

UPGRADING SPENT LIQUORS FROM NSSC PROCESS:

III. SEPARATION OF SPENT LIQUORS COMPONENTS BY ULTRAFILTRATION

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Abstract

The present study examines the fractionation of NSSC spent liquors using membranes with different chemical composition and pore sizes. The experiments evaluated the use of this method for separating neutral sulfite spent liquors hemicelluloses from lignosulfonates with the aim of recovering these by-products. Four ultrafiltration membranes with molecular weights cut-off of 500, 2000, 3000 and 10000 Dalton (AMICON type YC05, YM2, YM3 and PM10 respectively) were used. The fractions obtained by ultrafiltration and the original spent liquor were hydrolyzed and hemicellulose content was estimated by HPLC as xylans. Ultrafiltration behavior of spent liquor was estimated by determining molecular weights of the obtained fractions (retentate and permeate) by GPC (IR and UV detection) and lignosulfonate and ash content. BOD and COD of the original spent liquor and of some of the ultrafiltration fractions were also determined. The results showed that, for the separation of lignosulfonates, the membrane with a pore size of 3000 Dalton (YM3) gave the best results, with the lowest rejection of lignosulfonates. Permeates contain lower amounts of hemicelluloses than that of lignosulfonates, organic acids and ashes. The membranes with smaller pores retained more lignin, acetic acid and ash than YM3 and PM10 membranes. Trials at different concentrations show no difference between 1% and 7%. Definitive trials involved re-dilution of the YM filter retentates and further separation of ashes with the YC05 membrane.

Keywords

Semichemical pulping - neutral sulfite pulping – spent liquors– hemicelluloses – lignosulfonates – ultrafiltration – membranes – molecular weights.

Introduction

Modern trends ask for the use of pulping processes friendlier to the environment. In neutral sulfite pulping a major drawback, need to be resolved. In many cases, NSSC spent liquors are sent directly to water courses as effluents. Despite great efforts from its beginning, spent liquors chemicals recovery is still to be addressed.

In previous works, we used a design of experimental approach (Central Composite Design: 29 cooks including five central points) to optimize operating conditions. First, we optimized physical properties of NSSC pulps (1). Spent liquors containing the lowest ratio of inorganic/organic solids were obtained afterwards (2), their organic components were evaluated (3) and the average molecular weights (MW) and MW distributions of lignosulfonates and hemicelluloses obtained were determined (4).

The comparison of molecular weight distribution of hemicelluloses and lignosulfonates indicates that they seem to have different molecular sizes. If only molecular weights are considered, their main fractions could apparently be separated by ultrafiltration if an appropriate membrane cut-off is selected.

Ultrafiltration (UF) is a pressure-modified, convective process that uses semi-permeable membranes to separate species by molecular size, shape and/or charge. Ultrafiltration is gentler to the solutes processed than non-membrane processes. The microporous membranes used are generally rigid, continuous meshes of polymeric material with defined pore sizes. They generally have two distinct layers: a thin (0.1-1.5 μm), dense skin and an open substructure of progressively larger voids, largely open to the permeate side of the ultrafilter. Any species capable of passing through the pores of the skin can therefore freely pass the membrane (5).

In selecting ultrafiltration membranes, desired cut-off of molecular mass and suitable flow must be therefore followed by and adequate chemical composition of the membrane. These factors must be determined in actual operating conditions (6).

Lignosulfonates (LS) in bisulfite spent liquors has been separated by ultrafiltration in several works (6, 7, 8, 9, 10), but that is not the case of NSSC spent liquors, we found only one reference (11). Antecedents in the fractionation of sodium and calcium LS solutions showed no variation in permeate MW, and established that the nature and cut-off of the membranes did not affect permeation rates. Fouling rates were related more to the nature of the membrane than to the cut-off (7).

Spent liquors ultrafiltration from magnesium-bisulfite pulping using three types of membranes (pore size, 2000-10000 Dalton) showed that the membrane with a pore size of 10000 Dalton gave the best separation of lignosulfonates (8). The same results were obtained by other authors (9). They also found that flow rate through the membrane and selectivity depended on both, the pore size and the concentration of substances in the feed. They mentioned that finer separation could be obtained using a 2000 Dalton cut-off membrane, but the flux was too low to be suitable for industrial use.

Our problem in the contrary is to retain hemicelluloses (HC) (higher MW than LS) with the lowest LS rejection. This situation is originated by the particular MW distribution of HC and LS in our NSSC system (4). The two lignosulfonate fractions present in NSSC spent liquors obtained under different pulping conditions have weight-average molecular weights of about 1500 and 300. Hemicellulose molecular weight distributions depend on pulping conditions. Under stronger cooking conditions higher molecular weight materials are dissolved. Hemicelluloses average molecular weights vary between 8000 and 19600 for one fraction, and being 1000 for the other one.

The present study examine the fractionation of NSSC spent liquors using membranes with different chemical composition and pore sizes. The experiments evaluated the use of this method for separating neutral sulfite spent liquors hemicelluloses from lignosulfonates with the aim of recovering these valuable byproducts.

The economy of ultrafiltration depends partially on the membranes permeability. High flows of permeate at high concentrations make possible to obtain the desired LS purity at relatively low cost. Then, the influence of both solid concentrations in the feed and pore size on selectivity and on flow rates through the membrane was studied. Trials were run at three spent liquor concentrations (1, 3 and 7%) and on four membranes.

Experimental

The raw material used was the spent liquor corresponding to the central point of the experimental design performed in a previous work. The pulping procedure and spent liquors characteristics were described in previous articles (1-4). The percentage of different organic materials present in all spent liquors was 59 to 69 % of lignosulfonates, 2 to 24 % of hemicelluloses (simple sugars were not detected), 12 to 29 % of acetic acid and 1.6 to 2.4 % of formic acid. All pulping conditions generate soluble lignosulfonates with the same molecular weight distribution.

Four ultrafiltration membranes with molecular weights cut-off of 500, 2000, 3000 and 10000 Dalton (AMICON type YC05, YM2, YM3 and PM10 respectively) were used. YC filters (cellulose acetate) are high-flow hydrophilic membranes for concentrating low-MW solutes. YM filters (regenerated cellulose) are high-recovery ultrafilters with low non-specific binding of biomolecules. PM filters (polyethersulfone) are high-flux ultrafilters made of inert, non-ionic polymer; but they may absorb hydrophobic molecules.

A batch, thin channel 600-ml TCF10 ultrafiltration system was used. The high performance thin channel system employs cross-flow to minimize accumulation of retained species on the membrane.

Ultrafiltration was always conducted under a pressure of 3.69 kg/cm² (52.5 psi). Recommended pressure of 3.9 kg/cm² (55 psi) could not be attained by our equipment. All separations were lead to 65% of volume reduction.

The characterization of each membrane was determined by permeability, measuring the flow of demineralized water. Filters were conditioned by floating then, skin (glossy) side down, in a baker of distilled water for one hour, changing water three times. Effective area of the membranes was considered as 63 cm².

The efficiency of the process was controlled by determining hemicelluloses, lignosulfonates, acetic acid and ash content in both, retentates and permeates.

The fractions obtained by UF and the original spent liquor were hydrolyzed using 3% sulfuric acid and 4 hours of digestion. The resulting solutions were filtrated and the liquid was passed through a chromatographic column Aminex-hpx87h (Bio-Rad) for sugar content determinations (3). Xylans were considered as hydrolyzed hemicelluloses. Acetic acid (A.A.) content was also estimated. Chromatographic conditions were; eluent: H₂SO₄ 4 mM; flow rate: 0.6 ml/min; detection: refraction index.

The molecular weights of the obtained fractions (retentate (R) and permeate (P)) were analyzed by GPC using a Ultrahydrogel Linear (Waters) column. Chromatographic conditions were as follows; flow rate: 0,5 ml/min; mobile phase: 20% aqueous solution of methanol containing 0.1 N NaNO₃ and 0.1 N glycine; detection: refraction index and UV at 254 nm.

Lignosulfonate concentration was measured by absorbancy determinations, using UV spectroscopy at 274 nm.

Solids were determined weighting aliquots of fractions before and after oven dry drying.

The relationship between ash content at 900°C (TAPPI st 629 os-53) and conductimetric values was determined. The regression equation for these properties is:

$$\text{Ash (\%)} = -0.123 + 0.958 * \text{Conductivity} \quad R^2 = 0.99$$

As conductivity is easier to perform, ash content of all samples was therefore obtained using this equation.

Stability of membranes in long-term performance was measured by fouling behavior. Fouling is defined as the irreversible decline in membrane flux due to the deposition and accumulation of submicron particles and solutes on the membrane surface. The effect of fouling on flux was determined measuring flux in function of running time in conditions of total recycle, i.e., permeate and concentrate returned to feed 5 times each 2 hours. This was performed with the YM3 filter at 3% spent liquor concentration.

Definitive trials for further purification involve re-dilution of the YM filter retentates. Permeates were additionally purified by an ulterior separation with the YC05 membrane.

BOD and COD of the original spent liquor and some UF fraction were also determined.

Results and Discussion

Flows obtained in permeability measurements with demineralized water were:

- YC05: 0.033 ml/min cm² (nominal value: 0,03-0,04)
- YM2: 0.032 ml/min cm² (nominal value: 0,04-0,06)
- YM3: 0.066 ml/min cm² (nominal value: 0,06-0,08)
- PM10: 0.680 ml/min cm² (nominal value: 1,5-3,00)

Even permeability values followed the sequence of membrane cut-off; they were in general lower than nominal ones. We verified however that increasing wetting time enlarges flux.

Preliminary trials with the original spent liquor were performed using the YM2 membrane at spent liquors concentration of 1% y 7% (Figure 1). As there was not noticeable difference, an intermediate concentration of 3% was adopted for posterior experiences using membranes YM2, YM3 y PM10.

Flow rates for SL using different membranes (each 30 –min.) are presented in Figure 2. As solid concentration of the retentate increases, the drop of flux is the same for all membranes. At 60% of volume reduction during batch concentration (180 min), YM3 fluxes are approximately 0.014 ml/cm² min.

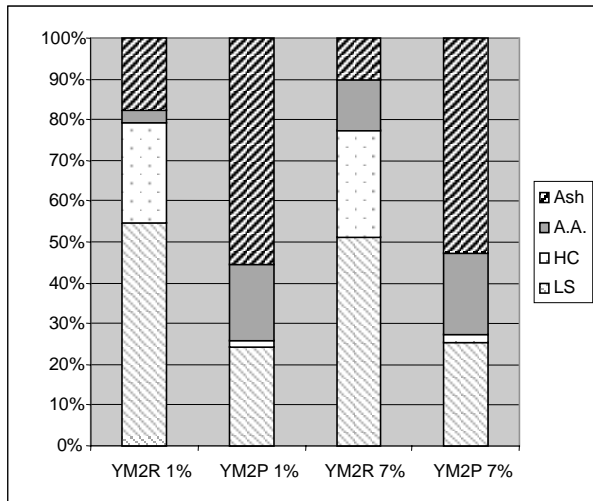


Figure 1: LS, HC, A.A. and Ash in SL, R and P separated by YM2 (1% and 7%).

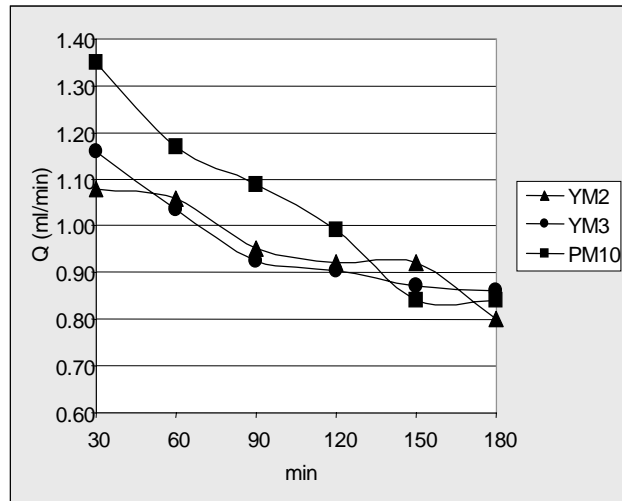


Figure 2: Flow rates of permeate for the different membranes (means each 30 min).

Maximum values of variation coefficients for separations using the same membrane in identical conditions are approximately: 4% in flows, 6.5% in total solids, 2% in lignosulfonates, 5.5% in hemicelluloses, 4% in acetic acid and 3.5% in ash determinations. Variation coefficient is defined as the ratio between standard deviation and repetition mean in percentage.

To see the separation evolution, six fractions of permeates were obtained at 15 minutes each (named P1 to P6). Lignosulfonates (LS), hemicelluloses (HC, represented by xylans content), acetic acid (A.A.) and ash concentrations in retentates (R) and different permeates are shown in Table 1. Original spent liquor feed concentrations (C) are also shown in the same table. Rejection values for each substance and membrane are also included.

Figures 3 y 4 shows the LS, HC, A.A., and ash quantity (in percentage over total solids content in each fraction and in the original spent liquor) in retentates (R) and permeates (P) separated by the different membranes. Spent liquor composition was; LS: 33%, HC: 12%, A.A.: 17%, Ash: 37% (based on total solids).

Table 1: Lignosulfonates, hemicelluloses and acetic acid contained in SL, R and P (mean values).
SL concentration: 3%, volume reduction: 65%

Membrane	LS (g/l)	HC (g/l)	A. A. (g/l)	Ash (g/l)
SL concentrations	9.0	3.3	4.7	10.1
YM2 R	16.2	5.9	6.1	10.3
YM2 P	3.7	2.2	4.6	8.1
YM2 Rejection	77	62	24	21
YM3 R	13.6	5.0	5.4	11.2
YM3 P	6.6	1.9	4.3	9.4
YM3 Rejection	52	63	21	16
PM10 R	15.4	5.1	4.5	11.3
PM10 P	5.4	2.3	4.3	9.2
PM10 Rejection	65	54	6	19

Rejection results showed that in all cases HC and LS can be recovered from spent liquors by ultrafiltration in retentates, and the ratio of organic to inorganic solids in the starting feed can be increased significantly.

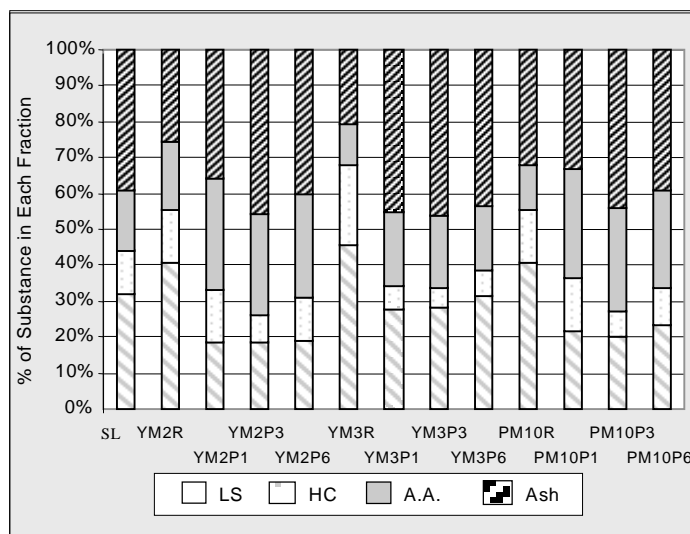


Figure 3: LS, HC, A.A. and Ash in R and P, separated by YM2, YM3 and PM10 (based on total solids of the fraction).

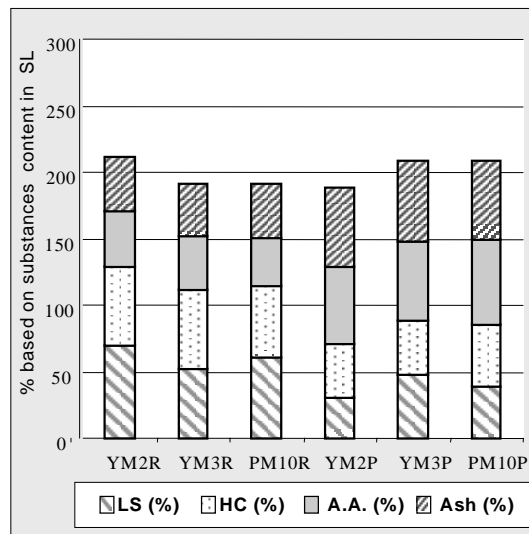


Figure 4: LS, HC, A.A. and ash in R and P separated by YM2, YM3 and PM10 (based on substances content in spent liquor).

YM2 membrane having smaller pores retained more lignosulfonates (LS rejection is high) compared with that of the YM3 and PM10 membranes (Figures 3 and 4). The YM3 filter (pore size of 3000 Dalton) gives the best results for lignosulfonates separation, having the highest selectivity (Figures 3 and 4).

PM10 performance was not as good as expected. Lignosulfonate rejection is high like the hemicelluloses presence in the permeate. These peculiarities are possible due to membrane characteristics: its chemical composition and its high cut-off can be the reasons for low selectivity.

All retentate and permeate fractions were diluted to the same level and, after filtration, they were analyzed by GPC using IR or UV at 254 nm detection. Figures 5 to 8 show the MW distributions for all the substances in the original spent liquor and fractions.

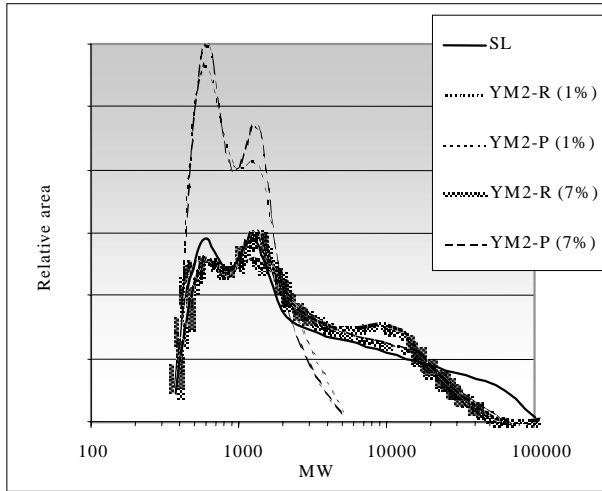


Figure 5: MW of substances (YM2 filter, IR detection).

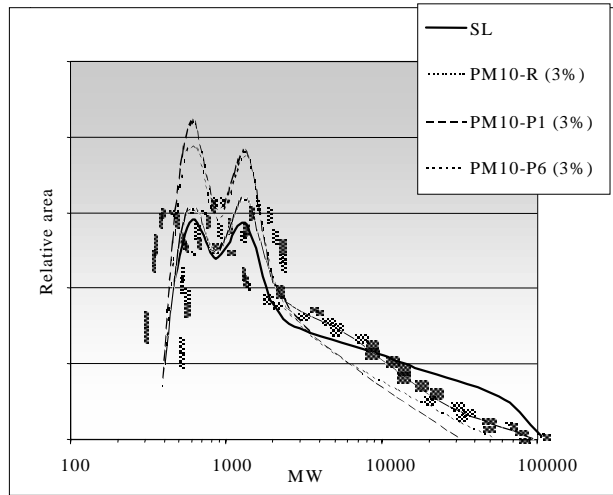


Figure 6: MW of substances (PM10 filter, IR detection).

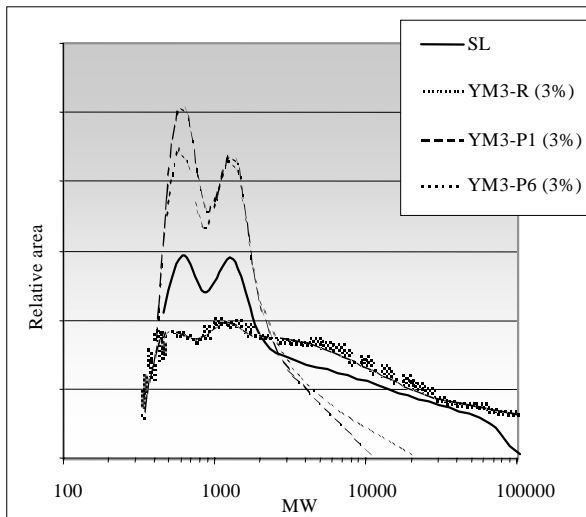


Figure 7: MW of substances (YM3 filter, IR detection).

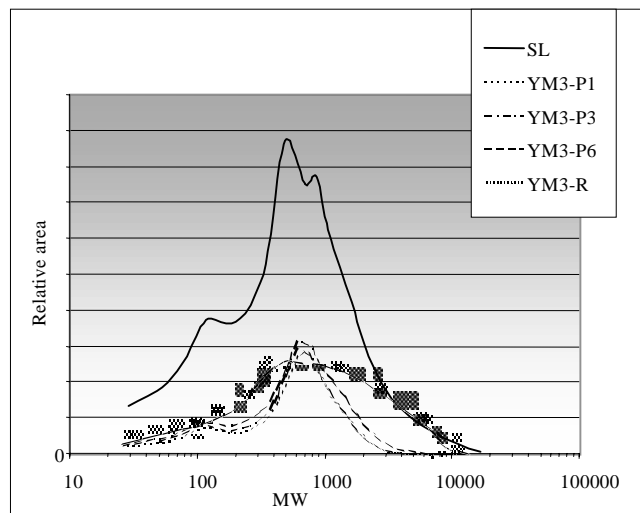


Figure 8: MW of substances (YM3 filter, 3%, UV at 254 nm detection).

Chromatogram shape is almost the same in all cases. Differences are evidenced by the level of molecular weights that are retained and those that passed the filters. Figure 5 shows that the molecular weight distributions obtained for permeate and retentates at 1% and 7% of spent liquors concentration are almost the same. Maximums MW values in permeate from YM2 filter are 5000. In contrast, these values are higher than 40000 for PM10 (Figure 6). PM10

retentate shows a great concentration of substances of low MW. These results reflect the low selectivity of the PM10 filter. Therefore, this membrane is not adequate to our separation needs. Differences in maximum MW of the different fractions of permeates when PM10 is used are also displayed (20000 in P1 and 40000 in P6).

In the separation with YM3, an important increase in selectivity was observed (Figure 7). A low concentration of substances having MW of about 1000 is present in the retentate and the amount of high MW materials present in permeates is low.

Figure 8 exhibit the MW distributions obtained with UV detection in the separation with YM3 filter. Only lignin derivatives are detected by this method. All permeates present the same shape and it is clear that the retentate contains lignosulfonates with higher molecular weights (weight-average molecular weights are: SL: 1434, R: 1594, P1: 680, P2: 653, P3: 724).

Table 2 presents the result of the application of a separation scheme shown in Figure 9, including re-dilution to the original volume of retentates and further separation in five successive ultrafiltration cycles (YM3 filter). Results are showed, first based on the total quantity of each substance in spent liquor considered as 100%, and secondly as percentages based on total solids in each fraction.

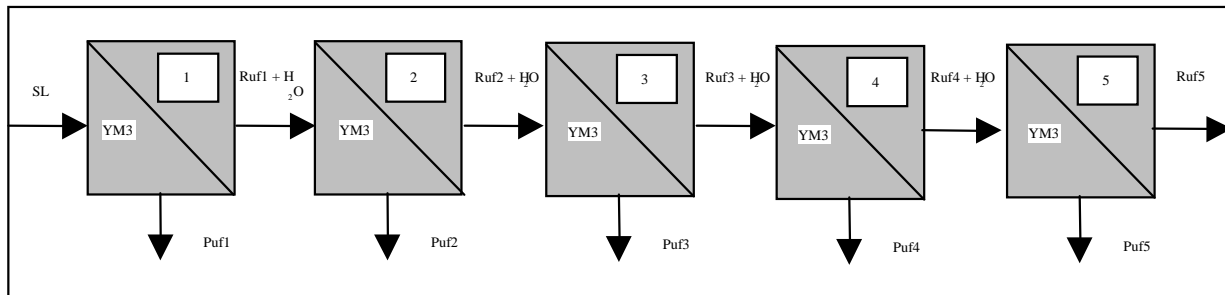


Figure 9: Separation scheme including cycles of retentate dilution and re-filtration.

Table 2: Results obtained by application of the separation scheme showed in Figure 9.

	% based on substances content in spent liquor				% based on total solids of the fraction			
	LS (%)	HC (%)	A. A. (%)	Ash (%)	LS (%)	HC (%)	A. A. (%)	Ash (%)
Fed	100	100	100	100	36.5	11.5	16.4	35.6
Puf 1	36.0	34.4	55.6	61.8	29.1	8.9	18.9	43.1
Puf 2	24.6	20.4	31.8	36.7	32.3	8.6	17.5	41.6
Puf 3	8.0	5.6	9.5	1.5	53.0	11.9	26.4	8.7
Puf 4	2.7	0.8	Nd	Nd	Nd	Nd	Nd	Nd
Puf 5	1.1	0.3	Nd	Nd	Nd	Nd	Nd	Nd
Ruf 5	27.6	38.4	3.1	0	67.0	29.8	3.2	0

Even when 61% of lignosulfonates present in spent liquors are found in permeates after two stages, 28% of them will remain in the retentate after five stages of ultrafiltration. Almost the same percentages of hemicelluloses passed to permeates and final results show that the retentate fraction is little enriched in hemicelluloses. Initial LS/HC ratio is 3.2 and final one after five cycles is 2.2. The retentate after two cycles is consequently rather enriched in HC, LS/HC = 2.7.

In a previous work (2) we found that LS molecular weight distribution in NSSC spent liquors present two peaks, one of Mw 1000 (47%) and other of 150 (53%). Hemicelluloses present also two peaks of Mw 18000 (43%) and 1500 (31%). Even when the highest molecular weight of HC is ten times greater than that of LS, these ultrafiltration results show that percentages of substances separated in retentates are coincident with high molecular weight fraction contents of both components. As ultrafiltration membrane separation involves hydrodynamic radius of the particle (12), the low rejection of HC can be justified by the flexibility of linear molecules. On the contrary, the three-dimensional molecule of LS explains its high rejection. A retentate fraction having high molecular weight LS and HC is therefore obtained.

A retentate like this can be used as a concentrated source of relative high molecular weight LS and hemicelluloses, being the quantity present almost 60% of the original one in both cases. The inorganic to organic solids ratio changed from 0.55 in the spent liquor to 0.015 in this retentate.

Acetic acid and ash content in the two first permeated represent 87% and 98%, respectively, of the amount found in the original spent liquor. The third stage produces negligible separation.

Results in Table 2 indicate that only two separation stages are necessary to obtain an acceptable separation.

Fouling trial results, measured as the flux reduction for de spent liquors with respect to pure water flux, are presented in Figure 10. The flow rate for SL drops about 64% in relation to pure water flux after 10 hours of continued ultrafiltration.

The separation scheme combining YM3 and YC05 membranes in two cycles of retentates redilution and filtration is presented in Figure 11 and results are shown in Table 3. This separation system is intended to obtain fractions suitable for further transformation of components in derivatives with possible industrial use.

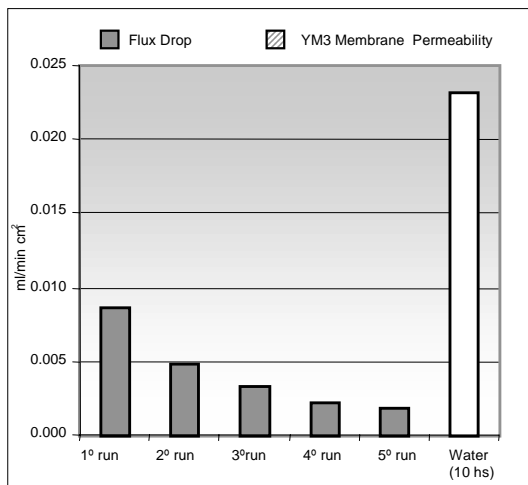


Figure 10: SL and pure water flux drops respect to the initial water flux.

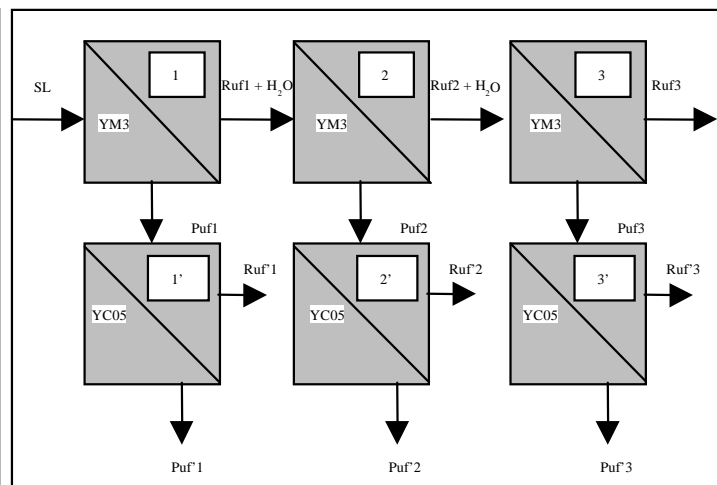


Figure 11: Separation scheme with cycles and the incorporation of the YC05 membrane.

Results show that almost the total quantity of free inorganic solids is eliminated in the first YC filtration. The ash remaining in the YC05 is probably originated from sodium acetate and sodium lignosulfonates having very low molecular weights.

Further separation of the Ruf' 1 retentate with another YC05 filter shows that LS and Ash rejections are 95 and 92% respectively (60% of volume reduction). Thus, this stage can be considered as unnecessary.

Table 3: Results of separations combining the YM3 and YC05 membranes: LS and Ash percentages based on substance content in feed solutions (YM permeates)

Membrane	LS (%)	LS Rejection (%)	Ash (%)	Ash Rejection (%)
YC05R'1	68.4	85	72.7	66
YC05P'1	31.5		27.3	
YC05R'2	>95	>95	97.4	94
YC05P'2	Nd		2.6	
YC05R'3	>95	>95	>99	>99
YC05P'3	Nd		Nd	

BOD, COD, and soluble solids determined values are shown in Table 4.

Table 4: BOD, COD and soluble solids of selected permeates.

	BOD mg/l	COD mg/l	Soluble solids (%)
SL (from the digester)	12470	59410	9.0
SL (feed to the UF system)	4156	19803	3.0
YM3P1	4090	13570	1.8
<i>YM3 stage reduction</i>	<i>2 %</i>	<i>31 %</i>	<i>40 %</i>
YC05P'1	1230	5590	0.69
<i>YC05 stage reduction</i>	<i>70 %</i>	<i>59 %</i>	<i>61 %</i>
Total reduction (YM3 + YC05)	70 %	72 %	77 %

Comparing BOD and COD values, results show the high content of non-biodegradable substances in NSSC spent liquors. These materials could only be eliminated with a separation involving the two membranes. Our batch ultrafiltration system removed 70 % of the BOD, 72% of the COD, and 77% of the soluble solids in two stages using different membranes, YM3 and YC05.

A possible NSSC SL separation-concentration scheme could involve two YM3 stages and two YC05 stages. The YC05 first retentate (Ruf'1) would be mixed with the second YM3 (Puf2) permeate as feed to the second YC05, and the YC05 second permeate (Puf'2) could be partially recirculated as dilution water of the second YM3 ultrafilter.

The scheme combining YM and YC membranes could be used to produce a NSSC spent liquor separation in three fractions. A retentate (Ruf2) containing high molecular weight LS and HC, another retentate (Ruf'2) having low molecular weight LS, HC, sodium acetate and a permeate (Puf'1) enriched in inorganic substances.

Comments found in the literature state that ultrafiltration is more cost effective (when compared to other processes such as evaporation or freeze crystallization) for flow rates less than 7 m³/ADt of pulp (13). From this point of view, our separation-concentration scheme could be valid. Nevertheless, as power demand for ultrafiltration pumping at high pressure is about 15 kWh/m³ (13), costs could be greatly increased as YC05 flux is rather low (0.008 ml/min cm²).

The operative limitations inherent to the equipment used in this research could be a source of errors. This can be attributed to the low volumes used. Manipulation losses of little quantities of liquid produce important errors at this level. Therefore, the process should be scaled up to confirm the results discussed in this paper.

Conclusions

- There is not noticeable difference in separating spent liquor at concentrations of 1% y 7%.
- As concentration of the retentate increases, the drop of flux is the same for all tested membranes.
- YM2 membrane retained more lignosulfonates (LS rejection is high) than YM3 and PM10 membranes.
- YM3 filter gives the best results for lignosulfonates separation, having the highest selectivity.
- PM10 performance showed low selectivity, presenting important quantities of high MW substances in permeates and low MW substances in retentates.
- After two separation stages (scheme Figure 9) results are not enhanced by re-dilution of the retentates and separation in ulterior stages. They indicate that only two stages of separation produce substantial differences in permeates and retentates composition.
- A retentate fraction having high molecular weight LS and HC is obtained after two cycles. This retentate can be used as a concentrated source of high molecular weight LS and hemicelluloses, being the quantity present almost 60% of the original one in both cases.
- Acetic acid and ash content in the two first permeated represent 87% and 98%, respectively, of the amount found in the original spent liquor.
- Fouling trials results show that pure water flux drop is about 64% after 10 hours of continued use.
- The scheme combining YM and YC membranes produce a SL separation in three principal fractions: a retentate containing high molecular weight LS and HC, another retentate presenting low molecular weight LS, HC and sodium acetate, and a permeate enriched in inorganic substances.
- Our batch ultrafiltration system removed 70 % of the BOD, 72% of the COD, and 77% of the soluble solids in two stages using different membranes, YM3 and YCO5.

List of Abbreviations and Formulas

A.A.: acetic acid

HC: hemicelluloses

LS: lignosulfonates

MW: molecular weight

Nd: non-determined

NSSC: neutral sulfite semi-chemical

P: permeate

Puf: permeate of schemes including cycles of retentate dilution and ulterior filtration

Q: permeate mean flow rate each 15 minutes (ml/min).

R: retentate

Ruf: retentates of schemes including cycles of retentate dilution and ulterior filtration

Rejection coefficient = $1 - C_p/C_r$ (5)

C_p : permeate concentration (g/ml)

C_r : retentate concentration (g/ml)

SL: original spent liquor.

UF: ultrafiltration

X: xylans

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