PHYSICAL PROPERTIES AND VISCOSITY CONTROL FOR STRONG BAGASSE BLACK LIQUOR BY SALT ADDITION

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ABSTRACT

Considering the increasing cost of petroleum oil, cooking chemicals and severe pollution problems, pulp mills should have suitable chemical recovery system. For design and smooth monitoring of chemical recovery operation it is important to know the behavior of spent pulping liquors. In this work, density of black liquor was measured over a wide range of temperature and solid concentration covers up to 100°C and 70% solid content. The rise in boiling point of black liquor with different solid contents at normal conditions (NBPR) was also determined where, its value was increased from 1.5 to 22°C when solid content increased from 20 to 75%. Viscosity of untreated, thermally and chemically treated black liquors at high solid content (40:75%) was measured at different temperatures ranged from 80 to 110°C. Ammonium thiocyanate salt was added to control black liquor viscosity. In order to evaluate effects of thiocyanate salt and determining the optimum dosage, it was added to achieves 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8M in black liquor. New reliable correlations are obtained to correlate both density and normal boiling point rise (NBPR) with black liquor solid content.

Keywords: Wastewater, Black Liquor, Recovery, Viscosity Control.
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1 INTRODUCTION

The kraft process, accounting for around 80% of world pulp production is the most common chemical pulping process, Hodges & Cullinan (2006). In this operation, the cellulosic materials, wood, rice straw and bagasse, and various chemicals (e.g., NaOH and Na_2S), collectively known as white liquor, are cooked at high temperature and pressure in a digester to produce pulp and a complex residual filtrate, referred to as black liquor due to its dark color. Black liquor contains a mixture of inorganic chemicals and a large amount of organic chemicals, chiefly lignin.

Pulp and paper manufacturing is energy and capital intensive. Energy costs represent around 30% of the total manufacturing costs for a pulp and paper mill , Maheshwari & Sahasrabudhe (2006). The increase in energy and chemical costs in kraft pulping mills has pushed mill managements towards the programmes that will lead to efficient use of energy and, optimal energy and chemical recovery schemes where, the economic success of a kraft pulp mill depends significantly on the operation of its chemical recovery facilities, Piccione (2005). In order to regenerate these chemicals, black liquor is subjected to several environmentally deleterious and energy-intensive treatments such as evaporation and burning. Therefore, any procedure that is potentially capable of improving the recovery boiler operation where the pulping chemicals are regenerated, simultaneously producing steam and energy for the entire mill should be given special consideration.

It has been reported that recovery boiler operations can be enhanced by firing black liquor at high solids contents, Porter & Maki (2004). There are a number of operational and economic benefits accruable from firing black liquor in the recovery boiler at high solids concentrations. Such benefits include: improvement in thermal efficiency, higher reduction efficiency, reduction in environmental emissions, increased liquor throughput, increased pulping capacity, improved bed stability and control, Brewster (2007). Although it is both economically and operationally beneficial to fire black liquor at high solids concentrations in the recovery boiler, the corresponding increase in viscosity of the liquor is the limiting factor. Viscosity beside density affect the heat transfer in the evaporation units, capacity of pumps and the spray characteristics of the liquor in the recovery boiler, Porter & Sands (2010).

Improved process design begins with using accurate physical property data of the process streams especially in the preliminary design stages. Several studies on the physical properties of black liquor from different resources of cellulosic materials have been found in the literature, Branch Muller (1991), Nassar et al., (2007). Although salting-in has been recognized for many years and has been employed in applications such as cloud point manipulation, its effectiveness in modifying the rheological behavior of complex aqueous solutions such as black liquor has not been fully examined. Addition of NaSCN salt to control viscosity of different polymers have been investigated, Prevysh et al., (1996b). Since the goal of this research is to enhance black-liquor processing through tailored viscosity reduction, ammonium thiocyanate (NH_4SCN) was examined as a structure-breaking salt in order to reduce black liquor viscosity. NH_4SCN was added with different molar concentration to evaluate the effect of dosage. Beside examination of viscosity, both density and boiling point rise for the thermally treated black liquor (process stream in Quena company) has been measured.

2 MATERIALS AND MEASUREMENTS

Black liquor: The black liquor used in this study was an Egyptian black liquor resulting from Kraft pulping of bagasse, it was provide from Kous pulp mill, Quena Paper Industry Company, Egypt. The black liquor was taken after evaporation unit at a 65% dry solid content as a weight percent. Other concentrations of the black liquor test samples were prepared by appropriate dilution or evaporation. The chemical analysis of black liquor used in this study is presented in Table 1.

Table 1. Constituents of bagasse kraft black liquor, wt% (without ash).

Particular	Value	Elemental analysis	Value
Concentration	65.0	Total carbon, C	33.9
pH	12.5	Total hydrogen, H	3.40
Organic	79.3	Total oxygen, O	41.8
Inorganic	20.7	Total sulfur, S	0.72
Lignin	25.9	Total Sodium, Na	19.1
Carbohydrates	53.4	Total potassium, K	< 0.1
Residual Active Alkali (RAA) as Na_2O, g/l	4.30	Total nitrogen, N	0.20
Total Alkali (TA) as Na_2O, g/l	15.5	Chlorine, Cl	0.07
		Silica, Si	0.75

Measurement: Viscosity of black liquor of different concentrations from 40 to 75% (TDS) and different temperatures up-to 110ºC was measured using a rotational viscometer, Brookfield DV-II+Pro viscometer. Density of black liquor at different concentrations (from 5% to 70%) and different temperatures up to 100°C was measured using density bottle and oil bath (±0.2°C). The normal boiling point rise (NBPR) is the difference in boiling temperature between the solution and the pure solvent when measured at normal pressure.

3 RESULTS AND DISCUSSION

Viscosity: The untreated black liquor viscosity at different concentrations up to 75% solid content and different temperatures covers up to 110°C was presented in "Fig. 1". It is clear that viscosity has a direct proportional with concentration and an inverse proportional with temperature. The viscosity increased dramatically for dry solid contents above 60% for all temperature ranges. It increases from 128 to 2200 c.poise when concentration increases from 40% to 75% at 80°C, the corresponding values at 100°C are 85 to 1726 c.poise respectively. The sharp increase in viscosity above 60% dry solid contents can be generally attributed to an entanglements effect of the dissolved polymeric lignin and carbohydrate (hemicellulose) molecules. McNaughton et al. (1967) observed that the degree of polymerization of dissolved lignin molecules increased from 10 to 300 during Kraft pulping of spruce saw dust. Condensation reactions between polymeric lignin fragments split off from chips during pulping can also be expected to give higher values of degree of polymerization for the lignin in commercial black liquor.

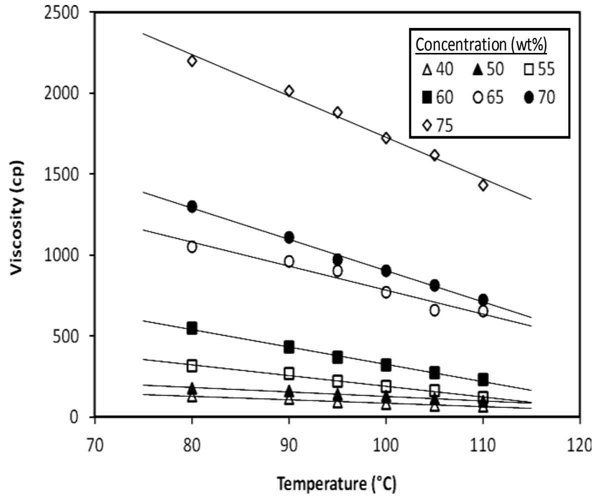

Figure 1. Viscosity of thermally untreated black liquor.

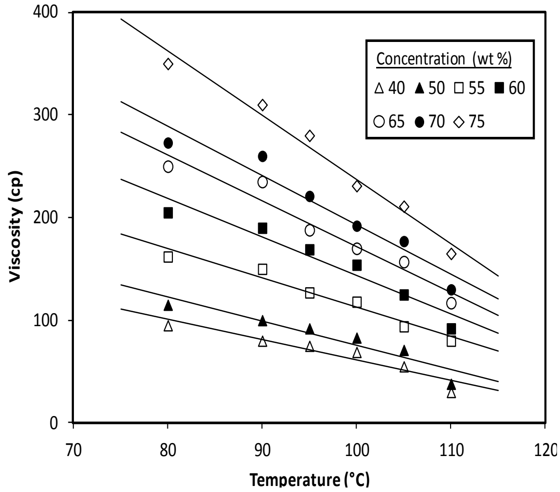

Figure 2. Viscosity of thermally treated black liquor.

One of the acceptable ways to control black liquor viscosity is the thermal treatment process, where black liquor is heated to a temperature higher than cooking temperature for a specified time. Figure 2 represents viscosity measurements for thermally treated black liquor at different concentrations and temperatures. The viscosity was increased from 95 to 350 c.poise when concentration increased from 40% to 75% at 80°C, while it was increased from 30 to 165 c.poise corresponding to 110°C. Comparing with data of the untreated black liquor presented in Fig.1 viscosity is decreased to a lower range when treated thermally. The dramatic increases of viscosity at higher concentrations is not present, only viscosity increased gradually with concentration. The heat treatment depolymerized the high molecular weight lignin and polysaccharides. The effect of heat treatment increases with concentration of black liquor i.e., at 80°C for 40% concentration the viscosity was 95 and 128 and c.poise for treated and untreated black liquor respectively, in other way the reduction in viscosity at this conditions was 25.8%. Conversely for 75% concentration the reduction was 84.1%.

An alternative approach based on the concept of salting-in to achieve lower viscosity of black liquor. Addition of thiocyanate (SCN-) salts permits control and reduction of black-liquor viscosity by more than two orders of magnitude in some cases. The effect of adding ammonium thiocyanate (NH_4SCN) salt on the black liquor viscosity with different solids concentrations and temperatures was examined. In order to investigate effects of NH_4SCN concentration on black liquor viscosity, different weight of it was added to achieves 0.3M, 0.4M, 0.5M, 0.6M, 0.7M and 0.8M of ammonium thiocyanate. Salt-modified black liquor solutions were prepared by adding predetermined quantities of NH_4SCN salt crystals to already concentrated black liquor samples (thermally untreated). The mixtures, covered to avoid premature water evaporation, were then stirred vigorously and heated at approximately 40°C for 30 min to promote salt dissolution. At each concentration from NH_4SCN, black liquor viscosity was measured for all concentrations (40% to 75%) and temperature ranges (80°C to 110°C). Figures 3 represents viscosity for black liquor treated with 0.3M, 0.4M, 0.6M, and 0.8M NH_4SCN respectively. It is clear from plots, that the addition of NH_4SCN substantially decreases the viscosity of black liquor over a broad solids range, the relative efficiency of salting-in is strongly dependent upon the concentration of salt added. Values of viscosity for all treated black liquor exhibit a substantial decrease with increasing salt concentration, supporting the idea that SCN- ions break the structure of water and salt-in the polymeric components of black liquor. The illustrated figures indicate reveal that addition of salt to a more concentrated liquor yields a more pronounced effect on measured viscosity.

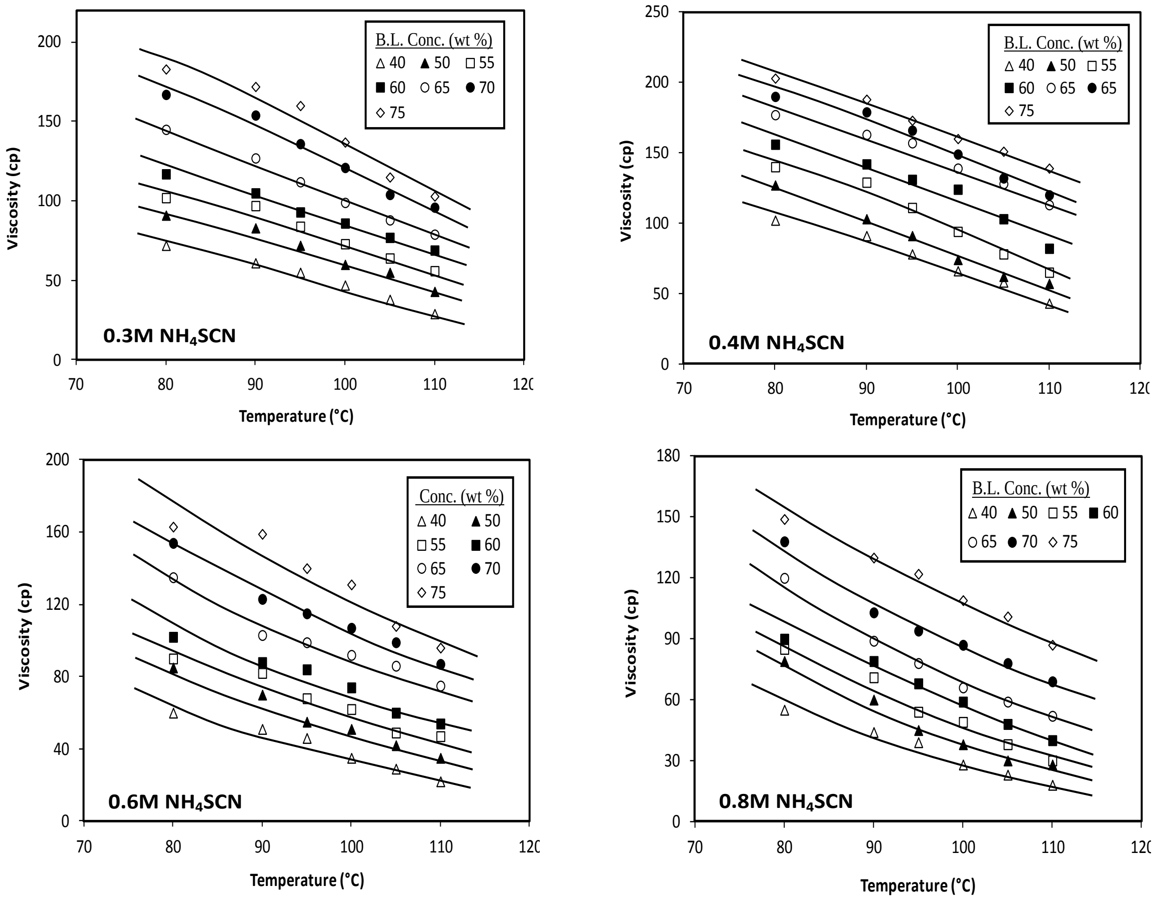

Figure 3. Viscosity of black liquor treated with different dosages of NH_4SCN.

Close examination of black liquor treated with 0.3M NH_4SCN, the viscosity of the 75% solids, decreases by 90.8%, whereas for 40% solids is reduced by a factor of 20.3%, this comparison at 80°C when compared with the viscosity of virgin black liquor. Another comparison for black liquor treated with 0.8M NH_4SCN, the viscosity of the 75% solids black liquor, decreases by 92.0%, whereas it decreases by 57.0% for black liquor of 40% solid content at 80°C. Conversely, at temperature 110°C, viscosity of the 75% solids black liquor, decreases by 93.9%, whereas the viscosity of the 40% solids sample is reduced by a factor of 73.1%. With less water present in a concentrated liquor solution, the salt may have a more noticeable effect because a larger number of salt molecules are present per water cluster. In this case, more water structures may be broken, reducing the viscosity more dramatically than in a lower solids content liquor.

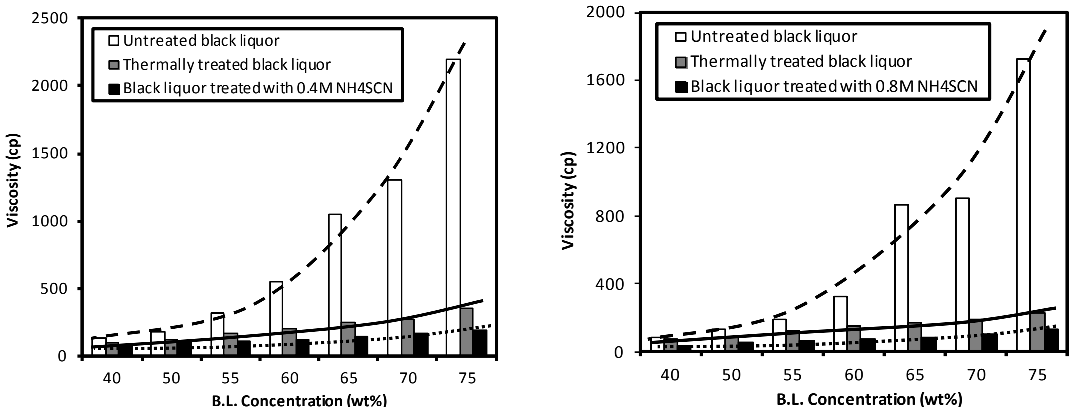

Figure 4. Comparison between viscosity of untreated, thermally treated and the treated with NH_4SCN black liquors at 80°C.

The chemical treatment of black liquor with NH_4SCN to reduce viscosity is evaluated by comparing it with the heat treatment process as well as the untreated black liquor (virgin black liquor). Figure 4 represents this comparison at two different conditions, 80°C for 0.4M NH_4SCN and 100°C for 0.8M NH_4SCN respectively. In general, effect of the two treatment processes increase with increasing concentration, and viscosity of black liquor which treated with NH_4SCN is lower than that treated thermally for all concentrations and temperatures range studied. There is a sustainable decreases in viscosity with increasing salt concentration, confirming that SCN^- ions break the structure of water and salt-in the polymeric components of black liquor.

Density: Black liquor density at different solids content ranged from 5% to 70% and different temperatures up to 100°C was measured using density bottle where different temperature was achieved by temperature control water bath. The results obtained indicated that, black liquor density increases with concentration and decreases with increasing temperature "Fig. 5". The presented data are average of two determinations. Density of low concentration black liquor at 100°C is not include due to evaporation effects while values for high concentrations at low temperatures also not includes due to non fluidity effects. The slopes of these lines increased from low concentration to the high concentration, means temperature affects more on the higher black liquor concentrations. The density data was correlated in an empirical correlation to predict density of black liquor "ρ" (kg/m^3) as a function of concentration "S" (wt%) and water density "ρ_{water}" (kg/m^3) where the later is a function of temperature as follow:

$$\rho = \rho_w[1 + 0.00628(S)]$$

A comparison between measured and predicted density values was done and approximately all values fall on the 45º line, i.e the measured and the predicted values are identical with $R^2 = 0.96$.

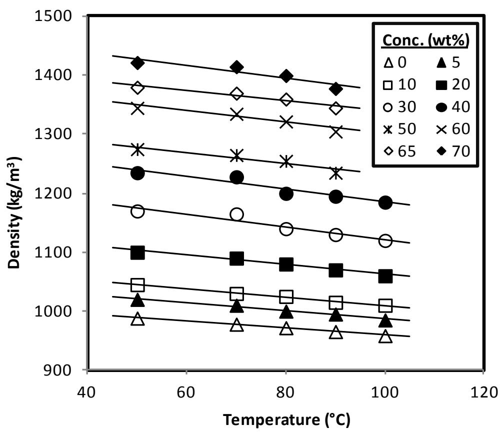

Figure 5. Density of thermally treated black liquor versus temperature.

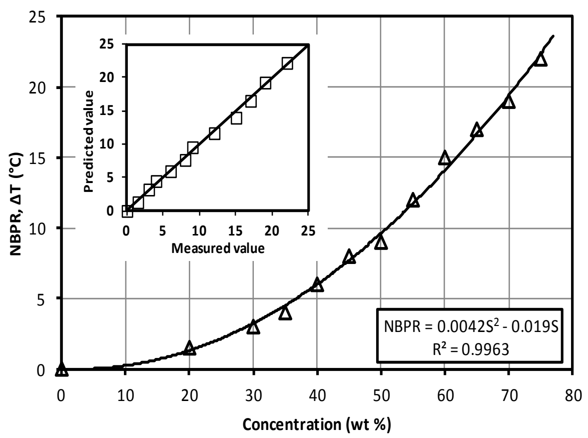

Figure 6. NBPR as a function of black liquor concentration (thermally treated).

Boiling Point Rise (BPR): BPR and its changes with the black liquor concentration is an important knowledge during evaporation process as well as for all processes include thermal energy transport. Boiling point of bagasse kraft black liquor at normal pressure (101.3 kPa) has been measured over a wide range of liquor concentrations (20%:75%), it named as normal boiling point (NBP). Since normal boiling point of bagasse kraft black liquor has been measured, the normal boiling point rise (NBPR) has been calculated and illustrated in "Fig. 6". Initially, the BPR increases slowly but above 40% dry solids it increases very rapidly. The measured values of NBPR can be correlated in an empirical equation as follow,

$$NBPR = 4.2 * 10^{-3}(S^2) - 0.019(S)$$

where, NBPR is in °C and. The normal boiling point is calculated from $T_{sat}^{n} = 373.15 + NBPR$.

In order to evaluate the validity of the estimated equation, a comparison between measured and predicated values over the studied concentration range has been done on 45° line as presented in "Fig.6" inner plot. It is clear that all points contacts with the 45° line, means the predicted equation simulates the data well, the correlation coefficient, R^2 was > 0.99. The above equation applies for normal pressure conditions (101.325 kPa) and to account for pressure effects, the following equation is necessary, Gullich & Fogelholm (2000).

$$BPR / NBPR = 1 + 0.6\left(T_p - 3.7316\right)/100$$

where, *NBPR:* is the normal boiling point rise (°C), *BPR*: is the boiling point rise for specified pressure (°C), T_p : is the boiling temperature of water at specified pressure (K).

4 CONCLUSIONS

The results demonstrate that black liquor viscosity reduction through addition of NH_4SCN is extremely promising. Treatment of black liquor with NH_4SCN, increases solubility where, SCN-ions break the structure of water and salt-in the polymeric components of black liquor. The observed increase in viscosity reduction at higher solids content. A correlation for density of bagasse kraft black liquor has been proposed and evaluated using 45° line. 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.

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