Closing the Loops in the Pulp and Paper Industry with Membrance Technology

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Membrane technology is a relative new technology in the pulp and paper industry with interesting applications in the water loop, the by-product loop and the chemical loop. The technology was pioneered in the pulp and paper industry by DDS Filtration, now Alfa Laval Nakskov in the 1970'ies and this article reviews the opportunities to use membrane technology in the different loops investigated over the years. The first part of the article focuses on the water loop and demonstrates the use of membrane technology to (1) prepare and purify in-take water, (2) recycle water in processes, and (3) to treat water before discharge. For the water loop, the use of membrane technology to polish evaporator condensate will be given as an application study. In the second part of the article membrane opportunities in the by-products loop of the sulphite and Kraft pulping process will be highlighted. The use of membrane technology for the concentration and purification of spent sulphite liquor in a sulphite pulp mill will be described in application study. The final part of the article will discuss membrane applications in the utilities and chemicals loop. The use of membranes for the Kraft bleach purification and for the paper coating recovery will be presented. Further, an application study will detail the use of membranes for purification of Kraft bleach effluent. Overall, the paper demonstrates potential of membrane technology for the pulp and paper industry ranging from water purification and preparation to the recovery of valuable products.

INTRODUCTION

The history of membrane technology is relatively short compared to the long history of the pulp and paper industry, which can be dated back to around 100 AD. Today's membrane technology started in the 1960'ies, when Loeb and Sourirajan developed asymmetric membranes produced by phase inversion (1). This type of membranes was adopted and further developed by DDS Filtration, one of the leading European membrane producers, today Alfa Laval Nakskov (Denmark), in the beginning of the 1970'ies. Being located in the North of Europe, one of the forest-riches regions in Europe, development activities focused early on the pulp and paper industry and resulted in the first full-scale membrane plant for Kraft black liquor purification installed at Metsäliitto (Finland) in 1975.

The key membrane processes applied nowadays in the pulp and paper industry are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The main features of these processes are summarized in Table 1.

In the following, the different alternatives for using membranes in the pulp and paper industry investigated by Alfa Laval Nakskov are introduced. The focus is on membrane applications in the water loop – to improve water management and reduce water consumption – the by-product loop – to extract key by-products – and the utilities and chemicals loop – to recover chemicals and pigments. For each loop the key applications will be briefly discussed and one application study will be presented.

Water loop

The average water consumption to produce one ton of paper is 20 m^3 (2). Due to increasing water prices and tightening discharge limits, the aim is to reduce the water consumption to 10 m^3 per ton of paper. In the water loop, membranes can be generally found in three positions:

1. Preparation and purification of in-take water.

2. Recycling of water in processes, and

3. End of pipe treatment of water before discharge.

In following, different membrane applications in the three positions in the water loop will be briefly discussed.

Preparation and purification of in-take water

Membrane processes such as MF, UF, NF and RO can be used to prepare and purify in-take water for different applications in the pulp and paper industry. Depending on the water usage membrane processes are used to remove salts, colloidal and suspended

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Table 1

Overview on Membrane Processes, Key Features, and Selected Applications

Membrane process	Key features	Selected applications
Microfiltration (MF)	• Pore size 0.1–1 μm • Typical operating pressure < 2 bar • Only suspended solids, bacteria and fat globules are rejected	• Membrane bioreactor (MBR)
Ultrafiltration (UF)	• Molecular Weight Cut-off (MWCO): 1,000–100,000 Dalton • Typical operating pressure 1–10 bar • Allows salts, sugars, organic acids and smaller peptides to pass • Rejects proteins, fats and polysaccharides	• MBR • White water purification • Spent sulphite liquor concentration and purification • Kraft bleach effluent
Nanofiltration (NF)	• $MgSO_4$ rejection > 99% • Slightly more open than RO • Typical operating pressure 5–35 bar • Allows monovalent ions to pass • Rejects divalent and larger ions and most organic components	• Kraft bleach effluent • White water UF permeate polishing
Reverse osmosis (RO)	• NaCl rejection > 95–99.99% • Only water will pass • Typical operating pressure 15–150 bar • Concentration of liquids with low molecular compounds at low solid levels	• Boiler water make-up water • Evaporator condensate • White water UF permeate polishing • Spent sulphite liquor UF retentate

matter as well as dissolved organics and inorganics. One of the most established processes is the demineralization of boiler makeup water by RO. Using RO not only 99 % of salts are rejected by the membrane but also over 95 % of dissolved organics and inorganics as well as all suspended and colloidal matters are removed. Hence, using RO to prepare boiler make-up water can reduce its fouling potential significantly and thus lead to an improved long-term performance of the boiler.

Recycling of water in processes

The white water from the paper machine is one of the major streams in the paper production. Applying UF combined with NF/RO it is possible to recycle the white water to the paper machine. Before entering the membrane process, the white water is pre-treated by passing it through disc or sand filter to remove the fiber material. Depending on the water quality required for recycling, the white water is then either passed through a UF unit alone or through a combination of UF followed by NF/RO. The combination of UF followed by RO will provide higher water quality for recycling compared to UF alone but it is also associated with higher investment costs. By applying this concept it has been shown that it is possible to use membranes as part of a water kidney around the paper machine, which reduces the water consumption significantly.

Another more general application in both pulp and paper industry is the polishing of evaporator condensate. Depending on the position in the process line, the condensate from evaporators can contain a high level of COD (Chemical oxygen demand) and BOD (Biological oxygen demand) resulting from carry-over. Depending on the molecular weight of the carry-over, UF, NF and RO can be used as polishing step by concentrating the COD/BOD and purifying the condensate stream for recycling.

End of pipe treatment of water before discharge

Despite the best efforts to recycle water in the processes there is still a need for end of pipe treatment in a biological reactor. In recent years, membranes have established themselves as a part of wastewater treatment plants. These so called membrane bioreactors (MBRs) are hybrid systems combining the biological activated sludge treatment process with a membrane unit as separating/filtering step and thus replacing the secondary sedimentation stage in the wastewater treatment process. The key advantages of MBRs

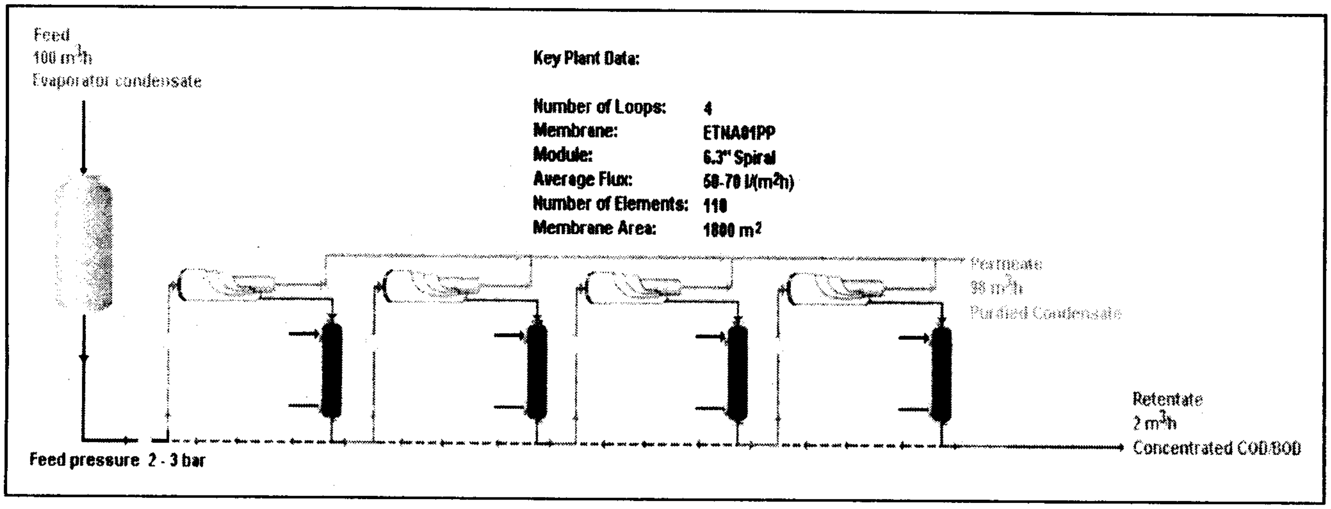

Fig. 1 Process Design : Evaporator Condensate Polishing

over conventional alternatives are: (1) Improved effluent quality after treatment due to complete retention of biomass, (2) compact design, (3) reduced sludge production and (4) process intensification due to higher biomass concentration in the bioreactor. The membranes used in MBRs are typically MF or UF membranes.

After the MBR or the secondary sedimentation stage, the purified wastewater is either discharged or recycled. In order to reuse the purified wastewater often a polishing step is required. Using NF/RO the purified wastewater can be polished for either direct recycling or mixing with the in-take water of the factory.

Application study: Evaporator condensate Polishing

The evaporator condensate in an integrated pulp and paper mill has to be polished according to environmental standards to a COD/BOD of less than 200 mg/l. To achieve this ultrafiltration is considered to concentrate the COD/BOD of the condensate by volume concentration factor (VCF) of 50, while the permeate stream should fulfill the discharge limits. An important design parameter is the flux of the ultrafiltration unit, which changes with volume concentration factor. For an operating pressure of 3- 4 bar and a temperature of 60°C the flux decreases from 55-60 l/(m²h) at VCF of 10 Brix to 45–50 l/(m²h) at a VCF of 50. Based on this the following ultrafiltration system to treat approx. 100 m³/h in four loops has been proposed, see Figure 2. The plant is equipped with 1800 m² of ETNA10PP membranes (Alfa Laval Nakskov, Denmark), which concentrates the evaporator condensate 50 times and obtains permeate stream with a COD/BOD < 200 mg/l. In Figure I a process design of this application is given.

This results in a permeate stream of 98 m³/h and a retentate stream of 2 m³/h. The plant is equipped with five pumps (1 feed and 4 booster pumps) and a CIP (cleaning in place) section to perform the internal cleaning of the ultrafiltration by circulation of the cleaning solution. Cleaning is typically carried out every 20 hours for 2 – 4 hours.

By-products loop

The applications of membrane technology in the by-product loop are related to the two most common chemical pulping processes – the sulphite and the Kraft process.

Sulphite process

In the sulphite process, membrane processes can be applied to both fermented and unfermented spent sulphite liquor (SSL).

UF can be used to simultaneously concentration of SSL and for classification of low and high molecular weight components in the SSL. The low molecular weight contents of the SSL such as sugar and low molecular lignosulphonates will pass through the membrane, while the high molecular lignosulphonates are concentrated to purities up to 90%. This concentrated lignosulphonates can be used as e.g. adhesive or dispersant. Further, low molecular weight components in the UF permeate can be concentrated by RO and fermented.

Another use of SSL is to use it directly for alcohol and protein production by fermentation. In this case UF can be used to separate the products and the by-products of the fermentation.

Kraft process

Kraft black liquor (KBL) contains similar to the SSL valuable components such as alkali lignin and tall oil. Using UF it is possible to purify and fractionate high molecular alkali lignin from KBL. Similar to lignosulphonates it is possible to use alkali lignin as e.g. adhesive.

KBL concentration by RO is another application. In this case RO is used as

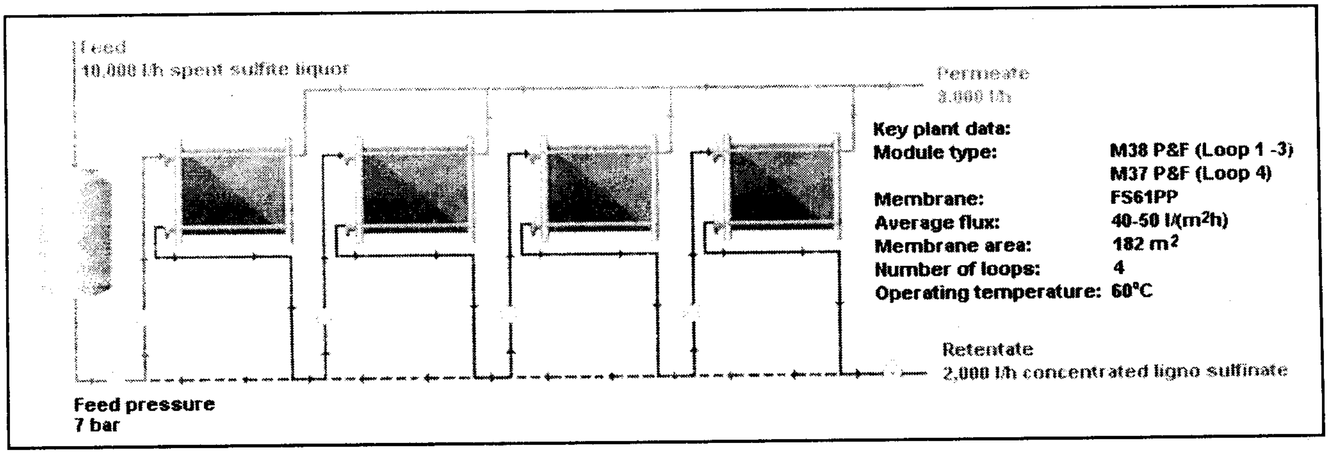

Fig. 2 Process Design : SSL Concentration and Purefication

pre-concentration step of the KBL before evaporation and can be used to de-bottleneck evaporator capacity as well as to save energy by reducing the evaporator load.

Application study: Concentration and Purification of SSL

In a sulphite pulp mill the 10 m^3/h of SSL should be concentrated by a VCF of 5 and the lignosulphonates should be purified. Therefore, a UF system with four loops has been designed, see Figure II.

The first three loops are consisting of M38 Plate and Frame modules (Alfa Laval Nakskov, Denmark), while for the final concentration in the fourth loop an M37 Plate and Frame module (Alfa Laval Nakskov, Denmark) is used. The system is equipped with 182 m^2 of FS61PP membranes (Alfa Laval Nakskov, Denmark) concentrating the lignosulphonates in the SSL by a volumetric concentration factor of 5. This results in a permeate stream of 8 m^3/h and a retentate stream of 2 m^3/h. The operating pressure is 7 bar and the operating temperature is 60 °C, which is maintained by four multi-tube heat exchangers in the process, s. The system is equipped with five pumps (1x feed and 4x booster pumps).

The permeate stream from the UF system is further concentrated by VCF of 3 in a four loop RO system, see Figure III. Each loop consists of one pressure vessel equipped with four spiral wound elements. The total membrane area in the system is 352 m^2 of HR98PP membranes (Alfa Laval Nakskov, Denmark). In the system the permeate of the ultrafiltration unit is concentrated by a volumetric concentration factor of 3, resulting in a permeate stream of 5.3 m^3/h and retentate stream of 2.7 m^3/h. The operating temperature of the system is 40 °C and the operating pressure is 60 bar. The system is equipped with six pumps (2x feed and 4x booster pumps).

Both units include a CIP unit for a daily cleaning cycle of 2 hours.

Utilities and chemicals loop

Membrane technology can be used to reduce chemical costs in the utilities and chemicals loop by concentrating and purifying used chemical for recycling. This will be highlighted in two examples; one from the pulp and one from the paper industry.

Kraft bleach purification

The effluents from the Kraft bleach process are generally considered as a pollution problem. About 60 – 70 %

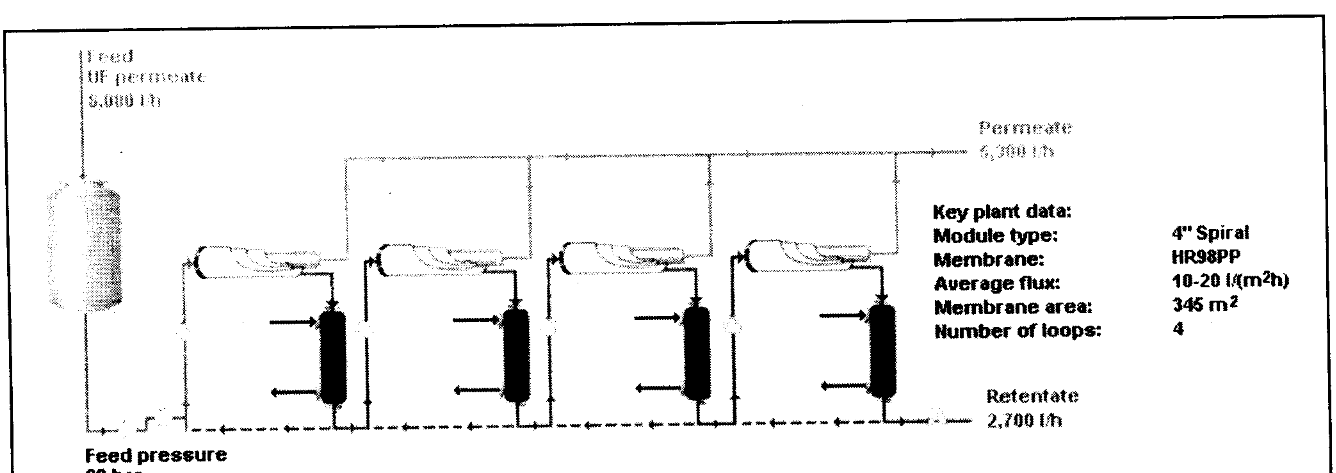

Fig. 3 Process Design : SSL UF Retentate Purification

of the strongly colored chlorinated lignin components are concentrated in the effluent from the first alkali extraction stage (E1-effluent). UF/NF has been identified as one approach to remove the color bleach stream. The concentrate from the UF/NF containing most of the color components can be concentrated by evaporation and then combusted in the soda recovery plant, while the permeate can be recycled as wash water in the bleaching plant or discharged to a wastewater treatment plant.

Paper coating recovery

The coating of paper generally requires that an excess of coating material is used. If not recovered this expensive coating material is lost in the process. The coating effluents are commonly a diluted stream with a total solid content of < 5 %. Using UF, these coating effluents can be concentrated by VCF > 10. Hence, the concentrate stream containing the coating material can be recycled, the permeate stream with < 0.5 % total solids can be further treated and directly discharged.

Application study: Purification of Kraft bleach effluent

In a Kraft pulp mill, the practiced flocculation-sedimentation technology to reduce COD was found to be insufficient. Therefore, UF was considered to concentrate the bleaching effluent for recycling to the chemical recovery system and to reduce the COD in the permeate by over 80 % before treatment in a sewage plant. Before entering the eight loops UF system the feed stream was pre-filtered by continuous sand filtration to reduce the fiber contents. The UF system has a membrane area of 336 m^2 GR81PP in spiral wound configuration (Alfa Laval Nakskov, Denmark) to treat 50 m^3/h of Kraft bleach effluent, see Figure 4. The feed stream is separated in 46 m^3/h permeate stream with a COD reduced by more 80 % and 4 m^3/h concentrate stream containing most of the COD.

The operating pressure of the plant is 4 - 5 bar and the operating temperature is about 70 °C maintained by 9 plate heat exchangers in the process. The system is equipped with nine pumps (1x feed and 8x booster pumps) plus CIP unit for 1 - 2 cleaning cycles per day.

CONCLUSION

The use of membrane technology in the pulp and paper industry was pioneered by Alfa Laval Nakskov (Denmark), previously DDS Filtration, in the beginning of the 1970s and led to the establishment of membranes in different positions of the pulp and paper production. The applications of membrane processes range from water preparation and purification to the recovery of valuable products from the processes. Current research efforts are on the updating and optimization of established applications in the pulp and paper industry and the development of new applications.

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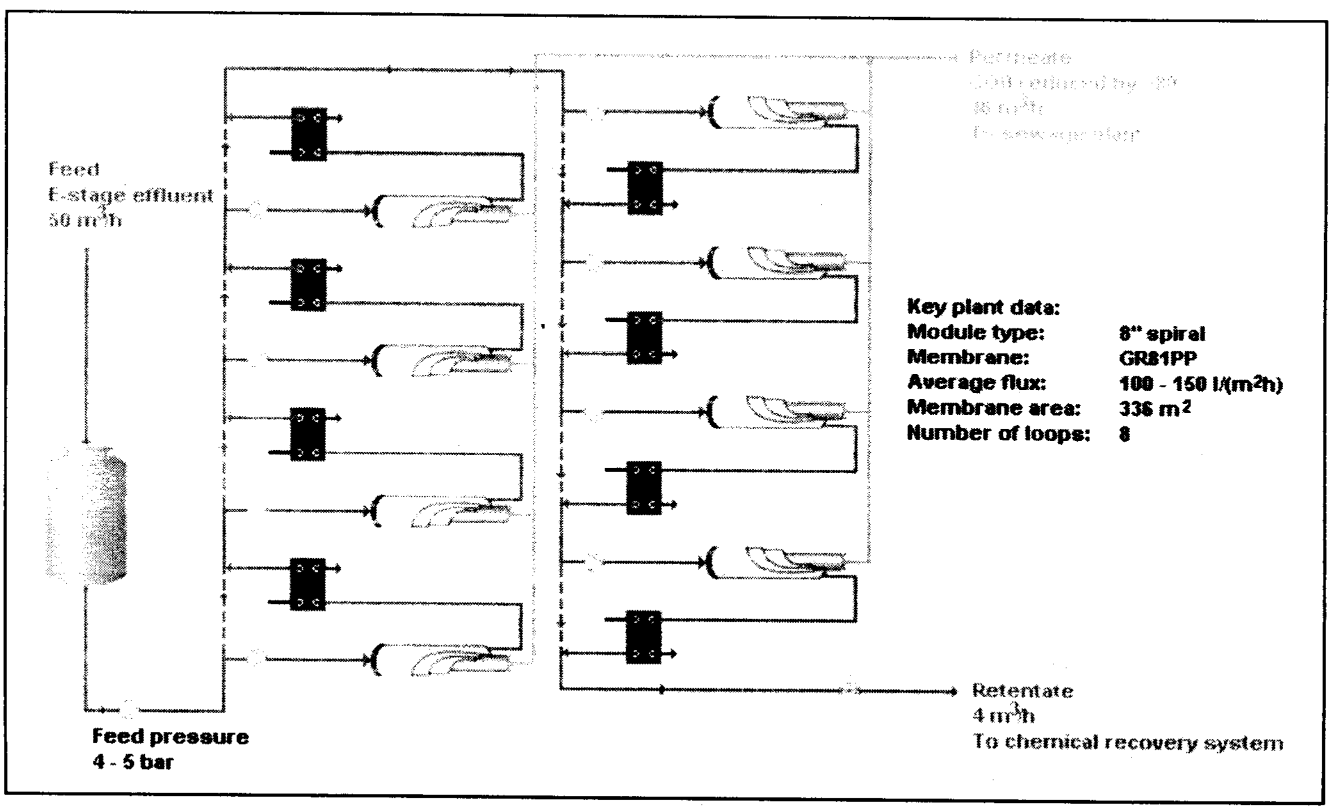

Fig. 4 Process Design : KBE Purification