

# Ultrafiltration of Industrial Hardwood Kraft Black Liquor with Regenerated Cellulose Membrane

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## Abstract:

**Background:** Kraft black liquor is a repository of valuable chemicals with potential application in high-value products. Fractionation of black liquor into low and high molecular weight fractions is imperative for the efficient isolation of these chemicals.

**Materials and Methods:** This study investigated the performance of a 1KDa regenerated cellulose membrane (RCM) in the ultrafiltration of industrial hardwood kraft black liquor. The effect of pH on lignin recovery was evaluated, and resultant lignins were characterised with FTIR, DSC, TGA, Py-GC/MS and SEC.

**Results:** The results revealed that RCM was effective in the ultrafiltration of black liquor into low and high molecular weight lignin fractions. At ambient temperature and maximum volume reduction of 72.5%, recovery (%) of lignin was 35% and 65% at pH 5 and 10, respectively. The molecular weight of permeate lignins (2600 & 3900 gmol<sup>-1</sup>) was lower than that of retentate lignins (5600 & 11,600 gmol<sup>-1</sup>) at pH 5 and 10, respectively. A slight difference in the distribution of monovalent and divalent ions in the permeate and retentate was observed. Based on the Py/GC-MS analysis, syringol compounds were found to be higher in the lignin fractions than guaiacol compounds.

**Conclusion:** This study showed that regenerated cellulose membrane could be effectively applied for the ultrafiltration of kraft black liquor and recovery of lignin.

**Key Word:** Kraft black liquor; Fractionation; Ultrafiltration; Regenerated cellulose membrane; Pulping; Lignin; Hardwood

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## I. Introduction

Fractionation of valuable chemicals from lignocellulosic biomass is currently an area of significant research interest. This is due to the urgent need to provide viable alternatives to fossil-based resources, which have hitherto been the mainstay of man's sustenance albeit now considered to pose proven health and environmental challenges (Thompson *et al.* 2009). Using bio-based resources is an attractive prospect because of its wide availability, relatively low cost, and low or no toxic effect.

Kraft pulping, which involves the use of aqueous solution of NaOH and Na<sub>2</sub>S as the primary pulping chemicals, is the most widely used process for the delignification of wood owing to the high quality of resultant pulp. During this process, wood components such as lignin and hemicellulose are dissolved in the pulping liquor resulting in a byproduct called black liquor (Cardoso *et al.* 2009). Black liquor is a complex mixture of valuable organic and inorganic compounds, which can be isolated and processed into value-added bio-products (Niemi *et al.* 2011; Mänttari *et al.* 2015). Although isolation of individual components of black liquor remains a challenge, several process technologies have already been investigated and established to fractionate high molecular weight lignin and various classes of compounds (Garron *et al.* 2015; Kumar and Alén 2015; Fatehi 2016; Schmitt *et al.* 2017). Membrane separation technique is a major technological process in this field.

Ultrafiltration (UF) is the most studied membrane process for fractionating lignin and other chemicals from black liquor (Toledano *et al.* 2010a; Fernández-Rodríguez *et al.* 2015). UF permits the separation of black liquor into high and low molecular weight fractions with varying degrees of distribution of chemical components in the fractions. The distribution of inorganic and organic components in the fractions may depend on other operating conditions such as pH, temperature, feed velocity and interaction with the membrane (Wallberg *et al.* 2003a). UF can be performed in two main filtration modes: direct flow filtration (DFF), also known as 'dead-end' filtration and tangential flow filtration (TFF), also known as crossflow filtration. In DFF, the feed stream is applied perpendicular to the membrane surface under applied pressure, while in TFF feed stream passes tangentially along the surface of the membrane as one portion passes through the membrane (permeate). At the same time, the remainder (retentate) is recirculated back to the feed reservoir. TFF is the most commonly used UF process because, unlike DFF, retained components do not build up at the surface of the

membrane. Instead, they are swept along by the tangential flow (Kevlich *et al.* 2017). The build-up of retained components on the membrane surface during DFF makes the system susceptible to fouling at a relatively short operating time.

Operational problems associated with other lignin fractionation methods have validated the increasing application of UF in the pulp and paper industry and, by extension, in different fields such as pharmaceuticals, wastewater treatment and food (Galanaki *et al.* 2013; Conidi *et al.* 2017). One of such problems is the formation of colloids during precipitation at low pH values (García *et al.* 2009). These colloids complicate separation and purification, leading to the production of low purity lignin. In addition, membrane technology generally offers an attractive alternative approach mainly due to the associated low energy requirement and operational reasons (Kevlich *et al.* 2017).

However, membrane filtration process is not without its technical challenges. The continuous quest to achieve high and consistent membrane flux, limited by fouling, relatively poor selectivity of desired compounds, amongst other associated challenges, is well documented (Bhattacharjee *et al.* 2006). Conversely, to circumvent these problems, the use of hyphenated processes for improved outputs has been considered (Hellstén *et al.* 2013; Arkell *et al.* 2014; Mänttari *et al.* 2015). Shen *et al.* (2013) investigated the application of a combined membrane, activated carbon adsorption and ion exchange resin in the separation of liquor from the production of dissolving pulp. This process resulted in a highly concentrated stream of hemicellulosic sugars. In addition, during the fractionation of lignin and other important chemicals, acid precipitation of black liquor before or after membrane separation was considered an important step (Ziesig *et al.* 2014). As reported by Mänttari *et al.* (2015), acid precipitation before UF reduced the fouling tendency of the membrane, but precipitation after UF may induce early fouling and affect flux in subsequent separation steps.

A wide range of membrane types such as cellulose acetate, polyethersulfone, polysulfone, ceramic and polymeric membranes have been utilised to fractionate lignin from black liquor (Adikane *et al.* 2004; Bhattacharya *et al.* 2005; Wallberg 2006; Kevlich *et al.* 2017). A careful study of the performance evaluation of these membranes reveals divergent valuable opinions and recommendations without a consensus on the most efficient membrane for lignin fractionation from black liquor. The highly alkaline nature and high solid content of kraft black liquor suggest a membrane that can withstand extreme conditions should be the most appropriate on an industrial scale (Holmqvist *et al.* 2005). Nevertheless, opportunities for more research with membranes of varying material properties still abound.

Regenerated cellulose membranes (RCM) are membranes with very high hydrophilicity and low resistance to fouling. They are more compatible with organic solvents than polyethersulfone-based membranes. With hydrophilic RCM, high purity hemicellulose was separated from hot water extract of spruce-saw dust (Al Manasrah *et al.* 2012). Also, in the UF of process water from pulp and paper mill, RCM showed high filtration capacity and high-temperature stability under the studied operating conditions (Kallioinen *et al.* 2006). The resulting high filtration capacity was attributed to the extreme hydrophilicity and weak charge of the membrane. RCM was also employed with relative success in the UF of phenolic compounds from sugar solution (Wei *et al.* 2010), removal of humic acid from drinking water (Lowe and Hossain 2008) and isolation of high purity lignosulfonate from spent sulphite liquor (Ringena *et al.* 2005).

The recovery of lignin from black liquor is imperative because of its vast industrial potential as raw material and building block for renewable chemicals. Over the years, lignin's multifunctional and structural features have been exploited to develop products for various applications such as dispersants, binders, carbon fibers, biofuels, and phenolic resins (Jablonsky *et al.* 2015). The inherent special characteristic features also make lignin a veritable resource in developing functional materials which are sustainable, toxic-free, and cost-effective alternatives to fossil-based resources (Matsushita 2015). Lignin separation from black liquor is also a way of increasing the economic value of the output from kraft pulp mills, as exemplified by the LignoBoost technology (Tomani 2010). Further cause for lignin fractionation is the variation in property characteristics of different lignin fractions from UF compared to lignin from acid precipitation. In the comparative study of lignin fractionation from these two methods, Toledano *et al.* (2010b) reported that UF lignin fractions are less contaminated by lignin-carbohydrate complex than lignin obtained by selective acid precipitation. Thus, lignin of improved purity and physicochemical properties are essential for the expansion of the biobased economy.

In addition, the presence of inorganic elements in black kraft liquor can be detrimental to the operation of the recovery plant in the pulp mill. These elements can form complexes with organic compounds, resulting in crust formation on the wall surfaces of heat exchange evaporators. The long-term effect of this is equipment corrosion and reduction in production efficiency (Cardoso *et al.* 2009). Therefore, removing these elements from black liquor through UF or other separation methods is imperative to maintain the longevity of pulp mill equipment and plant.

In this present work, the performance of RCM in the ultrafiltration of industrial kraft black liquor was investigated vis-à-vis process flux, lignin recovery and contents of inorganic elements in the resultant retentate and permeate fractions. Subsequently, acid precipitation was used to isolate lignin from the fractions. To

accurately evaluate the membrane's selectivity, the physicochemical characteristics of the obtained lignin samples were studied using FTIR, DSC, TGA, Py-GC/MS and SEC. In addition, the properties of lignin samples were also compared to lignin isolated via direct acid precipitation.

## II. Experimental

### 2.1 Materials

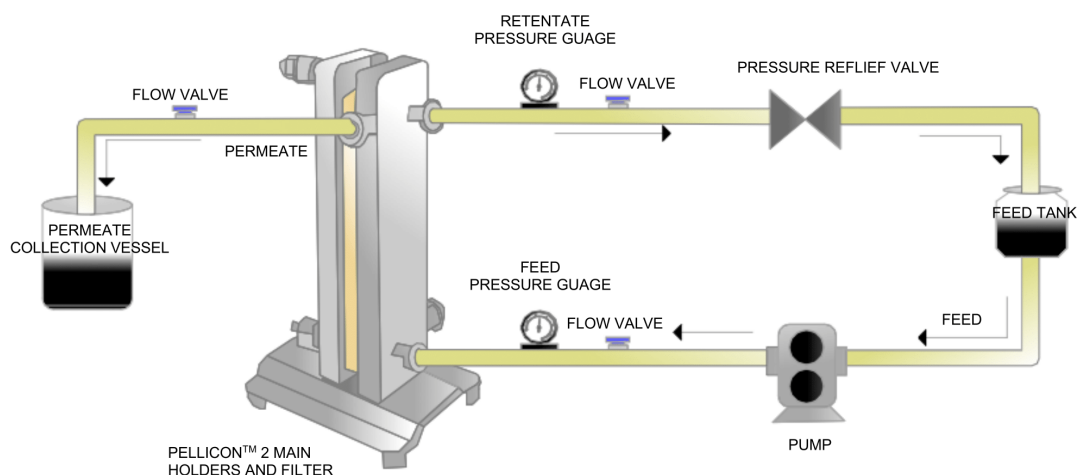
The industrial hardwood kraft black liquor used in this study was kindly supplied by a Slovakian pulp mill. According to the supplier, the black liquor was produced from a continuous batch cooking kraft pulping process. The pH and density of the black liquor were 13.5 and 1279.8 g/L, respectively.

### 2.2 Ultrafiltration Process

Crossflow ultrafiltration was performed using lab-scale membrane equipment as reported by Ringena *et al.* (2005). The membrane unit consisted of a Pellicon 2 mini stainless steel cassette holder (Millipore) equipped with a hydrophilic 1 KDa regenerated cellulose membrane (Millipore, USA) with an area of 0.1m<sup>2</sup>. The cassette holder comprised two steel plates; one acted as a flow distribution manifold and the other as a mating solid flat surface. A peristaltic pump (LP-1A, Amicon) was used to supply the black liquor from the 2 L glass beaker feed tank into the membrane unit. Inlet pressure (feed side) and outlet pressure (retentate side) were controlled by two pressure gauges, considering the maximum pressure resistance of the connecting tubes. The operating pressure called transmembrane pressure (TMP), representing the average pressure (bar) difference between the permeate side and retentate side of the membrane, was manually controlled by adjusting the retentate valve and calculated using Eq. 1,

$$TMP (bar) = \frac{P_{in} - P_{out}}{2} + P_p \quad (1)$$

where P<sub>in</sub> and P<sub>out</sub> are the inlet and outlet pressure of the membrane, P<sub>p</sub> is the pressure at the permeate side (zero with this system). A schematic drawing of the UF set-up is shown in Fig. 1.



**Fig. 1.** Schematic view of the ultrafiltration set-up

Before sample ultrafiltration, the membrane was flushed with deionised water for about 90 minutes to remove the cleaning and storage solution in the system. The original pure water flux was thereafter measured at a flow rate of 0.5 l/min, feed inlet pressure 0.7bar, retentate outlet pressure 0.35 bar. Water was recirculated for about 20mins to achieve stability and constant flow before collection of permeate began. The variation of pure water flux with TMP was also monitored to assess the membrane permeability and fouling condition. The retentate solution from the membrane was recycled back into the feed tank and permeate collected in a glass graduated cylinder. The time taken to collect permeate was monitored with a laboratory stopwatch.

Permeate flux was calculated using Eq. 2,

$$J = \left(\frac{V}{AT}\right) \quad (2)$$

where J is permeate flux (Lm<sup>-2</sup>h<sup>-1</sup>), A is membrane area (m<sup>2</sup>), V is permeate volume (L), and T is Time (hr).

Ultrafiltration was performed at ambient temperature (23.5°C) with black liquor samples at pH 10 and 5. pH adjustment was done by the slow and controlled addition of 1M sulphuric acid to the black liquor. At first, the system was set in recirculation mode to study the influence of TMP on the permeate flux. This also allowed for the selection of optimum pressure for the concentration of black liquor. In this mode, both retentate and

permeate were recirculated to the feed tank. Permeate was collected every 20 mins after a constant flow was observed. The experiment was then continued in the concentration mode, where permeate was continuously withdrawn and recorded until a maximum volume reduction (VR) was achieved. The maximum VR was signaled by the drastic reduction in flux which remained constant over a period. VR was calculated as the ratio between the permeate volume ( $V_p$ ) and the initial feed volume ( $V_o$ ) and expressed in % Eq. 3.

$$VR = \frac{V_p}{V_o} \times 100 \quad (3)$$

The experiment was rounded up with diafiltration to ensure maximum recovery of the targeted components and obtain a more purified fraction. To achieve this, water of approximately the same volume as permeate removed was added to the retentate, and the filtration was continued until completion. After the filtration process, membrane cleaning was done as recommended by the supplier. First, the membrane was flushed with deionized water (30 °C) for 1 h and then cleaned by recycling 0.1 M NaOH solution through the system. Washing was then repeated with warm deionised water. Retentate and permeate were collected until the outflows were no longer coloured. After cleaning, the membrane was stored in 0.1% sodium bisulphite solution in the refrigerator (4 °C).

### 2.3 Isolation of Lignin

A total of 200 mL of permeate and retentate from the UF process were treated with 5 M sulphuric acid to obtain lignin fractions. The pH value was measured with a WTW pH330 pH meter. The resulting suspension was centrifuged at 4000 rpm for 20 min, and the supernatant was removed via filtration with a glass filter. The lignin sample was washed with acidified water two times with follow-up centrifugation and filtration both times. The solid lignin was then dried in a vacuum oven at 50 °C. The physicochemical characteristics of the isolated lignins were evaluated using FT-IR, TGA, DSC, GPC and Py/GCMS.

### 2.4 Analysis of Feed, Retentate, and Permeate

The feed, retentate, permeate and original black liquor were analysed for total dissolved solids (TDS), lignin content, organic content, density and inorganic elements. TDS was determined by the gravimetric method (TAPPI 1999), and the density was determined by the pycnometric technique (Cardoso *et al.* 2009). The organic content was determined by heating the residue from the TDS measurement at 700°C for 5 h. The amount of organic content was calculated as the difference between the weight of the residue before and after heating at 700°C.

Lignin concentration was measured with a Perkin Elmer Lambda 650 UV/VIS spectrometer using the UV method described by Wallberg *et al.* (2003b). Samples were diluted with deionised water and 0.1M NaOH before the measurement. Lignin concentration was calculated using the Beer-Lambert relationship (Eq. 4),

$$LC \left( \frac{g}{l} \right) = \frac{A}{b \times a} \times df \quad (4)$$

where LC is Lignin concentration (g/L), A is Absorbance, a = absorption constant (24.6 g/Lcm) (Alen and Hartus 1988), B is cuvette path length (1cm), and df is dilution factor.

The concentration of inorganic elements was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES) with a Thermo iCAP6300 Duo. Before the analysis, the samples were pre-treated to remove the organic component. Then, 400ul of the sample was pipetted into the reaction vessel and mixed with 6mL concentrated nitric acid and 1 mL hydrogen peroxide. The mixture was heated for about 30mins under a high-pressure rotor. The final solution after treatment is then diluted to 10 mL and analysed.

### 2.5 Analytical Characterization of Lignin

Fourier Transform Infrared Spectroscopy (FTIR) of lignin fractions were recorded on a Bruker Vector 33 instrument from 3750 to 530  $\text{cm}^{-1}$  with 60 cumulative scans.

The molecular mass distribution of the lignin samples was analysed by size exclusion chromatography (SEC) as described by Ringena *et al.* (2006). The eluent consisted of DMSO with 0.1w% LiBr at a flow rate of 0.5mL/min, while Polyethylene glycol standards were used as the calibration system.

Glass transition temperature ( $T_g$ ) was determined using a Mettler Toledo DSC 3+ differential scanning calorimeter. Before the measurement, lignin samples were dried in a vacuum overnight to remove residual water. Approximately 3 mg was weighed into an aluminum pan and sealed hermetically with a hole in the cover. Sample measurement was done at a scan rate of 10°C/min over a temperature of -60 to 220 °C. In total, three heating scans were done for each sample. The first scan was from 25 °C to 105 °C to remove the moisture. The heated sample was maintained at 105 °C for 2 mins and then cooled to -60 °C. The second scan was from -60 to 220 °C to eliminate the thermal history. The sample was cooled again to -60 °C and then finally heated to 220 °C. The glass transition ( $T_g$ ), defined as the midpoint of the temperature at which the change in heat capacity occurred, was evaluated using the STARE software.

Thermogravimetric analysis (TGA) was performed with a NETZSCH STA 409 thermo-analyser. The

analysis was carried out under air at a constant heating rate of 10/min up to 1000 °C.

Analytical Py-GC/MS analyses of lignin samples were carried out in a Frontier Lab Micro furnace multiple-shot pyrolyzer (EGA/Py-3030iD) equipped with an autosampler (AS-1020 E). Approximately 100 µg of the samples were weighed in the crucibles and directly introduced into the pyrolysis system. Each sample was pyrolysed at 500 °C for about 0.5s, with the interface temperature set at 320 °C. Pyrolysis and gas-chromatographic separation were done with Helium as the carrier gas at a flow rate of 1.0 mL/min. After pyrolysis, the pyrolysate is transferred directly into the GC column with a split ratio of 30:1 using a DB-5 capillary column (Phenomen 7HG-G002-11; 30 m × 0.25 mm i.d., 0.25 µm film thickness). The initial oven temperature of the gas chromatograph was 45 °C for 4 min, and then the temperature was ramped to 320 °C at a rate of 5 °C/min with an equilibration time of 0.50 min. Mass spectral detection was done using Agilent 5973 inert MSD with electron impact ionisation energy of 70 eV. The transfer temperature from GC to MS, ionization source and quadrupole temperature were set at 320 °C, 230 °C, and 150 °C, respectively. Scanning parameters also include low mass (15.0), high mass (550.0) and threshold (150). Quantification of the lignin degradation compounds was based on the percentage area of integrated peaks.

### III. Results and Discussion

#### 3.1 Performance of UF System

Permeate flux at a varying TMP is one of the experiments employed for characterizing the performance of a membrane filtration system. The result of pure water flux measured as a function of TMP at ambient temperature before UF of black liquor is shown in Fig 2. Pure water flux increased with TMP without any indication of fouling. Furthermore, an increase in the feed flow rate did not have any effect on the flux.

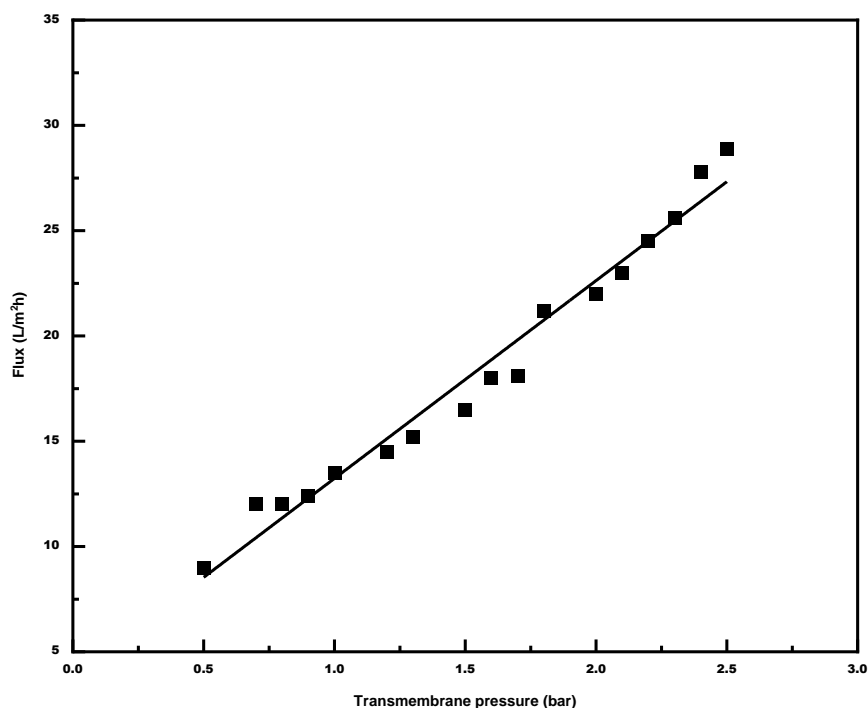
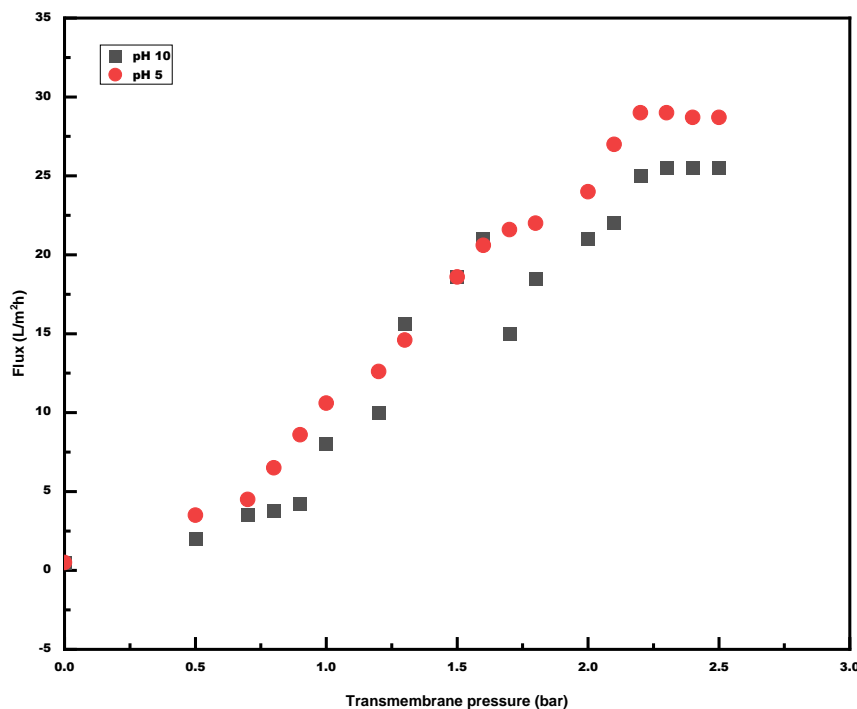


Fig. 2. The variation of pure water flux with transmembrane pressure

The kraft black liquor used in this study was pre-filtered before UF to remove colloidal particles. A high level of colloidal particles in the feed was likely to cause the blockage of the membrane pores by quickly building up a cake on the membrane surface, which could ultimately limit the permeate flux through the membrane and reduce the filtration efficiency. To avoid this limitation, pre-filtration of black liquor was imperative, especially with the filtration being carried out at room temperature and on a laboratory scale with associated devices having low driving force. In the study on UF of spent sulphite liquor, Al-Rudainy (2017) reported an increased flux and reduced fouling when the liquor was pre-filtered before ultrafiltration. Likewise, Cortifias *et al.* (2002) employed microfiltration to this effect, and Kallioinen *et al.* (2010) suggested the pre-treatment of feed to enhance the filtration capacity of regenerated cellulose membrane.

The influence of TMP on the permeate flux of kraft black liquor at pH 10 and pH 5 was studied in recirculation mode, as earlier mentioned. Results presented in fig 3 showed that flux achieved at pH 5 (28.7 L/m<sup>2</sup>h) was higher than flux at pH 10 (25.5 L/m<sup>2</sup>h). These results were not unexpected because the inherent

lignin hydroxyl groups dissociated at higher pH, making the usually hydrophobic lignin more hydrophilic with a negative surface charge. With a hydrophilic regenerated cellulose membrane, hydrophilic lignin interacted more strongly with the membrane surface resulting in a decreased flux (Zabkova *et al.* 2007). On the other hand, at a low pH, the hydrophilicity of positively charged lignin was reduced. As a result, the interaction with the hydrophilic membrane diminished. Therefore, low pH resulted in higher flux.



**Fig. 3.** The influence of transmembrane pressure on the flux of kraft black liquor during ultrafiltration with a regenerated cellulose membrane.

At both studied pH, flux increased gradually with TMP but began to level off at a value of 25 L/m<sup>2</sup>h. At TMP higher than 2.5 bar, the UF system was generally unstable; connecting tubes started to show signs of swelling which eventually led to breakage. Flux also became inconsistent. A reduction in flow rate was not enough to calm the system. To avoid further breakage, the TMP was reduced by adjusting the retentate valve. Accumulation of solid particles at the surface of the membrane may have led to the resistance to filtration. Therefore, at increased TMP, membrane porosity decreased, which led to an increase in the hydraulic resistance and flux decline. A higher TMP might have produced a higher flux, but the connecting tubes were too fragile to cope with TMP higher than 2.5 bar.

Consequently, UF was performed at 2 bar and pump speed of 0.7l/min until 72.5% VR was achieved. At this point, the flux had slowed down, and there was little or no permeate flowing through the membrane. It is noteworthy that the first permeate retrieved from the UF system showed a distinct colour difference from the feed (fig. 4), thus confirming the UF system's filtration efficiency.



**Fig. 4.** (L-R): original black liquor, retentate and permeate at pH 10

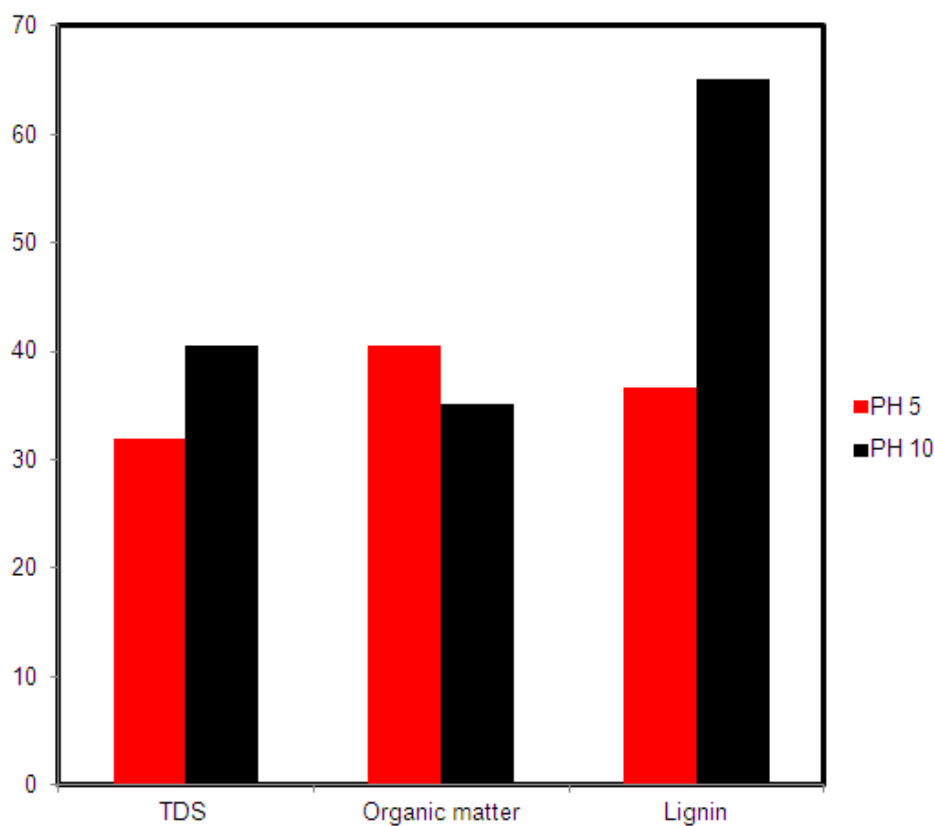
### 3.2 Lignin Ultrafiltration

The performance of the UF system was further evaluated from the concentration and recovery of lignin from the permeate and retentate fractions. Recovery of a solute depends on the selectivity of the membrane towards the solute. Therefore, high recovery indicates a low concentration in the permeate stream and a high concentration in the retentate. Conversely, a low recovery means a high concentration of solute in the permeate and a low concentration in the retentate. Recovery was calculated as the fraction of a component found in the retentate and expressed in % (Eq. 5),

$$Recovery (\%) = (1 - VR) \times \frac{C_r}{C_o} \quad (5)$$

where VR is Volume reduction (l),  $C_o$  &  $C_r$  are concentration (g/L) in initial feed & retentate respectively.

The analytical composition of feed, permeate, and retentate during the UF process showed that lignin concentration, TDS and organic matter in the feed are significantly lower than the original black liquor (Table 1). This was attributed to the pre-filtration step before UF. Lignin concentration in the retentate increased from 70.15 g/L to 93.64 g/L and 70 g/L to 132.76 g/L at pH 5 and 10, respectively. The average recovery of lignin was 36 % and 65 % at pH 5 and 10, respectively (Fig. 5). TDS concentration increased from 43% to 50% and 26% to 38% at pH 5 and 10, respectively. The average recovery of TDS was 31% and 40% at pH 5 and 10. Higher recovery at pH 10 was due to the low flux earlier discussed. Compared with other UF systems and membranes reported in the literature, values obtained in the study fall within the range, considering variation in operating conditions such as higher pressure and operating temperature (Wallberg and Jönsson, 2006 and Mänttari *et al.* 2015).



**Fig. 5.** Recovery (%) of total dissolved solids, organic matter and lignin in the retentate during concentration of kraft black liquor at pH 5 and 10 with a regenerated cellulose membrane

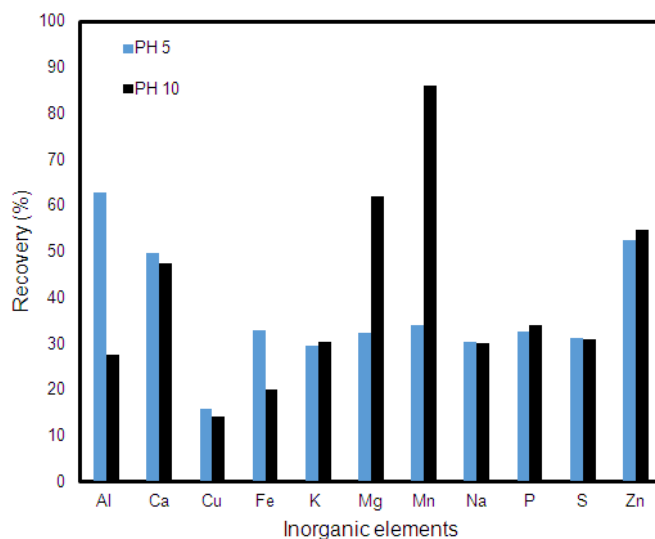
**Table 1.** Characteristics of Kraft Black Liquor, Feed, Permeate and Retentate at 72.5% VR during Ultrafiltration With 1kda Regenerated Cellulose Membrane

	Original black liquor	Feed	Permeate	Retentate	Feed	Permeate	Retentate
pH	13.5		5			10	
Lignin, g/L	103.04	70.15	46.05	93.64	70	25.57	132.76
TDS, %	48.97	43.94	43.07	50.75	26.20	20.07	38.03
Organic matter, %	67.01	31.56	27.29	41.04	52.41	42	66.83
Density, g/L	1279.8	1056.66	1059.95	1063.05	1021.81	1024.55	1035.98
Al, mg/L	23.05	7.18	5.425	16.41	29.35	23.81	29.48
Ca, mg/L	41.21	37.22	21.14	13.45	22.93	15.39	39.63
Cu, mg/L	0.89	0.08	0.6125	1.63	7.55	1.25	3.86
Fe, mg/L	22.14	4.11	3.46	19.86	32.24	24.89	23.54
Mg, mg/L	93.07	86.51	80.2	101.73	40.61	17.82	91.56
Mn, mg/L	29.22	21.85	18.51	26.97	10.11	0.54	31.65
P, mg/L	48.63	51.175	46.87	60.95	30.65	28.51	37.8
Zn, Mg/L	3.82	1.89	1.83	3.59	2.69	1.88	5.34
Na, g/L	33.6	43.06	39.98	47.56	21.9	20.85	23.89
K, g/L	27.121	27.51	25.98	29.63	13.82	13.28	15.29
S, g/L	17.55	42.62	41.01	48.44	14.74	14.06	16.64

### 3.3 Composition of Inorganic Elements

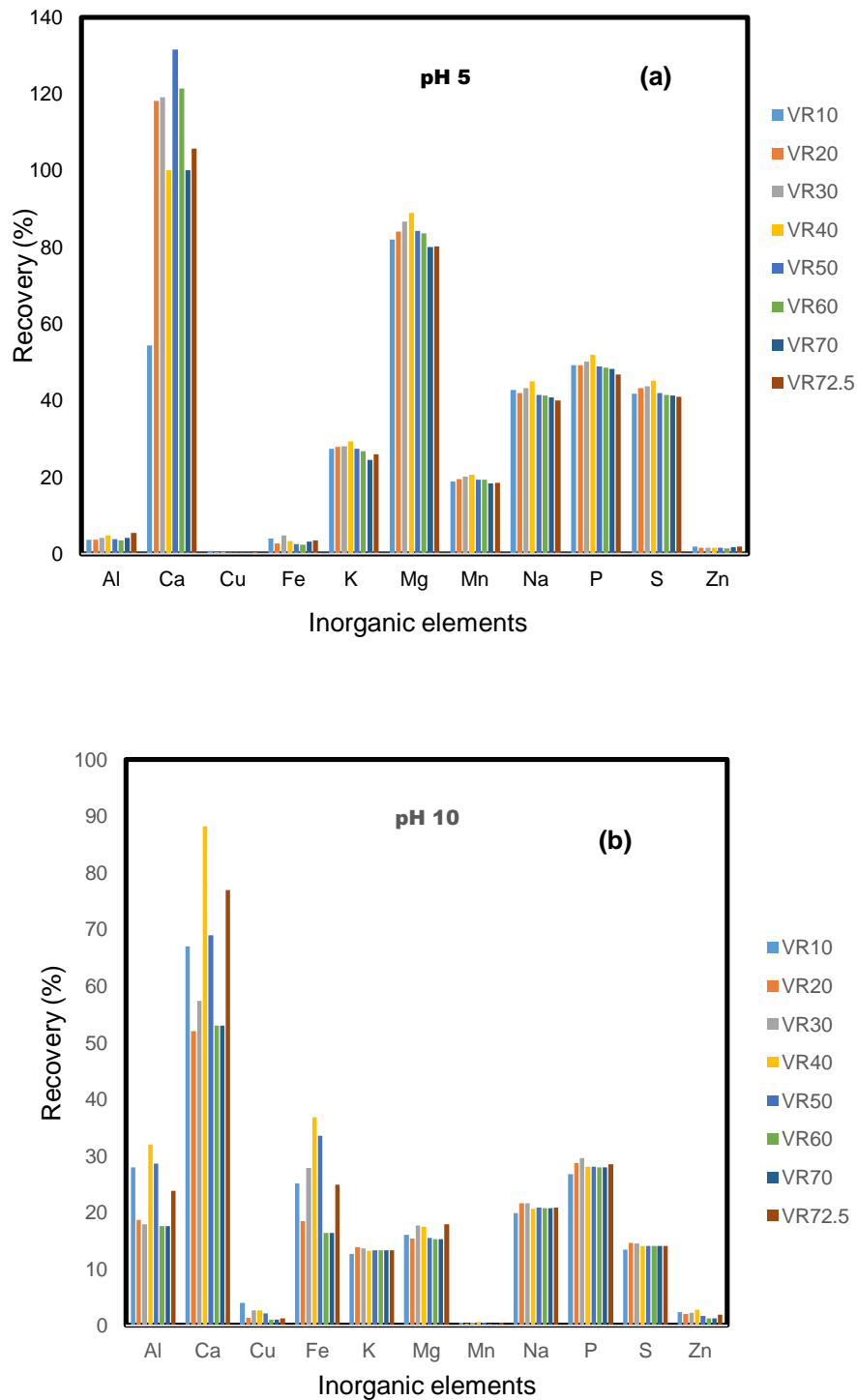
The concentration of inorganic elements in black liquor is essential to estimate its properties and potential hazardous effect on processing equipment. Removal of these elements through membrane separation depends on the ion charge, size, and interaction with the membrane surface. The pH of the liquor could also have a telling effect. The concentrations of Al, Cu, Fe, Mg, Mn, P, and Zn significantly increased at about 120% in the retentate at pH 5 (Table 1). Ca was concentrated in the permeate, while Na, K and S were evenly distributed in the permeate and retentate. However, at pH 10, a 72% increase in the Ca content of retentate was observed. A similar increase was also observed for Mg and Mn. Unlike the results obtained at pH 5, low retention of Cu and Fe was observed at pH 10, while the variation in the concentration of Al, P, Zn, Na, K and S was not high. At both pHs, higher concentrations of Na, K and S were in the permeate. This result agrees with Kirbawy and Hill (1987), who reported the presence of these monovalent ions and higher valence ions in permeate and retentate, respectively. Considering the high lignin retention at pH 10, the high retention of Ca, Mg and Mn were not out of place since they are multivalent ions that may strongly associate with high molecular weight components and organic matters in kraft black liquor (Wallberg *et al.* 2003b). The low retention of monovalent ions, Na and K, may also be attributed to their strong association with low molecular weight components of kraft black liquor, such as inorganic salts and organic acid salts.

Recovery (%) of inorganic elements computed from the concentration in retentate against feed concentration is shown in fig. 6. High valence ions (Al, Zn, Ca, Mg, & Mn) had higher recovery (50-65%) than Na, K, S and Cu. At various VR, the concentration of Na, S, K and P in the permeate remained essentially unchanged at both pH all through the UF process (Figure 7). Mn was significantly lower at pH 5 than at pH 10. Ca, Mg, Al and Fe showed some degree of variation.



**Fig. 6.** Recovery (%) of inorganic elements during the ultrafiltration of kraft black liquor at pH 5 and 10.





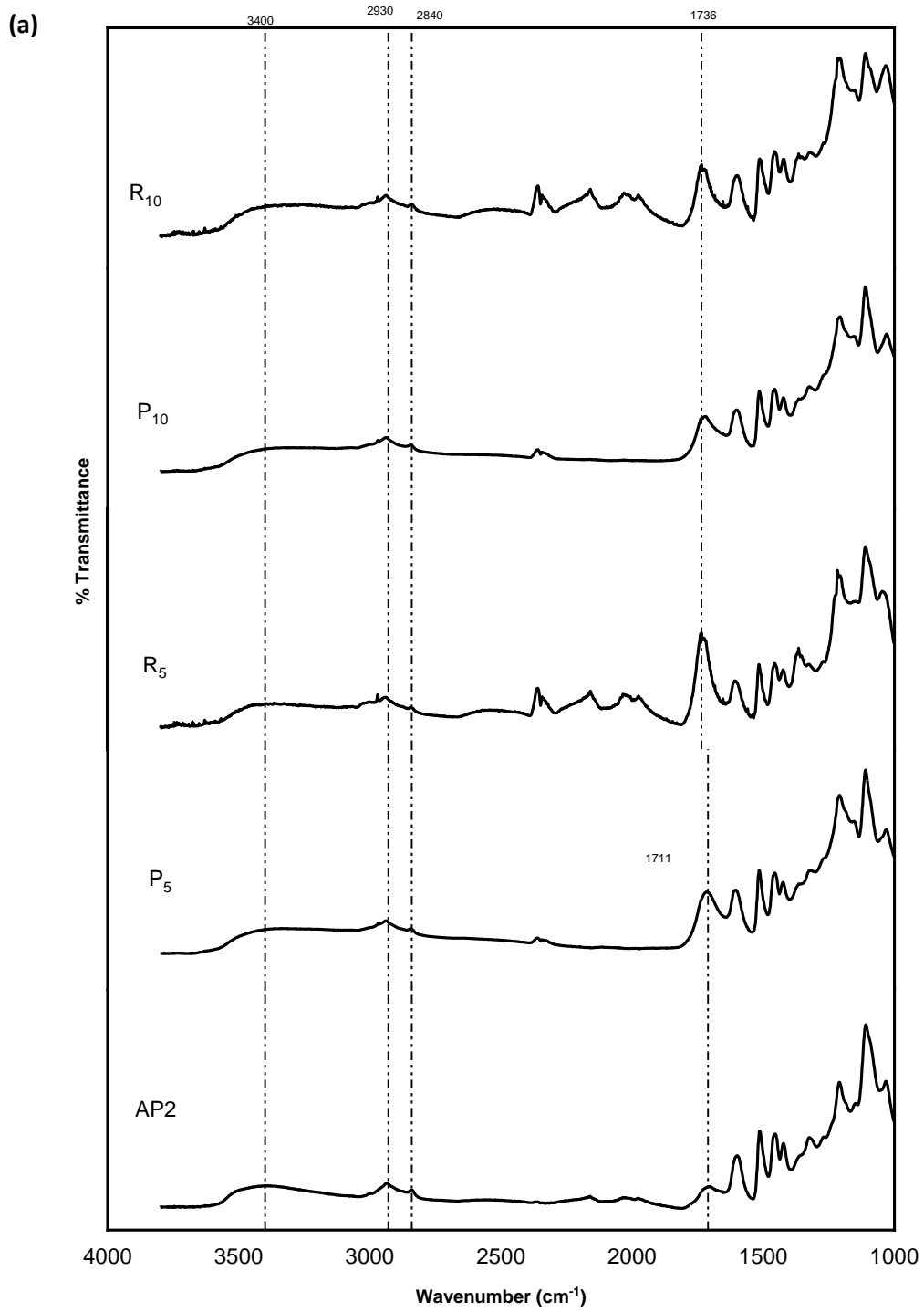
**Fig. 7.** Variation of the concentration of inorganic elements content of permeates with volume reduction (VR) at (a) pH 5 and (b) pH 10.

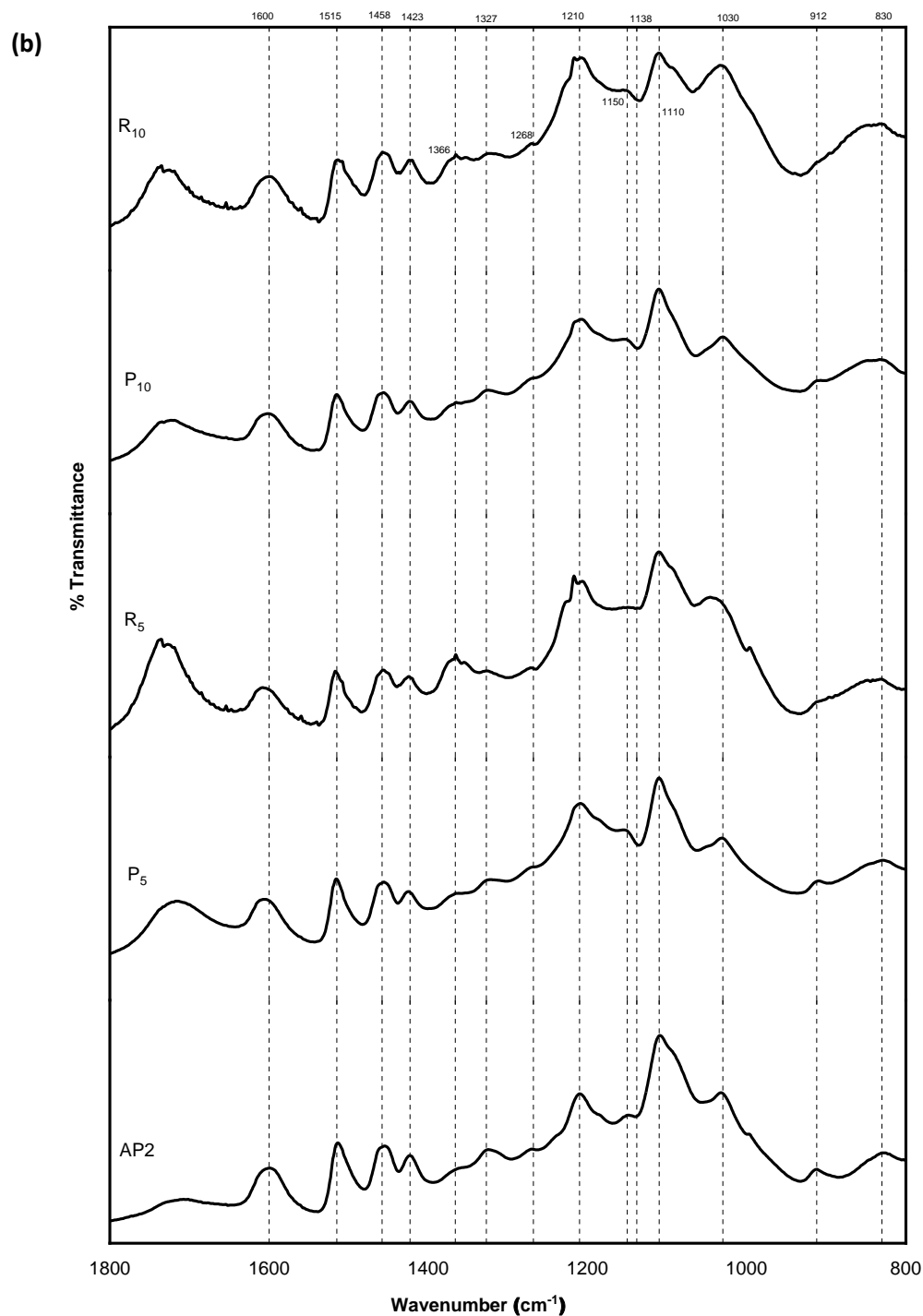
### 3.4 Analytical Characterization of Lignin

Four lignin fractions were obtained from the UF process at pH 5 and 10, namely, P10 & P5 (lignin from permeate at pH 10 and 5 respectively), R10 & R5 (lignin from retentate at pH 10 and 5 respectively). In addition, lignin (AP2) was obtained via direct acid precipitation at pH 2. Each fraction was characterised for its structural features, thermal stability, molecular mass distribution, and lignin macromolecules feature using FTIR, SEC, TGA, DSC and Py-GC-MS.

### 3.5 Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the five lignin samples are presented in **Fig. 8**. The full spectra from 4000 to 1000 $\text{cm}^{-1}$  are labeled **a** while the fingerprint 1700 to 700  $\text{cm}^{-1}$  are labeled **b**. The summary of the assigned bands of all spectra is presented in Table 2. All studied lignin samples showed similar vibrational features expected of lignocellulosic materials (Faix 1992), albeit with varying intensities. There was no major alteration in the chemical structure of lignin during ultrafiltration. Characteristic broad absorption band attributed to stretching vibrations of phenolic O-H groups in lignin was found at 3400  $\text{cm}^{-1}$ . Signals representing C-H stretching vibrations in the methyl and methylene group were also visible at 2930  $\text{cm}^{-1}$  and 2840  $\text{cm}^{-1}$ . Stretching vibrations of C=O for unconjugated ketone and ester groups are typically found between 1740  $\text{cm}^{-1}$  and 1710  $\text{cm}^{-1}$ . In this region, a noticeable difference was observed. R5 & R10 showed higher intensity at 1736  $\text{cm}^{-1}$  while P5 & P10 and AP2 showed weaker intensities at 1711  $\text{cm}^{-1}$ . Low carbonyl concentration may suggest low carbohydrate concentration and, hence, relatively higher purity (Passoni *et al.* 2016). In the fingerprint region, sharp peaks at 1600  $\text{cm}^{-1}$ , 1515  $\text{cm}^{-1}$  and 1423  $\text{cm}^{-1}$  were attributes of lignin's pure aromatic skeletal vibration. These peaks, which are typically very strong in softwood and hardwood lignin (Stark *et al.* 2016), were higher in the AP2 samples and may result from UF or membrane interaction. The presence of syringyl (S) and guaiacyl (G) moieties in all lignin samples was confirmed with peaks found at 1327  $\text{cm}^{-1}$  and 1110  $\text{cm}^{-1}$  associated with the syringyl structure and 1210  $\text{cm}^{-1}$ , 1268  $\text{cm}^{-1}$  related to C-O vibrations in the G aromatic ring. Higher intensity of these peaks was also found in AP2 (García *et al.* 2009). Peak associated with C-O deformations in primary alcohol 1030  $\text{cm}^{-1}$  was observed in all the spectra. Furthermore, the peak at 1138  $\text{cm}^{-1}$  can be assigned to C=O deformations in conjugated ester groups present G, S & H lignins. This peak appeared only as a weak shoulder in the retentate and permeated lignins. Similarly, all lignin samples showed a weak peak at 830  $\text{cm}^{-1}$  attributed to C-H deformations typically in S and H units of lignin.





**Fig. 8.** FTIR spectra of UF lignin R5 & R10 (retentate), P5 & P10 (permeate) and lignin directly precipitated at pH 2 (a) with enlarged views of the corresponding fingerprint regions (b)

**Table 2.** Assignment of Bands in FTIR Spectra of Studied Lignin Samples

No.	Band (cm <sup>-1</sup> )	Structure correspondence
1.	3400	O-H stretching
2.	2930	C-H stretch methyl and methylene groups
3.	2840	C-H stretch methyl and methylene groups
4.	1711	C=O stretch, unconjugated ketone, carboxyl and ester groups
5.	1736	C=O stretch, unconjugated ketone, carboxyl and ester groups
6.	1600	Aromatic skeletal vibrations
7.	1515	Aromatic skeletal vibrations
8.	1423	C-H in-plane deformation in aromatic ring stretching
9.	1327	C-O stretch, syringyl (S) ring
10.	1110	C-O stretch, syringyl (S) ring
11.	1210	C-O stretch, guaiacyl (G) ring
12.	1268	C-O stretch, guaiacyl (G) ring
13.	1030	C-O deformation, primary alcohol
14.	1138	C=O deformation, in conjugated ester (G, S & H)
15.	912	C-H deformation of out of plane, aromatic ring
16.	830	C-H deformation of out of plane, aromatic ring

### 3.6 Molecular Size Distribution

The molecular weight of lignin is essential for material applications. The values obtained for the number average molecular weights ( $M_n$ ), the weight average molecular ( $M_w$ ) and the polydispersities ( $M_w/M_n$ ) are presented in Table 3. P5 and P10 had lower molecular weights – 2600 and 3900  $\text{gmol}^{-1}$ , respectively, than R5 and R10 – 5600 and 11600  $\text{gmol}^{-1}$ . In addition, lignin polydispersity ranged between 2 and 5. These results show that the regenerated cellulose membrane was effective in the ultrafiltration of black liquor into low and high molecular weight fractions.

**Table 3.** Average Molar Mass and Polydispersity

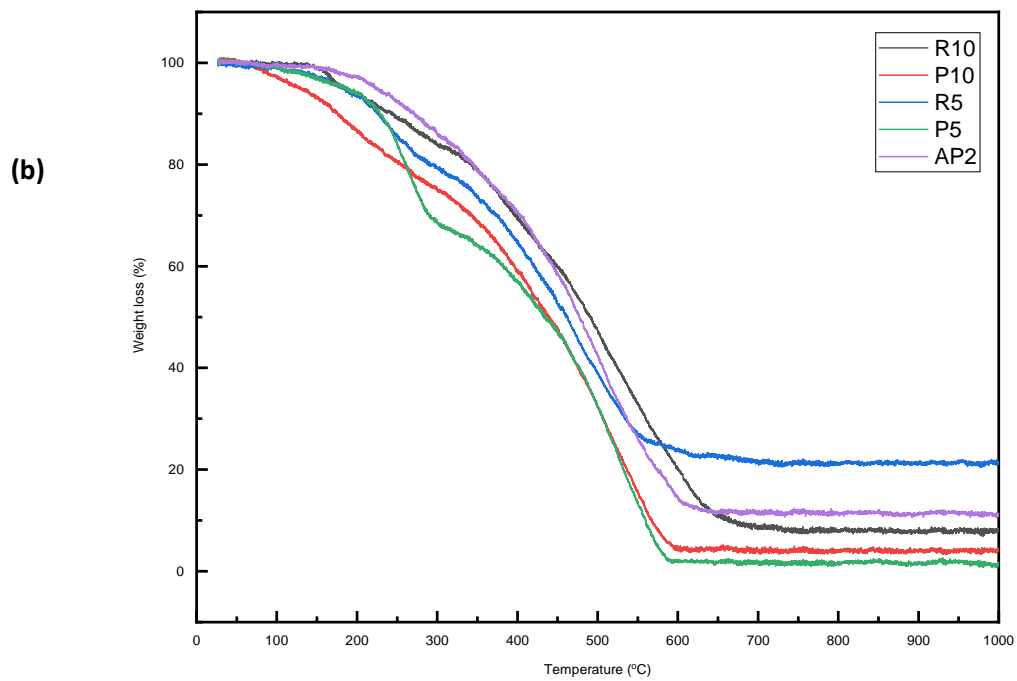
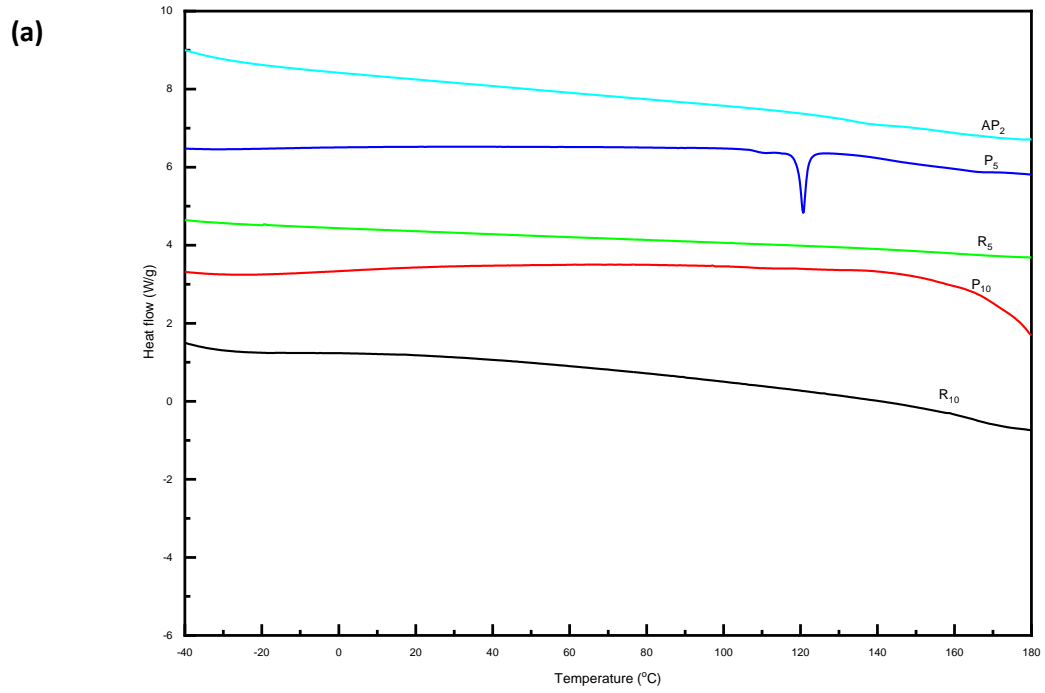
Lignin	$M_n$ ( $\text{gmol}^{-1}$ )	$M_w$ ( $\text{gmol}^{-1}$ )	$M_w/M_n$
P5	900	2600	2.8
R5	1500	5600	3.6
P10	1100	3900	3.4
R10	250	11600	4.6
AP2	1350	5900	4.4

### 3.7 Thermal Characteristics

The utilization of lignin in various applications such as thermoplastic or carbon fiber is dependent on its thermal properties (Duval *et al.* 2016). The results of the thermal analyses are presented in Table 4. R10 and P10 had the highest  $T_g$  of 163 and 165°C, respectively. The  $T_g$  of AP2, R5 and P5 were 141°C 109 °C and 108°C, respectively. TGA, DTG and DSC graphs are shown in **fig. 9** (a-c). TGA provides information about degradation temperatures and other phase transition temperatures. TGA curves show the weight loss of lignin as a function of temperature, while the first derivative of the TG curve (DTG) shows the corresponding weight loss rate. Evaluation of TGA results shows that all lignin samples have a similar degradation pattern. The first peak of the DTG seen around 100°C corresponds to the loss of absorbed water through evaporation. The second peak between 200 – 300 °C could be attributed to polysaccharide degradation (Wang *et al.* 2010). All lignin fractions exhibited this peak. Typically, the thermal degradation of lignin takes place in a wide temperature range between 180 – 800 °C. In this temperature range, several competing reactions, including fragmentation of inter-unit linkage, the release of monomeric phenols and decomposition of the aromatic ring, are known to occur (Sahoo *et al.* 2011). For all studied lignin fractions, the maximum degradation temperature was around 500 °C.

**Table 4.** Thermal Characteristics of Lignin Samples

Lignin sample	$T_g$ (°C)	Maximum Degradation Temperature (°C)
R10	163	502
P10	165	502
R5	109	474
P5	108	510
AP2	141	511



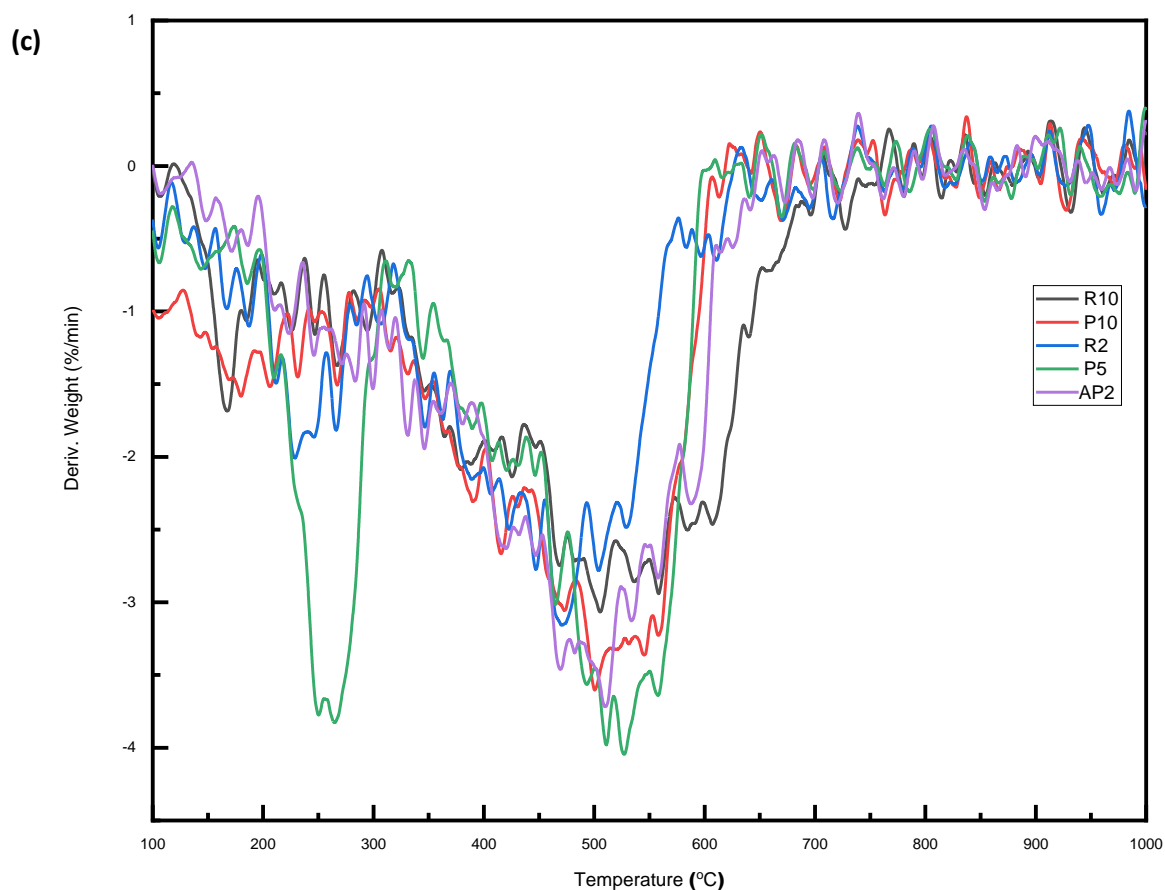


Fig 10. DSC (a), TGA (b) and DTG (c) curves of lignin fractions

### 3.8 Analytical Py-GCMS

Hardwood and softwood lignins comprise various syringyl (S) and guaiacyl (G) type degradation compounds. The presence and amount of these compounds in lignin are essential because of their reactivities during valorization (Lourençon *et al.* 2015). The ratio of these compounds in the lignin isolated from the retentate and permeate and lignin obtained from direct acid precipitation was determined using the analytical pyrolysis-GC/MS. Results shown in Table 5 indicate that syringyl compounds are dominant in all lignin samples. S-type compounds common to all studied lignin include Syringol, 4-Methylsyringol, syringaldehyde and acetosyringone. Of these compounds, syringol was the most abundant. Guaiacol was the most abundant of the G compounds, including 4-Methyl-guaiacol, 3-Methoxy-catechol, vinyl-guaiacol, and vanillin. Higher S unit compounds are characteristic of hardwood (Park *et al.* 2018). In general, AP2 had more G and S units than the lignin samples from ultrafiltration. This result suggests that some of these compounds were distributed in the retentate and permeate fraction during UF. It also agrees with the result of the FTIR measurement, which indicated that AP2 is richer in syringol units. In addition, P5 produced the lowest S and G type compounds while there was no major difference in other lignin samples. The size of these compounds and their interaction with the membrane are possible reasons for these variations. The average S/G ratio of the lignin samples fall within the range reported for hardwood species (Rodrigues *et al.* 1999).

**Table 5.** Relative Peak Areas of Lignin Degradation Compounds

Peak no.	Retention Time (mins)	Compound	Type	Area percentage (%)				
				AP2	P5	R5	P10	R10
1.	11.57	Phenol	H	0.1	0.1	0.3	0.1	0.3
2.	13.89	2-Methylphenol	H		0.2	0.2		0.2
3.	14.54	3-Methylphenol	H			0.2		
4.	14.65	4-Methylphenol	H		0.4	0.1		0.1
5.	14.89	Guaiacol	G	2.7	1.2	1.9	1.9	2.6
6.	17.67	2-Methoxy-3-methyl-phenol (Creosol)	H	0.9	0.1	0.2	0.2	
7.	18.07	4-Methyl-guaiacol	G	0.3	0.8	1.3	1.0	1.0
8.	19.99	3-Methoxy-catechol	G	0.8	1.0	1.0	1.4	2.1
9.	20.49	4-Ethyl-guaiacol	G	0.4	0.3	0.7	0.4	
10.	21.45	Vinyl-guaiacol	G	1.5	0.7	1.0	0.7	0.7
11.	22.41	Syringol	S	8.8	3.8	5.9	5.3	7.1
12.	23.80	Vanillin	G	0.2	0.1	0.3	0.2	0.1
13.	23.96	Isoeugenol (cis)	G	0.1	0.1			
14.	24.89	4-Methyl-Syringol	S	1.5	2.3	3.4	1.8	2.2
15.	24.95	Isoeugenol (trans)	G	1.3		0.1		
16.	25.25	Homovanillyl alcohol	G			0.1		
17.	25.28	Homovanillin	G		0.1			0.1
18.	25.31	4-Propylguaiacol	G	0.3			0.1	0.2
19.	25.95	Acetoguaiacone	G	0.8	0.3		0.5	0.2
20.	26.05	Acetovanillone	G			0.6		0.1
21.	26.85	4-Ethyl-Syringol	S	0.8		1.0	0.5	0.4
22.	27.75	4-Vinyl-Syringol	S	3.5	1.8	2.8	1.5	1.5
23.	28.26	Propiovanillone	G			0.1		0.1
24.	28.66	trans-4-Propenylsyringol	S	0.4		0.6		0.3
25.	28.77	4-Propyl syringol	S			0.1		
26.	29.75	cis-4-Propenylsyringol	S			0.1		0.1
27.	29.97	Syringaldehyde	S	1.1	0.4	0.8	0.7	0.5
28.	30.95	Homosyringaldehyde	S	0.5				
29.	31.53	Acetosyringone	S	2.8	1.5	2.4	1.8	0.6
30.	32.34	Syringylacetone	S	0.6		0.4	0.4	0.1
31.	33.43	Propiosyringone	S			0.2		
32.	36.60	Sinapaldehyde	S	0.2				
33.		Sum (H-type)		1	0.8	1	0.3	0.6
34.		Sum (G-type)		4.6	4.6	7.1	6.2	7.2
35.		Sum (S-type)		20.2	9.8	17.7	12	12.8
36.		Total		25.8	15.2	25.8	18.5	20.6
37.		S/G		<b>4.4</b>	<b>2.1</b>	<b>2.5</b>	<b>1.9</b>	<b>1.8</b>

#### IV. Conclusion

The performance of 1KDa regenerated cellulose membrane (RCM) in the crossflow ultrafiltration of industrial hardwood kraft black liquor was studied. The effectiveness of the membrane was confirmed by the isolation of low and high molecular weight lignin fractions in the permeate and retentate, respectively. In addition, a more transparent, purer, and less opaque liquid fraction was obtained after the UF. At ambient temperature and maximum volume reduction of 72.5%, recovery (%) of lignin was 35% and 65% at pH 5 and 10, respectively. The molecular weight of permeate lignins (2600 & 3900  $\text{g mol}^{-1}$ ) was lower than that of retentate lignins (5600 & 11,600  $\text{g mol}^{-1}$ ) at pH 5 and 10, respectively. The UF process did not alter the chemical properties of the isolated lignins. This study showed that regenerated cellulose membrane could be effectively applied for the ultrafiltration of kraft black liquor to recover lignin of varying properties for high-value applications. Application of this membrane in industrial settings would require further pilot scale experimental study.

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