

Membrane Technology For Recovery of Chemicals In Pulp Mills

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SUMMARY

Membrane technologies namely, reverse osmosis and ultrafiltration have been shown to be highly cost effective future technologies for Indian pulp and paper industry for complete recovery of pulping chemicals, lignin and water from black liquor. Availability of pressure driven membranes which can be used over a wide range of pH, temperature and pressure have broadened the application of reverse osmosis and ultrafiltration to pulp and paper industry. The effective utilisation of this technology for fractionation and preconcentration of black liquor are some of the potential applications. Pure lignin, a feedstock for chemical industries, can be fractionated into different molecular weight distribution lots from black liquors by appropriate selection of ultrafiltration membranes. Highly cost effective reverse osmosis is useful in preconcentration of black liquor for energy conservation.

INTRODUCTION

Recovery of pulping chemicals is an integral part of a pulp mill not only for economic reasons but also to maintain the ecological balance. Unfortunately many small pulp mills in our country find it unaffordable due to heavy investment required on conventional recovery systems. To overcome this and to ensure clean environment around pulp mills many new processes have been suggested by various groups from India and abroad. These processes have been successful to various degrees depending upon the cellulosic raw materials, pulping processes and location of the mill. Some of these processes are: (i) Direct Alkali Recovery Systems (DARS), (ii) Wet Air Oxidation, (iii) Anaerobic Digestion, (iv) Acid Treatment to Black Liquor to produce Lignin Products etc. Among the listed processes DARS appears to hold the highest success rate for the Indian small pulp and paper mills based on soda process. The details on these processes are well presented by Ku karni¹, Rao², Daraney³ and Mittal⁴ in various issues of IPPTA journal.

A closer look at the above mentioned recovery processes make it clear that these are mainly designed for the recovery of either inorganic or organic constituents, such as lignin, from the black liquor. No process is capable of recovering all the constituents i.e.

pulping chemicals, lignin and water. The complexity of the black liquor coupled with variations in the cellulosic raw material for the production of pulp make it extremely difficult to achieve the goal of complete recovery. However, this complex problem of recovery can be made easier to solve by the application of membrane technologies namely, reverse osmosis (R.O.) and ultrafiltration (U.F.). This paper deals with R.O. and U.F. applications in the pulp and paper industry for recovery of chemicals.

Membrane Technology

There are various membrane technologies available for different kinds of separations. The technologies relevant to pulp and paper mills are U.F. and R.O. In both the cases separation takes place, in the same phase, across a polymeric membrane under a pressure gradient. The basic difference between U.F. and R.O. (also known as Hyperfiltration) is in the pore size of the membranes and applied pressure range. R.O. membranes have very small pores in the order of 5–15 Å which practically rejects all solute molecules from a solution. The typical applied pressure in R.O. ranges from 28 to

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60 kg/cm² with solvent flux above 50 L/M²/day. In the case of U, F. membranes, the pore size varies from 15-1300 Å with applied pressure ranging from 1 to 10 kg/cm². The permeate flux in U.F. is generally much higher than that of R. O., U.F. membranes are tailor made by varying the pore size distribution for different molecular weight cut-off. These processes are illustrated in figure. 1. The illustrations show the membrane in the tubular form. Although other configurations (namely hollow fibre, plate-and-frame, spiral wound) are used, tubular membranes are ideal when looking for a system with well-defined flow channels which are not prone to blocking and through which the feed liquor can be pumped at velocities high enough to prevent deposits forming on the membranes.

ii) Recovery and purification of valuable byproducts by fractionation of black liquor with U.F.

Availability of membranes capable of withstanding high temperatures and pressures over a wide pH range has broadened the field of applications of membrane technologies from mere desalination to separation of the complex liquid streams such as black liquor. Cost of removing huge quantity of water from this black liquor by evaporation can be reduced to the extent of 25-30% through R. O. at the preconcentration stage, where 60% of the total water is removed. This cost reduction is possible due to the fact that less thermodynamic work is required in this separation involving no phase change. A comparison of the costs of water removal by R.O. and that of by evaporation techniques is given in table 1. Steam cost for R.O. system is not to be considered as electrical energy is required in this case. It is evident from the table that R.O. is decidedly a cost-effective technique for concentrations of dilute solutions.

In the concentration of thin black liquor, R. O. is useful in the preconcentration stage only i. e. from 10% total dissolved solids (TDS) to 20-25% TDS. For concentration beyond 25% TDS conventional evaporation have an edge over R. O. as the osmotic pressure of the feed stream increases to such an extent that it would require very high applied pressure to effect any separation. The benefits of preconcentration of black liquor by R.O. followed by evaporation over that of evaporation alone is well depicted in figure 2.

Apart from preconcentration, fractionation of black liquor can also be done by membranes technology. Application of properly chosen U. F. membranes for black liquor fractionation yields various molecular weight fractions of lignins in pure form. The purified lignin thus obtained has enormous market potential as a feed stock for chemical and allied industries. The lignin chemical market in the United States alone has touched 200M dollar per year, which is likely to increase manifold according to trade prognostication. The economics of lignin suggest that a vast reservoir of lignin now being wasted by burning may be diverted to useful applications if conditions improve. In 1986 lignin sold for 5 to 25 times its fuel value and yielded 25-50% of the price of competing polymeric materials from synthetic sources. The utilities of lignin as a feed

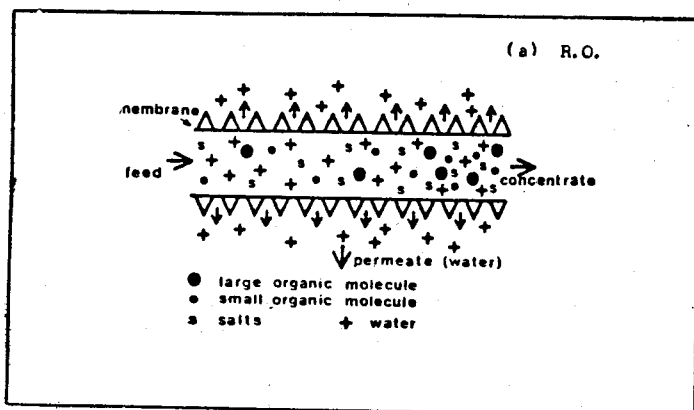
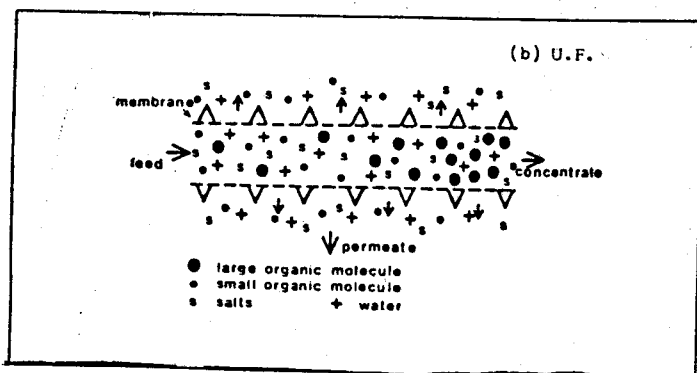


FIG.1 Illustration of (a) R.O. and (b) U.F. processes



Reverse Osmosis and Ultrafiltration of Black liquor

There are two areas for the use of pressure driven membrane processes in pulp and paper industry :

i) Water removal by R. O. prior to evaporation in order to reduce steam cost or expand evaporation capacity.

TABLE-1
Energy Requirements by evaporation and R. O. Techniques for Water Removal⁶

System	K. Cal/M ³ of Water Removal (K. Cal)	Steam Req'd. (T/M ³)	Cost of Steam (Rs/M ³)
6 Stage M.E.E.	118250	0.219	37.23
5 Stage M.E.E.	148500	0.275	46.75
4 Stage M.E.E.	189750	0.351	59.67
3 Stage M.E.E.	236500	0.438	74.46
R. O.	8250	0.015	09,59*

*Cost of electricity/M³ of water removal.
M.E.E.—Multi Effect Evaporator
Cost of Steam—Rs. 170.00/Ton
Cost of Electricity—Rs. 1.00/Kwh
1 Kwh = 860 K Cal

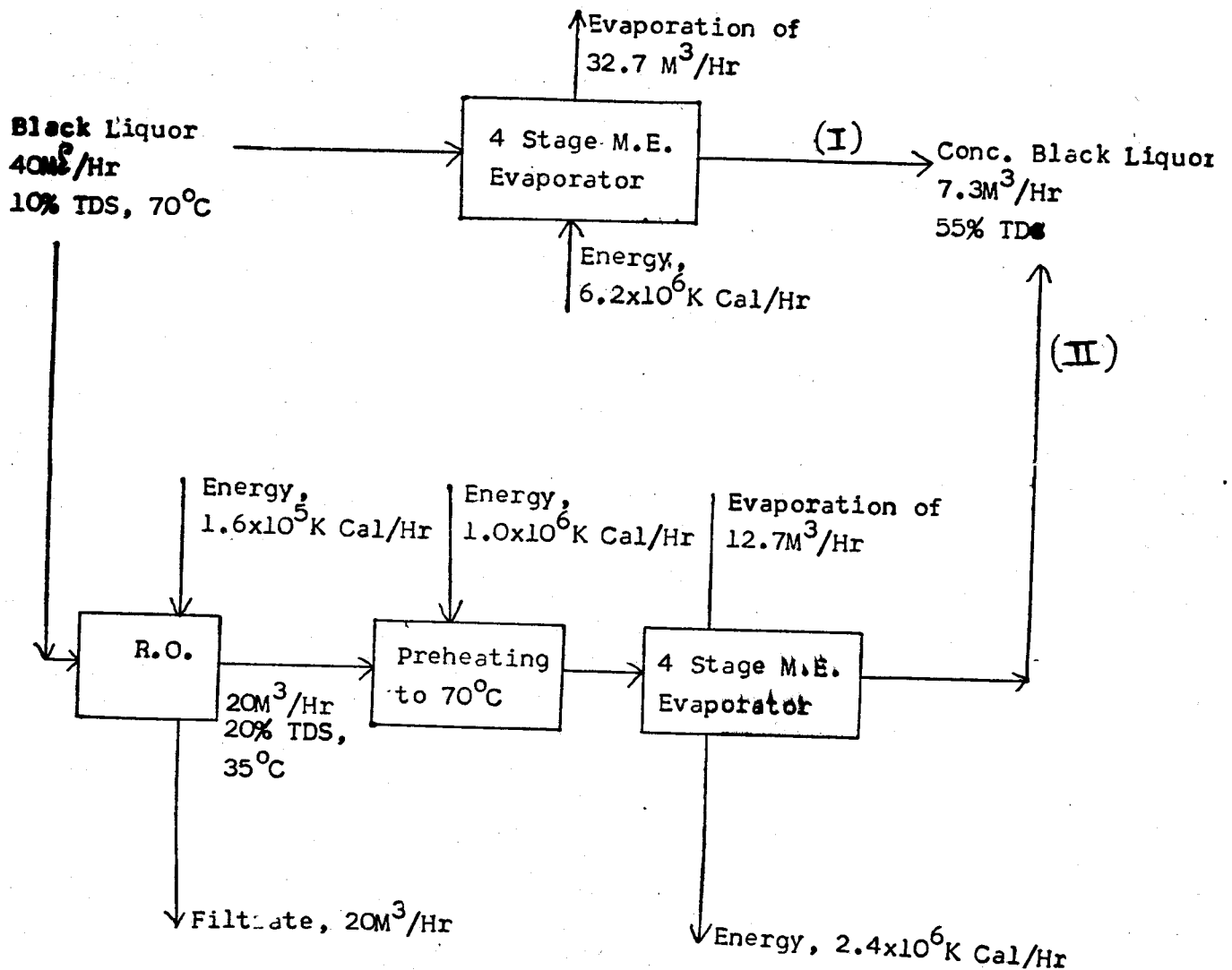
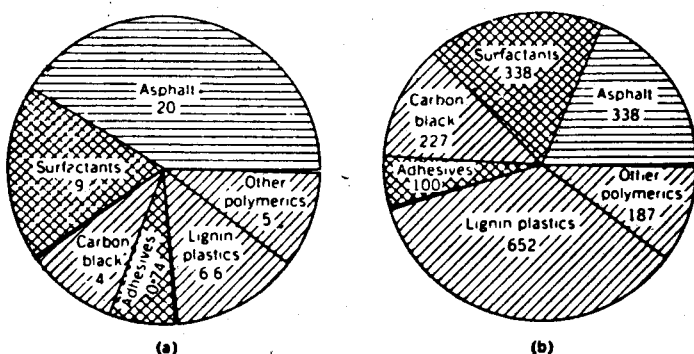


FIG.2 Alternative routes for concentrating black liquor
(I) 6.2x10⁶ K Cal/Hr and (II) 3.56x10⁶ K Cal/Hr

stock for chemical industries is an established fact, more than 3700 patents have been granted till 1984 on utilisation of lignin and lignin derivatives⁶. The marketable products which could be produced from lignin are adhesives agricultural, water treatment, drilling, tanning and rubber chemicals, dispersing agents and for the cement and battery industries. Projected U. S. Market for lignin by the turn of this century is given in figure 3⁷.



F. 3.3 Projected U.S. market for lignin derivatives by the year 2000. (a) in volume, 10^5 t/yr (b) in value 10^6 \$/yr.

In spite of the voluminous informations on utilisation of lignin not much has been done for its commercial exploitation in India and many parts of the World which is largely due to unavailability of homogeneous lignin at an affordable cost. Lignin is generally separated by precipitation from black liquor by lowering the pH to a value of around two followed by washing and filtration. Lignin produced by acidification is not very pure due to simultaneous precipitation of other low molecular weight organic chemicals. It also contains the whole range of lignin molecules which may not be suitable for its further conversions into marketable products. Puddington and Sirianni⁸ have shown that removal of low molecular weight fractions result in an enhanced reinforcing property of kraft lignin in the rubber industry. Similarly high molecular weight lignosulfonates and kraft lignin fractions were shown to form a better adhesive for plywood than the unfrac-tionated material⁹.

Lignin heterogeneity plays a key role in defining its products performance properties. It had been impossible to produce lignin chemicals of consistent quality unless the sources of lignin non-uniformity is better understood and methodology to eliminate the

deterimental lignin components are devised. It is for this purpose U.F. offers a decided help in lignin fractionation. Appropriate selection of U.F. membranes with defined molecular weight cut-off values can produce very narrow molecular weight distribution fractions of lignin without affecting its chemical structure, unlike the separation methods based of precipitation.

In actual practice, suspended solid free black liquor is passed through U. F. membranes under a pressure gradient when inorganic chemicals alongwith low molecular weight fractions of lignin and other organic chemicals permeate across the membrane leaving the high molecular weight fractions enriched in the retentate compartment. The enriched lignin stream is diafiltered to produce 95% pure lignin. The principle in construction of plant is shown in figure 4. Examples of gel-chromatograms illustrating the molecular weight distribution of lignosulfonates in the crude sulfite liquor, ultrafiltration concentrate and permeate is shown in figure 5. It is evident from this figure that all the constituents having molecular weight less than 5000 are filtered whereas larger molecules have been retained. In this particular experiment, the larger molecules were concentrated 25 times. The dried concentrated mass showed very low amount of monosaccharides and acetic acid. This exemplary experiment demonstrates the usefulness of U.F. in recovering pure lignin with a narrow molecular weight distribution. Purified lignin fractions of even narrower molecular weight distribution can be obtained by arranging different molecular weight cut-off U F. membranes in series and allowing the black liquor to flow through them under an applied pressure. Various fractions starting from lowest molecular weight can be collected from the corresponding U.F. permeate.

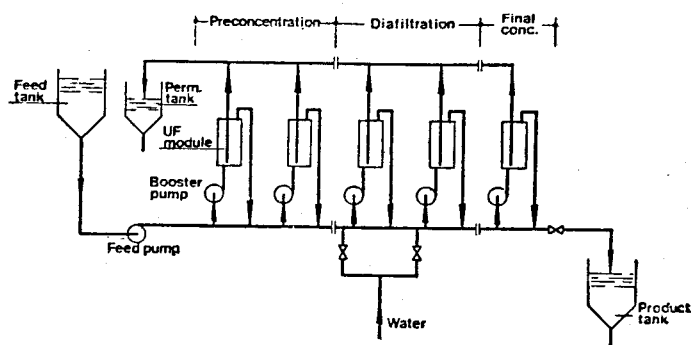


Fig 4 Continuous Ultrafiltration Plant

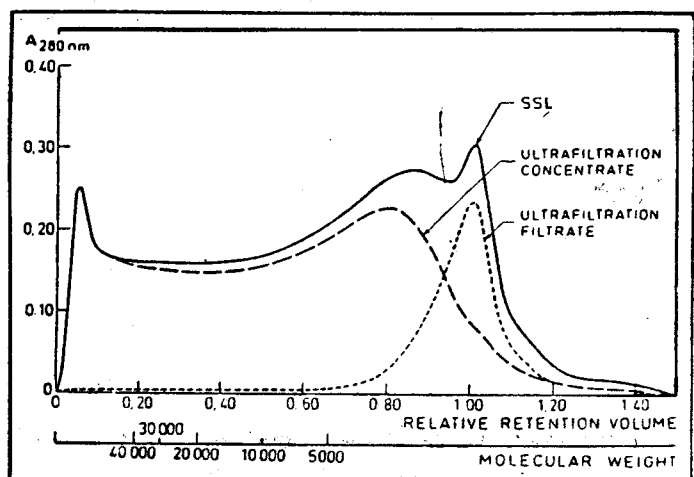


Fig. 5 Gel Chromatograms illustrating the molecular weight distributions of the lignosulfonates before and after ultrafiltration.

CONCLUSIONS :

The potential of membrane technologies (R.O. and U.F.) in complete recovery of black liquor constituents is discussed. The ideal recovery system for future would be ultrafiltration of black liquor followed by hyperfiltration of the ultrafiltrate. The concentrated black liquor thus obtained can be further processed in the existing recovery systems. Suggested recovery system would allow smooth expansion of pulp mill capacity without additional evaporators. Increased profit margin is expected from the sale of recovered lignin and its derivatives whose demand is increasing. Due to lower prices of lignin based chemicals, these are likely to compete well against petrochemicals. Another advantage of lignin chemicals over those of petrochemicals is that the former is obtained from a renewable source whereas the later is available in limited stock in the earth's crust.

Whereas DARS process is being exclusively developed for the recovery of chemicals from soda processes, R.O. and U.F. find acceptance in the recovery of chemicals from sulfite, sulfate and soda processes.

In fact R.O. can also be hooked up with DARS for concentration of soda black liquor to around 25% TDS prior to its mixing with Fe₂O₃ followed by burning in the fluidized bed reactors. Availability of R.O. and U.F. membranes with good resistance to high and low pH, high pressure and high temperature have made it possible for isolation of soluble substances and their consequent utilisation in the pulp and paper industry. Such separations were uneconomical even few years ago. There are likely to be significant variations from one mill to another, therefore pilot scale testing under local conditions are needed in almost every case.

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