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ULTRAFILTRATION OF KRAFT BLACK LIQUOR FROM TWO SWEDISH PULP MILLS

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Extraction of lignin by ultrafiltration of black liquor from two Swedish pulp mills has been studied. One of the mills employs batch digestion and the other continuous digestion. At both mills softwood was used as raw material. The black liquor was withdrawn before the evaporator unit. A ceramic membrane with a cut-off of 15 000 g mol^{-1} was used in the experiments. The average flux during concentration to 90% volume reduction was 160 and 110 L m^{-2} h^{-1} for the liquors from the batch and the continuous digestion processes, respectively, when the temperature was 90°C and the transmembrane pressure 200 kPa. The retention of lignin was about the same for both liquors, 35%. A cost estimate of extraction of lignin fuel from black liquor was made, based on experimental data from ultrafiltration at various operating conditions. The cost was found to be about 20 € per MWh of calorific value of the lignin fuel.

Keywords: kraft black liquor; lignin; ultrafiltration; ceramic membrane; economy.

INTRODUCTION

In pulp mills where the recovery boiler has become a bottleneck the extraction of lignin by ultrafiltration is an alternative to increase pulp production. Cooking liquor can be divided into two streams by ultrafiltration: one stream consisting mainly of lignin and the other a lignin-depleted liquor. The lignin-rich stream can be exported from the pulp mill and be further processed into a fuel, while the lignin-depleted liquor containing the cooking chemicals can be used for pre-impregnation of wood chips.

Fractionation of cooking liquor has hitherto been used primarily to recover lignin as it is a valuable chemical (Bansal and Wiley, 1974; Eriksson, 1979; Forss *et al.*, 1979; Glimenius, 1980; Olsen, 1980; Kovasin and Nordén, 1984; Kirkman *et al.*, 1986; Barnier *et al.*, 1987). Polymeric membranes have been used in most previous studies. However, the temperature of black liquor is high, as is the pH. It is therefore advantageous if the membranes can withstand extreme conditions removing the need for adjustment of the pH or cooling of the liquor. This calls for ceramic membranes, as polymeric membranes have limited temperature and pH resistance. In the R & D programme 'Future Resource Efficient Pulp Mill—FRAM' the performance of ceramic membranes for extraction of lignin from kraft black liquor is being studied (Wallberg *et al.*, 2003; Wallberg, 2003; Wallberg and Jönsson, 2003; Wallberg and Jönsson, 2004). The present investigation is part of this programme. Other studies on ceramic membranes have recently been published (e.g., Cortinas *et al.*, 2002; Liu *et al.*, 2004; Keyoumu *et al.*, 2004).

The aim of this investigation was to study the membrane performance during concentration of kraft black liquor from two pulp mills: one employing batch and the other continuous digestion. A ceramic ultrafiltration membrane with a cut-off of 15 000 g mol^{-1} was used in the investigation. A cost comparison between an ultrafiltration plant used to extract lignin from kraft black liquor from batch and continuous digestion is presented.

MATERIALS AND METHODS

Black Liquor

The kraft black liquors used in this investigation were supplied by the Södra Cell Värö pulp mill and the Södra Cell Mönsterås pulp mill, both in Sweden. The Värö mill has an annual capacity of 330 000 tonnes of bleached softwood totally chlorine-free (TCF) pulp. The Mönsterås mill has an annual capacity of 750 000 tonnes of bleached TCF hardwood and softwood pulp. Batch digesters are used at Värö and continuous digesters at the Mönsterås mill. The cooking temperature is about 165°C at the Värö mill and about 155°C at Mönsterås. The lower temperature at Mönsterås mill is partly compensated for by a higher sulphidity and alkalinity in the cooking liquor. The degree of delignification is kappa 27–30 at the Värö pulp mill and kappa 29–31 at the Mönsterås pulp mill. At both mills softwood was used as raw material when the black

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liquor was withdrawn. The black liquor was withdrawn before the evaporator unit. The characteristics of the two black liquors can be found in Table 1.

Analysis

The total dry solids (TDS) content was determined by drying weighed samples at 105°C and determining the weight of the residue. The ash content was measured by heating the residue from the TDS measurement to 950°C, and weighing the sample afterwards. The ash content is the ratio between the weight of residue after and before heating to 950°C.

Lignin contains phenolic groups which absorb light. The lignin concentration can therefore be measured as the light absorption at a wavelength of 280 nm (Hill and Fricke, 1984; Hill *et al.*, 1988). The UV light absorption was measured using a Shimadzu UV-160 spectrophotometer. Before measurement of the light absorption, the samples were diluted with deionized water. The absorption constant used was 24.6 g $(\text{L cm})^{-1}$ (Fengel *et al.*, 1981).

The concentration of inorganic elements was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Perkin Elmer Optima 3000DV ICP AES instrument. The samples were pretreated in order to remove the organic content, which would otherwise have interfered with the analysis. The pretreatment involved dilution of 10 ml of the sample with 5 ml concentrated nitric acid. The sample was heated under pressure in a microwave oven for 30 min. During heating the carbon is oxidised which raises the pressure inside the container. The excess carbon dioxide is released through a valve and the sample is heated again for 2 h to remove the remaining organic material. The final solution is then diluted to 50 ml and analysed.

Equipment

The membrane filtration equipment used in the experiments was constructed at the department. In the experiments a K01 membrane module from Orelis, France, was used. The module was erected vertically because ceramic membranes have a poor resistance to bending stress induced by vibration in the equipment. The membrane used throughout all experiments was a KERASEP membrane from Orelis with a cut-off of 15 000 g mol^{-1}, made of $Al_2O_3-TiO_2$. The membrane has seven parallel channels, each with a diameter of 6 mm, and the length of each channel is 1.2 m.

Table 1. Characteristics of the kraft black liquors used in the investigation.

	Continuous digester (Mönsterås)	Batch digester (Värö)
Lignin, g L^{-1}	62	57
TDS, wt%	22	14
Ash content, %	43	34
Sodium, g L^{-1}	40.6	26.4
Sulphur, g L^{-1}	11.0	4.8
Potassium, g L^{-1}	8.6	3.1
Iron, mg L^{-1}	3.4	3.1
Calcium, mg L^{-1}	23.5	32.7
Magnesium, mg L^{-1}	12.0	41.0
Manganese, mg L^{-1}	9.2	10.4

A centrifugal pump (NB32/25-20, ABS Pump Production AB, Sweden) regulated with a frequency converter (LUST CDA3000, Lust Antriebstechnik GmbH, Germany) provided the cross-flow velocity and feed pressure needed. The feed pressure and cross-flow velocity were regulated by the frequency converter and a valve on the retentate side after the module. The transmembrane pressure was regulated by a valve on the permeate side of the module. The pressure was measured before, P_{before}, and after, P_{after}, the membrane module and on the permeate side, P_{permeate}. The transmembrane pressure, P_{tm}, is given by:

$$P_{\text{tm}} = \frac{P_{\text{before}} + P_{\text{after}}}{2} - P_{\text{permeate}} \qquad (1)$$

As the temperature of the black liquor was close to its boiling point, evaporation from the tank must be kept to a minimum. This was achieved using a sealed lid with only a small hole for a temperature probe. The feed tank was heated with steam which condensed inside a coil in the feed tank. The steam pressure was 300 kPa. When the feed solution had reached the desired temperature this was maintained by a regulated electrical heater inside the tank.

Two 200-litre feed tanks were connected to the plant. One was used as the feed tank during the experiments and the other was used when cleaning the membrane. Samples of the feed solution were withdrawn through a valve at the bottom of the feed tank. The flux was determined by measuring the permeate flow with a balance. The analogue signals from the pressure transmitters were transformed with an AD converter (INTAB AAC-2) before they were transferred to the computer. The data were recorded and analysed with LABVIEW 6 software.

Performance of Experiments

Initially the pure water flux was measured at 50°C and 50 kPa to ensure that the membrane was clean and not cracked (which can happen since ceramic membranes are somewhat fragile). The manufacturer recommends that the maximum heating of the feed solution is 2°C min^{-1} as ceramic membranes can be damaged if they are subjected to rapid temperature fluctuations.

The initial feed volume was 170 L of black liquor. The black liquor, which had been preheated in the feed tank to the same temperature as the pure water (50°C), was circulated in the plant, while being heated to the temperature required for the experiment. During the heating period the permeate valve was closed. When the solution had reached the desired temperature (90°C in all experiments) the permeate valve was opened. The liquor was recirculated to the feed tank for 24 h before concentration was initiated. During concentration permeate was continuously withdrawn at constant temperature, transmembrane pressure and cross-flow velocity.

After the experiment the membrane was cleaned. Cleaning started by rinsing the membrane at the operating temperature used in the experiments. The rinsing liquid was either deionized water or permeate collected during the experiment. During the first 15 min of the rinsing operation