

SURFACE ACTIVITY OF LIGNIN FRACTIONS OBTAINED BY MEMBRANE-SEPARATION TECHNOLOGIES OF INDUSTRIAL BLACK LIQUORS

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Abstract

In this investigations it is demonstrated the ability of industrial black liquor -obtained after alkaline digestion of tropical woods- and the fractions obtained by membrane separation thereafter, as stabilizer of liquid-liquid and solid-liquid interfaces.

Alkali-lignin fractions of different molecular sizes were obtained by ultrafiltration by employing polymer-based membranes having molecular weight cut off (MWCO) 100 000; 10 000; 5 000 and 1 000. Solutions separated sequentially with membranes of increasing MWCO produced fractions with lower lignin content and a significant reduction of the color of the permeate was attained. The highest solid separation was observed with the membranes of MWCO 100 000 in which case the relative concentration of phenolic groups was the highest. Surface activity of the different lignin fractions (both from the permeate as well as from the retentate) was studied by employing the Wilhelmy plate technique under different conditions of pH and solids content.

From the surface tension results it is concluded that the effectivity and efficiency of the separated lignin solutions are similar to those obtained for commercially available alkali-lignins. Solid (bentonite) dispersion experiments were conducted and it is demonstrated that the raw black liquor, the retentate and permeate fractions of the membrane of MWCO 100 000 and the retentate from the membrane of MWCO 30 000 have the highest dispersion power. Therefore, high molecular weight fractions are more effective as solid dispersants.

O/W emulsions were prepared using as emulsifier solutions obtained after black liquor ultrafiltration. Small drop sizes (< 5 μm) along with high stabilities were observed for the emulsions prepared following standard emulsification protocols. The results demonstrate the potential of black liquor and lignin fractions obtained by membrane filtration as dispersant and emulsifier in industrial applications.

Keywords: Black liquor, Lignin, Membrane, Ultrafiltration, Stabilizer.

Introduction

Pulp mills worldwide are confronted with serious problems related to the discharge of residual liquids containing spent liquors from wood (or lignocellulose raw material) digestion. On the other hand, lignins and their derivatives can be isolated from spent liquors (black liquors) and then used advantageously in a broad list of applications. The main sources for lignin derivatives are black liquors from pulping plants. Depending on the application, lignin compounds can be separated with different purity degrees and in some cases it is desirable to keep the molecular structure as close as possible to the original one (phenolic groups content, as well as primary and secondary alcohols, methoxyl groups, carboxylic and carbonyl groups, etc.). In other cases, it is desirable to derivatize the lignin structure by insertion of functional groups such as sulfonates, sulfates or to modify the structure more intensively so as to obtain new compounds (Huttermann, Mai y Kharazipour, 2001).

It has been reported (Conrad, 1980) that lignin has potential uses due to its physicochemical properties in fields such as road pavement, in animal feed, as industrial cleaner, as a sequestering agent, in leather tanning, as deposits inhibitor in boilers and heat exchangers and can be used in cement mixes and concrete admixtures (Bialski y Navak, 1987). Additionally several other uses include dispersion of carbon black; as a wettability enhancer in dyes and pigments applications; in printing inks; in plywood and particle boards; in dispersions of pesticides; in emulsion colloidal protection and in the manufacture of insulation materials with phenol-formaldehyde-based (adhesive) resins (Nada, Flady y Dawy, 1992). Degradation of lignin by-products to obtain low-molecular weight fractions is interesting in other areas such as in food industry, especially vanillin production (Ribbons, 1987); animal feed (Giger, 1985) and pharmaceutical industry (Sjoostrom, 1981).

In the formulation of drilling muds for oil exploitation the intensive use of lignin is demonstrated by the consumption figures. In this case the function of lignin is centered in the control of filtration losses towards regions of low permeability and in the reduction of the consistency of the mud (thinning effect). In these applications the surface activity of lignin compounds play a key role. Lignin assists in drilling muds conditioning due to its dispersant properties (by adsorption of lignin molecules to clay surfaces) and by stabilization of the dispersion obtained thereafter. These combined effects are traduced in a reduction of the apparent viscosity of the suspension and in the control of filtration properties due to solvation with the aqueous phase of the mud (Linfield, 1976; Kumar, Neale y Hornof, 1974; Salager, 1986). In well cementing operations lignosulfonates are used to modify the wettability of the cement and they also reduce the losses by penetration (Chilingarian y Vorabutr, 1981).

In pumping and pipe transportation lignin derivatives have found use as stabilizers of emulsions. These compounds have competitive costs as compared to the non-ionic surfactants which are normally recommended in these operations (Monsalve, 1986).

The effect of lignin as dispersant comes basically from electrokinetic effects since electrical charge of the solid surfaces is modified by lignin adsorption. Thus, electrical barriers are produced enhancing the stability of solid dispersions. Additionally, due to the polymeric nature of the molecule, steric effects also contribute in the stabilization of the dispersions.

Obst and Kirk (1988) have forwarded an excellent review of the different lignin types obtained following various isolation/purification methods both at an industrial and at a laboratory scale. As was mentioned before, black liquors constitute one of the main sources available for lignin separation. Generally speaking, the most commonly applied treatment involves the concentration and incineration of black liquors so that inorganic chemicals can be recovered and at the same time energy can be generated during the combustion of the organic fraction. In any case, the recovery process involves the destruction of organic compounds (specially lignin) from the black liquor which carries the loss of any potential for obtaining high-valuable products such as lignin derivatives that are recognized to have many uses in a number of applications. In the case of pulping mills of small to medium size the spent liquors are usually handled in

effluent treatment units and therefore the contamination problem is here an additional issue of concern.

One of the technologies most recently used for lignin treatment is the Lignin Removal Process (LRP) that has been implemented on a pilot-scale level and is available for its commercialization. This method, developed in India and Finland, is based on the removal of organic matter by the use of acidified fibers muds (Hynninen, 1992). By using acid precipitation, lignin can then be separated with high yield and purity. Conventional filtration operations are usually employed. However, with this process caution should be exercised since colloidal aggregates of lignins may be formed and additional coagulation stages may be required.

Rojas and Salager (1994) have reported yields of the order of 40-60 % in acid precipitation of lignin from black liquors (from pulping of sugar cane bagasse). Selectivities of the order of 60-80 % are also reported. Complete separation of lignin is attained after reduction of pH of the black liquor in a multi-step process (till pH of 3 or lower). Alternative methods for lignin separation have been suggested, such as reverse osmosis separation, electrolytic process, liophilization, etc. Nevertheless their use at an industrial scale is still very limited (Sarkanen y Ludwig, 1971).

Previous studies conducted in our laboratory has shown that lignin fractions separated from black liquors have high surface activity and also have good properties as dispersant and emulsifier (Padilla, 1989; Rosquete, 1987; Sánchez, 1991; Contreras, 1991; Aldana, 1991; Romero, 1992; Rojas and Salager, 1994; González, 1995; Lorenzo, 1995).

Currently, pulp mills in Venezuela, and for that matter in Latin America, have difficulties in the handling of spent black liquors. In many cases the residual liquors are treated in effluent plants and therefore the separation and use of lignin as the main organic component is desirable, especially if products of high value in targeted applications are obtained taking advantage of the dispersing, binding, complexing and emulsifying properties of lignin.

Methodology

Black Liquor

The industrial black liquor was obtained from Smurfit-Mocarpel pulp mill (Yaracuy, Venezuela) where a low-sulfidity Kraft process is used to digest *Pinus caribaea*. The waste liquor from the digestion process has a dark coloration and it is an alkaline aqueous solution that contains organic and inorganic solids. The 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 of the obtained black liquor was 13.5 and had a density of 1.2 g/ml. The black liquor solid content was 31% after measurement of weight loss in an oven at 100 °C overnight and Klason lignin was determined to be 17.8 %.

Membrane Ultrafiltration

Ultrafiltration (UF) separation was conducted with a MinitanTM (Millipore) unit using polysulfone and regenerated cellulose semi permeable membranes in a plate-and-frame set up. Table 1 shows the membranes MWCO used in the experiments

Table 1: Membranes used for black liquor ultrafiltration.

Membrane	Molecular weight cut off (MWCO)
Polysulfone	100 000
Polysulfone	30 000
Polysulfone	10 000
Celulose acetate	5 000
Celulose acetate	1 000

The initial feed consisted of black liquor solution diluted to 15 % total solids content. This solution was fed to the membrane of MWCO 100 000. The retentate in each UF step was recycled to the feed stream. The permeate from the membrane of MWCO 100 000 was filtered using the membrane of MWCO 30 000 and the same was done successively for the membranes of MWCO 10 000, 5 000 and 1 000, respectively. Samples from the retentate and permeate in the membrane separation stages were analyzed in terms of UV/VIS absorbance, phenolic groups content and surface tension.

Solids Content

The total solids content for both the permeate and retentate of black liquor after membrane separation was obtained from measurement of weight loss in an oven at 60 °C until constant weight was achieved

UV/Vis Spectrophotometric Analysis

For UV/Vis spectrophotometric analysis, a Lambda 3B (Perkin-Elmer®) spectrometer was used. In a typical run, 5 µL of the sample (original black liquor or permeate/retentate after membrane separation) was dissolved in 10 mL of 0.1 N NaOH solution. Samples were scanned over the wavelength range from 200 to 600 nm using PECSS program (Perkin-Elmer®, Computerized Spectroscopy Software, version 3.2). The absorbance maximum of lignin was measured at 280 nm (Janshekar, et al., 1981).

Phenolic Groups Concentration

Phenolic groups concentration was measured using the procedure of Markwell *et al.* (Markwell, 1978) with a solution of known concentration of precipitated Kraft black liquor as standard and by employing the Folin – Ciocalteus phenol reagent (Merk).

Surface Tension

Surface tension of black liquor samples was measured by employing the Wilhelmy plate technique in a Dataphysics tensiometer, model DCAT11 (Germany). A thermostated bath with circulating water at 25 °C was used to ensure constant temperature conditions throughout the measurements. Surface tension calculations were performed following SCAT 11/12 program (ver. 2.01).

Solid Dispersions

Aqueous solutions (0.5% solids content) of permeate and retentate solutions after black liquor membrane ultrafiltration were used to disperse bentonite solids. Five grams of bentonite were added to the respective aqueous solution so as to obtain 10% bentonite concentration. The dispersion were stirred under controlled conditions (1 min stirring at low shears) and after a resting period of 10 minutes (without agitation) the apparent viscosity of the dispersion was obtained by employing a Brookfield V-03-00 (model LVF) viscometer (operating at a shear rate of 240 min⁻¹ and 25 °C).

O/W Emulsions

Oil-in-water emulsions with different internal phase content and different pHs of the aqueous (continuous) phase were prepared using a Taurus stirrer using a standard emulsification protocol (one minute stirring at 25 °C at the highest rpm attainable). The oil phase consisted of technical-grade kerosene and the aqueous phase consisted of 1.5 % w/v black liquor solution. The resulting emulsions were analyzed in terms of drop size distribution by laser light diffraction (Malvern) and stability. The stability was estimated by a phase separation technique as follows. The emulsion samples were poured in graduated tubes that were then capped and placed in a vertical position at a constant temperature. The separated phase volumes were monitored from time to time and the stability was expressed as the time required for half the settling percentage to take place. The rheological behavior of the emulsions and viscosity were studied with a rheometer (Rheometric Scientific SR-5000) using parallel plates geometry (40 mm diameter, 1 mm gap).

Results

In this section the main observations regarding the efficiency of lignin separation by using ultrafiltration and also the surface activity of the fractions obtained herein are presented (see Tables 1 to 6 and Figures 1 to 6).

Figure 1 shows the appearances of the permeate solutions after filtering the black liquor with membranes of different molecular weight cut-off (MWCO). It is observed that the permeate optical density is decreased as the porous diameter of the membranes are reduced. This effect is due to an effective rejection of solids by the respective membranes.

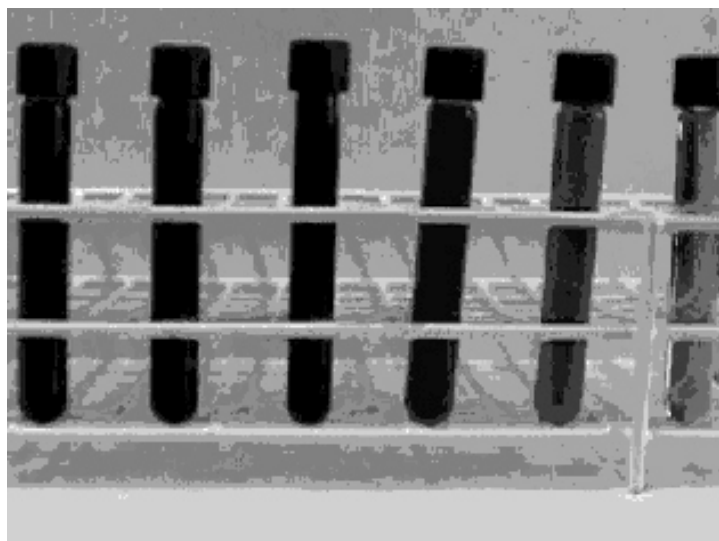


Figure 1.- Photos of the permeates after membrane separation of industrial black liquor. From left to right the feed and the permeates of membranes with MWCO 100 000, 30 000,10 000, 5 000 and 1 000 are presented.

Table 2 shows the solids content in the retentate and permeates. It is observed that the solids content is lowered as the MWCO of the respective membrane is successively reduced. For the membrane of MWCO 1 000 a low retention is observed while the highest retention was attained in the case of the membrane of MWCO 100 000. It is important to point out that the membrane of MWCO 30 000 rejects almost half of the solids present in the feed. This indicates that the high molecular weight fraction (nominal membrane MWCO > 30 000) of lignin molecules is ca. 50% of the total solids.

Table 2: Solid content (%) of permeate and retentate after black liquor ultrafiltration.

Sample	% solids	Solids Retention, %
Feed	14.7	
Permeate MWCO 100 000	7.5	26.52
Retentate MWCO 100 000	15.5	
Permeate MWCO 30 000	5.8	23.20

Retentate MWCO 30 000	8.7	
Permeate MWCO 10 000	3.9	20.22
Retentate MWCO 10 000	6.7	
Permeate MWCO 5 000	3.0	17.86
Retentate MWCO 5 000	3.9	
Permeate MWCO 1 000	2.0	10.55
Retentate MWCO 1 000	1.9	

In Figure 2 UV spectra for different permeate samples are showed. In most of the cases it is evident an absorbance maximum at 280 nm which is characteristic of aromatic compounds. In this UV region there is a reduction of the permeate absorbance from 0.34 to 0.02 as the membrane MWCO is reduced. This phenomenon is directly linked to the reduction of lignin concentration.

In the case of the permeates of membranes of high MWCO there is a distinctive peak at 220 nm which is likely to occur due to presence of carbohydrate degradation by-products and carbohydrate-lignin complexes that absorb in this UV region.

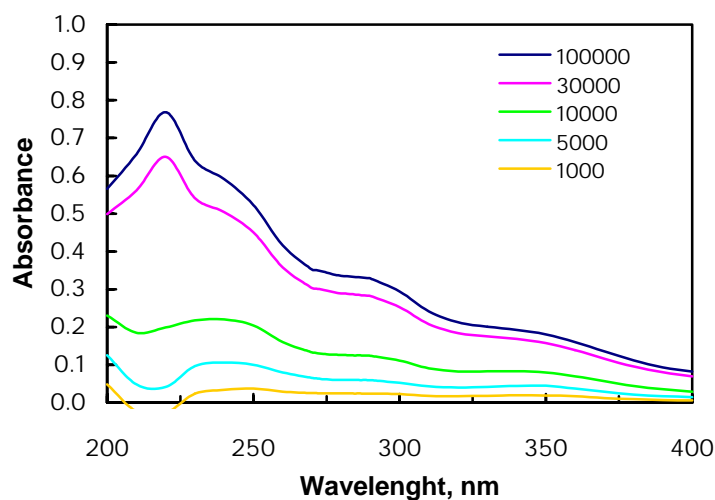


Figure 2: UV spectra of the permeate after ultrafiltration of industrial black liquor using membranes of different MWCO.

UV spectra for the retentate samples after black liquor ultrafiltration are shown in Figure 3. For the membranes with MWCO 100 000, 30 000 and 10 000 the absorbance between 200 and 280 nm is higher than 1. Comparing the data from Figure 1 and 2 it is concluded that lignin concentration is higher in the retentate than in the permeate for the membranes with higher MWCO and therefore an important fraction of the lignin molecules is retained by these membranes. However, the fact that permeate in the same membranes has non-negligible absorbance indicates that some medium- and lower- molecular weight lignins are not fully retained. The absorbances at 280 nm are reduced as the membrane MWCO is reduced which is an indication that lignin concentration is lowered as the pore diameter is successively reduced.

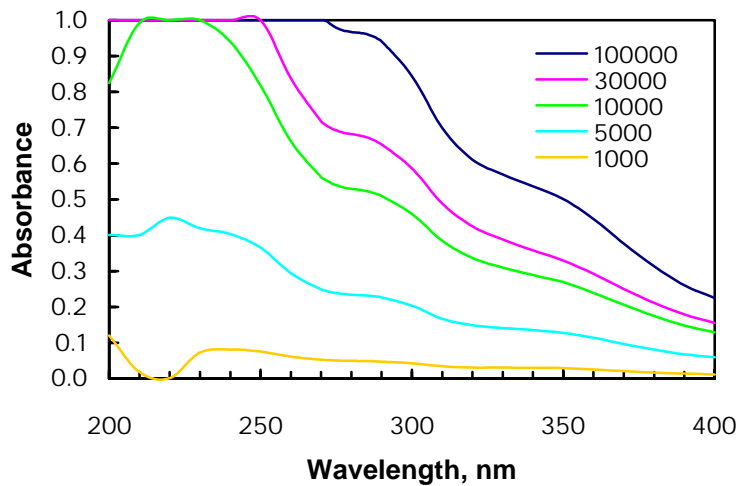


Figure 3: UV spectra of the retentate after ultrafiltration of industrial black liquor using membranes of different MWCO.

Phenol groups concentration was measured for both, the permeate and retentate of all used membranes (see Table 3). A higher phenol-group concentration is observed for the retentate solutions compared to that of the permeate solutions. This confirms the rejection of lignin compounds by the employed membranes. Furthermore, phenol-bearing compounds are more strongly rejected by the membrane with MWCO 100 000 where the lignin fractions are of the highest molecular weight.

Table 3: Phenol concentration (g/l) in permeate and retentate after black liquor membrane filtration

Sample	Phenol groups concentration (g/l)	Phenol groups retention (%)
Feed	26.9	26.2
Membrane 100 000: Retentate Permeate	28.0 20.9	
Membrane 30 000: Retentate Permeate	20.5 18.2	19.6
Membrane 10 000: Retentate Permeate	18.2 16.3	17.5
Membrane 5 000: Retentate Permeate	16.6 15.7	18.2
Membrane 1 000: Retentate Permeate	15.3 15.2	16.4

Surface tension was measured on different filtration permeates as depicted in Figure 4. Here the surface tension is plotted against the concentration in a semi-log scale. The surface tension for the fed black liquor is also included in the same plot. Permeate solutions for the membranes with MWCO 100 000 and 30 000 show high surface activity. However, this is not the case for the permeate of the membrane of MWCO 1 000. Minimum surface tensions of the order of 50 mN/m were observed. These figures are similar to those reported by Rojas and Salager (1993) for sugar cane bagasse lignins and commercially available lignin derivatives. From these results it can be concluded that lignin fractions of higher molecular weight are more surface active than the lower molecular weight counterparts. The amphiphilic nature of these anionic polyelectrolytes is explained by the hydrophobicity of the molecule balanced by a high number of anionically-charged groups. As the lignin size is reduced, the hydrophilic/hydrophobic balance is changed making the molecule less hydrophobic and surface activity is also reduced.

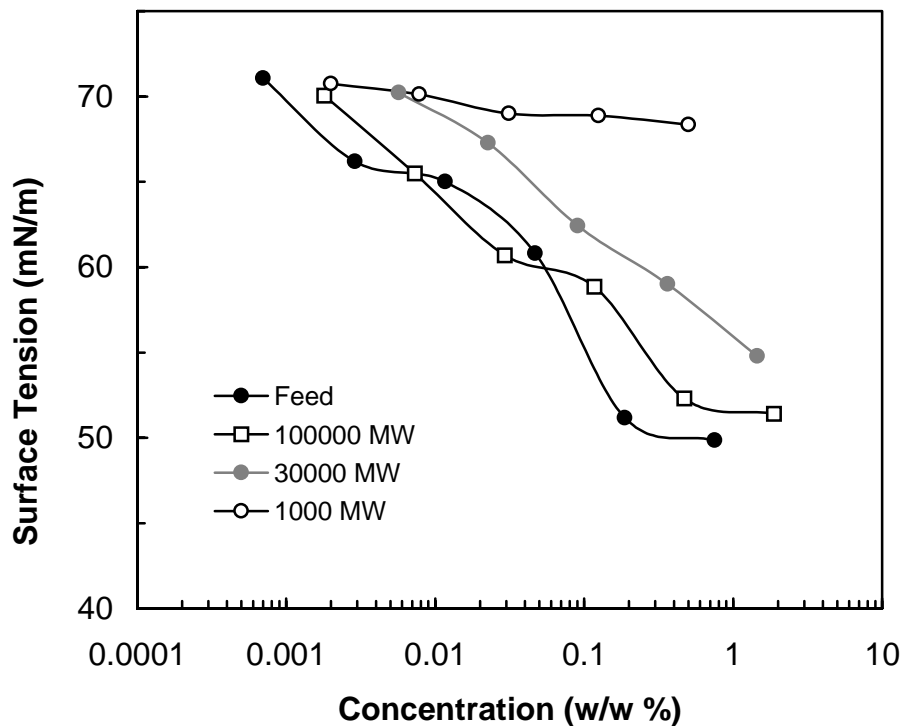


Figure 4: Surface tension of various permeates after ultrafiltration of industrial black liquor (feed) with membranes of MWCO 1 000, 30 000 and 100000.

Bentonite dispersions were prepared by using the permeate and retentate fractions after ultrafiltration of the black liquor as dispersant (see measured viscosities for the respective dispersions in Table 4). It was observed that only the fractions from the membranes with highest MWCO produced good dispersions whereas the fractions from membranes of lower MWCO were not able to disperse bentonite solids. This behavior is in agreement with the observed surface tension tendency where it was argued that only the high molecular weight fractions show surface activity. The permeate from the membrane of MWCO 30 000 was not able to disperse the solids even though it showed surface activity similar to that of higher MWCO fractions. This fact cannot be explained yet and further investigation is underway to comprehend more fully the relationship between surface tension and dispersion efficiency of the different lignin fractions. An interesting fact is that the apparent viscosities of the dispersions obtained by using the black liquor (feed) and those obtained by using the high MWCO fractions are similar and therefore the stabilization of the solid-liquid interface is attained by the highest molecular weight lignin molecules and the role of smaller molecules is not as important.

Table 4: Viscosity of dispersions of bentonite at 25 °C using various black liquor permeates as dispersant.

Dispersant	μ (cP)	Observation
Feed	830	Disperses
100 000 Mw Membrane: Permeate	860	Disperses
Retentate	885	Disperses
30 000 Mw Membrane: Permeate	-	Do not disperses
Retentate	871.7	Disperses
10 000 Mw Membrane: Permeate	-	Do not disperses
Retentate	-	Do not disperses
5 000 Mw Membrane: Permeate	-	Do not disperses
Retentate	-	Do not disperses
1 000 Mw Membrane: Permeate	-	Do not disperses
Retentate	-	Do not disperses

Figure 5 summarizes the drop size distribution for O/W (kerosene-in-water) emulsions prepared by using black liquor as emulsifier. The drop size distribution gives a statistical inventory of the dispersed phase fragmentation and it is therefore the best way to describe an emulsion.

The laser light scattering technique employed in this investigation is one of the most accurate ways to measure drop size and distribution in emulsions. This technique is based on the fact that within the usual macroemulsion range (1-100 μ m) the diffraction angle increases as drop size decreases. The distribution frequency coming from the analyzer is generally in volume, i.e., the proportion of drops included into a class is the volume proportion of these drops with respect to the whole internal phase volume. Nevertheless, if the distribution follows a log-normal statistics (as it is often the case) the volume distribution frequencies can be translated into equivalent distribution and average parameters.

Drop size distributions are often plotted as frequency versus logarithm of the diameter, to test the symmetry around the first arithmetic mean value of an assumed log-normal distribution. The average size or distribution central tendency can be calculated in many different ways that may

not be equivalent among them. Some of the most frequently used statistical parameters to describe the drop size are reported in Table 5 which includes the median (symbolized as $D[0.5]$) which represents the size so that half the internal phase volume is fragmented in smaller drops, and half in larger ones and the mean distribution in volume symbolized as $D[4,3]$.

A slight displacement of the average particle size towards higher drop sizes is observed as the internal phase concentration is increased (see Table 5 for details on the numerical values for the different average parameters). This behavior can be simply explained by the fact that as the internal phase concentration is increased less lignin is available to stabilize the higher surface area produced and therefore larger drops are produced. Alternatively, more coalescence occurs. In both cases it should be stressed that lignin stabilization capabilities are due to the electrostatic and steric barriers provided by the adsorbed lignin molecules.

The apparent viscosities of the emulsions reported in Table 5 are in agreement with the expected behavior, i.e., emulsion viscosity increases as the internal phase content is increased (more tightly packing, i.e., and more inter-drop interactions). A relatively much higher apparent viscosity was observed for emulsions of high internal phase concentration (e.g., WOR 30/70). This is related to structure (possible gel) formation. The rheological behavior for emulsions of low internal phase content (WOR > 50/50) is typical of Newtonian fluids whereas a departure from the Newtonian behavior is observed at higher internal-phase contents.

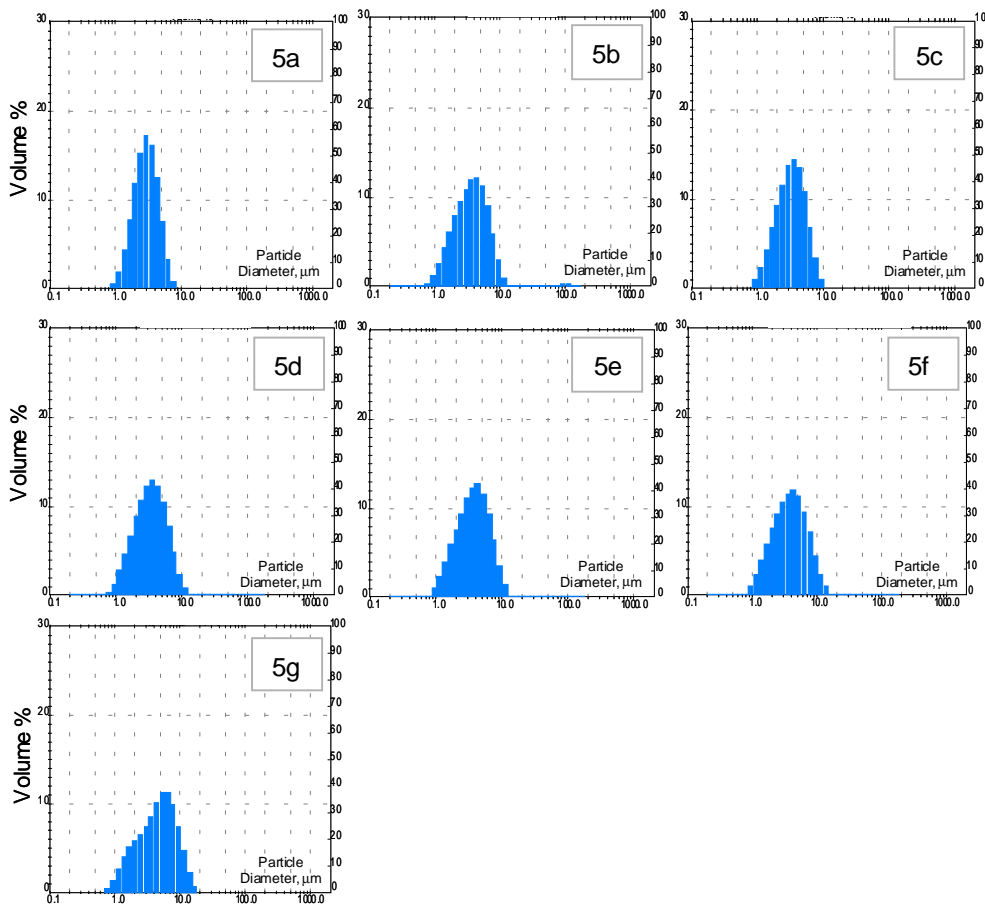


Figure 5: Particle size distribution for kerosene-in-water (O/W) emulsions of different internal phase concentrations (different water-to-oil ratios, WOR): 90/10 (a); 80/20 (b); 70/30 (c); 60/40 (d); 50/50 (e); 40/60 (f) and, 30/70 (g). The employed emulsifier was black liquor at a concentration of 1.5 %.

Table 5: Properties (mean diameters D; span and apparent viscosity at a shear rate of $\dot{\gamma}=200\text{ s}^{-1}$ and 25 °C) of kerosene-in-water (O/W) emulsions of different internal phase concentrations (different water-to-oil ratios, WOR). The employed emulsifier was black liquor at a concentration of 1.5 %.

WOR	90/10	80/20	70/30	60/40	50/50	40/60	30/70
D[0.5], μm	2.95	3.62	3.29	3.36	3.69	3.81	4.59
D[4,3], μm	3.17	5.31	3.6	3.77	4.15	4.43	5.17
D[0.1], μm	1.65	1.58	1.62	1.59	1.63	1.65	1.61
D[0.9], μm	4.99	7.3	6.0	6.51	7.31	8.05	9.57
Span, μm	1.13	1.58	1.33	1.47	1.54	1.68	1.74
App.Visc, cP	4.12	5.11	5.89	8.71	16.7	97.18	760.3

The concept of emulsion stability is linked either to the persistence or the decay of the dispersed system under certain circumstances. The only absolute way to define stability is to count the number of drops in the system, and to evaluate how it changes as time elapses. This is however impractical because most of the measurement techniques require dilution and thus modification of the emulsion. As a consequence stability is normally associated with a visual change in emulsion appearance or tactility, or with the phase separation by drop coalescence according to an experimental set up which mimics the conditions of use of the emulsion (rest, shearing, transport, temperature change, gravity change etc)

As such, the emulsion stability was measured using the time required for phase separation as described in the methodology section and it was observed that in all cases the emulsion stability was of the order of 47 days which implies that the obtained emulsions can be classified as highly stable.

Emulsions with WOR 40/60 were prepared to investigate the effect of pH of the internal aqueous phase on the emulsion drop size (and size distribution) and viscosity (see Figure 6 and corresponding Table 6). The average drop size is distinctively increased as the pH of the aqueous phase is reduced. This behavior agrees with the fact that as the system becomes more acidic and the surface activity of lignin molecules is reduced due to protonation of the charged groups.

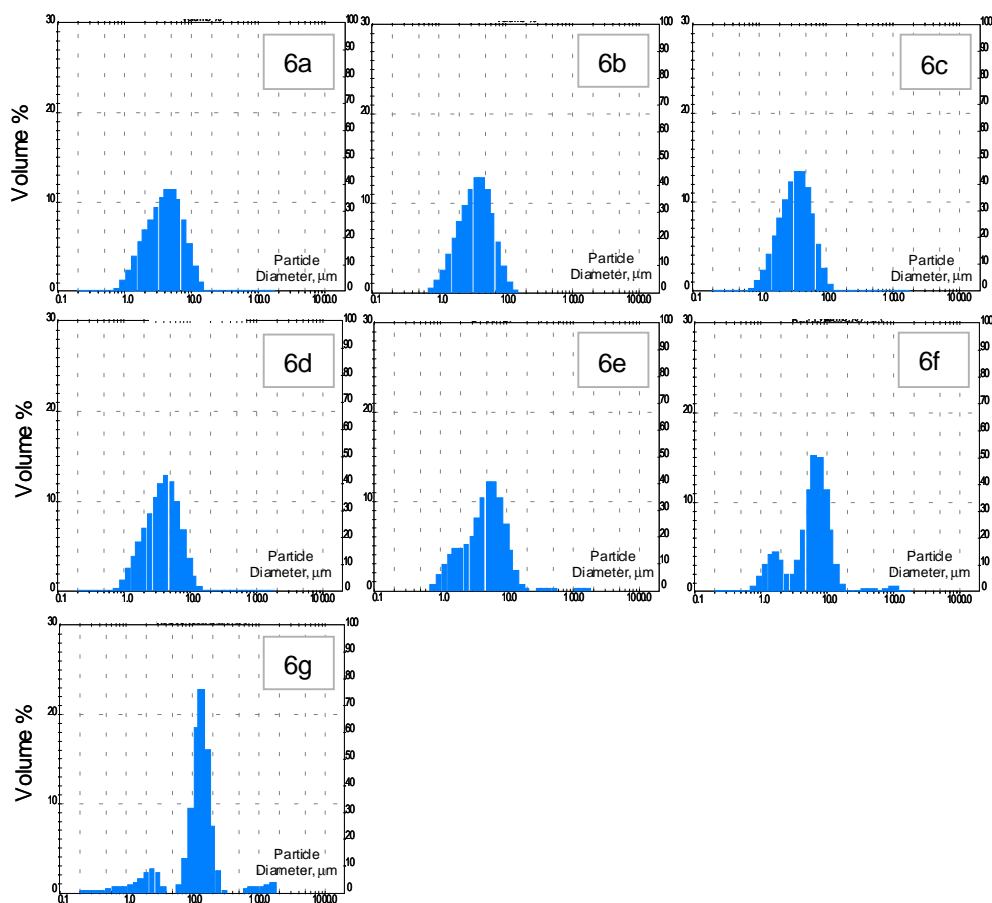


Figure 6: Particle size distribution for kerosene-in-water (O/W) emulsions with WOR 40/60 and aqueous phase at different pH: 12.2 (a); 10.02 (b); 9.35 (c); 7.2 (d); 6.3 (e); 4.6 (f) and 2.58 (g). The employed emulsifier was black liquor at a concentration of 1.5 %.

Table 6: Properties (mean diameters D; span and apparent viscosity at a shear rate of $\dot{\gamma}=200\text{ s}^{-1}$ and 25 °C) of kerosene-in-water (O/W) emulsions (at WOR 40/60) with aqueous phase at different pHs. The employed emulsifier was black liquor at a concentration of 1.5 %.

pH	12.2	10.02	9.35	7.2	6.3	4.6	2.58
D[0.5], μm	4.03	3.59	3.54	3.84	4.89	6.29	12.78
D[4,3], μm	4.62	4.02	3.93	4.29	6.38	8.61	16.39
D[0.1], μm	1.62	1.61	1.64	1.63	1.55	1.54	2.53
D[0.9], μm	8.45	7.01	6.75	7.53	9.91	11.53	19.85
Span, μm	1.7	1.51	1.44	1.54	1.71	1.59	1.36
App. Visc, cP	87.95	61.14	57.16	70.06	79.09	760.23	795.70

The viscosity, on the other hand, is reduced as the pH is reduced down to pH 9 but, at lower pHs a markedly increase in the apparent viscosity is observed. This effect is most probably caused by the formation of structures due to more favorable inter-drop interactions due to the fact that the electrostatic repulsions between the molecules are reduced (more protonated polyelectrolytes as the pH is reduced). These structures produce a more elastic behavior as confirmed by rheometric measurements, i.e., the departure from the Newtonian behavior is more apparent as the pH is reduced. Emulsion stability was of the order of 37 days, which again, confirms the fact that the black liquor is an excellent stabilizer of liquid-liquid interfaces.

Discussion

From the point of view of the reduction of organic contamination, it is confirmed that by using ultrafiltration techniques the detriment effects of residual black liquor can be alleviated. The results (see Figure 1) show a notable removal of color (removal of lignin compounds) upon black liquor ultrafiltration in agreement with observations on removal of organic contaminants by Huuhilo et al. (2002), Bodzek (1977), Sato (1986) and Lundahl et al. (1980). The reduction in color is usually associated with a reduction in the COD and BOD of the effluent (Tipisev, 1980 and Jain et al., 1998). However, the removal of inorganic salts would require the use of nanofiltration technologies. Higher purity of the concentrates, on the other hand, could be obtained by complementing the ultrafiltration process with diafiltration as reported by Tanistra et al. (Tanistra et al., 1998).

Ultrafiltration of black liquor by polymeric membranes proved to be an effective way to separate different lignin fractions as observed from the results shown in Table 2. However, the nominal MWCO of the employed membranes need to be taken as a relative value since the actual molecular size separated by the different membranes employed may not correspond to the reported pore sizes. Thus, it is advisable to discuss the separated molecule size in terms of an effective membrane pore size as reported by Li et al (1996). Calibration of cut-off values are currently underway by using size exclusion chromatography experiments.

The employed regenerated cellulose and polysulfone semipermeable membranes were effective in removing lignin due to their hydrophilic character since this type of characteristic is preferable for refining lignin-containing wastewater (Kochkodan et al. 1994). This also helps to keep membrane fouling at minimum. Even though this subject was not considered in this study it is expected to be an important issue since it has been reported that lignin concentration has an effect on the extent of membrane fouling and permeate quality (Gomez et a., 2000).

The concentration of lignin molecules of high molecular weight is appreciable as judged by the measured rejection of membranes of nominal MWCO 100 000 and 30 000 (see Table 2 and 3). Even though the lignin concentration in the retentates were not measured directly, it is expected that the purity is rather high as reported in other studies on the isolation of lignin from spent liquors by ultrafiltration (Drouin et al., 1988; Ren et al., 2001). This fact is evident from the difference between the measured absorbances for the retentate and permeates in every membrane used (see Figures 2 and 3). This reveals the efficiency in separation of UV-absorbing species, i.e., lignin molecules.

The content of phenolic groups in the fractions was shown to decrease by reducing the membrane MWCO (Table 3), or equivalently, the content of phenolic groups is reduced as the hydrodynamic radius and molecular weigh are reduced in agreement with observations by Norgren et al. (Norgren et al., 2000). Based on the observations of the same authors, it is expected that the median surface charge densities of the macromolecules are approximately constant. However, this may not be the case for the high molecular weight fractions where the surface activity was shown to be higher than for the low molecular weight counterparts (see Figure 4 and corresponding dispersion efficiency of the different lignin fractions).

Surface activity for the different lignin fractions was shown to be high (see Figure 4), except for the case of lignins separated by membranes on low MWCO (1 000). The fact that the surface

tension curves of the black liquor is similar to those of the lignin fractions separated by membranes of MWCO 100 000 and 30 000 reveals that only those molecules with high molecular weight are surface active and selectively adsorb at the air-water interface. The same behavior was observed at solid-liquid interfaces (see Table 4). These observations are supported by reports of the improvement of the surface activity of lignin after ultrafiltration (Liu et al, 1989 and Wu et al., 1988).

The emulsifying capability of the black liquor is demonstrated by the high stability and small drop size found for O/W emulsions (see Figures 5 and 6 and also Tables 5 and 6). The effect of the internal phase concentration is as expected in terms of drop size and emulsion viscosity. The effect of the acidity of the aqueous phase is explained by the protonation of lignin molecules as the pH is reduced. The growth of large, stable associated complexes from smaller lignin moieties as the pH is reduced can also explain the observed behavior. This has been discussed by Woerner and McCarthy (Woerner et al., 1988) who employed light-scattering to indicate a large increase in the average molecular weight (i.e., from ca. 3 500 to 200 000) when the alkalinity is reduced. In the same study it is suggested that the controlling step is the protonation of phenolic hydroxyl groups.

Conclusions

Permeable ultrafiltration membranes were used successfully to separate lignin fractions from industrial black liquor. It was observed that the highest membrane rejection occurs when membranes of high MWCO are employed. The phenol groups concentration is reduced as the membrane MWCO is reduced. The highest surface activity and stabilizing effectivity (for both liquid-liquid and solid-liquid interfaces) was found to be that corresponding to high molecular weight lignin fractions. Excellent emulsifying and dispersant properties were observed by employing black liquor.

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