3. Membrane Processes for Energy Saving in Japan

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1. Introduction

Over the last 20 years, membrane separation processes, such as reverse osmosis, ultrafiltration and microfiltration, have been widely adopted by different industries. Commercial uses of membrane have displaced conventional separation processes, such as distillation, evaporation, precoat filter and so on.

Membrane separation processes are often more capital and energy efficient when compared with conventional separation processes. Membrane devices and systems are almost always compact and modular. These are the well-known advantages of membrane separation processes. The disadvantage of the membrane process is that the process does not have scale merit and thus the membrane process is suitable for the small and middle size applications.

Energy saving is, of course, the biggest advantage of the membrane process, and in many industries the membrane processes are employed because of this reason.

Membrane process has other big advantage. In many applications membrane processes provide much higher quality of product than conventional processes. The example is ultrapure water production by membrane processes in semiconductor industry. Conventional technologies never offer such good quality of pure water.

If you can obtain both energy saving and higher quality of product at the same time by membrane processes, this is the best application of membrane processes. One example is the concentration of orange juice by membrane, which has already been commercialized in Japan. Comparing with the conventional vacuum evaporation process, juice concentrated by the membrane process has much better taste and flavor and the energy consumption in the membrane process is much less than the evaporation process.

In this paper, first membrane separation technology will be classified and then Japanese membrane manufacturers and new modules and devices under development in Japan will be introduced. Fourth energy saving in membrane process will be discussed and finally practical applications of membrane processes in Japan will be shown.

2. Membrane Separation Technology

A membrane separation process requires two bulk phases, the feed and the permeate, physically separated by a third phase, the membrane. Membrane separation technology can be classified into three groups based on state of the feed and permeate.

In the first group both feed and permeate are liquid and driving force for permeation is mechanical pressure difference applied over the membrane. In the second group feed is liquid and permeate is vapor. Driving force for this group is vapor pressure difference over the membrane. In the third group both feed and permeate are gas or vapor and the driving force is partial pressure or vapor pressure difference. In Table 1 all membrane processes commercialized are classified.

Table 1 Membrane separation technology commercially applied.

Liquid-Liquid System

Technology	Size or Molecular Weight of Species Rejected	Pressure Difference
Microfiltration(MF)	0.02 to 10 μm	Vacuum to 200kPa
Ultrafiltration(UF)	8,000 to 300,000(Mw)	Vacuum to 500kPa
Nanofiltration(NF)	350 to 8,000(Mw)	500kPa to 3MPa
Reverse Osmosis(RO)	< 350(Mw)	3 to 5MPa

Liquid-Vapor System

Technology	Species Rejected	Pressure Difference
Pervaporation(PV)	Organic Solvents, Water	Vacuum(10torr <)

Gas(Vapor)-Gas(Vapor) System

Technology	Species Rejected	Pressure Difference
Gas Permeation(GP)	Gas	Vacuum to 3MPa
Vaporpermeation(VP)	Volatile Organic Compounds Water, Gas, Air	Vacuum(10torr <)

Nanofiltration listed in Table 1 is rather new membrane separation technology and its separation characteristics is in between ultrafiltration and reverse osmosis. Main suppliers of this type of membrane are Film Tech(USA), Toray(Japan) and Nitto(Japan). Especially in Japan, both Toray and Nitto have commercialized many types of NF membranes because large area of the membranes is used in producing ultrapure water in semiconductor industry. Table 2 shows separation performance of the typical nanofiltration membranes.

Table 2 Rejection performances of thin-film composite membranes

Manufacturer	Nitto				Toray			Film Tech		
	NTR-				SU-			BW-	NF-	
Solute(Mw)	759HR	729HF	7250	7450	700	600	200S	30	70	40HF
NaCl(58)	99.5	92	60	51	99.5	80	65	98	70	40
Na_2SO_4(142)	99.9	99	99	92	99.9		99.7			
$MgCl_2$(94)	99.8	90	90	13	99.8		99.4	98		20
$MgSO_4$(120)	99.9	99	99	32	99.9	99	99.7	99	98	95
EtOH(46)	53	25	26		54	10		70		
IPA(60)	96	70	43		96	35	17	90		
Glucose(180)	99.8	97	94					98	98	90
Sucrose(342)	>99.9	99	98	36	99.8	99	99	99	99	98
Conc.(%)	0.15	0.15	0.20	0.20	0.15	0.10	0.10	0.20	0.20	0.20
Pressure(MPa)	1.5	1.0	2.0	1.0	1.5	0.75	0.75	1.6	0.6	0.9
Temp.(°C)	25	25	25	25	25	25	25	25	25	25

3. Membrane Manufacturer in Japan

There are many membrane manufacturers in Japan and they are shown in Table 3 with membranes they made and their materials. There are two inorganic membrane manufacturer, NGK Filtech and Noritake, and they make alumina microfiltration membranes and titania ultrafiltration membranes.

Ube makes gas permeation and vaporpermeation membranes. Vaporpermeation membranes are also made by Nitto and there is no manufacturer of commercially available pervaporation membrane.

Table 3 Main Membrane Manufacturer in Japan

Manufacturer	Membranes Produced	Membrane Materials
Fuji Photo Film	MF(Flat, Capillary, Cartridge)	CTA, PSf
Kuraray	MF(Capillary)	PVA
Mitsubishi Rayon	MF(Capillary, Hollow Fiber)	PE
Daicel Chemical Industries	UF(Tubular, Capillary) RO(Tubular, Spiral)	PAN, PES CA, Composite
Nitto Denko	UF(Tubular, Capillary, Spiral) NF(Tubular, Spiral) RO(Tubular, Spiral) VP(Flat)	PES, PVA Composite CA, Composite Silicon Rubber + PI
Toyobo	RO(Hollow Fiber)	CTA, PA
Toray Industries	NF(Spiral) RO(Spiral)	Composite CA, Composite
NGK Filtech	MF(Tubular, Monolith) UF(Tubular, Monolith)	Alumina Titania
Noritake	MF(Tubular, Monolith)	Alumina
Ube Industries	GP(Hollow Fiber) VP(Hollow Fiber)	PI PI

CTA:Cellulose triacetate, PSf:Polysulfone, PVA:Polyvinyl alcohol, PE:Polyethylene, PAN:Polyacrilonitrile, PES:Polyethersulfone, CA:Cellulose Acetate, PI:Polyimide, PA:Polyamide

4. Energy Consumption in Membrane Processes

Membrane processes are well-known as an energy saving process, but few energy consumption data have been reported. Therefore, here, an amount of energy required in membrane process will be calculated for desalination of sea water as an example, and compared with the amount required in other processes.

(1) Theoretical energy consumption

$$W_{id} = -RT \ln a \qquad (1)$$

where a is activity of sea water. When the activity is known, energy can be calculated by this equation. However it is rather difficult to find activity data for a certain solution, thus the following approximate calculation is often employed by using vapor pressure or osmotic pressure data.

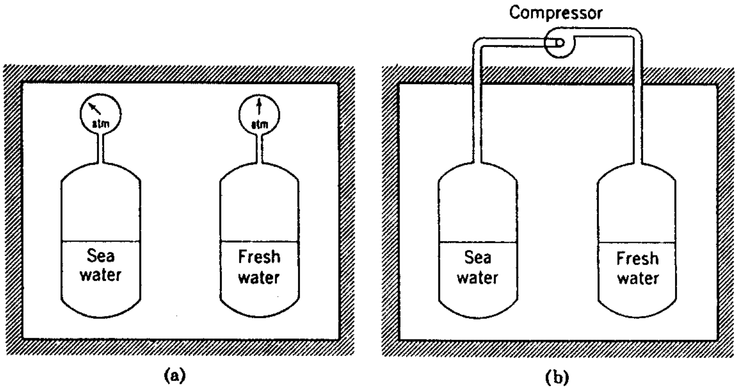
Supposing the hypothetical simple desalting process shown in Fig.1. Consider first the situation in which the two reservoirs are not connected. In both reservoirs water evaporates into the empty space and the pressures reach the equilibrium vapor pressures of sea water, P_s, and pure water, P_w. The vapor pressure of sea water is always less than that of pure water, therefore it is necessary to install a pump or compressor between the vessels which raises the pressure of the water vapor coming from the sea-water reservoir to a value just a little higher than in the pure-water reservoir.

The work done by a hypothetical pump of this kind equals the pressure difference times the volume of water vapor. At 27°C, P_s/P_w=0.982 and thus the work for obtaining 1kg pure water can be calculated as follows.

$$W_{id} = (P_w - P_s)\cdot\left(\frac{1\times10^6}{18}\right)W_{id} = (P_w - P_s)\frac{1000}{18}\frac{RT}{P_w} = (1-0.982)\frac{1000\cdot8.3\cdot300}{18}$$

(2)

$$= 2.5\text{kJ}/\text{kg} = 0.70\text{kWh}/\text{m}^3$$



(a) (b)

Fig.1 Illustration of energy requirements for sea-water purification. Pressure gages show schematically pressure difference. Compressor is needed to transfer pure water vapor from left to right vessel.

Assuming osmotic equilibrium between sea water and pure water which are separated by an ideal semipermeable membrane, the work done by an hypothetical pump which moves pure water from sea-water side to pure-water side equals the osmotic pressure difference times the volume of water. At 25°C the osmotic pressure of sea water is 2.5MPa and thus the work is given as follows.

$$W_{id} = 2.5 \times 10^6 \cdot \frac{1}{1 \times 10^3} = 2.5\mathrm{kJ/kg} = 0.70\mathrm{kWh/m^3} \tag{3}$$

(2) Energy consumption in reverse osmosis process

In reverse osmosis processes applied pressure is usually two times higher than the osmotic pressure of sea water. The energy to operate the process equals the applied pressure, ΔP, times the volume flow rate of feed, Q. The amount of pure water produced depends on recovery, usually 0.3. Thus the energy requirement in reverse osmosis process is given as;

$$W_{RO} = \frac{2.5 \times 10^6 \times 2}{0.3} = 1.7 \times 10^4 \mathrm{kJ/m^3} = 4.7\mathrm{kWh/m^3} \tag{4}$$

This energy is supplied as electric energy. When comparing to other processes in which energy is supplied as heat energy, the electric energy above calculated must be converted into heat energy. Using conversion coefficient of 0.3, the energy consumption becomes,

$$W_{RO} = \frac{4.7}{0.3} = 16\mathrm{kWh/m^3} \tag{5}$$

(3) Energy consumption in evaporation process

In evaporation process energy mainly consumes for evaporation of water and energy is calculated by using latent heat of water, that is about 540kcal/kg at 100°C. Of course energy efficiency can be increased by heat recovery and by employing multiple-stage flash evaporation and the energy requirement decreases at least down to one tenth.

$$W_{EV} = \frac{540 \times 4.18}{10} = 230\mathrm{kJ/kg} = 63\mathrm{kWh/m^3} \tag{6}$$

It is quite obvious from these results that reverse osmosis process is greatly energy saving comparing to evaporation process. Membrane processes driven at lower pressure, such as ultrafiltration and microfiltration, require less energy than in reverse osmosis process.

5. New modules and Devices Recently Developed for Energy Saving in Japan

5.1 Rotating-type modules equipped with disk membrane

High concentration suspensions, such as fermentation broth, non-clarified juice, waste water and so on, have been filtrated by using precoat filters. However this technique has many problems:

1) Suspended matters leak through a filter, especially in an initial filtration stage.
2) Filter aid, such as diatom earth, costs much.
3) From the view point of global environmental protection, disposal of waste filter-aid becomes difficult.

Therefore, membrane separation processes are introduced for suspension filtration.

High concentration suspensions have high potential for membrane fouling. Recently crossflow filtration technique has been widely employed to prevent fouling, and feed solutions are usually fed with flow velocity of 2 to 5 m/s. This high velocity requires huge amount of energy, nevertheless permeate flux is not so high.

In Japan, in order to remove above mentioned problems in both precoat filter and crossflow filtration, a new type of module, a rotating-type module equipped with disk membrane has been developed and commercialized. Figures 2 and 3 schematically illustrate this type of modules. Membrane fouling is prevented by rotation of a membrane itself(Fig.2) or by rotation of a blush placed between two disk membranes which are fixed and do not rotate(Fig.3).

Energy required for preventing fouling in these modules is only energy for rotating disk membranes or blushes, and this consumes quite small amount of energy, namely these modules greatly save energy.

The other advantage of these modules is that suspensions and polymer solutions can be concentrated up to extremely high concentration at which solution viscosity is greatly high. Therefore these modules are used combined with conventional tubular and/or capillary modules which work only at low viscosity.

Figures 4 and 5 show permeate flux obtained with these modules during microfiltration of yeast suspensions. Influence of rotation of disk membrane and scraping by rotating blush is quite large.

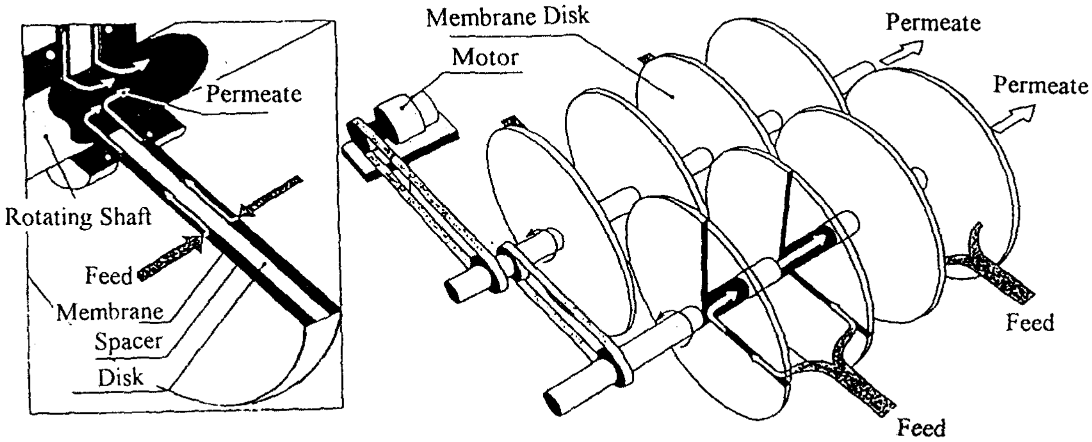


Fig.2 Schematic illustration of rotating disk-membrane module.

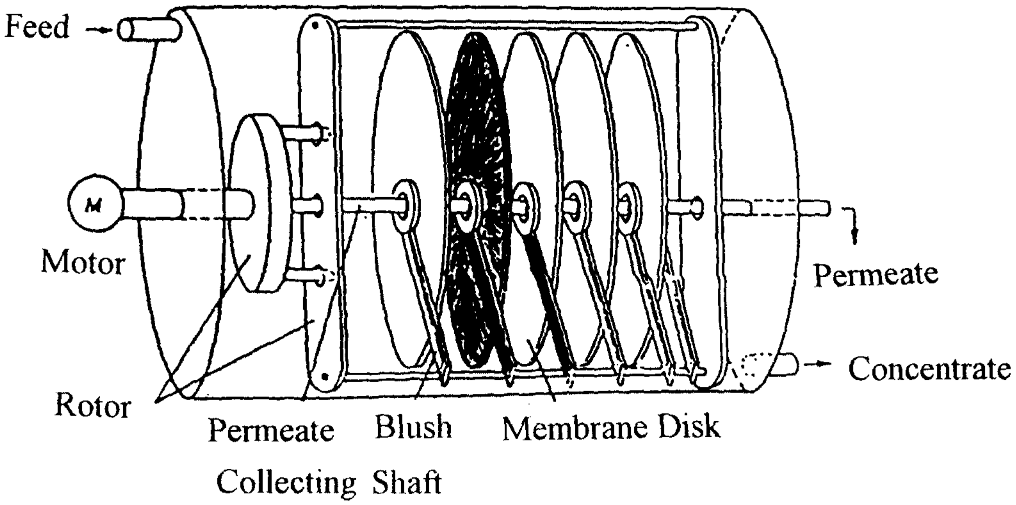


Fig.3 Schematic illustration of rotating blush module equipped fixed disk-membranes.

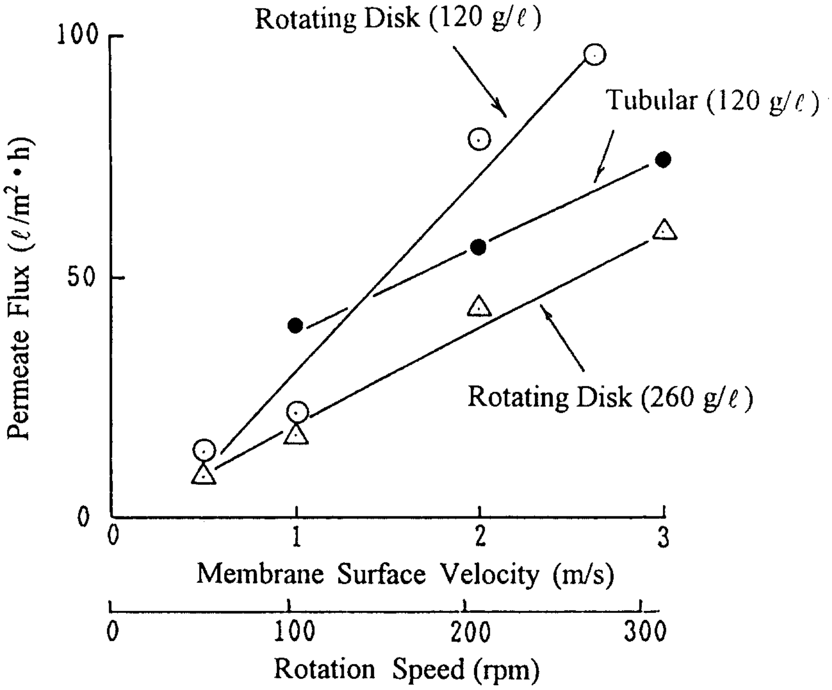


Fig.4 Permeate flux obtained during microfiltration of yeast suspensions using a rotating disk-membrane module. Ceramic membrane 0.1μm, pressure 0.1MPa.

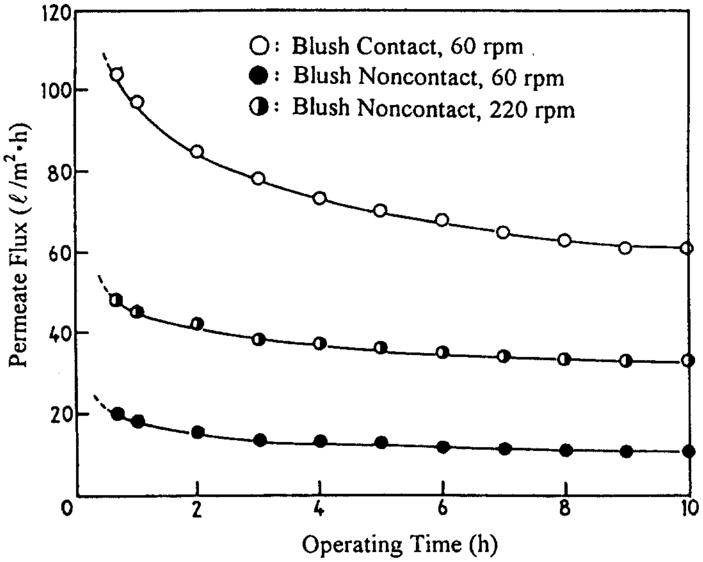


Fig.5 Permeate flux obtained during microfiltration of yeast suspensions using a rotating blush module equipped with disk membrane. PTFE membrane 0.2μm, pressure 0.05MPa, concentration 15w/v%.

5.2 Housingless membrane devices

In membrane processes, feed solution generally flows from feed tank to membrane modules (and then flows back to the tank), and requires energy for feed flow and circulation. In order to reduce this energy new membrane devices have been developed. Flow diagram of an example is shown in Fig.6. As mentioned before, high flow rate of a feed is necessary on membrane surface to prevent membrane fouling.

When membrane is just immersed in the feed tank, the membrane is fouled very much. As shown in Fig.6 membrane surface is washed by air bubbles which also keep dissolved oxygen concentration high. Therefore this device is often employed in activated sludge process and in water treatment process for public water supply, and deduces energy very much. Because no energy for feed flow and circulation consumes. This system also deduces total system volume, almost one tenth of the volume of the conventional process.

In the system shown in Fig.6 ceramic tubular membranes are used. Envelope type membrane made by organic flat sheet membrane and bundle of organic capillary membrane are also used in this housingless type device.

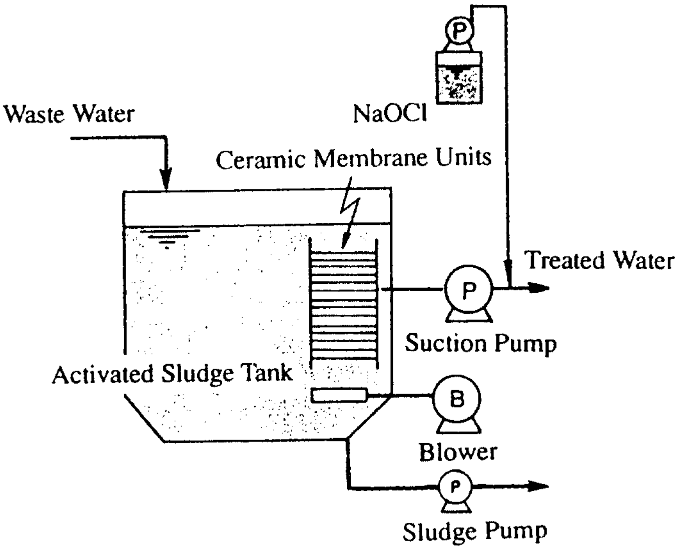


Fig.6 Schematic flow sheet of activated sludge process coupled with housingless membrane device.

6. Practical Applications in Japan

In Japan, membrane processes have wide industrial applications in the chemical, petrochemical, environmental, water treatment, waste water treatment, pharmaceutical, medical, food, dairy, beverage, paper, and electronic industries.

Membrane applications are summarized in Table 4. Reasons for employing membrane processes are energy saving and/or obtaining higher quality, and these reasons are also shown in Table 4.

Table 4 Practical applications of membrane processes in Japan

Application	Membrane Process	Reason(s)
Sea water desalination for drinking water for boiler water	RO	ES
Ultrapure water for semiconductor for pharmaceutical usage	MF, UF, NF, RO	HQ, ES
Public water supply	MF, UF, NF	HQ, ES
Waste water treatment	UF, NF, RO	VR, HQ, ES
Juice and milk concentration	RO, NF	ES, HQ
Clarification of juice, sake, soy sauce, honey	MF, UF	HQ, ES
Beer filtration	MF	HQ
Suspension filtration	MF	EQ
Protein removal/concentration	MF, UF	ES
Dehydration of alcohol	PV	ES
VOC removal	PV, VP	ES

MF: microfiltration, UF: ultrafiltration, NF: nanofiltration, RO: reverse osmosis
PV: pervaporation, VP: vapor permeation
ES: energy saving, HQ: high quality, VR: system volume reduction

When membrane process is used for concentration purpose, permeation flux decreases along with increase in concentration factor, because osmotic pressure of the feed increases and effective pressure over the membrane deduces. Therefore osmotic pressure limitation always exists and we can not concentrate up to feed osmotic pressure higher than applied pressure.

This is big disadvantage of membrane process in concentration use. In order to overcome this limitation, multistage recycle membrane process has been developed and already commercialized for juice concentration. Mass balance for two stage system concentrating apple juice is illustrated in Fig.7. In the first stage high rejection reverse osmosis membrane is used and thus the permeate concentration indicates Brix 0%. Through this stage the juice is concentrated from 9.3% Brix to 19.5% Brix, about 2 times higher, and the osmotic pressure at module outlet becomes about 3.5MPa.

To continue concentration, thus, is difficult under the same operation pressure, so in the second stage low rejection reverse osmosis membrane is employed. The permeate concentration is 2.9% Brix and osmotic pressure difference between feed and permeate side of the membrane is maintained less than the applied pressure. As a result product concentration reaches Brix 38.5% and the osmotic pressure becomes about 8MPa. This process is very effective for concentrating solutions with energy saving.

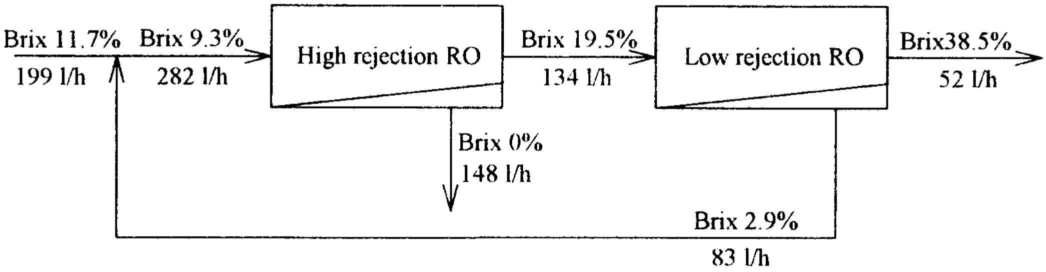


Fig.7 Mass balance for two stage system concentrating apple juice