Design of ultrafiltration process for extraction of lignin from kraft black liquor

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Abstract

Ultrafiltration of kraft black liquor for the extraction of lignin has been studied in several previous investigations. The overall aim has been to produce a marketable bio-fuel which could replace fossil fuel in heat plants, thereby reducing greenhouse gas emissions. Lignin is a suitable bio-fuel, which is available in large quantities from pulp mills. Also, by extracting lignin potential benefits in the pulping processes could be gained.

In this investigation relevant boundary conditions are applied to the ultrafiltration process for lignin extraction from kraft black liquor. The analysis is based on previously presented data of ultrafiltration of kraft cooking liquor. The boundary conditions represent material balances which a lignin extraction process by ultrafiltration should fulfil. The analysis shows that a suitable membrane should have lignin retention between 50% and 80%. It is also shown that of the two membranes investigated in previous studies with cut-off 5,000 Da and 15,000 Da the lower cut-off membrane will be more economical when extracting equal amounts of lignin even though the flux of this membrane is considerably lower.

Keywords: Ultrafiltration, Kraft black liquor, Lignin, Design, Boundary conditions

Introduction

Within the two Swedish national research programmes Ecocyclic pulp mill (KAM) and Future Resource Adapted pulp Mill (FRAM) lignin extraction from kraft black liquor using ultrafiltration have been studied [1-6]. The lignin in kraft black liquor is usually burnt in the recovery boiler at mills, thus providing the energy needed in the pulping processes. As more energy efficient technologies are introduced in pulp mills there will be an energy surplus in the form of lignin in kraft black liquor. Provided that the lignin in this liquor can be successfully separated from the cooking chemicals also present in the liquor and concentrated the energy surplus could be turned into a potentially profitable chemical or external bio-fuel for the mills to market. Lignin extraction also reduces the load on the recovery boiler as less fuel has to be burnt. As the recovery boiler in many cases is the bottleneck in a pulp mill a lignin extraction process can lead to an increased pulp production. The permeate from the ultrafiltration process could also have a value in the mill operation. The permeate can be recirculated to the digestion thereby achieving kraft cooking at lower lignin concentration which could be beneficial. More about the different aspects of lignin extraction from kraft black liquor can be found in [6,7].

Based on results from previous investigations the production cost of a concentrated lignin solution has been made [8]. Some of the results from these calculation are also included in the published papers [4,5]. In these calculations no constraints on volume reduction or recovery were used. It was shown in the work by Holmqvist [8] that the membrane replacement cost was one of the most significant parts in cost calculations, even with a calculated membrane lifetime of 6 years. It has also been reported by others that the cost of a membrane plant is in many cases directly related to the installed membrane area [9].

The purpose of this study is to investigate the influence on required lignin retention when relevant constraints, or boundary conditions, are introduced on the lignin extraction process. Some of these boundary conditions are dictated by the ultrafiltration process itself and some are...
dictated by external processes in the mill and by the processes used to perform the final purification of the lignin. The exact values of all boundary conditions are not known as they are dictated by external processes. However, reasonable assumptions can be made in order to illustrate the influence of different boundary conditions on the process design. The aim of this investigation is also to demonstrate the influence of lignin retention on the investment cost of an ultrafiltration plant for lignin extraction.

**Theory**

To describe the influence of volume reduction on retentate concentration Eq. (1) can be used [9]:

\[ C = C_0 \left( \frac{1}{1 - VR} \right)^R \]  

(1)

where \( C \) is the concentration in the retentate, \( VR \) the volume reduction and \( R \) the retention. Subscript 0 indicates the initial condition. The volume reduction is calculated as:

\[ VR = \frac{V_p}{V_0} \]  

(2)

where \( V \) is the volume and subscript \( p \) indicates permeate.

The yield of lignin, or recovery, is an important parameter as it will determine the amount of lignin that can be extracted from the liquor. The recovery, which is the fraction of lignin that remains in the retentate, can be calculated as:

\[ \text{Recovery} = (1 - VR)^{1-R} \]  

(3)

The flux during concentration of the liquor can be described with a polynomial function of volume reduction as was done in [1]:

\[ J = a + b \cdot VR + c \cdot VR^2 + d \cdot VR^3 \]  

(4)

where \( a, b, c \) and \( d \) are polynomial coefficients. The average flux during batch concentration is obtained by integration of Eq. (4). The average flux, \( J_{av} \), is then:

\[ J_{av} = \int_0^{VR} J dVR = a + \frac{b}{2} \cdot VR + \frac{c}{3} \cdot VR^2 + \frac{d}{4} \cdot VR^3 \]  

(5)

Eq. (5) can be used to calculate the average flux of the solution when the liquor is concentrated to a certain volume reduction.

**Boundary conditions**

One of the boundaries is the maximum lignin concentration which could be achieved by ultrafiltration. It has been reported that the maximum lignin concentration which could be achieved during ultrafiltration is 320 g/l [10]. This is however higher than the lignin concentration achieved in previous investigations which was 240 g/l [5]. The exact upper boundary in lignin concentration when treating black liquor using the methods employed in the experimental studies are unknown, but it is probably not as high as 320 g/l.
If the lignin should be further refined by precipitation another boundary is added. Lignin precipitation is usually performed with liquor having a lignin concentration between 130 and 150 g/l, but it should be possible to perform the precipitation at higher concentrations [11,12]. Lower concentrations are however not advisable as the volumes treated in the precipitation equipment would be too high.

There are different possible routes to take to achieve concentrations within this upper and lower limit (assumed to be 140 g/l and 300 g/l). Either a high volume reduction with a membrane with low lignin retention or a membrane with high lignin retention processed to a lower volume reduction could be used. This is demonstrated in Figure 1.

![Figure 1. Lignin concentration at different volume reductions calculated for different lignin retentions using Eq. (1). The initial lignin concentration was 60 g/l in these calculations. Values outside the boundary conditions have been omitted.](image)

Only data that fulfil the boundary conditions in lignin concentration have been considered in Figure 1. Other requirements, besides maximum and minimum concentration, must also be considered. If the lignin is extracted from the pulp mill in order to increase the capacity of the recovery boiler, as described in the introduction, the lignin recovery cannot be too low as too small amounts of lignin would be extracted. It have been reported that 25% of the lignin in a pulp mill can be withdrawn without disturbing the operation of the recovery boiler [6, 11]. At least 25% recovery of lignin is therefore needed. This then introduces a lower limit in recovery. If the lignin recovery in the ultrafiltration process is higher then 25% a smaller volume flow of black liquor could be treated in order to not withdraw a too large amount of lignin. In Figure 2 the lignin recovery as a function of volume reduction with different lignin retentions is shown.
Figure 2. Lignin recovery at different volume reduction calculated with Eq. (3) using different lignin retentions. The initial lignin concentration was 60 g/l in these calculations. Values of lignin recovery not obeying the boundary condition (25% recovery, 140 g/l in lower lignin concentration and 300 g/l in upper lignin concentration) have been omitted.

The shaded area in Figure 2 represents the area of interest in this investigation. An additional boundary condition of a minimum volume reduction of 80% has also been included. A high volume reduction would be required in the ultrafiltration process if the permeate should be recirculated to the digester.

In Figure 3 the retention required to fulfil the boundary conditions in Figure 1 and Figure 2 is shown.

Figure 3. Lignin retention required to fulfil the boundary conditions in Figure 1 and Figure 2. In the shaded area the boundary conditions are fulfilled.

As can be seen in Figure 3 there is a limited interval in lignin retention and volume reduction which is interesting for process design purposes. Retentions between 40% and 100% are of
interest when membranes and operating conditions are selected and the boundary conditions are as specified above.

In the experimental studies [1-5] the performance of two membranes with cut-off 5,000 Da and 15,000 Da, has been investigated. It is however only with the lower cut-off membrane that retentions above 40% can be achieved during concentration of the liquor except at very low cross-flow velocities with the cut-off 15,000 Da membrane [2].

**Plant size**

A continuous ultrafiltration plant can be divided into several stages to minimize the membrane area. Increasing the number of stages decreases the membrane area but also increases the complexity of the plant. As a rule of thumb the optimum number of stages is between 3 and 5 stages [9]. As the cost of membrane constitutes a large part of the investment it is also important to minimize the membrane area as much as possible, which is why the cost estimates in the previous investigations have been made with an 8 stage continuous layout [4,5,8]. The average flux from a continuous plant is, when properly staged, in the order of 10 % lower then the corresponding batch plant [9].

To calculate the required membrane area the feed flow must be known. The feed flow can be calculated by deciding the amount of lignin to be withdrawn from the black liquor. In previous investigations the membrane area has been calculated when treating a certain volume flow of kraft liquor, not the actual production of lignin [4,5,8]. The recovery of lignin in the retentate can be calculated using Eq. (3) and the feed flow can then be calculated as:

\[
\text{Feed flow} = \frac{\text{Extracted lignin}}{\text{Lignin recovery} \cdot \text{Initial concentration}}
\]  

The required feed flow will depend on the lignin retention and volume reduction as these variables decide the lignin recovery. The membrane area needed can then be calculated as:

\[
\text{Membrane area} = \frac{\text{Feed flow} \cdot \text{Volume reduction}}{\text{Average flux}}
\]  

where the average flux is calculated using Eq. (5). The lignin concentration at each volume reduction can be calculated using Eq. (1). The parameters used in the following calculations can be found in Table 1.

*Table 1. Parameters used to estimate the required membrane area. Data from [5].*

<table>
<thead>
<tr>
<th>Cut-off (Da)</th>
<th>5,000</th>
<th>15,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extracted lignin (kg/h)</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Initial concentration (g/l)</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Lignin retention (%)</td>
<td>57</td>
<td>30</td>
</tr>
</tbody>
</table>

In the calculations a lignin extraction of 1000 kg/h has been assumed. The results can be easily scaled to any other production capacity as the membrane area is directly related to the extracted amount of lignin. The retention and initial concentration have been collected from a previous investigation [5].

The calculated values of feed flow, average flux, membrane area and lignin concentration as a function of the volume reduction are presented in Figure 4.
Figure 4. Membrane area, lignin concentration, treated feed flow and average flux as function of volume reduction when the membrane with cut-off 5,000 Da is used to extract lignin.

The amount of liquor which has to be treated in order to extract the desired amount of lignin increases at higher volume reductions as the recovery of lignin decreases. Consequently, the membrane area which is needed in the process increases both because of the increased feed flow as well as the lower average flux.

An interesting question is if there exits an optimum concentration to which the lignin should be concentrated before the final purification is performed. The most likely candidate for the final purification is acid precipitation of lignin followed by filtration [11]. The major operational cost in the precipitation process is the carbon dioxide used to precipitate lignin. The carbon dioxide neutralizes both lignin and the hydroxide ions in the solution. By increasing the lignin concentration by ultrafiltration without increasing the hydroxide concentration the cost of carbon dioxide can be reduced. In Figure 5 the membrane area needed to extract lignin from kraft liquor, using cut-off 5,000 Da and 15,000 Da membranes, at certain concentration is shown.
Figure 5. Membrane area needed to achieve different lignin concentrations in the retentate when using ultrafiltration membranes with cut-off 5,000 Da and 15,000 Da.

It is first of all obvious from the data presented in Figure 5 that it is possible to achieve much higher lignin concentration using identical membrane area with the lower cut-off membrane. It can also be seen that the relation between achieved lignin concentration and membrane area, and consequently plant cost, is not linear. In the case of the cut-off 5,000 Da membrane the derivative of the function is decreasing at higher lignin concentrations. Each step in lignin concentration is therefore more economical then the previous step. With the cut-off 15,000 Da membrane the opposite is true as the derivative increases when the lignin concentration is increased.

Conclusions

In this study relevant boundary conditions have been applied to an ultrafiltration process for lignin extraction from kraft black liquor. By this analysis, with the boundary conditions set in this investigation, it is shown that the lignin retention needs to be in the interval between 40% and 80% in order to fulfil the boundary conditions. By using equal membrane area but with two different membrane cut-off the lower cut-off membrane is more favourable as the retentate will have a higher concentration. The consequence is that it is more beneficial to use a lower cut-off membrane with high retention to extract lignin from black liquor, at least when the final lignin concentration is important in the following treatment of the concentrated solution. It must however be remembered that this analysis is based on the boundary conditions applied, which are relevant in the context of bio-fuel production and digester integration. If other boundary conditions are chosen, other results could be achieved.
References


