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Process performance in lignin separation from softwood black liquor by membrane filtration

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ABSTRACT

Black liquor is a side-stream in the production of kraft pulp. The extraction of lignin and hemicelluloses from black liquor would reduce the load on the recovery boiler and give valuable by-products. Lignin was separated from black liquor by membrane filtration, using one ceramic and three polymeric nanofiltration membranes, with molecular weight cut-offs in the range of 200 Da to 1 kDa. Ultrafiltration was tested as a form of pretreatment prior to nanofiltration to separate hemicelluloses from lignin. The use of ultrafiltration prior to nanofiltration increased the flux drastically in the nanofiltration step with three of the membranes. The ceramic membrane exhibited a higher flux and lower lignin retention than the polymeric membranes. The two membranes with a molecular weight cut-off of 1 kDa were found to have the best performance in parametric studies, and were therefore used in concentration studies. The results were used for a preliminary economic evaluation of the process. These calculations showed that the most cost-effective alternative for the extraction of lignin was with the polymeric 1 kDa membrane without pretreatment, and that the production cost for a lignin solution with a concentration of 230 $g L^{-1}$ would be 46 € per ton of lignin.

Keywords: Black liquor; Ultrafiltration; Nanofiltration; Lignin; Hemicelluloses

1. Introduction

An average Swedish kraft pulp mill has an energy surplus of about 7 GJ per metric ton of pulp produced (Axegård and Backlund, 2000). This mainly originates from the combustion of organic matter in black liquor, which is a by-product in the production of pulp and paper. At pulp mills the black liquor is incinerated in a Tomlinson recovery boiler, where the organic matter is burnt to produce heat and power, and the cooking chemicals are regenerated. In many cases, the recovery boiler is the bottleneck of the pulp mill (Uloth and Wearing, 1989). Pulp production could be increased by extracting some of the organic matter from the black liquor. The main two organic constituents of black liquor are lignin and hemicelluloses (Sjöström and Alén, 1999).

Lignin and hemicelluloses can be used in a number of applications. Some of the lignin removed from the black liquor could be utilized on-site in the lime kiln to reduce the need of fossil fuels (Loutfi et al., 1991; Axelsson et al., 2006), or as a biofuel (Axelsson et al., 2006). Gargulak and Lebo (2000) have shown that lignin can be used as dispersants, binders and emulsifiers, while Kubo and Kalda (2005) used lignin as a precursor for carbon fibres. Lignin can also be employed in phenolic resins (Sarkar and Adhikari, 2000; Sellers et al., 2004) and as a wet strength additive to kraft liner (Antonsson et al., 2008; Elegir et al., 2007). Hemicelluloses are used in the production of barrier films (Hartman, 2006), and can also be used in hydrogels (Gabrielii et al., 2000; Söderqvist Lindblad et al., 2001) and as paper additives (Lima et al., 2003; Hannuksela et al., 2004). To use lignin and hemicelluloses in these applications they need to be separated from the kraft black liquor.

Several methods for the extraction of lignin and hemicelluloses from black liquor have been investigated previously. The most commonly used method for the extraction of lignin is precipitation and filtration (Merewether, 1961). Lignin is extracted from black liquor by acidification with, for example, carbon dioxide or sulphuric acid (Loutfi et al., 1991; Öhman and Theliander, 2001). When the solution has reached a certain pH it is filtered to extract the lignin (Öhman et al., 2007; Öhman and Theliander, 2001). Uloth and Wearing (1989)

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investigated a similar process in which waste acid from a chlorine dioxide generator was used as the acidifying agent (Uloth and Wearing, 1989). Hemicelluloses can also be extracted from black liquor using precipitation. Niemelä and Tamminen (2007) and Lisboa et al. (2005) demonstrated a method in which the precipitating agent consisted of dioxane and acetic acid. Other substances, such as methanol and ethanol, have also been used to extract hemicelluloses from kraft black liquor (Liu et al., 2012). A major drawback of the above methods is that they require the addition of chemicals to the process stream. Membrane filtration, on the other hand, requires no addition of chemicals to the process.

Membrane filtration can be used to extract various components from black liquor. Both ultrafiltration (Alén et al., 1986; Bhattacharjee et al., 2006; Paleologou et al., 1994; Wallberg et al., 2003) and nanofiltration (Keyoumu et al., 2004) of black liquor have been investigated, although ultrafiltration has been more extensively studied. These investigations showed that both methods are able to remove hemicelluloses and lignin from black liquor, but they are not able to separate the two components. This can be achieved by coupling the two types of membranes in series. When using ultrafiltration, a low retention of lignin and a high retention of high molecular weight hemicelluloses are preferred. This will lead to a high lignin yield, while reducing the concentration of hemicelluloses, in the permeate. Nanofiltration of the permeate from ultrafiltration increases the concentration of lignin, which will then be found in the retentate. To the best of the authors' knowledge, no thorough investigation of a configuration consisting of ultrafiltration and nanofiltration in series has been carried out.

The aim of this study was to investigate the performance of nanofiltration with and without pretreatment using ultrafiltration. By combining these two methods in series we were able to investigate how pre-separation of high molecular weight molecules affected the performance of nanofiltration. Both polymeric and ceramic membranes with different molecular weight cut-off were used to identify which gave the most cost-effective process.

2. Materials and methods

2.1. *Membranes*

Two tubular ceramic membranes and three tubular polymeric membranes were used. One of the ceramic membranes, the ultrafiltration (UF) membrane, was made of Al_2O_3 with a surface layer of TiO_2 (Atech Innovations GmbH, Gladbeck, Germany), and the ceramic nanofiltration (NF) membrane was made of TiO_2 (Tami Deutschland GmbH, Hermsdorf, Germany). The polymeric membranes, with different molecular weight cut-off (MWCO), consisted of a composite material and were used for nanofiltration (Koch Membrane Systems Inc., Wilmington, Massachusetts, USA). The characteristics of the membranes are given in Table 1.

2.2. *Experimental set-up*

Two different membrane filtration systems were used during this study, one for the ceramic membranes and one for the polymeric membranes. These are described separately below. The transmembrane pressure (TMP) is defined by Eq. (1), where P_{in}, P_{out} and P_p are the pressures at the inlet, the outlet and the permeate side of the membrane, respectively.

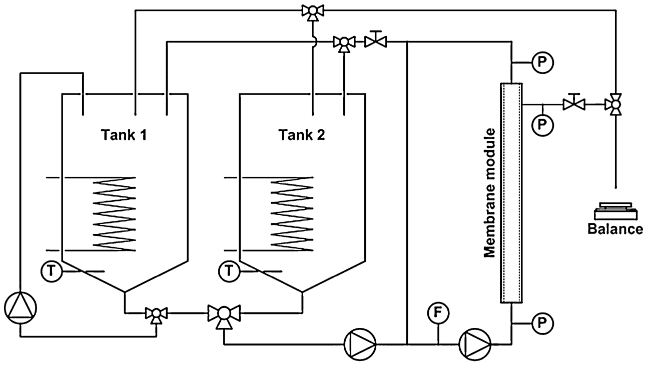

Fig. 1 – Illustration of the set-up used with ceramic membranes. *P*: pressure transmitter, *F*: flow meter, *T*: temperature transmitter.

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

The pressure drop (ΔP_f) over one membrane module is simply the difference between the inlet and outlet pressure: $P_{in} - P_{out}$.

2.2.1. *Ceramic membrane equipment*

The most important components of the set-up used with the ceramic membranes were two 200 L tanks, a circulation pump (NB32/25-20, ABS Pump Production, Mölndal, Sweden), a feed pump (Hydra-cell, G25XKSGHHECB, Wanner, Minneapolis, Minnesota, USA) and the membrane module. A schematic illustration of the ceramic membrane set-up is given in Fig. 1. The membrane housing used for UF was a M1 housing (Atech Innovations GmbH, Gladbeck, Germany), and for NF a KB01 housing (Orelis Environment SAS, Salindres, France), in which the membranes were installed. The cross-flow velocity (CFV) was controlled by adjusting the speed of the circulation pump using a frequency converter (CD3100, Lust Antriebstechnik GmbH, Lahnau, Germany). The feed flow was controlled by another frequency converter (MicroDrive MD409H, SIGBI System AB, Helsingborg, Sweden) connected to the feed pump. The TMP during the experiments was controlled manually by adjusting the retentate valve. Feed tank 1 contained the black liquor during the experiments, and tank 2 was only used during cleaning and start-up.

The permeate flow was measured with a balance (PL6001-S, Mettler-Toledo Inc., Columbus, Ohio, USA), and the circulation flow with a volume flow meter (Fischer&Porter Co., Ltd, Göttingen, Germany). The pressure was measured with pressure transmitters (dTrans p02, Jumo AB, Helsingborg, Sweden) before, after and on the permeate side of the membrane. The temperature in tank 2 was controlled with a temperature regulator (Shinko MCM, Shinko Europe BV, Haarsteeg, the Netherlands) connected to an electrical heater, and in tank 1 with a temperature regulator (PCT-30-2011X, Saab-Scania NAF, Solna, Sweden) regulating steam at a pressure of 5 bar in a heat exchanger coil inside the tank. The temperatures were monitored with two Pt-100 temperature probes (Pentronic, Gunnebo, Sweden) immersed in the feed tanks. An analogue-to-digital converter (AAC-2, Intab, Stenkullen, Sweden) was used to transform and transfer all instrument signals to a desktop PC, and all data were recorded using the software LABVIEW 2009 (National Instruments Co, Austin, Texas, USA).