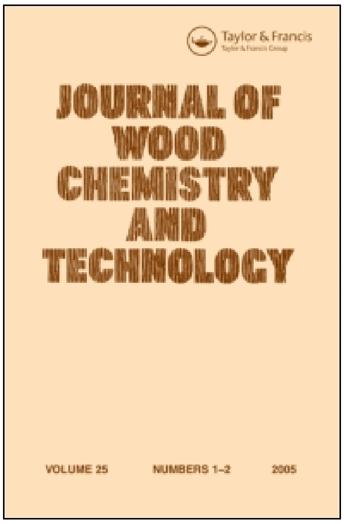

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CONCENTRATION OF ACID HYDROLYZATE BY REVERSE OSMOSIS AND MECHANICAL VAPOR RECOMPRESSION EVAPORATION

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ABSTRACT

The aim of this project was to investigate possible methods for the concentration of acid hydrolyzate obtained from hydrolyzing wood. A detailed study of concentration of sugar solution by reverse osmosis, RO, has been performed as well as a comparison with mechanical vapor recompression evaporation. The comparison has, in this specific case, shown that RO is currently more expensive. The result is, however, highly dependent on investment costs, and future expansion of membrane technology could mean lower area costs which would favor the technology.

INTRODUCTION

Energy prices have increased rapidly during recent years, and this has initiated extensive research into the production of liquid fuels as supplements to crude oil. Crude oil resources are limited and there is therefore a need to find renewable energy sources. One product which could be used as a fuel and which is renewable is ethanol produced from biomass, such as wood.

A flowsheet of a wood-ethanol process based on acid hydrolysis can be seen in figure 1[1]. In the first stage of this

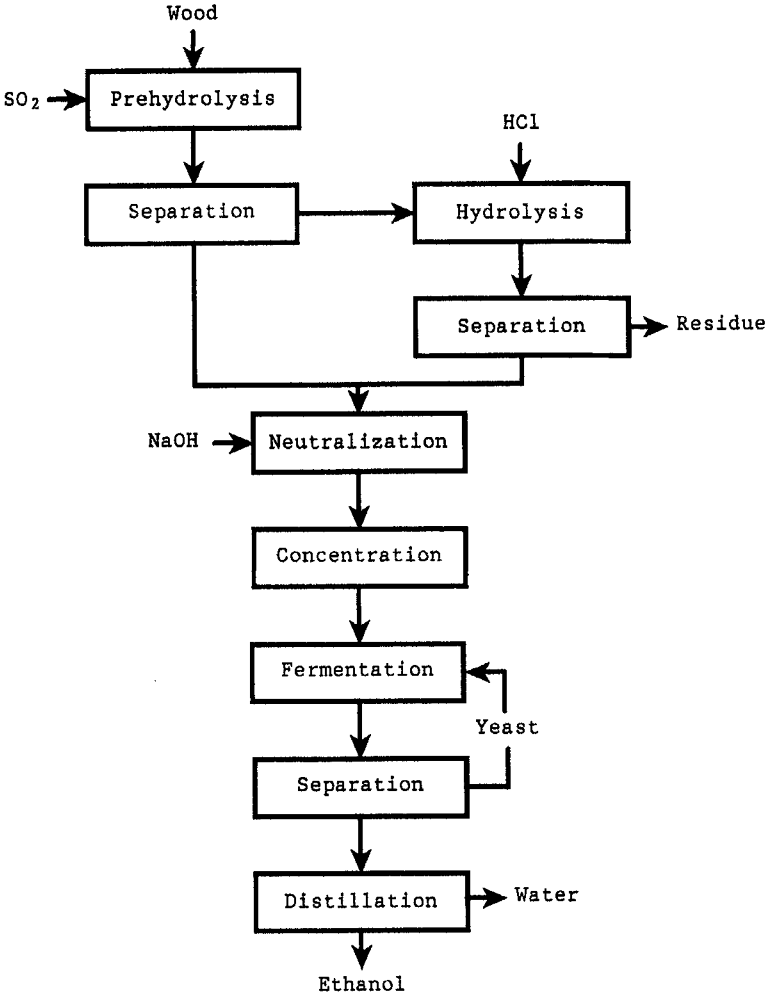

FIGURE 1. A flowsheet of a wood-ethanol process.

process, wood is prehydrolyzed with SO_2 in water. The sulfur dioxide solubilizes a smaller part of the lignin and degrades the hemicellulose, which is a heteropolymer of glucose, galactose, mannose, xylose, and other sugars. The prehydrolyzate will therefore contain all these sugars. After the prehydrolysis stage the remaining cellulose is separated from the sugar-containing prehydrolyzate.

The remaining cellulose can also be degraded to sugar. This is performed in the hydrolysis stage. In this process stage the cellulose is degraded by dilute acid (hydrochloric acid, for example), mainly to glucose. A residue, primarily containing lignin and ash, is then separated from the hydrolyzate.

The hydrolyzate, both from the prehydrolysis and the hydrolysis, which contains about 3-5 %(w/w) sugar, is neutralized with NaOH before fermentation. In some processes the sugar solution is also concentrated before fermentation.

The yeast species used in ethanol fermentation and of primary interest to industrial operations is *Saccharomyces cerevisiae*. Generally, 0.40 - 0.51 kg ethanol (or 0.51 - 0.62 liters ethanol) can be produced from 1 kg fermentable sugar (glucose). When the sugar conversion in the fermentation stage is completed, the yeast is separated and recirculated to the fermentor while the water-ethanol mixture is treated in a distiller. In this process stage water is removed until the final concentration of the product is obtained.

The production of ethanol from cellulose has, so far, been limited by technical and economical problems. In order to make the cellulose-ethanol process profitable, further steps must be taken to improve the process.

Several approaches may be taken to reduce the total cost of the process. One possibility is to remove water after hydrolysis, i.e., before fermentation, instead of after fermentation. If water is removed at an early stage of the process, less volume of sugar solution needs to be treated in the following stages, and investment costs for equipment can be reduced. Normally, the fermentation is performed at a low concentration, because a higher sugar concentration yields a higher alcohol concentration, which inhibits the fermentation. Recently, a process requiring higher sugar contents (18-19 %) has been developed[2].

The traditional way of concentrating sugar solutions is by evaporation, but reverse osmosis is an interesting alternative. In the reverse osmosis process, water is separated without a phase change. The energy requirement is therefore considerably lower than that in thermal evaporation. A positive effect if the concentration is performed by reverse osmosis before the neutralization is that a smaller amount of neutralization chemicals is required.

Another interesting technique of concentration is mechanical vapor recompression evaporation, where the produced vapor can be recompressed and used as a heating agent. In this process the energy is supplied only in the form of electrical energy to the compressor.

In this paper a detailed study of concentration of sugar solutions by reverse osmosis is presented, as well as a comparison with mechanical vapor recompression evaporation.

THEORY OF REVERSE OSMOSIS

The concentration of sugar solutions by reverse osmosis was investigated some decades ago by the sugar industry. However, at that time there were no suitable membranes and the process was not economical. Membranes with better performance characteristics have been developed recently, and therefore interest in concentrating sugar solutions by reverse osmosis has been re-established. Comprehensive literature surveys have recently been published[3,4].

In membrane operations some parameters are of vital importance. The most important operating parameters are pressure, feed concentration, temperature, velocity and, to some extent, pH. The influence of some of these parameters may be explained by basic transport equations. There are several theoretical models[5-9] which predict the influence of various parameters, but one simplified expression of the fluid flow through a membrane can be written as follows:

$$J = (\Delta P - \Delta\pi)/(\mu \cdot R_m) \tag{1}$$

Equation (1) shows that the flux, J, is influenced by the operating pressure (ΔP), the osmotic pressure ($\Delta\pi$) of the solution, the temperature (which effects the viscosity μ) and the membrane permeability (which effects R_m, the hydraulic resistance of the membrane).

A change in pressure will change the driving force, the difference between the operating pressure and the osmotic pressure. An increase in operating pressure increases the driving force and thus the capacity is improved.

The concentration of a solution has an apparent effect on the capacity. The reason is a change in the osmotic pressure. A higher concentration will lead to a higher osmotic pressure which in turn results in a lower driving force and, accordingly, a flux decrease.

The temperature affects the viscosity. The permeation of water through the membrane is facilitated by decreasing the viscosity. Since the viscosity decreases with increasing temperature, this has a positive effect on the capacity. The upper temperature is, however, determined by the membrane material's thermal resistance.

The circulation velocity affects the concentration polarization. This is due to a concentration boundary layer effect. Since the osmotic pressure increases in this layer the flux is reduced, as earlier discussed. The boundary layer is significantly decreased by increasing the velocity at low Reynolds numbers, but at higher numbers the layer-induced resistance becomes constant, and thus the permeate flow is no longer influenced by the velocity.

If the membrane contains charged groups, charged components in the solution can interact with the membrane. Since the charge on these compounds is determined by the solution pH, this can have a considerable influence on the capacity. It can be very difficult to predict how the interaction will affect the capacity and retention performance of the membrane, but knowledge in this area may be helpful in improving the performance of the membrane.

EXPERIMENTAL

In this work an extensive parameter study using three thin film composite membranes has been made. To reduce the influence of variations in the composition of the hydrolyzate solution, pure sugar solutions were used in the parameter study. Detailed results are reported elsewhere[10]. The membrane performance during the concentration of hydrolyzate under optimized conditions has also been studied.

The choice of the operating parameters used during concentration of the hydrolyzate was based on the parameter study. The operating pressure during concentration of the hydrolyzate was 4.0 MPa, the temperature 60 ^{o}C and the cross flow velocity 2.5 m/s.

The RO-membranes AFC30, AFC80 and AFC99, manufactured by PCI Membrane Systems Ltd, England, were tested. These polyamide membranes have NaCl retentions of 30, 80 and 99 %, respectively.

The inner diameter of the tubular membranes is 12.5 mm and the length of a membrane tube is approximately 1.2 m. The RO membranes were tested simultaneously in a single tube tester with separate permeate outlets for each membrane tube.

Hydrolyzate Solution

Hydrolyzate from the prehydrolysis stage was supplied by TVA (Muscle Shoals, Alabama, USA). The hydrolyzate was produced from yellow pine and contained 2.8 %(w/w) mannose, 1.7 % glucose, 1.5 % xylose, 0.6 % galactose and 0.4 % arabinose. The pH of the hydrolyzate was originally 1.8, but before transportation it was adjusted to 3.0 with NaOH. The TDS (total dry solids) content of the hydrolyzate from TVA was 8.2 %.

DISCUSSION

Preliminary tests on hydrolyzate solutions revealed severe fouling problems. This was due to fouling materials, such as proteins, lignin and other surface active substances. Removal of these by some kind of pretreatment was accordingly necessary. This pretreatment can be performed using different techniques. One method of pretreatment which is both technically feasible and sufficient is ultrafiltration[11,12].

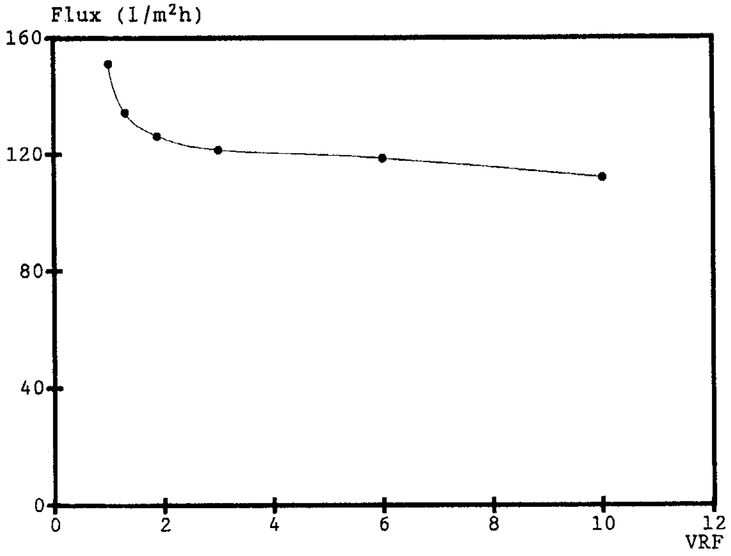

FIGURE 2. Flux as a function of VRF during hydrolyzate pretreatment using the FP100 membrane. T=60 °C, p=0.5 MPa and pH=3.

In tests of UF as a method of pretreatment a PVDF membrane (FP100) with a cut off of 100 000 (manufactured by PCI) was used. The large cut off of the membrane implies that the sugar molecules will pass through the membrane while larger molecules are retained. The test showed that it was possible to remove more than 90 % of the feed as the permeate, i.e. pretreated hydrolyzate, while still maintaining an acceptable flux. An average flux of 110 l/m^2h was obtained. Figure 2 shows the flux as a function of VRF (volume reduction factor).

The TDS contents in the permeate and the retentate were 7.6 and 9.1 %, respectively. Analysis for the determination of wood extractives in the untreated hydrolyzate and in the permeate was performed, and the results of this analysis showed that the two hydrolyzate samples contained 0.26 and 0.24 g/kg, respectively.

The conclusions which can be drawn from the TDS values and the wood extractives analysis are that only a minor part of the extractives was removed by the ultrafiltration pretreatment, and that most of the dry solids substance including suspended solids, apart from sugars, which account for 7.0 %, was removed. It was, therefore, probably substances other than wood extractives that caused membrane clogging when no pretreatment was used.

Concentration of Hydrolyzate by Reverse Osmosis

Two concentration tests were performed with the pretreated hydrolyzate. In these concentration tests approximately 100 liters of hydrolyzate were used, and each test was performed over a one-week period. The hydrolyzate originally contained 7.0 % sugar and this was the initial concentration in the first concentration test. The final concentration achieved in this test was 15.2 %.

In the second concentration test the feed hydrolyzate was diluted with deionized water to 3.0 % sugar, to simulate conditions in the concentration of dilute filtrate from a washing filter in the process. In this test the final sugar concentration was 9.1 %. The concentration was increased, in both tests, by the removal of AFC80 permeate while the permeates from the other membranes were recirculated.

The results from these two tests are presented in figures 3 and 4. The AFC30 membrane is the less dense membrane and the flux of this membrane started at about 80 l/m^2h at a sugar concentration of 3 %. As the concentration of the solution increased the flux decreased, and finally the flux was zero at a concentration of about 15 %. The retention of the AFC30 membrane was approximately 91 % during the period of concentration. It is remarkable that the AFC80 membrane exhibited the same high flux as the AFC30 membrane in spite of its much higher retention, about 95 %.

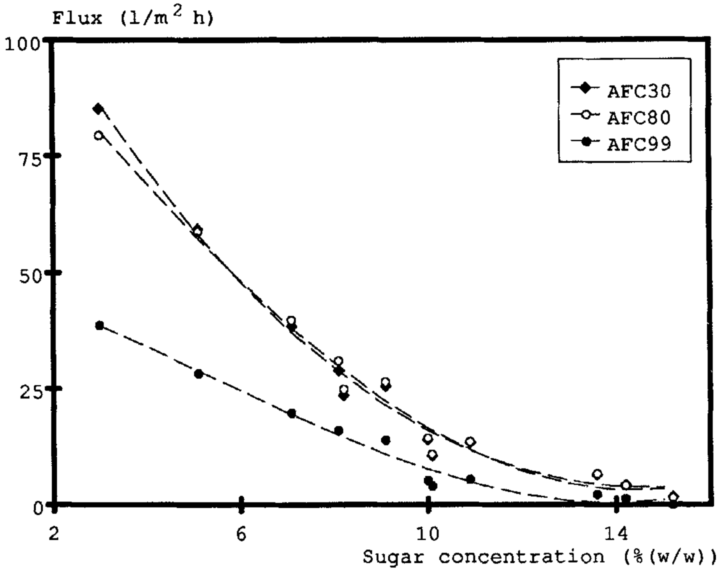

FIGURE 3. Flux of the AFC30, AFC80 and AFC99 membranes as a function of sugar content in the feed. T=60 °C, p=4.0 MPa and pH=3.

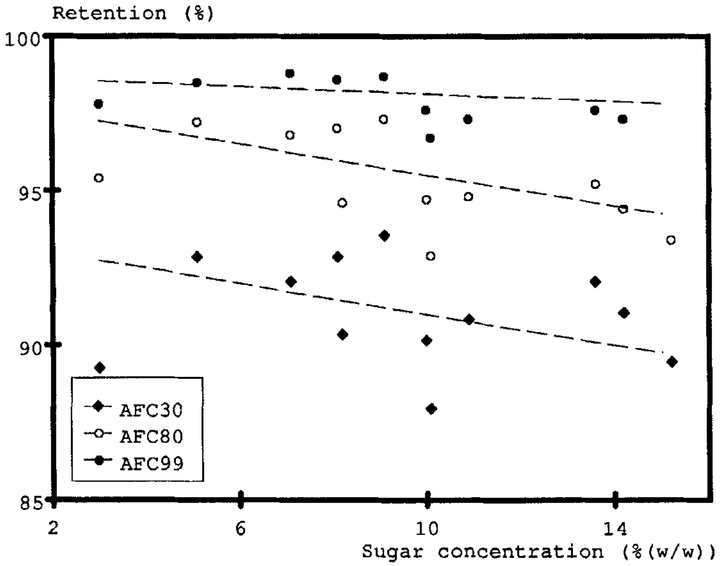

FIGURE 4. Retention of the AFC30, AFC80 and AFC99 membranes as a function of sugar content in the feed. T=60 °C, p=4.0 MPa and pH=3.

The densest membrane, AFC99, had as expected the lowest flux. At about 3 % sugar solution the flux was 37 l/m^2h and it decreased to zero at a sugar concentration of 15 %. As this membrane was the densest membrane included in the investigation it also had the best retention, about 98 %.

Concentration of Hydrolyzate by Mechanical Vapor Recompression

In separation processes where the waste heat consists of pure vapor, the vapor can be recompressed and used as a heating medium. In this process, mechanical vapor recompression (MVR), the energy is supplied in the form of electrical energy to the compressor. The economy of the process is therefore sensitive to the steam price/electricity cost ratio and the relation between energy costs and investment costs.

The heat flow, P, in the evaporator is dependent on the overall heat transfer coefficient, U, the size of the heat transfer area, A, and the temperature difference, ΔT.

$$P = U \cdot A \cdot \Delta T \qquad (2)$$

The overall heat transfer coefficient depends on the construction of the evaporator and the operating conditions, such as flow velocity and temperature difference. It is also influenced by the properties of the liquid that is to be concentrated.

Today, the most common type of evaporator in MVR applications is the falling film evaporator. This type of evaporator is characterized by a low pressure drop, satisfactory overall heat transfer coefficient and stable operation, even at low temperature differences.

The heat flow is, as mentioned above, affected by the flow velocity over the heat transfer surface, i.e. the Reynolds number. An increase in flow velocity will improve the heat transfer, and this may be achieved by recirculation in the evaporator.

The compressor power is determined by the total value of ΔT which means that the process requires more energy when the boiling point elevation increases. The process is thus favored by low concentration. The heat flow in the evaporator is also favored by low concentration, which means better heat transfer conditions (lower Prandtl number) and less fouling of the heat transfer area. Fouling decreases the overall heat transfer coefficient, U, and to compensate for this a higher value of ΔT is required, and thus a higher energy demand.

Equation (2) shows that the heat transferred is determined by the product of the heat transfer area and the temperature driving force. The compressor power, i.e. the energy consumption is in turn determined by ΔT which means that improved heat economy must be compensated for by an increase in the heat transfer area and thus an increase in capital costs. It is therefore very important to optimize the temperature difference in the evaporator.

The heat transfer coefficient was based on values from the literature[13]. The viscosity required for these calculations was determined experimentally and was found to agree well with values for pure sugar solutions.

The boiling point elevation for the hydrolyzate was also measured and found to be 1 °C at 15 % concentration. No foaming or fouling of the heat transfer area were observed in lab scale tests.

Economic Assessment

Cost estimates have been made for a plant concentrating 30000 kg/h 5 % sugar solution, during 300 days/year, to 12 %. An electricity cost of 0.036 USD/kWh valid for Swedish conditions and an annuity of 20 % of the capital cost have been used.

Membrane Plant

The RO plant is assumed to be a single pass system. Flux and retention from lab tests have been used to calculate the membrane area required and the sugar content in the permeate. Conditions used in the cost calculations are:

temperature	60	°C
pressure	40	bar
total investment cost	1250	USD/m^2 membrane area
electricity consumption	10	kWh/m^3 permeate
cleaning cost	0.16	USD/m^3 permeate
membrane cost	190	USD/m^2
membrane lifetime	1	year

Total investment and membrane costs were obtained from the manufacturer. The electricity consumption was estimated to be 2 kWh/m^3 permeate for the high-pressure pump and 8 kWh/m^3 permeate for the booster pumps. The cleaning cost was obtained from similar commercial plants and a membrane lifetime of 1 year was chosen, which is a conservative estimate.

The results obtained from the calculations show that a plant for the concentration of hydrolyzate would be more expensive with an AFC99 membrane (4.90 USD/m^3 permeate) than with an AFC80 membrane (2.60 USD/m^3 permeate). The significant difference in cost is due to the substantial difference in flux of the two

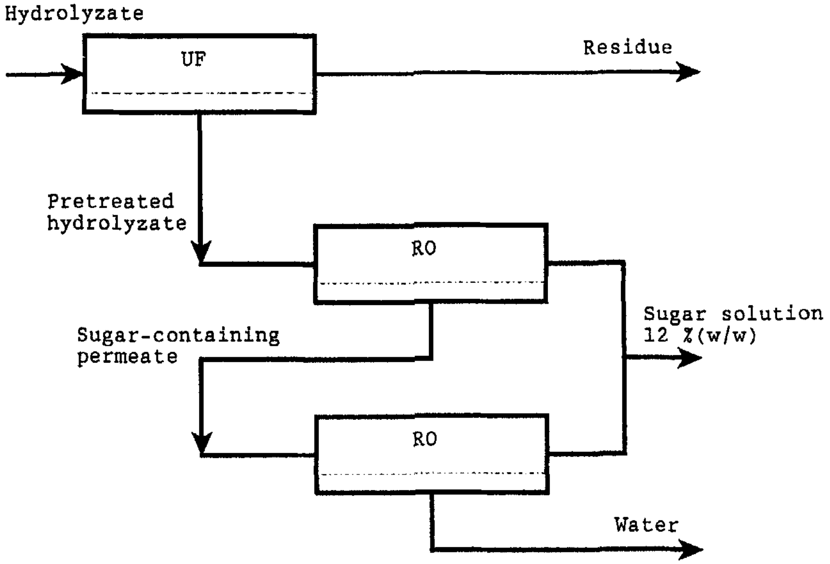

FIGURE 5. The suggested process configuration for concentrating the hydrolyzate by reverse osmosis.

membranes. But the permeate from the AFC80 membrane contains more sugar, 0.29 %. The AFC99 permeate contains only 0.13 % sugar. The loss of sugar in the permeate therefore becomes 3.4 % for the AFC80 membrane and 1.5 % for the AFC99 membrane. The sugar losses are considerable but can be reduced by a combination of low-retention and high-retention membranes[14]. In this investigation a direct follow-up RO stage has, however, been found to be more favorable. The suggested process configuration is presented in figure 5. Table 1 presents the hydrolyzate concentration costs for four possible combinations of the AFC80 and AFC99 membranes.

When the permeate from the first RO stage, which contains some sugar is subsequently treated in the second RO stage the fouling matter has been removed so results obtained from glucose tests[10] may be used.

TABLE 1

Costs of Hydrolyzate Concentration by RO.

Membrane in the first RO stage	AFC99	AFC99	AFC80	AFC80
Membrane in the second RO stage	AFC99	AFC80	AFC99	AFC80
Sugar content in the permeate (%(w/w))	0.001	0.003	0.002	0.006
Sugar losses (%)	0.013	0.033	0.027	0.067
Pretreatment costs	1.30	1.30	1.30	1.30
Investment costs	3.00	2.80	1.60	1.40
Operating costs	3.20	3.10	2.30	2.20
Total Cost (USD/m^3 permeate)	7.50	7.20	5.20	4.90

It can be seen from table 1 that it is more economical to use the AFC80 membrane in the first RO stage than the AFC99 membrane. The AFC80 membrane has a higher flux, therefore a smaller membrane area is needed. However, the AFC80 membrane does not have as good retention as the AFC99 membrane, and therefore more sugar passes through this membrane. If the AFC80 membrane is chosen in the second RO stage the concentration cost is minimized. However, the permeate contains more sugar and the sugar losses are more than doubled.

MVR Evaporation Plant

The temperature of the feed was assumed to be 130 °C as the hydrolysis was performed at this temperature, and this means that no heat exchanger is needed before the evaporator. Heat transfer areas and energy consumptions were calculated for three different

TABLE 2.

Calculated Heat Transfer Areas and Energy Consumptions.

ΔT (^oC)	3	5	10
Heat transfer area (m^2)	2240	1350	670
Energy consumption Compressor (kW)	137	205	372
Energy consumption Circulation pump (kW)	40	24	12

temperature driving forces and the results obtained are presented in table 2.

Investment costs were obtained from a budget quotation from a manufacturer as displayed below.

compressor (ΔT = 3 ^oC)	214 000	USD
(ΔT = 5 ^oC)	189 000	USD
(ΔT = 10 ^oC)	156 000	USD
cost of heat transfer area (> 1000 m^2)	390	USD/m^2
(< 1000 m^2)	470	USD/m^2
circulation pumps, piping and instrumentation	343 000	USD

Table 3 presents the investment and operating costs of an MVR evaporation plant at three values of ΔT. Figure 6 shows the cost of concentration as a function of ΔT in the evaporator for two different electricity prices.

TABLE 3.

Cost of Hydrolyzate Concentration by MVR-evporation.

ΔT (°C)	3	5	10
Investment costs	2.50	1.90	1.50
Operating costs	0.40	0.50	0.80
Total Cost (USD/m^3 evaporated water)	2.90	2.40	2.30

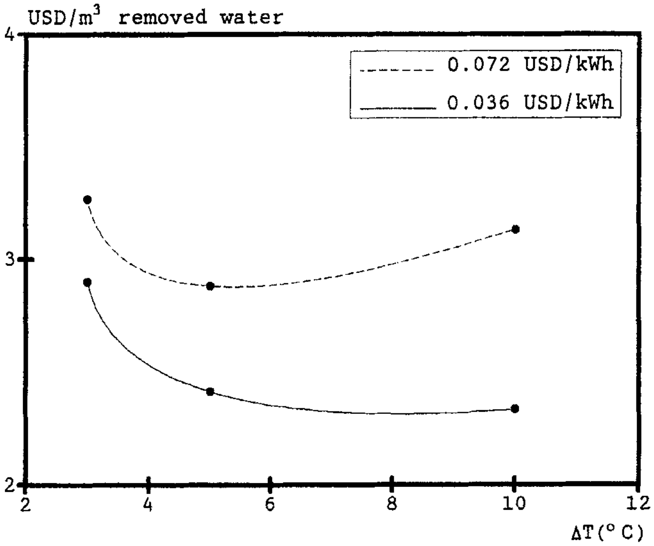

FIGURE 6. The cost of concentration by MVR evaporation as a function of ΔT in the evaporator.

CONCLUSIONS

A comparison between RO and MVR evaporation has, in this specific case, shown that RO is currently more expensive. The higher cost of the RO plant is due to the high investment cost for the plant and the high membrane costs. In order to make membrane technology competitive these costs must be reduced still further in the future.

MVR evaporation plants are sensitive to the relation between energy cost and investment costs. Therefore, calculations were carried out for three different values of ΔT. The cost calculations show that at current Swedish electricity prices the plant with the highest value of ΔT, 10 ^{o}C (i.e. the smallest heat transfer area), was favored. However, when the electricity cost was doubled, a cost minimum appeared at 5 ^{o}C.

The RO concentration is complicated by two factors, the need for pretreatment and the sugar losses. One technically feasible method of pretreatment is ultrafiltration. In order to minimize the sugar losses and avoid a discharge problem a follow-up RO stage could be used. The permeate from this second RO stage will only contain a small amount of sugar.

REFERENCES

1. R.A. Westmoreland, R.L. Griffith, S. Wannstrom and J. Kolar, VIII International Symposium on Alcohol Fuels, p. 55, New Energy and Industrial Technology Development Organization (ed.), Sanbi Insatsu Co. Ltd, Tokyo, 1988.

2. B. Atkinson and F. Mavituna, Biochemical Engineering and Biotechnology Handbook, p. 912, The Nature Press, New York, 1983.

3. G. Trägårdh and V. Gekas, Desalination, 69, 9 (1988).

4. Y. Blomgren, Report LUTKDH/(TKKA-7007)/1-21/(1988).

5. H.K. Lonsdale, W. Pusch and A. Walch, J. Chem. Soc. Faraday Trans., 3, 501 (1975).

6. S. Sourirajan and T. Matsuura, Reverse Osmosis / Ultrafiltration Process Principles, National Research Council Canada, Ottawa, 1985.

7. W. Pusch, Desalination, 59, 105 (1986).

8. G. Jonsson, Desalination, 35, 21 (1980).

9. V.L. Punzi and G.P. Muldowney, Rev. Chem. Eng., 4, 1 (1987).

10. Y. Blomgren, Lic. Thesis, Dept. of Chemical Engineering I, University of Lund, Sweden, LUTKDH/(TKKA-7006)/1-44/(1989).

11. T.S. Lee, D. Omstead, N.-H. Lu and H.P. Gregor, Ann. NY. Acad. Sci., 367 (1982).

12. T.R. Hanssens, J.G.M. van Nispen, K. Koerts and L.H. de Nie, Zuckerind., 109, 152 (1984).

13. S. Ragnarsson, Ph.D. Thesis, Dept. of Chemical Engineering I, University of Lund, Sweden, LUTKDH/(TKKA-1003)/1-11/(1980).

14. H.F. van Wijk, A.E. Jansen and R.J.M. Creusen, Desalination, 51, 103 (1984).