + NBPR$ $NBPR = 8.0 * 10^{-5}(TDS^{3}) - 5.2 * 10^{-3}(TDS^{2}) + 0.2(TDS)$

Keywords: Bagasse, Black Liquor, Rheology, Viscosity, Boiling Point

1. Introduction

Improved process design begins with using accurate physical property data of the process streams. Especially in the preliminary design stage, physical property data such as density, viscosity, thermal conductivity and specific heat can affect the overall performance of heat exchangers, re-boilers, heaters, absorbers and pumps. These properties can also influence temperature profiles in heat transfer equipment. One of the major process streams in the pulp and paper industry is black liquor and the pulp mill capacity is normally limited by the capacity of recovery system. Black liquor has physical properties which vary greatly with temperature, solids content and its chemical composition. The ability to reliably predict the physical properties of black liquor governs the overall quality of the design. Several studies on the physical properties of black liquor from wood pulp have been found in the literature [1-8]. Research in literature revealed lack information on kraft bagasse black liquor.

Viscosity of black liquor is the most important physical property in selection design and performance of chemical recovery equipment in a kraft pulp mill. Viscosity governs overall heat transfer coefficient and in turn controls liquor flow pattern and steam economy of multiple effect evaporators used for black liquor concentration. Other factors dependent on viscosity include: size distribution of droplets in black liquor spray to recovery boiler and performance of auxiliary units like heat exchangers (integral/external), pumps, pipelines, and oxidation tower. Viscosity data are also required in the various heat transfer and fluid flow correlations for process engineering calculations.

Viscosity vary with temperature, composition and concentration of dissolved solids in black liquor. Dissolved organic matter consists of sodium salt of degraded polymeric lignin that contributes significantly to the viscosity of the liquor. Viscosity of black liquor would also depend upon raw materials (softwood, hardwood, and agricultural residues), pulping process (kraft, soda, sulfite, and neutral sulfite), technical pulping conditions and pulp yield. Kraft black liquor viscosities of pine [1], western hemlock [2] and straw [3] have been reported. Viscosity of neutral sulfite spent liquor from hardwoods (poplar, oak, aspen, maple, gum) has been determined in [4].

Since black liquor is a heterogeneous mixture that consists of dissolved sugars, Swollen Colloidal Lignin Molecules (SCLM), inorganic chemicals, and water, the liquor may not be treated as a Newtonian fluid at all concentrations and temperatures. Ghalke and Veeramaini [9] found that black liquors from bamboo, bagasse, and eucalyptus woods exhibit Bingham plastic behavior when solids content exceed 45%.

In this study, behavior of kraft bagasse black liquor over a wide range of temperatures and liquor concentrations is investigated. Viscosity is determined at different conditions in order to obtain a reliable correlation useful for engineering design. The normal boiling point of the liquor is also measured and correlated in an empirical correlation as normal boiling point rise, NBPR, as a function of solid content. This study will help to understand the rheological behavior of black liquor and, consequently, will lead to better design and operation of the recovery system.

2. Black liquor solids

The black liquor used in this study was Egyptian bagasse kraft black liquor provided from Edfo pulp Mill, Aswan governorate, Egypt. The black liquor was obtained in three different concentrations 8.5%, 34% and 52%. The other concentrations of the black liquor test sample are prepared by appropriate dilution of the stock solutions. The percent of organic and inorganic solids and the percent of lignin are determined according to Ghalke and Veeramaini [9]. The chemical analysis of liquor is given in table 1. All data are presented on a dry weight basis.

Table 1
Chemical analysis of bagasse kraft black liquor

Property	Value
SCLM, %, w/w	8.5
pH	10
Organic, %,w/w	67.08
Inorganic, %,w/w	32.92
Silica and insoluble matter, %,w/w	3.31
Lignin, %	22.03
Carbohydrates, %,w/w	45.05
Residual Active Alkali (RAA) as Na_2O, g/dm^3	4.03
Total Alkali (TA) as Na_2O, g/dm^3	17.98
Elemental analysis	
Total carbon, %,w/w	33.1
Total sodium, %,w/w	23.54
Total sulphur, %,w/w	4.4
Total nitrogen, %,w/w	0.19
Total hydrogen, %,w/w	3.4
Total oxygen, %,w/w	31.4

3. Experimental techniques

Viscosity of black liquor of different concentrations up-to 52% SCLM and different temperatures from 20 °C to 85 °C was measured. Capillary viscometer (Ostwald) and constant temperature bath (± 0.1 °C) were used for samples up to 15% SCLM concentration. Rotational viscometer (Rheotest 2.1) was used for the range of 15% to 52% CLM. The latter unit consists of a system of coaxial cylinders with a fixed outer cylinder and rotating inner cylinder. The sample of black liquor placed in the annulus can be brought to the desired temperature level by circulating water from a constant temperature bath through the jacket surrounding the outer cylinder. The viscometer is provided with 36 different speeds for changing the shear rate. (0.2 – 1310 s^{-1}) and the corresponding shear stress measurements can be taken.

4. Results and discussion

Kinematics viscosity was measured using capillary viscometer and the dynamic viscosity was calculated using specific gravity data [7]. Rotational viscometer gives shear values corresponding to different applied shear rates for each sample. The flow curves of shear stress–shear rates data shown in figs. 1 to 6 for 15, 20, 30, 40, 45 and 52% concentration respectively. The data of 20, 30, 40, 45 and 52% concentration at temperatures above 40, 50, 60, 70 and 80 °C respectively as well as lower concentrations (SCLM < 20%) can be correlated according to eq. (1) for a Newtonian fluid.

$$S = \mu \frac{du}{dy}, \quad (1)$$

and can be correlated linearly according to eq. (2) typically for non-Newtonian fluid, exhibiting Bingham plastic behavior, at temperatures below 40, 50, 60, 70 and 80 °C for concentrations 20, 30, 40, 45 and 52% respectively.

$$S = S_0 + \mu \frac{du}{dy}. \quad (2)$$

The intercept S_0 in eq. (2) represents the limiting value of yield stress below which the internal structure of the fluid resists shear movement; flow begins at shear stress values above S_0.

The graphs in figs. 1-6 are suggested that a transition from Newtonian to non-Newtonian behavior can be expected for some black liquor systems (SCLM and temperature), this phenomena was observed by different authors for different types of black liquors [2, 3, 6 and 9]. Black liquor can not be handled above concentration 52% due to rapid drying of sample during transfer to the viscometer.

Bagasse black liquor exhibits Bingham plastic behavior at high concentrations and low temperatures. Yield stress values increase with liquor concentration and decrease with a rise in temperature, for example, yield stress increase from 9.8 to 30.4 Pascal for concentration rise from 30% to 40% SCLM at 50 °C and shear rate 220 s^{-1}, figs. 3 and 4; and decrease from 174.9 to 130.3 Pascal following temperature increase from 60 °C to 70 °C for 52% SCLM and shear rate 365 s^{-1}, fig. 6. Also the limiting value of shear stress depends on both concentration and temperature of liquor where it has a direct proportion with concentration and inverse proportion with temperature as given in table 2.

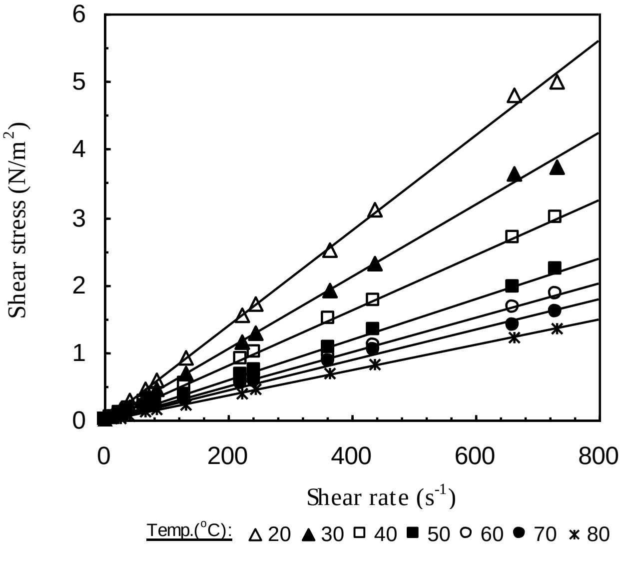

Fig. 1. Shear stress versus shear rate for 15% concentration at different temperatures.

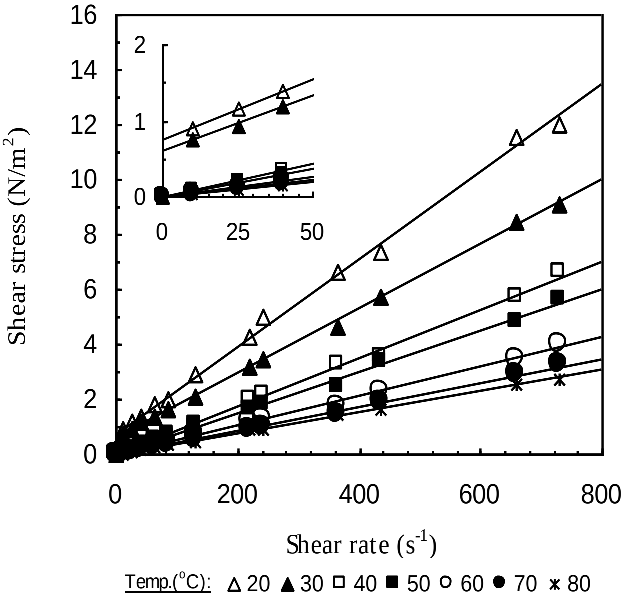

Fig. 2. Shear stress versus shear rate for 20% concentration at different temperatures.

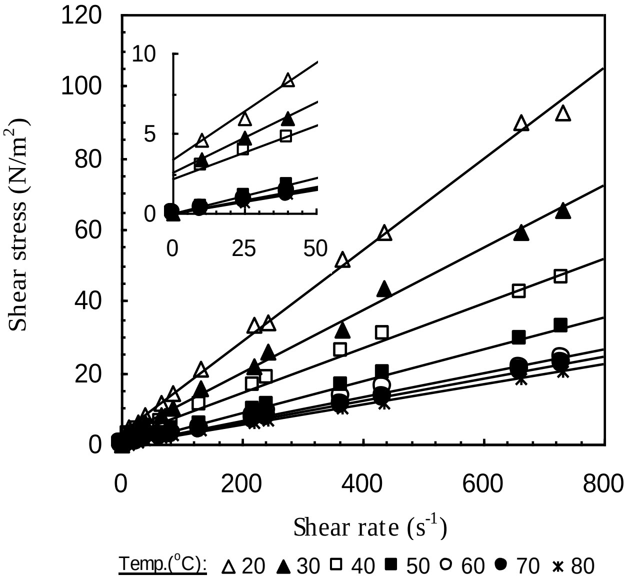

Fig. 3. Shear stress versus shear rate for 30% concentration at different temperatures.

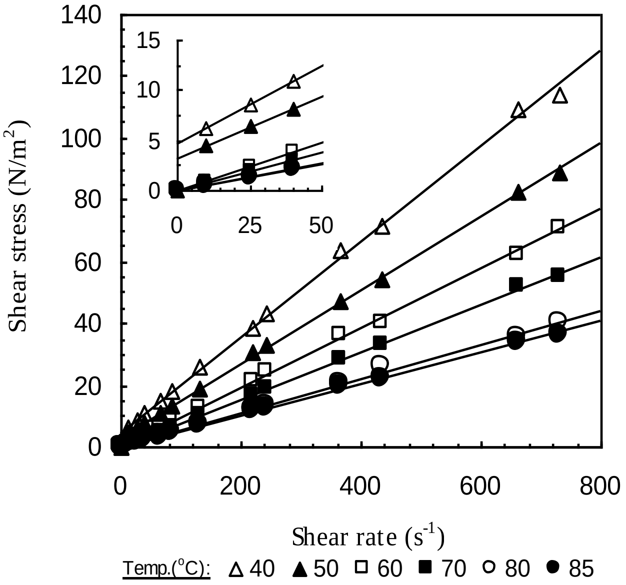

Fig. 4. Shear stress versus shear rate for 40% concentration at different temperatures.

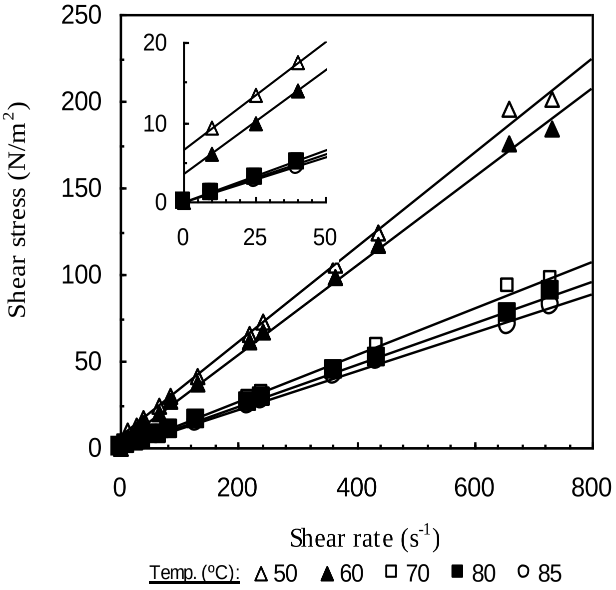

Fig. 5. Shear stress versus shear rate for 45% concentration at different temperatures.

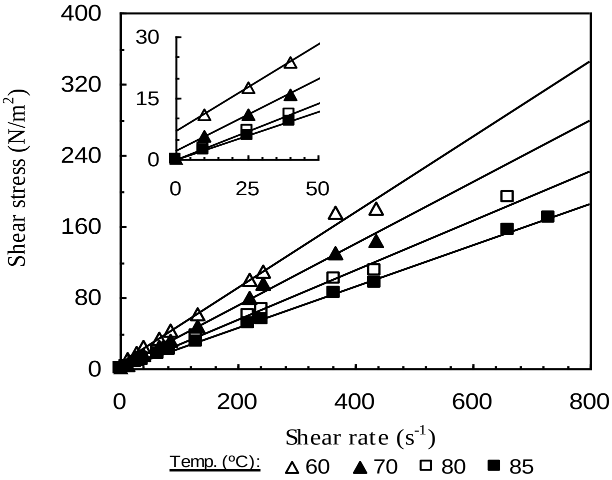

Fig. 6. Shear stress versus shear rate for 52% concentration at different temperatures.

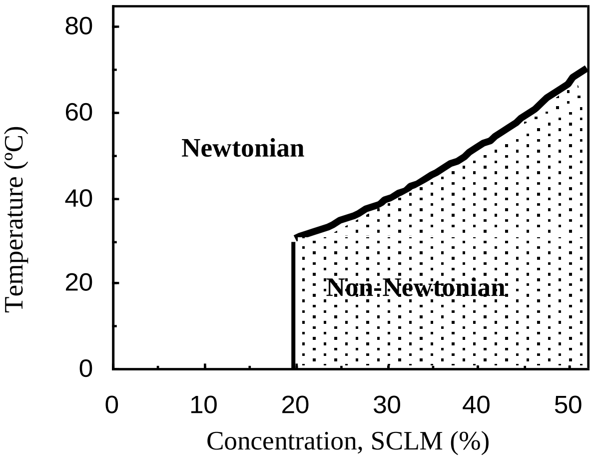

Fig. 7. Transition points from Newtonian to non-Newtonian behavior.

As stated above, there is a condition of temperature and concentration which black liquor behaves as a Newtonian fluid and at other conditions a Bingham plastic is observed. The situation can, at least approximately, be described by the sketch in fig. 7. Transition measurement points should lie on a curve as shown in the figure, clear area is the points representing Newtonian flow and shadow area is non-Newtonian flow. The figure shows that the range of non-Newtonian flow is extended as the temperature is reduced or SCLM increased, i.e. non-Newtonian behavior is more frequent in highly viscous black liquor.

Viscosity data from both capillary and rotational viscometers are summarized in table 2. For the non-Newtonian region, values of the slope of the Bingham model (viscosity or coefficient of rigidity) and the corresponding yield stress are given in table 2. A typical graphical correlation of viscosity data is illustrated in fig. 8 using temperature as a parameter.

Table 2
Viscosity of bagasse kraft black liquor

SCLM %	Factor	Temperature (°C)							
		20	30	40	50	60	70	80	85
0	μ	1	0.801	0.659	0.544	0.470	0.405	0.356	0.337
	S_0	---	---	---	---	---	---	---	---
2.5	μ	1.268	1.049	0.809	0.693	0.680	0.465	0.396	
	S_0	---	---	---	---	---	---	---	
5	μ	1.612	1.439	1.126	0.921	0.826	0.676	0.479	
	S_0	---	---	---	---	---	---	---	
10	μ	3.215	2.879	2.451	2.033	1.629	1.148	0.911	
	S_0	---	---	---	---	---	---	---	
15	μ	7.103	5.323	4.073	2.980	2.533	2.390	1.876	
	S_0	---	---	---	---	---	---	---	
20	μ	15.899	11.800	8.802	7.500	5.299	4.299	3.916	
	S_0	0.746	0.628	---	---	---	---	---	
30	μ	128.30	87.300	62.100	44.500	33.498	30.499	29.012	
	S_0	3.325	2.514	2.313	---	---	---	---	
40	μ			154.99	118.70	95.990	76.799	55.015	52.830
	S_0			4.656	3.295	---	---	---	---
45	μ				270.88	260.60	128.50	120.00	112.30
	S_0				6.684	3.441	---	---	---
52	μ					427.40	351.25	274.70	231.10
	S_0					6.945	2.046	---	---

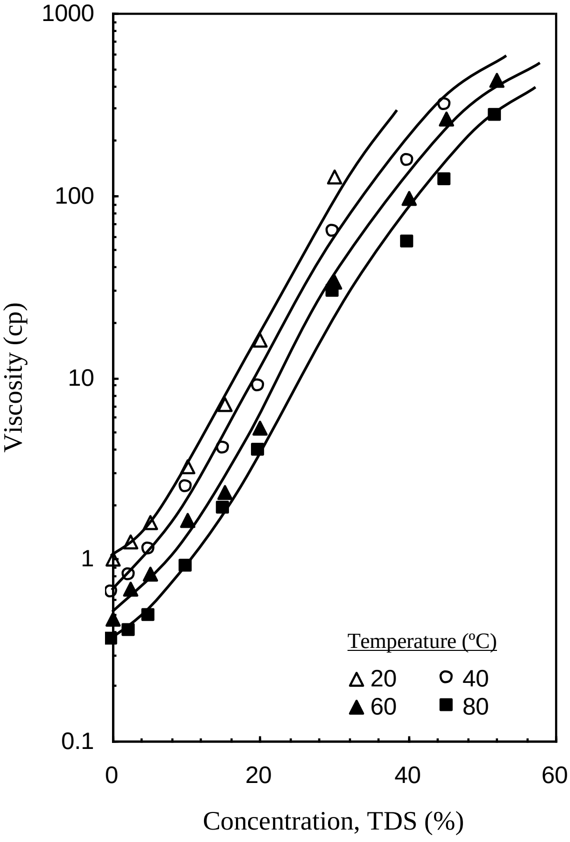

Fig. 8. Viscosity of black liquor a function concentration at different temperatures.

Viscosity of bagasse black liquor at 20 °C increases from 3.215 to 128.3 cP for concentration change from 10 to 30%, the corresponding values at 60 °C are 1.629 and 33.498 cP and at 80 °C are 0.911 and 29.012 cP respectively. The curves in fig. 8 show a sharp increase in viscosity above 20% SCLM that can be generally attributed to an entanglement effect of the dissolved polymeric lignin and carbohydrate (hemicellulose) molecules. Goring and coworkers [10] observed that the degree of polymerization of dissolved lignin molecules increases from 10 to 300 during kraft pulping of spruce saw dust in a laboratory digester with the continuous withdrawal of black liquor from the reaction zone. Condensation reactions between polymeric lignin fragments split of from chips during pulping can also be expected to give higher values of degree of polymerization for the lignin in commercial black liquor [11].

Viscosity data in table 2 can also represented by a linear correlation on a semi-logarithmic plot of ln(μ) vs. reciprocal of absolute temperature (1/T) with concentration as a parameter as illustrated in fig. 9. The sharp increasing in viscosity above 20% SCLM is more obvious in this figure. The viscosity data was correlated in an empirical correlation to predict viscosity of black liquor "μ" (cP) as a function of both concentrations "SCLM" (%) and water viscosity "μ_{water}" (cP) where the later is a function of temperature, eq. (3).

$$\mu = 10^{A}(\mu_{uater})^{B} , \qquad (3)$$

where,

$$A = \sinh\left[2.981(TDS/100)^{0.67}\right]$$

$$B = \cosh\left[1.462(TDS/100)^{0.38}\right]$$

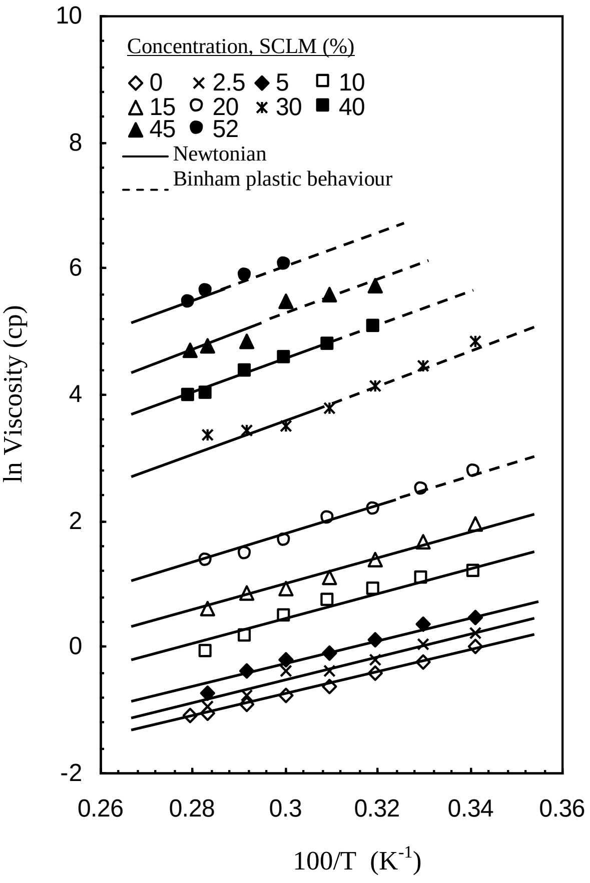

Fig. 9. Logarithmic plot of ln(μ) vs reciprocal of absolute temperature (1/T) with concentration as a parameter.

A comparison between measured and predicted viscosity values is shown in fig. 10. All values approximately fall on the 45° line, i.e the measured and the predicted viscosity values are identical.

Another comparison of present works with other published work that of ref. [9, 12] was carried out in fig. 11. Small differences were found that may be due to the difference in pulping conditions, raw materials, and the method used in determination of viscosity.

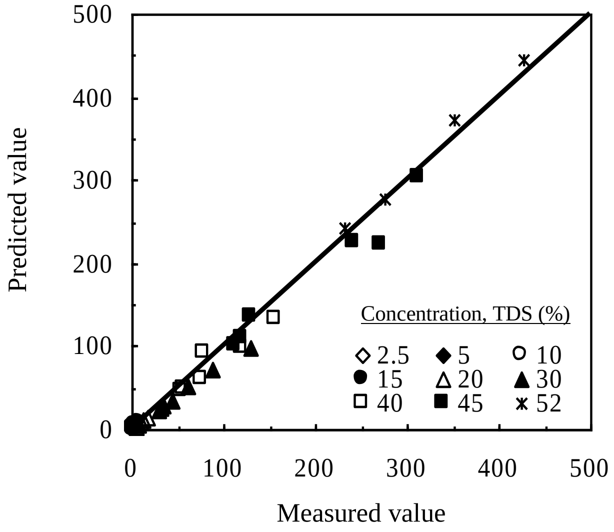

Fig. 10. Comparison between measured and predicted viscosity values for different conditions.

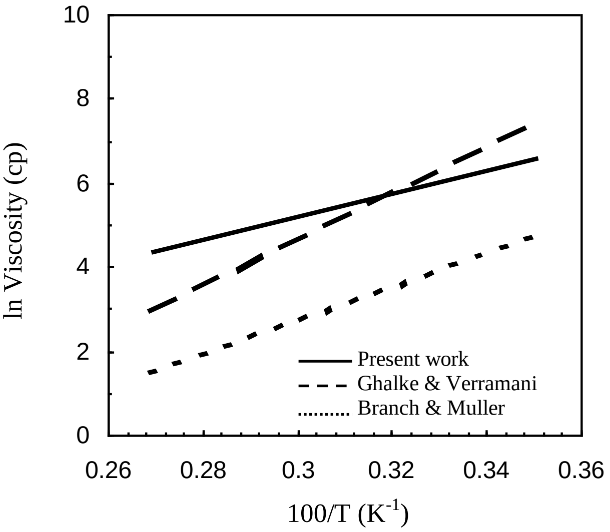

Fig. 11. Comparison between predicted viscosity with other values in literatures for 45% liquor concentration.

5. Boiling point rise

One of the most important knowledge during evaporation process is liquor boiling point and its change with concentration, since normal boiling point of bagasse kraft black liquor has been measured. The Normal Boiling Point Rise (*NBPR*) over the total range of concentrations (2.5%:52%) has been calculated and illustrated in fig. 12. The data of *NBPR* can be correlated in an empirical equation as follow,

$$NBPR = 8.0 * 10^{-5}(TDS^3) - 5.2 * 10^{-3}(TDS^2), + 0.2(TDS), \tag{4}$$

where,

$$T_{sat}^n = 373.15 + NBPR. \tag{5}$$

Eq. (4) applies for normal pressure (101.325 kPa) and to account for pressure effects, the equations used are,

$$\Delta T = \left\{T_{sat}^n \ln(P/P^n)\right\} / \left\{(\Delta h_v^n Mr / RT_{sat}^n) - 0.15\ln(P/P^n)\right\} * \left\{(0.041P/P^n) + 0.942\right\}, \tag{6}$$

where,

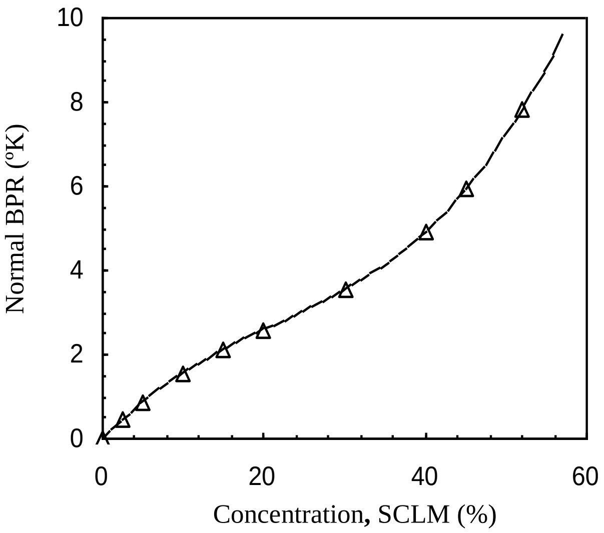

Fig. 12. Normal boiling point rise as a function of liquor concentration.

$$T_{sat} = T_{sat}^{n} + \Delta T \ . \tag{7}$$

Eqs. (6 and 7) are applicable for pressure between 50 and 500 kPa.

6. Conclusions

Viscosity data reported in this work is useful for process calculations in design of a new facilities of performance evaluation and for modifications to existing plant and equipment. Bagasse kraft black liquor behaves as a Newtonian fluid for lower solid concentrations and high temperatures, other than Bingham plastic is observed. Viscosity of bagasse kraft black liquor at low solid content is closed to that of water. Viscosity has a direct proportion with solid content where, it has inverse proportion with temperature. A sharp increase in viscosity was found above 20% of total dissolved solids. A correlation for viscosity of bagasse kraft black liquor has been proposed and compared with other values in literatures. The agreement between the measurements and predictions is excellent, confirming the reliability of the correlation. A small rise for normal boiling point is observed which increases with increasing soilde content in the liquor. The rise in normal boiling point for liquor is correlated in an empirical equation as a function of solid content.

Nomenclature

du/dy	is the shear rate (s^{-1}),
Mr	is the molar mass of water (18.02 g/mol),
$NBPR$	is the normal boiling point rise (K),
P	is the pressure (kPa),
P^n	is the normal pressure (101.325 kPa),
R	is the universal gas constant (8314 J/mol/K),
S	is the shear stress (N/m^2),
S_0	is the limiting value of shear stress (N/m^2),
T	is the temperature, °C or K,
$SCLM$	is the dry solid content "concentration", w/w (%),
Δh_v	is the latent heat of vaporization (kJ/kg), and
μ	is the dynamic viscosity (c.p).

Subscripts-superscripts

n	is the normal , and
sat	is the saturation.

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