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LOWERING KRAFT BLACK LIQUOR VISCOSITY BY ULTRAFILTRATION

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ABSTRACT

High viscosity is a major factor limiting the percentage total dissolved solids (%TDS) to which kraft black liquor (KBL), a spent pulping liquor, can be concentrated before it is burned to recover its fuel value and its inorganic chemicals. The effect on black liquor viscosity of removing high molecular weight lignin by ultrafiltration of 16% and 24% TDS liquors was studied.

Viscosities of ultrafiltration permeates were reduced relative to feed black liquors. When a permeate was concentrated to higher %TDS levels, its viscosity decreased yet further relative to feed samples evaporated to similar solids levels. Retentate viscosity was very high relative to both feed and permeate.

Ultrafiltration was carried out at 75°C using polysulfone membranes in a plate-and-frame or hollow fiber system. Flux rates varied greatly depending upon the specific liquor used. Flux was enhanced by increased temperature and increased linear velocity. The membrane molecular weight cutoff (MWCO) typically used was 50,000; increasing MWCO to 100,000 or 200,000 did not enhance flux.

INTRODUCTION

Kraft black liquor (KBL) contains high concentrations of inorganic salts, low molecular weight organic acids, and the degradation products of the complex polyphenolic compound, lignin.

The lignins in black liquor have molecular weights varying from <1,000 to >50,000. Ultrafiltration has been previously used with kraft liquor for several purposes. Forss and Fuhrmann recovered the high molecular weight retentate lignin for use in adhesives (1); and, Gregor et al. (2) and Alen et al. (3) examined the recovery of permeate low molecular weight organic acids. The possibility that ultrafiltration could be used to partially concentrate kraft liquor while removing high molecular weight lignin was considered by Woerner and McCarthy (4). Kirkman et al. recently published a work on the economic feasibility of recovering lignin by ultrafiltration (5).

The purpose of this study was to explore the feasibility of using ultrafiltration to significantly lower the viscosity of kraft liquor by removing high molecular weight lignin. Kraft liquor, after the removal of pulp and the addition of pulp wash water, has 15 to 16% TDS. This dilute liquor is concentrated to ca. 65% TDS before burning to recover both its energy value and inorganic salts. A major factor limiting liquor concentration beyond 65% is its high viscosity. If the viscosity could be lowered by removal of high molecular weight lignin, the liquor could potentially be concentrated to higher %TDS levels before burning. Resultant energy savings for a 1,000 ton/day pulp mill were calculated at ca. 2 x 10 10 Btu/yr for each percentage increase in %TDS (6). Another advantage of removing a portion of the lignin relates to the fact that many mills are recovery limited, i.e., concentration or burning of liquor solids is the limiting factor in pulp production. If a portion of the KBL solids could be advantageously removed, the production capacity of a mill could be increased.

EXPERIMENTAL

Kraft liquors. A Maine 70% hardwood-30% softwood liquor mix was most often used in the ultrafiltration runs. (Although hardwoods and softwoods are pulped separately, the liquors may be mixed before the concentration step.) Other liquors used, softwood and hardwood, were obtained from North Carolina and Alabama mills. After collection, liquors were filtered through bags with 100 micrometer pores to remove particulate materials. They were then refrigerated under N_2 until used.

Ultrafiltration systems and runs. The DDS Corp. Minilab 10 (Plate and Frame, 336 cm 2) and Romicon Corp. Lab 5 (Hollow Fiber, 0.46 m 2) were described earlier (7). Comparative work was also done with A/G Technology Corp. hollow fiber cartridges (327 cm 2). Polysulfone membranes and cartridges capable of withstanding the liquor pH of 12.5 to 13 and the liquor temperature of 75 C were used.

For ultrafiltration runs described in this study, a temperature of 75°C was used and 88% of the feed liquor was recovered as permeate.

Average transmembrane pressure was between 103 and 172 kPa. Linear velocities of the liquor across the membrane surface, if not otherwise noted, was 1.25 m/sec. Typically, 4 L of feed were used for the DDS Corp. Minilab 10 and A/G Technology runs and 24 L for the Romicon Lab 5 runs. Ultrafiltration runs were done using 16% TDS liquors or those partially evaporated to 24%.

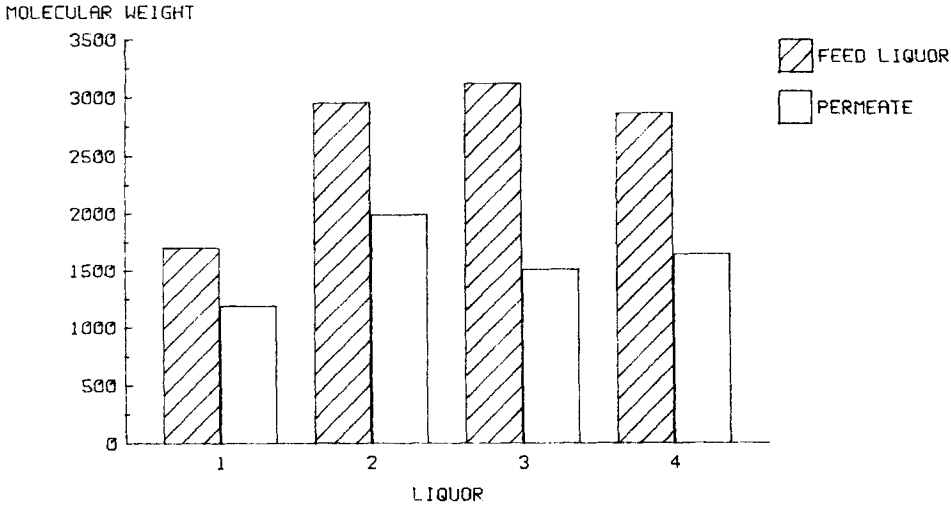
Evaporation of KBL and KBL fractions. Evaporations of small volumes (1 to 1.5 L) of feed liquors, permeates, and retentates were carried out in a hood using stainless steel beakers contained within heating mantles. Samples were constantly stirred during evaporation. Larger volumes (up to 90 liters) were evaporated using a Rototherm Agitated Thin Film Evaporator (Artisan Industries, Waltham, MA). Evaporations were taken to as high as 85% TDS for feeds and permeates, but to only 51 to 52% for the high viscosity retentates.

Analyses. Viscosity was determined with a Nametre vibrating sphere viscometer (shear rate, 4,500/sec) at 75 C and density with a Mettler density meter. For low solids samples, %TDS were determined by 105°C oven drying of weighed samples on weighed glass pads; for samples greater than ca. 35% TDS, a weighed amount of sample was mixed into a weighed amount of water before using the glass pad procedure. Lignin concentration was determined by absorbance of the diluted liquor at 280 nm (7). Lignin molecular weight was determined using Sephadex size exclusion chromatography at pH 13 (8).

RESULTS AND DISCUSSION

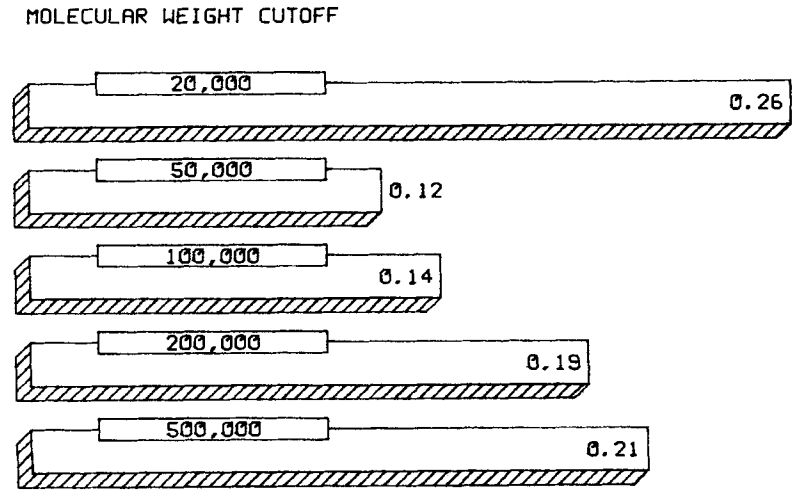
Lignin molecular weight. Figure 1 shows lignin weight average molecular weights for four liquors and their 50,000 molecular weight cutoff (MWCO) permeates. Since each liquor is produced under separate pulping conditions using varied species of wood, variability in the molecular weights of the feed lignins is expected. However, in all cases the permeate lignin molecular weight was clearly lower than that of its respective feed indicating that the membranes had removed higher molecular weight lignins from the liquor.

Lignin rejection. Since any lignin removed from a liquor would need to be dealt with separately in a mill situation, an objective of this work was to lower liquor viscosity while removing a minimum of lignin. Lignin rejection coefficient (R_{lig}) of each membrane was thus important. R_{lig} = 1 - (permeate lignin concentration/feed lignin concentration). A 20,000 MWCO membrane rejected more lignin into the retentate than did a 50,000. See Figure 2. However, membranes with pore sizes larger than 50,000 also rejected more lignin. This behavior was attributed to gel layer formation on the higher MWCO membranes. The gel layer could act as a lower MWCO membrane yielding greater lignin rejection into the retentate. Thus, of the membranes used, the 50,000 MWCO had the most desirable R_{lig} value.



Permeates from four separate liquors were generated as described in text using 50,000 molecular weight cutoff membranes.

Fig. 1. Lignin weight average molecular weight determined by size exclusion chromatography.



Rejection coefficient = 1 -(permeate lignin concentration/feed lignin concentration)
All membranes were polysulfone from DDS Corp.

Fig. 2. Lignin rejection coefficient as a function of membrane molecular weight cutoff.

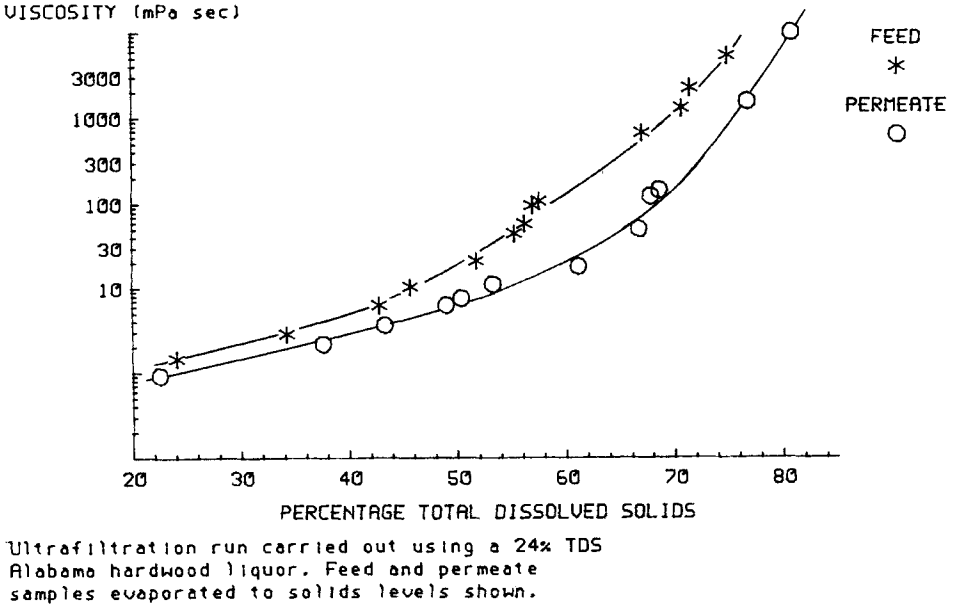


Fig. 3. Viscosity with percentage total dissolved solids for a kraft liquor and its 50,000 MWCO permeate.

Viscosity differentials. After ultrafiltration of a 16% or 24% TDS liquor, permeate samples were evaporated to higher %TDS. The viscosities of the concentrated samples were then compared to feed liquor samples evaporated to similar %TDS levels. As %TDS level increased, there was an increasing divergence between permeate and feed viscosities up to ca. 60% TDS for the Alabama hardwood liquor shown in Figure 3. To permit viscosity data at all solids levels to be expressed in one figure, the viscosity was expressed as its logarithm. The results shown indicated that the high molecular weight lignin removed by ultrafiltration had a beneficial result on resultant permeate viscosity, and that the effect was more marked at high %TDS levels. However, at solids levels greater than 65-70%, the difference between permeate and feed viscosity, although still marked, was not as prominent. Similar results were obtained using the Maine hardwood-softwood liquor mix.

When the retentate was evaporated to higher solids levels, viscosity increased more markedly than for either feed or permeate

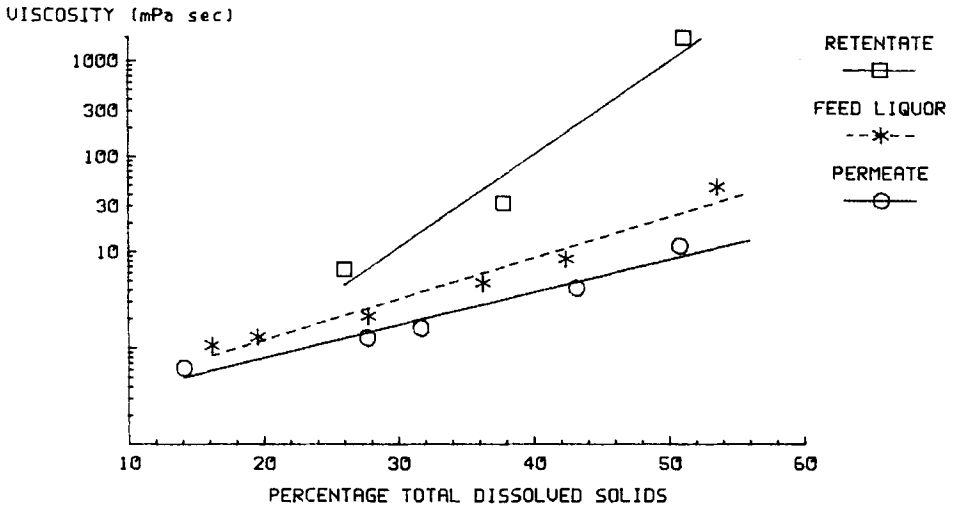


Fig. 4. Viscosity with percentage total dissolved solids for a kraft liquor and its 50,000 MWCO ultrafiltration fractions.

(Figure 4). Indeed, even 50% TDS retentates were difficult to handle. Other interesting properties of the retentate included a disproportionately high concentration of carbohydrate (7,9) and of multivalent metal ions (7,9,10). The retentate also had a lower sulfur content relative to the feed and permeate (11).

In the normal liquor recovery process, lignin (with a fuel value of 26,000 kJ/kg) and other organic chemicals are important sources of energy. Recovering only 88% of the feed in the permeate left between 20 and 25% of the lignin in the retentate. The value of this lignin would need to be recovered if ultrafiltration were to be useful to a mill. Ideally the retentate lignin would be used as a chemical feedstock, but the current market (12) is not large enough to make use of the lignin that would be generated by widespread use of the ultrafiltration process.

If the viscosity of the retentate could be reduced by recycling it to the chip digestor, the ultrafiltration process

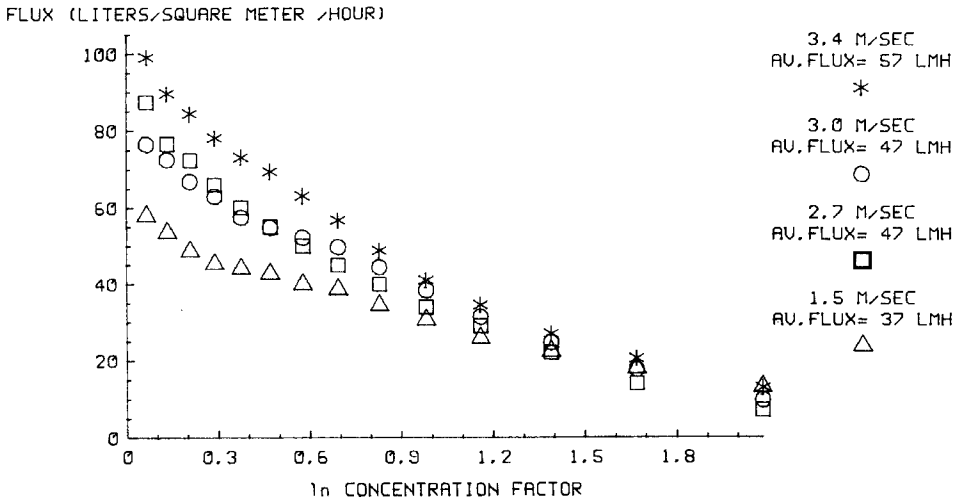


Fig. 5. Effect of linear velocity on flux.

might still be useful. A separate study (9) indicated that retentate viscosity could be greatly reduced by conditions simulating those found in the digestor, but the viscosity still remained double that of the feed liquor. Thus, this high viscosity retentate is an obstacle to the use of ultrafiltration in the recovery scheme.

Kraft liquor flux. Another factor important to the use of kraft liquor ultrafiltration would be a reliably maintained high flux rate. One set of 50,000 molecular weight cutoff polysulfone membranes (DDS Corp.) was used repeatedly in this study. After each run the membranes were rinsed thoroughly with hot water and then cleaned with hot 0.5% NaOH for approximately one hour. On occasion, after a long run with a fouling liquor, 0.3% Tide detergent was added to the alkali. Under these circumstances, the membranes showed only a slight drop in flux over a period of two years (9). Polysulfone was also the material of choice when hollow fiber membranes were used. On a short term basis these membranes in a polysulfone housing (Romicon Corp. and A/G Technology Corp.) worked as well as the flat sheet polysulfone; however, no longer term studies were carried out with the hollow fiber cartridges.

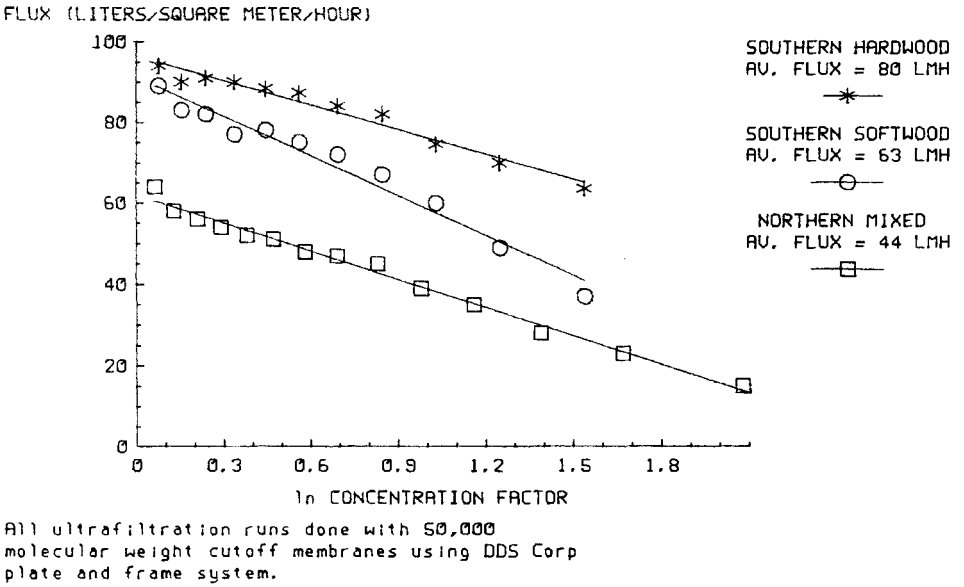


Fig. 6. Variation in flux with liquor used. All liquors 15-16% total dissolved solids.

Flux, expressed as liters/m 2 /hr (LMH), increased with temperature up to 80°C (7). However, since the plate and frame polysulfone cell leaked at 80°C, the routine operating temperature chosen was 75°C. Flux also increased with pressure up to ca. 186 kPa (7). Enhanced linear velocity of a feed stream across the membrane surface also increased flux (Figure 5). Using a A/G Technology Corp. hollow fiber cartridge, a 3.4 m/sec velocity had an average flux more than 50% greater than that seen at 1.5 m/sec. Increasing linear velocity also increased flux in the Romicon Lab 5 hollow fiber system and the DDS Minilab 10 plate-and-frame setup.

DDS Corp. 50,000 MWCO polysulfone membranes showed higher flux than the 20,000. However, when larger pore membranes were examined, there was no further enhancement of flux over that seen with the 50,000 MWCO (7,9). Indeed, the higher MWCO membranes cleaned up less well and showed decreased flux after only several runs. This behavior is consistent with the greater R_{lig} values seen with the higher MWCO polysulfone membranes (Figure 2).

The particular liquor used also greatly affected flux. Figure 6 compares the flux of two southern liquors to that of the Maine (northern) hardwood-softwood mix. A marked variation in flux relative to liquor used was noted. The southern hardwood of Figure 6 was from a cook of unusually high sulfur content which resulted in a lignin molecular weight much lower than that of the other liquors as noted in Figure 1 (Liquor 1). This lower molecular weight could have led to the enhanced flux noted. Despite the smaller quantities of high molecular weight lignin removed, the permeate of this liquor showed a significant viscosity drop (9).

CONCLUSIONS

Removal of high molecular weight lignin by ultrafiltration does indeed lower viscosity of a black liquor permeate, and the lowered viscosity is greater at higher solids levels. However, there is a limited market for the high molecular weight lignin, and dealing with the high viscosity retentate could be a disadvantage to the recovery process.

Flux rates and degree of membrane fouling varied greatly depending upon the type and source of the liquor ultrafiltered. However, even liquors exhibiting high flux would need an inordinate amount of membrane if the whole stream of a mill were ultrafiltered. As lignin markets develop, a portion of the liquor stream could be ultrafiltered to attain a portion of the lowered viscosity advantage. There could also be enhanced production in a recovery-limited mill if a portion of the lignin were removed from the stream.

ABBREVIATIONS AND DEFINITIONS

Concentration factor = Feed volume/retentate volume
KBL = kraft black liquor
LMH = flux expressed as Liters/square meter/hour
MWCO = molecular weight cutoff
R_{lig} = lignin rejection coefficient expressed as 1- (permeate lignin concentration/feed lignin concentration)
TDS = Total dissolved solids expressed as weight/weight.

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