Environment Protection Engineering

Vol. 13 1987 No. 1

NIKODEM CHLUBEK*, MARIA TOMASZEWSKA*

CONCENTRATION OF DAIRY WASTES BY MEMBRANE DISTILLATION

The membrane distillation process is a new method of separation and concentration of liquors. Its important applications can be seen in the technology of water treatment, sea water desalination, and especially in the recovery of costly matter from hot wastewater solutions. In our laboratory some experiments have been carried out on concentration of milk whey in order to recover milk sugars for their further utilisation. It has been shown that it is possible to concentrate lactose up to 300 g/dm^3 at the water removal rate approaching 0.45 m^3/m^{2}d, thermal gradient of 40 deg and the average temperature of 41 deg.

1. INTRODUCTION

It has been shown in the previous paper [3] that membrane distillation requires the application of hydrophobic membranes. Mass and heat transport across the membranes under non-isothermal conditions was described in a number of papers. For example APTEL [2] defined this process as pervaporation, VINK [10] as thermal osmosis, and GAETA [5] as thermodialysis.

Membrane distillation is a process in which a microporous and hydrophobic membrane separates a warm aqueous solution from the cold one. In these conditions water evaporates from the warm solution into the membrane pores and vapour is transported through the membrance as permeate. The vapour condenses directly in the stream of cold condensate on the other side of the membrane [1], [4], [6]–[9]. Due to surface tension forces the liquid phase is not allowed to penetrate into the pores and the contact between two liquid phases is impossible. According to the laws of thermodynamics, the driving force of the membrane distillation is assured by the difference of temperatures which, in turn, results in the difference of vapour pressure across the membrane. Evaporation takes place at the solution–membrane interface on the solution side if the vapour pressure is higher than that at the con-

*Technical University of Szczecin, 70-310 Szczecin, Al. Piastów 17, Poland.

densate–membrane interface. The vapour can then diffuse through the pores to the cooler interface where it becomes condensed. This simple model of the process presented above does not give sufficient information about the membrane distillation. There remain several questions such as membrane phobicidy and the effect of pressure which have not been answered yet.

The rate of evaporation is strongly influenced by the temperature of the warm solution t_w and that of the coolant t_c. With the increase of temperature, the vapour pressure increases and hence the driving force. This means that the evaporation rate increases with temperature of the warm solution, even though the temperature difference $\Delta t = t_w - t_c$ remains constant.

The length of the diffusion path is another significant factor. In membrane distillation the diffusion path is usually determined by the membrane thickness.

The hydrophobic properties [4] of the polymeric material of the membrane prevent bulk liquid transport of the liquid phase in the same direction as permeate. By applying a hydrostatic pressure on the warm solution, lower than the intrusion pressure P at which bulk liquid flow might take place, the vapour transport across the membrane can be increased.

Thus in membrane distillation process the main role of the microporous hydrophobic membrane is to prevent bulk flow of the liquid phase and to favour the evaporation of water. The dependence of mass and heat transport upon different process and membrane parameters, which are involved in membrane distillation, has been investigated theoretically [8], [9].

It has already been shown [4] that the membrane distillation can be used for concentration of sugar solutions. The possibility of concentrating solutions characterized by very high osmotic pressure is an interesting aspect of this technology. The low operation temperature of the membrane distillation system makes waste heat the preferable energy source, therefore the cost of energy can be reduced or even eliminated.

2. EXPERIMENTAL

The study has been carried out using a laboratory set-up shown in fig. 1. The construction of apparatus for membrane distillation was based on the filter press principle, shown in fig. 2. It consists of two compartments, a warm and a cold ones, separated by a microporous hydrophobic membrane of effective surface area equal to 73.8 cm^2. The warm compartment has been supplied continuously by thermostated liquid. The produced vapour was condensed in the cooling liquid in the cold compartment. Having in mind future technical applications of the process, we have used the tap water as a coolant. It is assumed that pure water evaporated from the wastewater can be directed into industrial water systems. Thus, in the further investigations the vapour phase was condensed directly in a stream of a cooling

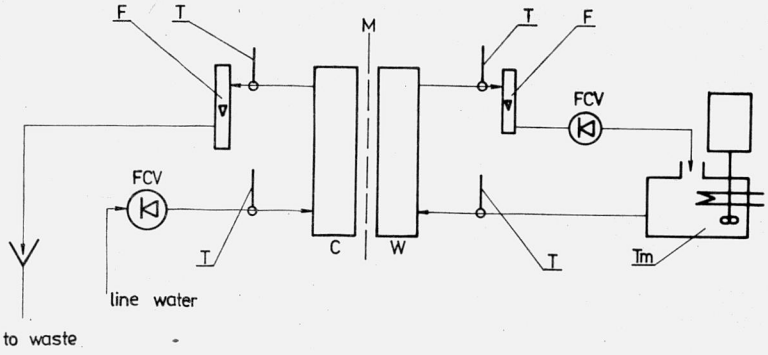

Fig. 1. Set-up for the membrane distillation experiments

M – membrane, *C* – cold compartment, *W* – warm compartment, *T*– temperature control, *Tm* – thermostat, *FCV* – flow control valve, *F* – flow meter

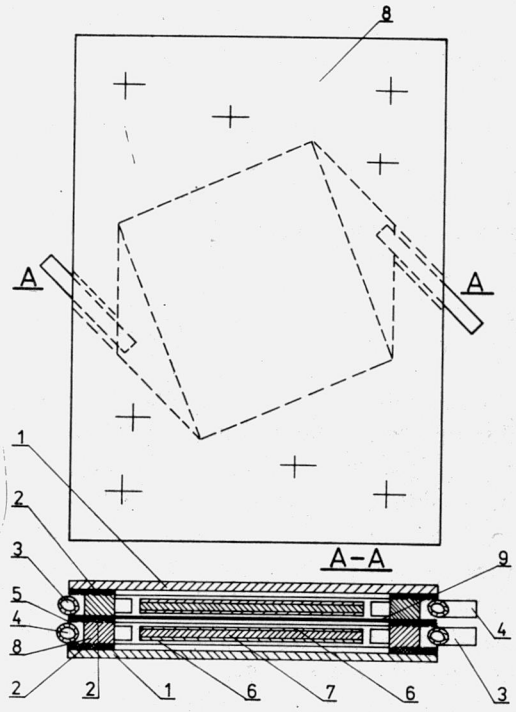

Fig. 2. Apparatus for membrane distillation

1 – PVC plates, *2* – rubber gasket, *3* – inlet, *4* – outlet, *5* – epoxy resin beting, *6* – supporting screen, *7* – turbulence promotor, *8* – PVC frame, *9* – membrane

water, flowing across the cold compartment. In order to increase the turbulence and improve the distribution of flows, turbulent promotors were placed in the cold and warm compartments. In our experiments the commercial microporous flat sheet membranes of various types (Gelman Inc., U.S.A.) made from Teflon ℛ have been tested. Membrane distillation process was tested with pure water, electrolyte

solutions (NaCl), non-electrolyte solutions (lactose), and milk whey at different concentrations and different temperature gradients. The tested solution circulated between the warm compartment and the thermostate. The distillate was removed with cold water flowing along the other side of the membrane. The flow rate of the warm solution was 0.084 m^3/h and that of cold water about 0.002 m^3/h. The concentration of commercial lactose solutions was carried out at two temperature differences, i.e., 22 deg and 40 deg. The feed solution was thermostated and completed periodically to its initial volume in the thermostate, each time using the lactose solution the concentration of which corresponded to that in actual concentration of feed solution. After every 20 hours the sides of the membranes were turned over by alternating the compartments.

Prior to the membrane distillation process the raw milk whey was neutralized to pH 6.2 and heated in 90 deg for 30 minutes. The whey proteins precipitated and were separated by filtration. This pretreatment was necessary to eliminate the negative effect of proteins in the feed solution on membrane distillation (fouling). Moreover, proteins could contaminate the concentrated whey and make crystallization of sugars difficult. The contents of sugars in pretreated whey were 45–47 g/dm^3.

The experiments were carried out at two constant whey-cold water temperature gradients which were equal to 32 deg and 42 deg. During the process the volume of thermostated liquor was completed periodically with fresh whey (containing 45–47 g of sugars/dm^3) to its primary level. The concentration of sugars and the flux of water across the membrane were measured during these experiments.

3. RESULTS AND DISCUSSION

The influence of salt (NaCl) concentration in the warm feed solution on water flux across the membrane at different temperature gradients is shown in fig. 3 and in table. The water flux across the membrane decreases exponentially with the increasing concentration of salt in the feeding solution. The effect of salt concentration is more distinct in higher temperature gradients. This observation indicates that a lower partial pressure of vapour at the membrane surface, which is due to the presence of salt in the feeding solution, reduces the driving force of the mass transport. This negative effect is intensified by the polarization of concentration at the membrane surface.

In order to reduce this effect the turbulence promotors were placed in both compartments. Moreover, the hydraulic flow conditions were improved by a special design of inlet and outlet in the apparatus (fig. 2), based on experimenal study. The heat exchange in the described apparatus was tested both under countercurrent and cocurrent flow conditions. It has been found that better results are obtained in countercurrent flow conditions, therefore they were applied in present work.

From the data in the table it can be seen that the rejection of sodium chloride

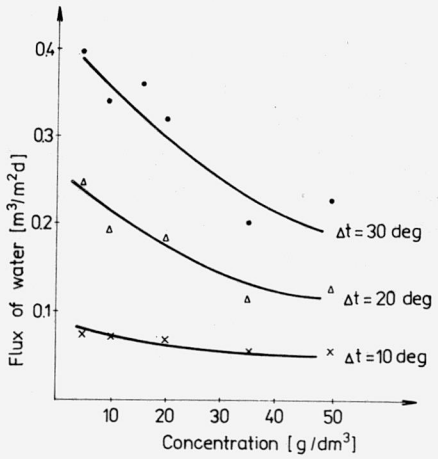

Fig. 3. Influence of sodium chloride concentration in warm solution on water flux at different temperature gradients

Membrane type – Gelman TF-450 (0.45 μm pore size)

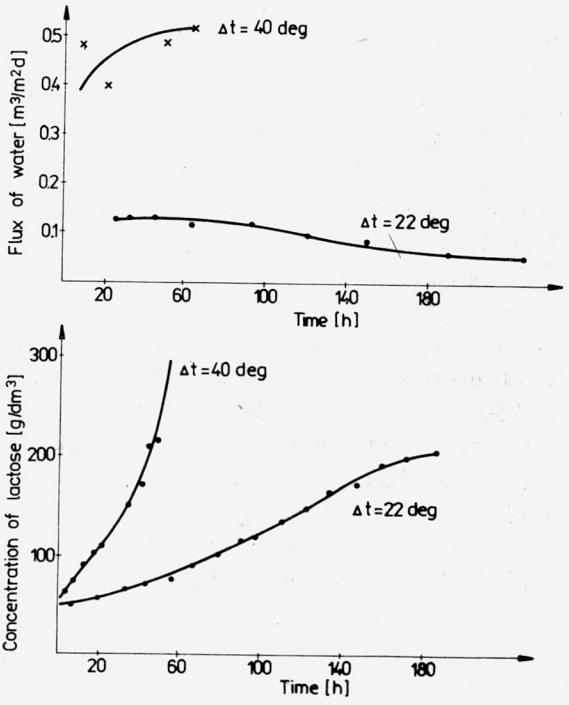

Fig. 4. Water flux and lactose concentration versus operation time of the process

Membrane type Gelman TF-200 (0.20 μm pore size)

Table

Membrane* distillation of water from sodium chloride solution

Temperature		Feed concentration	Salt rejection	Water flux
In warm compartment	In cold compartment			
°C		g/dm³	%	m³/m²d
50.2	19.5	4.51	97.6	0.392
30.3	19.8	4.33	96.6	0.072
48.7	20.2	9.90	99.4	0.340
27.8	17.7	9.32	98.4	0.072
49.8	20.0	20.57	99.7	0.320
29.5	19.0	18.86	99.2	0.070
50.2	20.7	50.2	96.7	0.226
29.8	17.8	48.1	96.8	0.058

*Membrane – Gelman, type TF-450.

from primary solution exceeded 95%, being lower than 100% predicted theoretically. Probably, the bulk flow of solution is caused by the vapour flux in a part of the largest pores. To compare the mass transport in membrane distillation and ultrafiltration, the same membrane was tested also in isotermic conditions. The applied hydraulic pressure was set so that the flow rate through the membrane be equal to the water flow rate in the process of membrane distillation. In these conditions the rejection was near zero.

The concentration of commercial lactose solution as a function of time is shown in fig. 4. In this experiment the membrane distillation of non-electrolytes was to be compared with the electrolyte concentration described above. Generally, the relationships between water flow across the membrane and the concentration of lactose depending on the time of the experiment were the same. An increase of temperature gradient from $\Delta t = 22$ deg to $\Delta t = 40$ deg caused considerable acceleration of the process. The rate of water flow across the membrane at $\Delta t = 40$ deg was more than 4 times higher than at $\Delta t = 22$ deg reaching about 0.5 m^3/m^2d (fig. 4). At $\Delta t = 40$ deg the concentration of lactose grew considerably faster than at 22 deg and the value of about 300 g/dm^3 was reached after 50 h operation of the system.

Concentration of whey sugars proceeded slowly (fig. 5). The fact of a periodical supply of raw whey (dotted lines in the figures) should be taken into account.

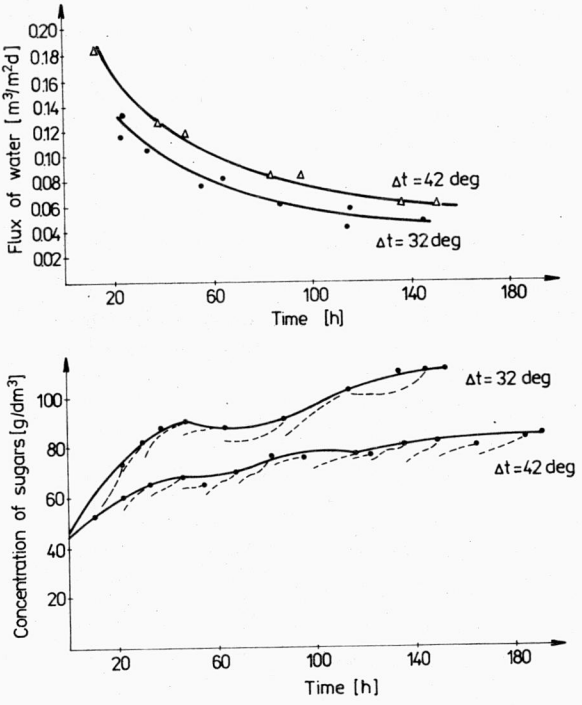

Fig. 5. Water flux and concentration of whey sugars in the membrane distillation process
Dotted lines indicate periodical raw whey supply. Membrane type – Gelman TF-200

Milk whey is a mixture of non-electrolyte and electrolyte solutions. Because the applied clarification was not perfect, an opalescence from colloidal particles of proteins occurred in feed solutions. This situation should be considered as typical as far as waste treatment by membrane distillation is concerned.

4. CONCLUSIONS

The membrane distillation process may find much interesting application, especially in concentration of diluted waste solutions. The possibility of utilizing low temperature gradients coming from different sources of waste heat makes this process very attractive from the economic point of view.

The ability of membrane distillation systems to operate effectively at ambient pressures greatly simplifies the operations.

REFERENCES

[1] ANDERSSON S. I., KJELLANDER N., RODESJÖ B., *Design and field tests of a new membrane distillation desalination process*, Desalination, 1985, 56, 345.

[2] APTEL P., CHALLARD N., CUNY, J., NELL J., *Application of the pervaporation process to separate azeotropic mixtures*, J. Mem. Sci, 1976, 1, 271.

[3] DRIOLI E., CHLUBEK N., PUNZO A., *Studio sui processi a membrana condotti sotto gradiente termico*, La Chimica E L'Industria, 1984, 66, 147.

[4] DRIOLI E., YONGLIE Wu., *Membrane distillation: an experimental study*, Desalination, 1985, 53, 339.

[5] GAETA F. S., MITA D. G., *Thermal diffusion across porous partitions: the process of thermodialysis*, J. Phys. Chem., 1979, 83, 2276.

[6] GORE D. W., *Gore–Tex membrane distillation*, Proc. 10th Ann. Conf. WSIA, July 25–29, Honolulu 1982.

[7] HANBURY W. T., HODGKIESS T., *Membrane distillation — an assessment*, Desalination, 1985, 56, 287.

[8] JÖNSSON A. S., WIMMERSTEDT R., HARRYSSON A. C., *Membrane distillation — a theoretical study of evaporation through microporous membranes*, Desalination, 1985, 56, 237.

[9] SARTI G. C., GOSTOLI C., MATULLI S., *Low energy cost desalination processes using hydrophobic membranes*, Desalination, 1985, 56, 277.

[10] VINK H., CHISHTI S. A. A., *Thermal osmosis in liquids*, J. Mem. Sci., 1976, 1, 149.

ZATĘŻANIE ŚCIEKÓW MLECZARSKICH Z WYKORZYSTANIEM DESTYLACJI MEMBRANOWEJ

Destylacja membranowa jest nową metodą rozdziału i zatężania roztworów. Wykorzystuje się ją głównie w technologii uzdatniania wody, odsalania wody morskiej oraz utylizacji cennych substancji ze ścieków o podwyższonej temperaturze. W naszym laboratorium zatężano serwatkę z mleka, aby odzyskać cukry w nim występujące. Wykazano, że podczas tego procesu można uzyskać roztwór laktozy o stężeniu około 300 g/dm^3 przy szybkości transportu wody wynoszącej 0,45 m^3/m^{2}d, różnicy temperatur 40 deg i średniej temperaturze 42°C.

КОНЦЕНТРАЦИЯ СТОКОВ МОЛОЧНОЙ ПРОМЫШЛЕННОСТИ С ИСПОЛЬЗОВАНИЕМ МЕМБРАННОЙ ДИСТИЛЯЦИИ

Мембранная дистиляция является новым методом разделения и концентрации растворов. Её используют, главным образом, в технологии водоподготовки, обессоливания морской воды и утилизации ценных веществ из стоков с повышенной температурой. В нашей лаборатории концентрировали сыворотку из молока с целью рекуперации выступающих в нём сахаров. Доказано, что в течение этого процесса можно получить раствор лактозы концентрацией в 300 г/дм^3 при скорости транспорта воды 0,45м^3/м^{2}д, разницы температур 40 дег и при средней температуре 42°Ц.