

Physical and Chemical Properties of Effluent from the Pre-Conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulp (P-RC APMP) Process

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The properties of P-RC APMP effluent, including relative density, Baume degree, viscosity, surface tension, specific heat capacity, boiling point rise (BPR), and elemental contents of the effluent, were studied. Results indicated that relative density, viscosity, Baume degree, and solids content all displayed a direct proportional correlation; however, there was an inverse linear relationship between Baume degree and temperature. Viscosity rose sharply when the solids content was more than 40%. Surface tension gradually decreased with the rise of solids content. However, when the solids content was over 35%, it increased with an increase in solids content. Specific heat capacity was closely related to the solids content, but it was reduced with an increase in solids content. BPR was proportional to effluent solids content, especially when the solids content exceeded 30% with an uptrend in BPR.

Keywords: P-RC APMP; Effluent

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INTRODUCTION

Pre-conditioning Refiner Chemical Alkaline Peroxide Mechanical Pulp (P-RC APMP) process is an advanced chemi-mechanical pulping technology for the production of high-quality high-yield pulps from hardwoods. To achieve zero-discharge of effluent at P-RC APMP or BCTMP pulp mills, effluent from the P-RC APMP or thermo-mechanical pulping process is treated in the recovery of black liquor from kraft pulping. The effluent is concentrated from about 2% solids to about 70% solids by evaporators. Then the concentrate is incinerated in a recovery boiler. An evaporation plant consists of heat transfer units connected in various configurations. To design the plant properly, several properties of the effluent require consideration. The recovery boiler performance may be affected by effluent properties as well. Therefore, several important properties of P-RC APMP effluent were studied in the current work.

Relative density, Baume degree, viscosity, surface tension, specific heat capacity, and the boiling point rise (BPR) of P-RC APMP effluent are the most important factors to consider for evaporator and recovery boiler design and operation. The density of P-RC APMP effluent has an effect on its flow properties and static pressure. At the same temperature, the density of low solids content P-RC APMP effluent is similar to that of water. But the density of a high solids content effluent depends on its inorganic and organic contents. The amount of inorganics has an important influence on density,

because typical inorganic-contaminated effluents are twice the density of water, whereas most organic effluents have a similar density to water (Sandquist *et al.* 1983).

The viscosity of an effluent is an important hydrodynamic parameter to consider, and it depends on its components, solids content, temperature, pulping variables, and wood species. Viscosity affects the evaporation rate and the heat transfer rate of effluent (Carroll *et al.* 2009). Evaporator capacity can be significantly affected by changes in viscosity.

Surface tension (ST) is important property in determining the droplet size at the time of atomization of concentrated liquor for combustion (spray drying) and nucleate boiling. Viscosity and surface tension influence spray size distribution and droplet combustion. Surface tension decreases with an increase in concentration and temperature of black liquor. At a fixed temperature, surface tension falls rapidly with increasing solids content (10% to 40% of total solids); in addition, the organic part of the black liquor strongly influences surface tension (PAPER MART 2009).

Surface tension is also an important factor for the reduction of foaming and surface activity of the P-RC APMP effluent, and it has a tremendous influence on the foaming tendency of effluent as induced by gas agitation. The smaller the surface tension, the stronger the foaming tendency.

The specific heat capacity represents the heat necessary to raise the temperature of 1 kg of a material by 1 °C (Sixta 2006). Enthalpy data for P-RC APMP effluent are essential for estimating energy balances of recovery boilers. The specific heat capacity of the effluent is also a necessary factor for the calculation of the heat evaporation.

Boiling point rise (BPR) refers to the difference of boiling point between the P-RC APMP effluent and pure water at the same pressure. BPR is useful for the design and operation of an evaporator system, and is generally specific for each effluent, and depends on the amount and composition of the dissolved substances (Clay and Grace 1984). BPR increases with increasing of solids and inorganic content of liquor. BPR is especially important in effluent evaporation because it reduces the available temperature differential for heat transfer (PAPER MART 2009).

EXPERIMENTAL

Materials and Instruments

Hardwood chips (mixed chips of poplar, eucalyptus, and acacia) P-RC APMP effluent used in the experiment was from the Sun paper Co., LTD., Yanzhou, Shandong Province.

The experimental instruments included a NDJ-5S rotary viscometer, an FD-LCD-A specific heat detector, a KRUSS K9-MK1 surface tension-automatic, and a Vario Micro Cube elemental analyzer.

Experimental Process

In a typical experiment, the physical properties of P-RC APMP effluent were measured by conventional methods, including the use of a Baume gauge for Baume degree, while relative density, viscosity, and surface tension were measured with a hydrometer, rotary viscometer, and surface tension-automatic, respectively. Before testing, the effluent was evaporated to a desired solids content with a RE-52AA rotary evaporator in the laboratory.

RESULTS AND DISCUSSION

Relative Density

The density of an effluent is usually expressed as relative density. At low solids content, the density of the black liquor is close to that of water. At higher solids contents, it depends on the nature of the inorganic and organic materials that constitute the solids.

Relative density is a function of solids content and temperature. Figure 1 shows the relationship between relative density and solids content. The relative density is nearly directly proportional to the solids content at 15 °C. From Fig. 2 it can also be seen that relative density of P-RC APMP effluent and temperature display an inversely proportional relationship.

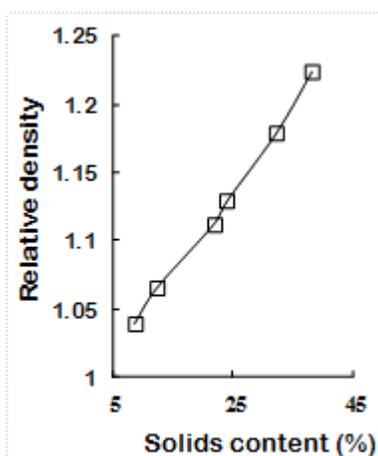


Fig. 1. Relationship between relative density and solids content (at 15 °C)

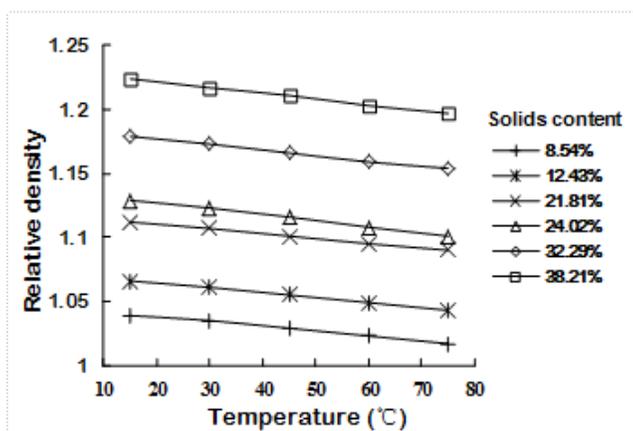


Fig. 2. Relationship between relative density and temperature

Baume Degree

The measurement of density takes a long time, and thus it cannot be carried out in a convenient enough manner to affect a mill change. Pulp mills measure the relative density by a Baume hydrometer scale to represent solids content. The readings from Baume hydrometer are called Baume degrees. Baume degree is a function of solids content and temperature. The results showed that Baume degree and solids content have a linear relationship at 15 °C (Fig. 3). Given the difference of temperatures, the Baume degree of P-RC APMP effluent varied at a fixed solids content. Figure 4 shows that the Baume degree and solids contents displayed an inverse linear relationship.

Viscosity

Results showed that the viscosity of P-RC APMP effluent increased as the solids contents rose and decreased as the temperature increased. Figure 5 demonstrates that when the solids content was low, it had no significant effect on the viscosity, but when the solids content surpassed approximately 40%, there was a sharp increase in viscosity, with the "critical solids content" of P-RC APMP effluent being about 40%. The influence of temperature on viscosity was not evident when the concentration was low, but as the concentration increased, the impacts of temperature on viscosity became more and more obvious. When the concentration and viscosity of effluent were both high, it was found

that the impact of low temperature was evident and the impact of high temperature was relatively small relative to viscosity.

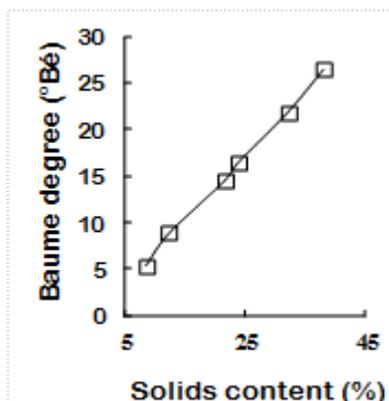


Fig. 3. Relationship between Baume degree and solids content

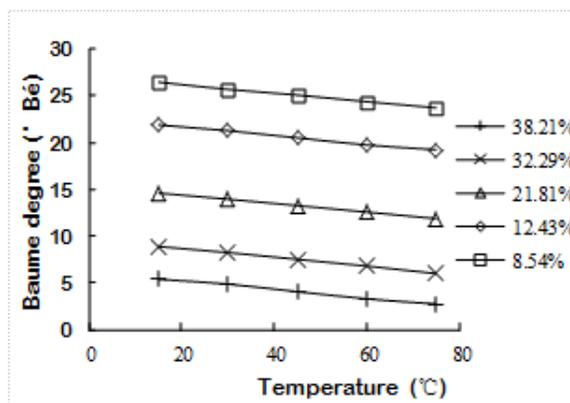


Fig. 4. Relationship between Baume degree and temperature

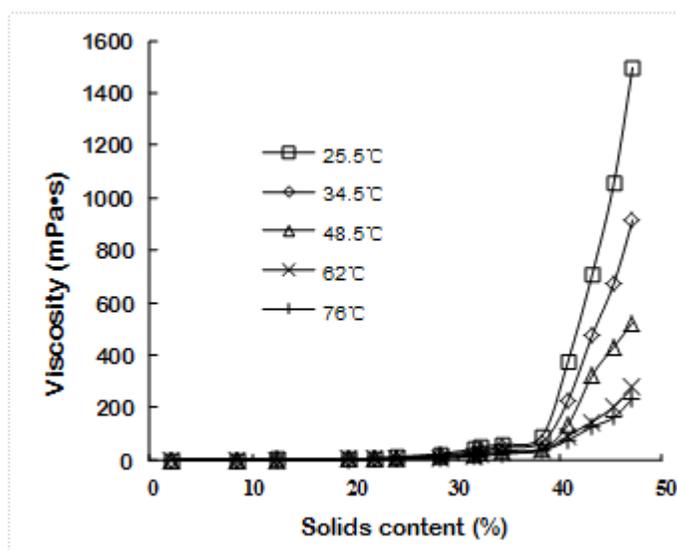


Fig. 5. Effects of solids content and temperature on viscosity

Surface Tension

For a binary solution, surface tension is a function of temperature (T) and solids content (c), *i.e.*, $\sigma = f(T, c)$. For various solutes, the relationship between surface tension and different solids contents is not so straightforward. For an inorganic electrolyte solution, the surface tension increases as the solids contents increases, but trends were opposite with organic aqueous compounds (Ali *et al.* 2006). At a given solids content, the surface tension of an inorganic electrolyte solution decreased linearly with increasing temperature, but displayed a different activity with organic compounds; the relationship of surface tension and temperature is more complicated. Some researchers have reported

that the surface tension over a certain temperature range increases as the temperature increases with a particular solids content (Gliński *et al.* 2000; Romero *et al.* 2007; Savinoa *et al.* 2007).

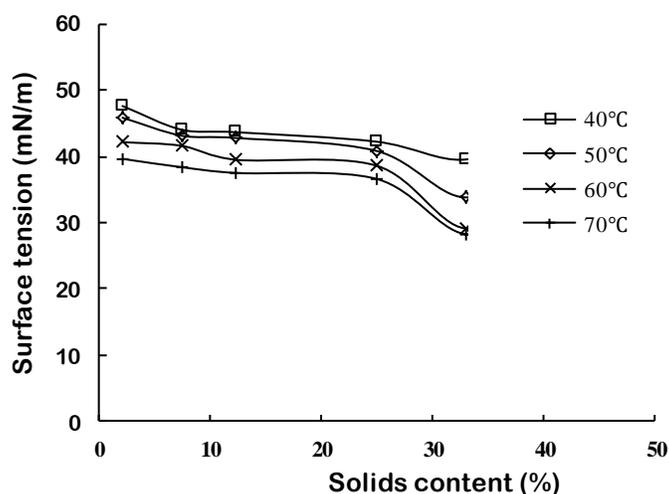


Fig. 6. Relationship between surface tension and solids content

Figure 6 shows that along with the increase of solids content, surface tension first decreased gradually, but when solids content exceeded about 35%, the surface tension increased. As the temperature increased, the surface tension of P-RC APMP effluent decreased gradually. At higher concentrations, the influence of temperature on surface tension was larger, while at lower concentrations, the temperature had less of an influence on surface tension.

Specific Heat Capacity

Specific heat capacity of P - RC APMP effluent depends on the heat capacities of the constituents. Any increase in dry solids content would decrease specific heat capacity (Fig. 7). This result is similar to the heat capacity of the kraft black liquor. The heat capacity of the black liquor decreases along with the increase in dry solids content (Sixta 2006).

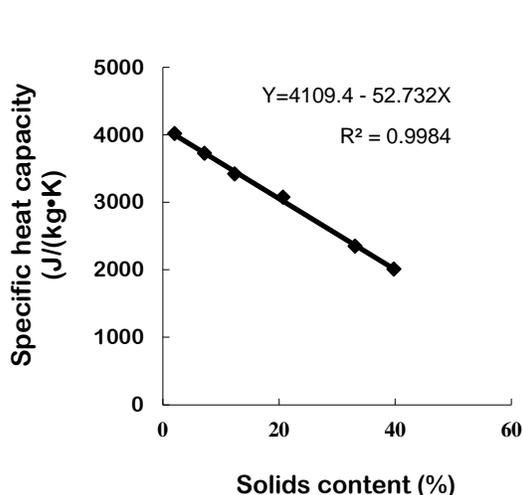


Fig. 7. Specific heat capacity as a function of solids content

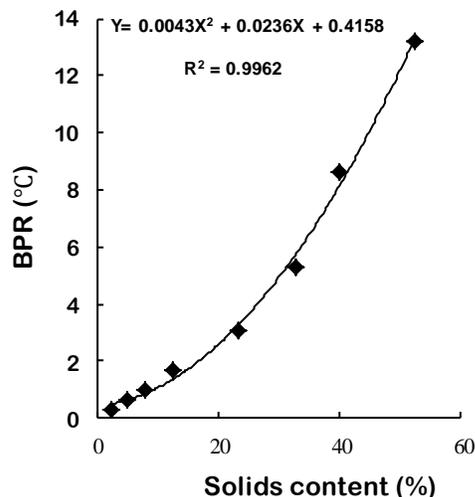


Fig. 8. BPR as a function of solids content (at atmospheric)

Boiling Point Rise (BPR)

BPR of the effluent is an important factor to consider for the design and operation of an evaporator system; high BPR obviously reduces the capacity for heat and mass exchange. BPR was proportional to solids content, as shown in Fig. 8. When the solids contents were lower, an increase in the BPR was not evident; however, when the solids contents were more than 30%, along with the increases of solids content, the BPR increased and more rapidly.

Element Analysis

A Vario Micro cube elements analyzer was used to determine the C, H, and N composition of P-RC APMP effluent dry solids. Results showed that the percentages of carbon, nitrogen, and hydrogen in P-RC APMP effluent dry solids were 31.18%, 0.46%, and 3.93% respectively.

CONCLUSIONS

Relative density and Baume degree were directly proportional to the temperature and have an inverse linear relationship with temperature.

The viscosity of the P-RC APMP effluent was increased along with an increase in solids content, and it was reduced with a rise in temperature. There were no significant effects of low solids content on viscosity until the density surpassed approximately 40%, where there was a sharp increase in viscosity; thus, the "critical solids content" of P-RC APMP effluent was judged to be about 40%. From a different perspective, the impact of temperature on viscosity becomes more and more significant along with an increase in solids contents.

Along with a solids contents increase, the surface tension of P-RC APMP effluent was reduced gradually, until it exceeded about 35%, at which point it went up. With an increase in temperature, the surface tension decreased. The higher the amount of solids contents, the greater the impact of temperature on surface tension.

With the content of solids rising, the heat capacity of P-RC APMP effluent decreased, where it showed a good inverse linear relationship with solids content.

Boiling point rise (BPR) became greater as the solids contents rose, where it showed a small change at low solids contents. However, when the solids contents exceeded 30%, the BPR increased much more rapidly.

Elemental analysis is important for the recovery boiler design. The proportion of the C element in the P-RC APMP effluent dry solids was the 31.18%, while nitrogen and hydrogen were 0.46% and 3.93%, respectively.

REFERENCES CITED

Ali, K., Anwar, H., Bilal, S., and Siddiqi, S. (2006). "Concentration and temperature dependence of surface parameters of some aqueous salt solutions," *Colloids and Surfaces A: Physicochem. Eng. Aspects* 272, 105-110.

- Carroll, K. C., Taylor, R., Grayb, E., and Brusseaua, M. L. (2009). "The impact of composition on the physical properties and evaporative mass transfer of a PCE-diesel immiscible liquid," *Journal of Hazardous Materials* 164, 1074-1081.
- Clay, D., and Grace, T. M. (1984). "Measurements of high-solids black liquor boiling point rise," *Tappi Journal* 67(2), 92-95.
- Gliński, J., Chavepeyer, G., and Platten, J. K. (2000). "Untypical surface properties of aqueous solutions of 1,5-pentanediol," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 162(1-3), 233-238.
- PAPER MART. (2009). "Black liquor properties and impact on Recovery Island Operation," (<http://papermart.in/2009/03/04/black-liquor-properties-and-impact-on-recovery-island-operation>.)
- Romero, C. M., Páez, M. S., Miranda, J. A., Hernández, D. J., and L. E. Oviedo (2007). "Effect of temperature on the surface tension of diluted aqueous solutions of 1,2-hexanediol, 1,5-hexanediol, 1,6-hexanediol and 2,5-hexanediol," *Fluid Phase Equilibria* 258(1), 67-72.
- Sandquist, K. (1983). "Rheological properties and evaporation of black liquor at high dry-solids content," *Pulp & Paper* 84(2), 30-34.
- Savino, R., and di Francescantonio, N., Fortezza, R., Abe, Y. (2007). "Heat pipes with binary mixtures and inverse Marangoni effects for microgravity applications," *Acta Astronautica* 61(1-6), 16-26.
- Sixta, H. (2006). *Handbook of Pulp*, Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim, Germany, 972 pp.

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