Orlando J. Rojas, John Song,
Dimitris S. Argyropoulos
Forest Biomaterials Laboratory,
College of Natural Resources,
North Carolina State University,
Raleigh, NC 27695-8005, USA
Juan Bullón
Department of Chemical
Engineering, Universidad de Los
Andes, Mérida (Venezuela)

LIGNIN SEPARATION FROM KRAFT BLACK LIQUORS BY TANGENTIAL ULTRAFILTRATION

Lignin from black liquors is a biofuel that is generated during chemical digestion of lignocellulosic materials. There is an increasing interest in separating these lignins into fractions with well-defined properties. Therefore, the objective of this study was to elucidate the characteristics of lignin fractions after ultrafiltration of industrial kraft black liquor by using tubular ceramic membranes. Overall, this effort represents an embarkation point for a fundamental understanding of membrane ultrafiltration efficiency for the concentration and fractionation of industrial black liquor lignins.

In chemical pulping a large part of the wood is dissolved during digestion. The dry matter content of the generated black liquor is typically 12 to 18 wt% [1, 2]. In the case of kraft black liquors four main groups of organic constituents are present, 30-45 wt% ligneous material, 25-35 wt% saccharinic acids, about 10 wt% formic and acetic acid, and 3-5 wt% extractives. It also contains about 1 wt% methanol and many inorganic elements, mainly sodium (17-20 wt%) and sulphur (3-5 wt%). The exact composition of the black liquor varies considerably between different mills depending on the cooking conditions and feedstock. The vast majority of lignin in the spent liquors of pulp mills is used as in-house fuel for the recovery of chemicals.

If liquid fuel production from biomass and solvent pulping reach commercial maturity the production of lignins will be enormous. Therefore, current and future availability of lignins in spent liquors together with their characteristic polydispersity will make mandatory the use of fractionation schemes for the production of streams with uniform characteristics and composition.

Fractionation of cooking liquor from kraft and sulphite pulp mills by ultrafiltration (UF) has been studied since ca. thirty years ago [2-19]. In most of these applications the objective of UF processes was to purify the lignin fraction in order to use it as a valuable chemical product. The use of pressure-driven membrane filtration processes for applications such as the clarification of solids, protein isolation and sterilization has become a well-established technology. However, in membrane separation many of the mechanisms that take place at the membrane surface and inside the pore structure during the separation are still under scrutiny.

Membranes can be classified under three general categories according to the sizes of the particle that they can retain. Reverse osmosis (RO) membranes are capable of rejecting salt ions while ultrafiltration (UF) membranes are often used to retain macromolecules. On the other hand, microfiltration (MF) or cross-flow filtration (CFF) membranes are used to filter out particles greater than 0.1 micron.

As is the case in general filtration, the permeate flux across the membrane is driven by a pressure gradient. As the filtration proceeds, an accumulation of particulate mater at the surface of the membrane produces a resistance to filtration: i.e. it reduces the filtration rate. This occurs because the fluid phase passes through the membrane while particulate material is retained. Eventually the retained solids may form a distinct gel layer that causes significant resistance to the solvent flux. The solids may move back into the bulk solution by natural diffusion and when the rate of solids being deposited at the membrane is counterbalanced by the rate of back diffusion, a concentration gradient of solids is set up near the membrane as represented in Figure 1. The flux J is directly proportional to the pressure gradient ΔP across the membrane and inversely proportional to the viscosity m and the resistance to flow of the membrane (R_m) and the solids accumulated on the surface of the membrane (R_s). This resistance includes the concentration polarization (CP) and the gel layer resistance (GLR) due to the irreversible adsorption of colloidal particles on the surface

$$J = \Delta P / \mu(R_m + R_s)$$

Membrane resistance is the product of pore size, pore density, pore depth, the materials' wettability, and the hydrodynamic resistance of the device holding the membrane. The interaction forces between solute, solvent, and membrane material play an important role as well. Gel polarization resistance is caused by convection through the membrane. If fluid flows through the membrane faster than the retained material can diffuse back into the bulk fluid, a saturated layer builds up next to the membrane. This layer creates a secondary dynamic membrane, with a measurable porosity and pore radius of its own. The layer's depth and its resistance to flow depend on the speed at which the retentate is circulated. The faster the flow, the thinner the gel layer.

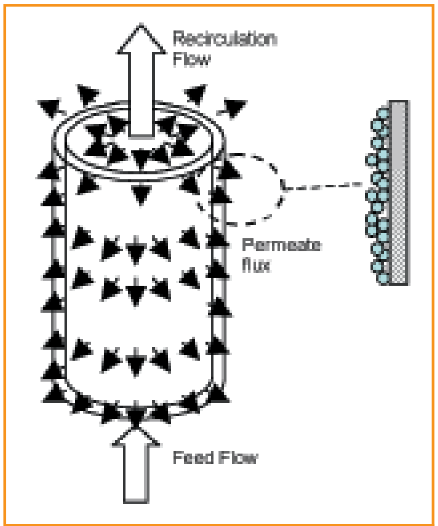

Fig. 1 - Microfiltration process

The optimal membrane cut-off during fractionation of kraft black liquor is not obvious. When a membrane with a high cut-off is used the lignin in the retentate is purer, as more of the low- molecular-weight compounds pass through the membrane. On the other hand, more low-molecular-weight lignin compounds are lost in the permeate. When producing lignosulphonate from spent sulphite liquor, membranes with a molecular weight cut-off of 20,000 are typically used [20].

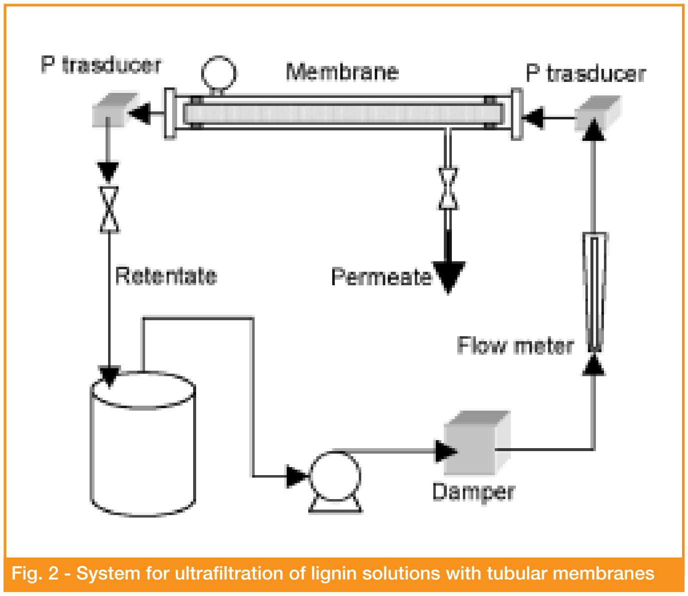

Fig. 2 - System for ultrafiltration of lignin solutions with tubular membranes

The aim of this investigation was to determine the retention of industrial kraft black liquor lignin and correlate this to the functional group distribution of the emerging fractions during UF. The performance of five commercial membranes with cut-offs of 150,000; 50,000; 5,000 and 1,000 was evaluated. The flux and retention for each membrane was measured and a systematic investigation of the molecular weight (via GPC) and main functional groups (via NMR) in lignin was studied for the various ultrafiltration streams.

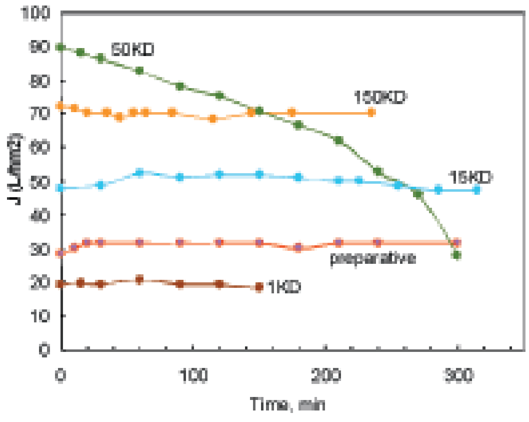

Fig. 3 - Permeate flux versus filtration time for the various UF tubular membranes operating at 1 bar trans-membrane pressure

Experimental

Black Liquor

The industrial black liquor used in this study was obtained from Smurfit-Mocarpel pulp mill (Yaracuy, Venezuela). In their process *Pinus caribaea* is digested in a low-sulfidity Kraft digestion. The black liquor samples were collected in the recovery boiler. Suspended solids were separated from the black liquor by filtration with a Whatman filter No. 1. The pH and density of the filtrated black liquor were 13.5 and 1.2 g/ml, respectively. The black liquor solid content was 31% after measurement of weight loss in an oven at 100 °C and Klason lignin was determined to be 17.8%.

Membrane Separation

Experiments were carried out in a UF unit with a filtration module made of stainless steel AISI 304, fitting ceramic tubular membranes (α-Al_2O_3) Schumacher GmbH-TI (Germany) and TAMI (France). The module was connected by means of tri-clamp connections allowing easy dismounting. A schematic drawing of the UF setup is shown in Figure 2.

The UF unit was operated as a recirculation batch. No dilution was necessary due to the high surface area of the employed system as compared to others (e.g., cross flow). The feed stream was pumped from a temperature-controlled tank through the membrane. Permeate was collected and the retentate (concentrate) returned back to the feed tank. The transmembrane pressure (TMP) was controlled by adjusting a valve in the retentate line.

The operating conditions during ultrafiltration involved a transmembrane pressure of 1 bar at room temperature. The permeate flow rate was measured with a digital flowmeter. The UF membrane was carefully cleaned after each experiment with a NaOH solution and rinsed with distilled water. The first membrane in the stage-wise operation was α-Al_2O_3 (Schumacher) mounted for preparative purposes (elimination of suspended material). Alter this conditioning membrane TAMI ceramic membranes with successively lower nominal MWCO were employed (150, 50, 15 and 1 KDa).

Both permeate and retentate from each stage were treated with sulfuric acid to precipitate lignin that was then separated by centrifugation and then re-dissolved in NaOH aqueous solution. The lignin solutions were then dried at 40 °C and stored for subsequent analysis. The total solids content for the permeates and retentates of black liquor after membrane separation was obtained from weight losses in an oven at 100 °C.

Molecular Weight Distribution of Acetylated Lignins by GPC

Approximately 100 mg of each of the lignin samples were suspended in pyridine (2 ml) and acetic anhydride (2 ml). The acetylation was carried out overnight in a water bath set at room temperature in order to dissipate any excess heat generated during reaction. The resulting solution was then poured in an excess (50 ml) of ice water and centrifuged/washed 3 times. After this the sample was freeze dried until use.

Prior to the GPC analyses, the solubility of acetylated samples in THF, MF, DMF containing 0.5% LiCl; 0.05 M and 0.5 M aqueous NaOH was qualitatively examined using 5 mg of the sample each in 5 ml of the selected solvent.

The obtained acetylated samples (2 mg) were dissolved in tetrahydrofurane to adjust the solids concentration to 0.1% w/v and filtrat-

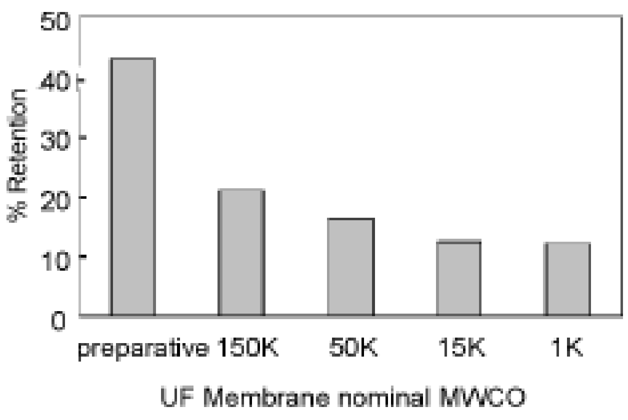

Fig. 4 - Solid retention for UF membranes at 1 bar transmembrane pressure

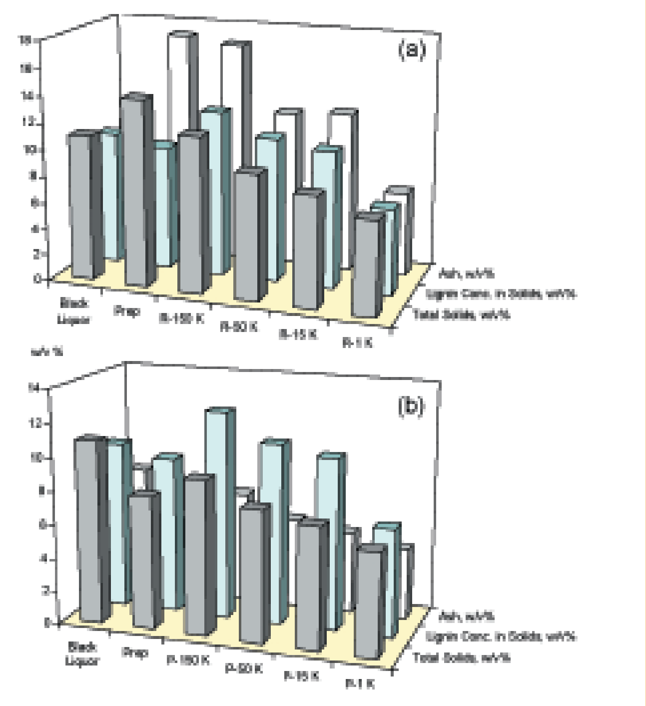

Fig. 5 - Total solids, Klason lignin and ash content in each of the retentate R (a) and permeate P (b) streams of the various stages of black liquor UF

ed through a 0.2 μm filter to remove any contaminant. The molecular weight characterization by a GPC consisted of a Waters U6K injector, a Waters pump 510, a UV Waters 484 detector (Waters) and a Waters refractive index 410 detector. The respective analyses were carried out at 40 °C using THF as eluent at a flow rate of 1 ml/min. The columns used were HR 5E and HR 1 (Waters), connected in series. Polystyrene standards in the molecular weight range of 890-186x10^4 g/mol were used to calibrate the columns. Millenium GPC software (Waters) was used for data processing.

Quantitative ^{31}P NMR Analysis of Lignins from BL

Quantitative ^{31}P NMR spectra of the lignin samples were obtained by using a Bruker 300 MHz spectrometer equipped with Quad probe dedicated to ^{31}P, ^{13}C, ^{19}F and ^{1}H acquisitions. Samples were completely dried using a vacuum oven set at 40 °C overnight.

Approximately 40 mg of each sample, weighted accurately, was transferred into a sample vial and dissolved in 600 μl Pyridine-$D_5/CDCl_3$ (1.6/1, V/V) solution. N-HNI (22 mg/ml in Pyridine-$D_5/CDCl_3$ (1.6/1, V/V)) was used as Internal standard, 50 μl $Cr(acac)_3$ (11.4 22 mg/ml in Py-$D_5/CDCl_3$ (1.6/1, V/V)) were added as relaxation agent and finally 100 μl Phosphitylation reagent was added. NMR measurements followed immediately after this preparation.

Results and Discussion

Ultrafiltration

Figure 3 shows the fluxes of lignin solutions for each of the tubular membranes (preparative and membranes of nominal MWCO of 150, 50, 15 and 1 kDa). In all cases (except for the 50 k membrane) the flow rates were constant which suggest the formation of a dynamic film (gel) on each of the membranes. The membranes and corresponding films exert a constant filtration resistance and therefore allow constant flux (in operations at constant transmembrane pressure). However, in the case of the 50 k membrane a reduction of permeate flux with time is observed. The effectiveness of the filtration process is limited in this case by fouling, which causes a decline in flux. This behavior can be rationalized in terms of pore blocking and plugging, or from the formation of external cakes with lignin molecules of specific dimensions. Fouling resistance builds as deposits chemically bind to the membrane. Fouling is distinct from polarization, in which the interfering layer is held against the membrane by hydrodynamic forces. If increasing the tangential flow increases flux, the effect is polarization.

In general, the measured fluxes (90 to 20 l/m^{2}h, depending of the membrane) are similar to those reported for the concentration of black liquor using similar operations [18].

Figure 4 shows the measured total solid retention in each of the stages of the tubular filtration for transmembrane pressures of 1

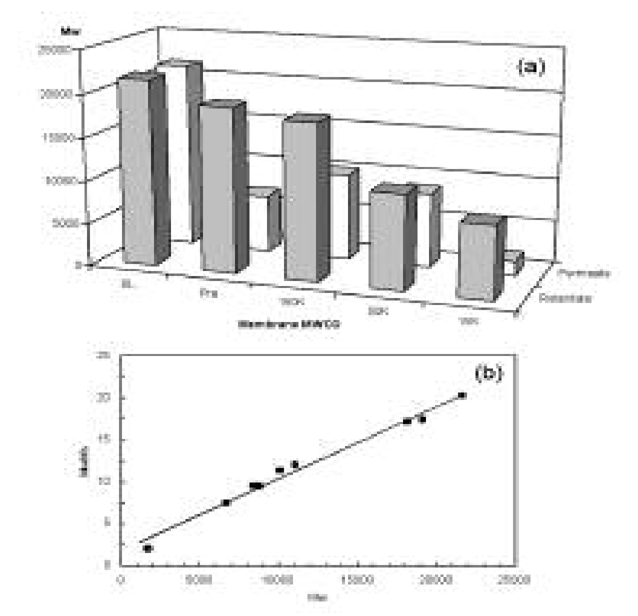

Fig. 6 - a) Weight average molecular weight for the retentate and permeate of the streams from the various UF stages and, b) relationship between the measured molecular weight and the lignin polydispersity (Mw/Mn)

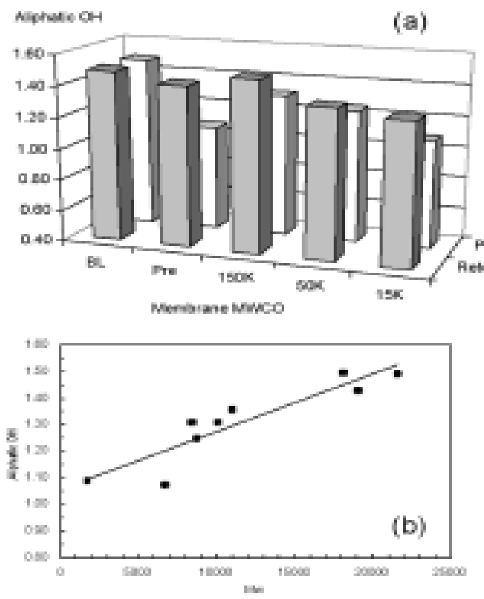

Fig. 7 - a) Aliphatic OH for the retentate and permeate of the various UF stages and, b) relationship between the aliphatic OH and the effective molecular weight of lignin in the black liquor

bar. Note that the filtration was conducted in a stage-wise mode with the membranes of largest nominal MWCO at the beginning and the membranes with smallest MWCO at the end. From this graph a first assessment of the mass distribution for the various particle sizes can be obtained. The total solids, ash content as well as lignin concentrations are presented in Figures 5 for the retentate *R* (Fig. 5a) and for the permeate *P* (Fig. 5b) (for each stream of the membrane separation process). In general, the aim is to obtain streams with low ash content and high lignin concentration. From Figure 5 it can be concluded that with each successive stage both the total solid and ash content are reduced. Furthermore, there is a correlation between the total solids and the Klason lignin concentration. This result is as expected since smaller molecular size entails a larger fraction of soluble lignin.

GPC and NMR Analysis

During this effort we used THF as the GPC solvent despite the fact that previous reports [21] state that size exclusion chromatographic analyses of dissolved lignins sometimes give different results, depending on the analytical conditions employed (i.e. nature of the mobile phase). The limitation of the use of polystyrene standards to calibrate and determine molecular weights and molecular weight distribution of lignin preparations has also been pointed out [22]. Figure 6a shows the results of GPC weight-average molecular weights obtained for the retentate and permeate of the various UF stages. As anticipated, as the nominal MWCO is reduced both the size of the lignin molecules in the retentate and permeate are reduced. However, it is important to point out that the nominal MWCO of the UF membranes does not match the measured (GPC) lignin molecular weight. Lignin molecules are known to have a small hydrodynamic radius in aqueous solution and the formation of a dynamic gel layer (membrane) on the ceramic surface is believed to induce a reduction in the actual size of the free area for flow during filtration. For this reason the effective MWCO is much smaller than the membrane nominal MWCO. Similar observations have been reported elsewhere [11, 23]. To further comprehend this effect a series of additional measurements utilizing light scattering and viscosimetric detectors with our size exclusion equipment are planned. The reports on kraft lignin number average molecular weight ($\overline{M}$n), weight average molecular weight ($\overline{M}$w) and polydispersity (PD=$\overline{M}$w/$\overline{M}$n) are, as expected, rather broad. Number average molecular weight ($\overline{M}$n) of lignin fractions from bleaching effluents after ultrafiltration were determined to be in the range 593-2,899, 432-1,852 and 161-215 [24]. The respective distribution of weight-average molecular weight was 3281-8,851, 917-2849, and 170-365. Norgren *et al.* [23, 25] obtained $\overline{M}$n ranging from 950 to 2,190 for different fractions after ultrafiltration (with respective $\overline{M}$w between

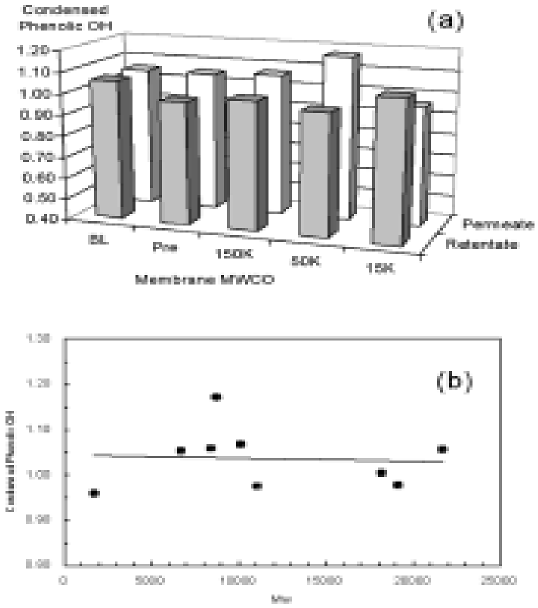

Fig. 8 - a) Condensed phenolic group content of the retentate and permeate in the various UF stages and, b) relationship between the concentration of condensed phenolic groups and the effective molecular weight of the lignin in the black liquor

1,910-41,400). Bikova *et al.* [26] measured the $\overline{M}$n of lignin fragments from spent kraft liquor to be in the range 1,500-3,000 (the respective $\overline{M}$w did not exceed 5,000). In the present study the lignin fragments have a number average molecular weight ranging from 880-1,200. This corresponds to about 5-7 phenol-propane units, i.e., lignin in this industrial black liquor is extensively broken into small fragments. The disparity in the reported ranges for $\overline{M}$n is explained by differences in the raw materials and pulping/bleaching methods employed.

The weight average molecular weight calculated in our study ranged from 1,7 to 21,6. This $\overline{M}$w is much broader than the number molecular weight distribution, which indicates that the high molecular tail in GPC elution contributes heavily to the weight average. Associative interactions between the compounds to form macromolecular complexes (aggregates); and non-size-exclusion effects are believed to play an important role in the determination of the molecular size. Our data agree very well with other reports [23, 25] except that our distribution is narrower and the maximum measured Mw is relatively smaller. It is important to point out that the molecular weight distribution (MWD) of kraft lignin is strongly dependent upon the isolation procedure and incubation conditions prior to analysis [27].

The polydispersity (PD) calculated from Ristolainen *et al.* (1996) was 1.1-4.5 and that calculated from Bikova *et al.* (2000) was approximately 1.3-1.5. In contrast, the PD in our system is broader (in the range 2-20 for the various stages) which agrees with the data reported by Norgren (PD in the range 2-19) [23].

The principal structure of softwood lignins is methoxy-hydroxyphenylpropane (guaiacyl) units. More than two thirds of these units are linked by ether bonds and the remainder by carbon-carbon bonds. In addition to aliphatic hydroxyl groups, the structure includes other functional groups such as methoxyl, carbonyl, and phenol groups in various amounts, depending on morphological origin [21]. During kraft processing of wood most of the lignin is removed from the pulp, and the main portion can be separated as soluble polymeric lignin from the black liquor (e.g., by ultrafiltration). In the following, a variety of functional groups, present in the fractions after ultrafiltration of the kraft lignin were investigated as a function of the membrane MWCO or rather the molecular weight of the separated lignins. The functional groups were determined by quantitative ^{31}P NMR spectroscopy. The lignin functional groups, being evaluated against the molecular weights, are reported only as a function of $\overline{M}$w since it was more sensitive than the $\overline{M}$n to the relative changes during the progress of ultrafiltration. From the chemical formula of piassava lignin $C_{9.00}H^{ar}_{2.25}H^{al}_{3.73}O_{0.89}(OH)^{ph}_{0.69}(OH)^{al}_{0.86}(OCH_3)_{0.57}$ [28], we can calculate the aliphatic alcohol content of about 5 mmol/g lignin. On the other hand, Wang [29] reports an aliphatic alcohol content in Klason lignin of 4.96 mmol/g lignin. The aliphatic alcohol content from our ^{31}P NMR reveals lower concentrations (see Fig. 7).

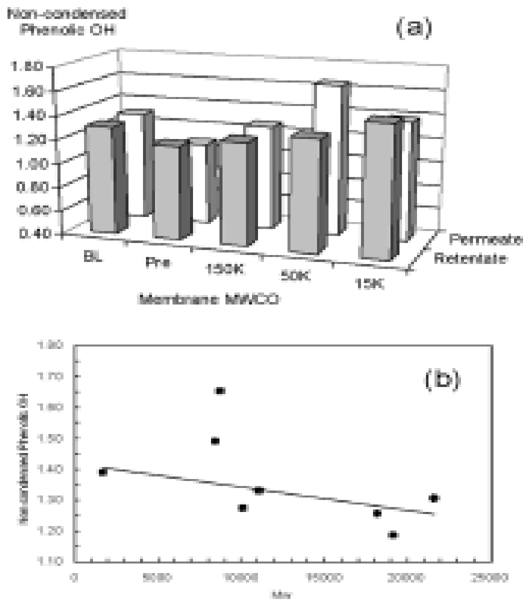

Fig. 9 - a) Non-condensed phenolic group content of the retentate and permeate in the various UF stages and, b) relationship between the concentration of non-condensed phenolic groups and the effective molecular weight of the lignin in the black liquor

It is known that in the course of delignification the residual kraft lignin molecular weight decreases. Our black liquor sample is the product of a continuous, industrial process in which all the lignin fractions are present (from the early until the final stages of the delignification). In general, both the retentate and permeate contain lignins with less aliphatic OH groups as the nominal MWCO is reduced (see Fig. 7a). In other words, the relative amount of aliphatic OH is reduced as the molecule size is reduced. This tendency is more clearly seen in Fig. 7b where a clear reduction of aliphatic hydroxyl groups is observed as the molecular weight of the lignins in black liquor is decreased. This decline is related to the elimination of Ca hydroxyl groups present in the β-*O*-4 structures.

Since this process is progressive, lignin of smaller molecular size contains less aliphatic OH. Since the integrity of the polymeric chains of lignins is largely due to the presence of the β-*O*-4 structures it is evident that once the chain length of a given lignin decreases, the content of such structures will be concomitantly reduced. In recent years, a great deal of attention has been devoted to determine

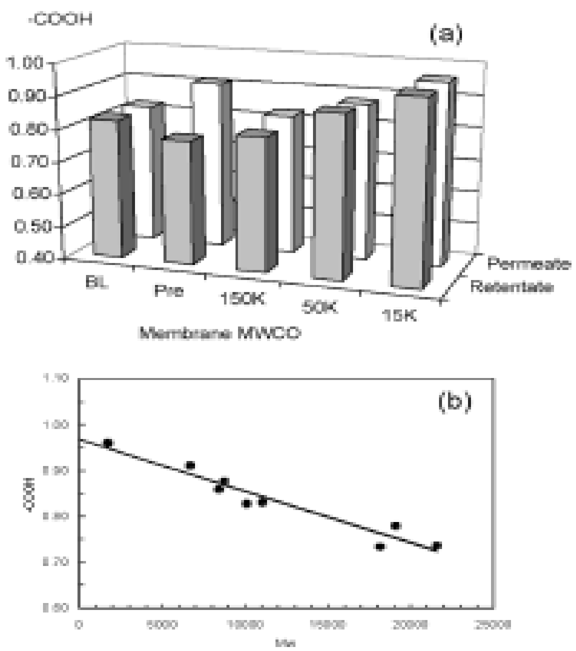

Fig. 10 - a) Carboxylic group content of the retentate and permeate of the various UF stages and, b) relationship between the -COOH concentration and the effective molecular weight of the lignin in the black liquor

the nature and the extent of condensation reactions that occur during kraft pulping. Therefore, we are now turning our attention to the concentration of total and condensed phenolic hydroxyl groups. In both cases it has been noted a progressive increase in their abundance within residual kraft lignins as a function of delignification.

Therefore, it would be interesting to compare and contrast this behavior for lignins from ultrafiltration of (whole) black liquors.

It is important to point out the significance of condensation reactions as has been discussed and rationalized in previous efforts [30, 31]. The total phenolic hydroxyl groups was showed to increase monotonically as the molecular weights of the residual kraft lignins decreases since they represent the majority of the end groups present in these biopolymers.

Gellerstedt and Lindfors have proposed that the lignin-carbohydrate linkages inhibit the delignification at its final stages, after most of the β-aryl ether linkages in lignin have been eliminated [32, 33]. Subsequent model compound work confirmed that lignin fragments containing non-phenolic and non-condensed β-aryl ether structures linked to polysaccharides, via α-ether linkages, were relatively stable in alkali [34] with the possibility of being cleaved only at the latter phases of delignification. Consequently, such structures, once formed, would only cleave relatively slowly contributing to the accumulation of non condensed phenolic OH only at the latter phases of delignification.

Figures 8 and 9 show the relative content of condensed and non-condensed phenolic groups in the UF fractions. Note that the results for the permeate of the 50k-column are unexpectedly high and this produces the outlier data in the respective graphs. This behavior may be related to the reduction in filtration flux discussed in earlier sections (due to membrane plugging or fouling) (see Fig. 3). If this observation is factored in the trends would indicate that total phenolic OH decrease with increasing membrane MWCO. This conclusion agrees with observations made by Norgren [23, 25] who noted that low molecular lignin fragments strongly influence the total amount of phenolic groups. However, in our case any conclusion in this regard is speculative since the results are not statistically significant and therefore more detailed studies are needed.

We now turn our attention to the content of carboxylic groups. A behavior opposite for that reported before for aliphatic OH groups is observed for the carboxylic groups. Figure 10a shows the -COOH content per lignin mass for the different UF stages (retentate and permeate). The overall reduction in the relative concentration of -COOH with increased molecular weight is clearly seen in Figure 10b.

Overall, in our study we found an aliphatic OH content ranging from 1.04 to1.46 mmol/g. The content of condensed and non-

Separazione della lignina da kraft black liquor mediante ultrafiltrazione tangenziale

ABSTRACT

La lignina derivata dai black liquor è un biocombustibile che viene generato durante la digestione chimica di materiali lignocellulosici. C'è un interesse crescente nel separare queste lignine in frazioni con proprietà ben definite. L'obiettivo di questo studio è di chiarire le caratteristiche delle lignine dopo ultrafiltrazione di kraft black liquor usando membrane ceramiche tubulari. Sono stati studiati Il flusso di cinque membrane ceramiche con differenti cut-off, la loro ritenzione di solidi, lignina e ceneri. Questo lavoro rappresenta un punto di partenza per la comprensione dell'efficienza della tecnica di ultrafiltrazione su membrana per la concentrazione ed il frazionamento di lignine da black liquor industriali.

condensed phenolic OH ranged from 0.98 to 1.19 and from 1.09 to 1.65 mmol/g, respectively. Finally, the carboxyl acid COOH content was found to be between 0.78 and 0.96 mmol/g.

The phenolic and total OH content measured in this study are about half of the values found by Morck [35] by using ^{13}C NMR (phenolic OH content from 3.9 to 5.0 mmol/g and total OH content from 5.4 to 7.3 mmol/g). Data reported by others agree with our results [21, 23].

Based on the data presented so far some additional observations can be made. For a given stage in membrane ultrafiltration, the retentate contains more aliphatic alcoholic units and less total condensed phenolic units than the permeate. No major differences were observed in the concentration of carboxylic groups for a pair of retentates and permeates in a given UF stage.

Conclusions

Our results show that the weight average molecular weight for the examined industrial black liquor ranged from ca. 1,700 to 20,000 Da. The Mw of the retentates and filtrates correlate with the membrane MWCO. The effective molecular size is smaller than the nominal membrane MWCO. As the membrane MWCO is reduced, the lignin streams are characterized by a reduced aliphatic OH concentration and an increased content in carboxylic groups. The separation with membranes of different MWCO produced little changes in the concentration of condensed and non-condensed phenolic OH.

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