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NOTE

Apparatus for Casting and Testing Tubular Cellulose Acetate Membranes for Reverse Osmosis

INTRODUCTION

Loeb's gravity drop technique for making tubular cellulose acetate membranes brought the latter into popular industrial use in reverse osmosis.[1,2] A continuous method for making such membranes has also been developed recently.[3] It has been shown [4,5] that, in addition to casting solution composition, temperature of film casting solution, temperature of casting atmosphere, and solvent evaporation rate and period during film formation are important controlling parameters affecting the porous structure and performance of resulting membranes in reverse osmosis. The effects of such parameters have been studied, and superior membranes have resulted from such studies with respect to flat membranes.[4-11] Similar studies with tubular membranes are far less extensive. This paper describes an apparatus with which the effect of the above controlling parameters affecting the porous structure of the tubular membranes can be studied in detail. Further, a design for membrane assembly in tubular reverse osmosis test cell is also described.

APPARATUS DESIGN

Apparatus for Casting 1-in. Diameter Tubular Cellulose Acetate Membranes

In this apparatus, the casting tube is held stationary, and the casting bob is pulled upward by means of a motor at controlled speed. After the required solvent evaporation period, gelation is brought about by pumping ice-cold water (gelation medium) into the casting tube at the same speed at which the film was cast. A water test tube is used to help set water flow at the above speed. A two-bob system, consisting of a leading bob and casting bob, is used for holding the casting solution and for film casting. An air disperser is connected directly to the casting bob. Fresh air (or gas) at controlled speed comes into contact with the membrane surface as it is formed. Figure 1 gives the general flow diagram of the apparatus. The casting tube may be surrounded by a jacket (not shown in Fig. 1) through which water (or any liquid) at the required temperature is circulated. This arrangement enables variation of the temperature of the film-casting surface as required. Figure 2 gives details of the two-bob assembly.

Referring to assembly on the left side of Figure 2, the casting bob (5) has a through-vertical center hole which is attached to an air disperser (7) at the bottom and to an air-flow tube (2A) at the top. The leading bob (4) is made up of three parts—a cylinder whose outside diameter is only slightly smaller than the inside diameter of the casting tube, a centering cap (3), and a press clip (1). The inside of the cylinder has a taper at the bottom corresponding to the taper in the casting bob so that when the bobs are coupled, there is metal-to-metal seal between the cylinder and the casting bob. The centering cap, which is screwed to the top of the cylinder, has a central hole for the insertion of the air-flow tube attached to the casting bob, a tapered part at the top from which the casting bob hangs freely, and air vent which releases the casting solution when the bobs are uncoupled. The press clip is pressed into two holes on the side of the centering cap and hangs from a hook in a cord or wire attached to the motor through a pulley. The air (or gas) hose is connected to the air-flow tube through the pivot cap (8).

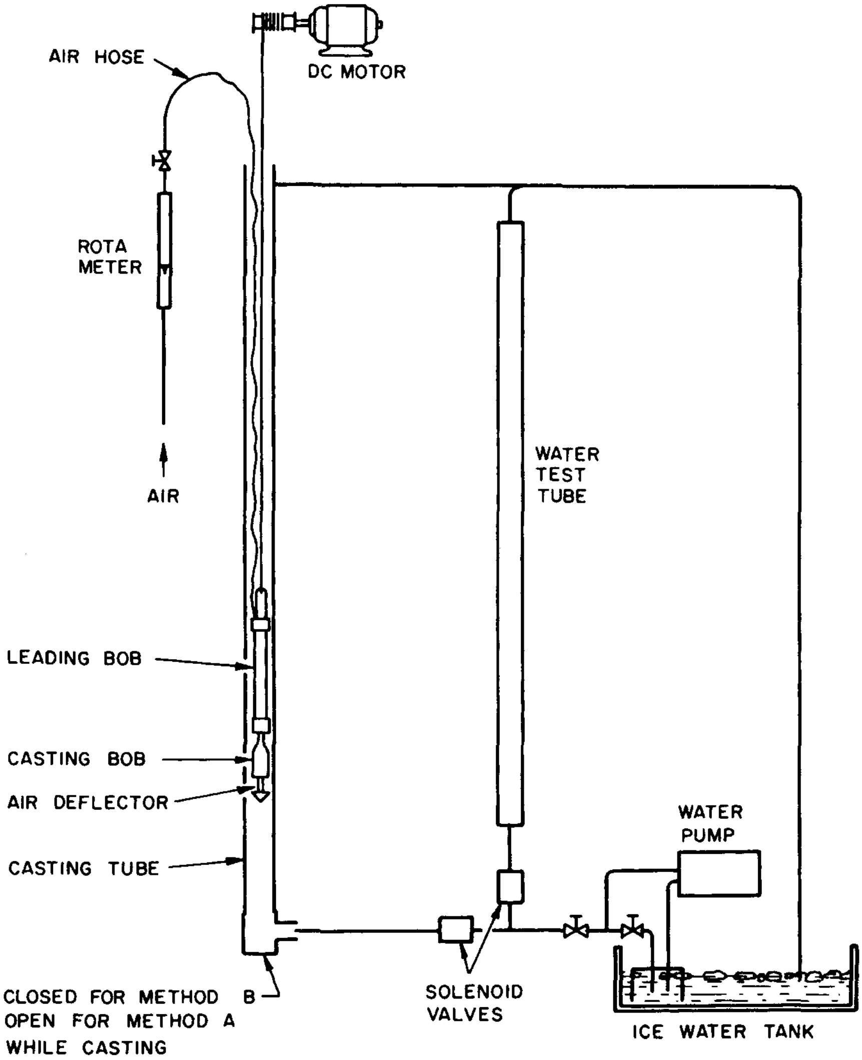

Fig. 1. Flow diagram of apparatus for making tubular membranes.

With the above assembly, the air leaves the casting tube through the bottom while the film is being cast. This mode of air exit is designated method A in Figure 2. An alternative mode of air exit, shown on the right side of Figure 2, is designated method B. Method B is used when the evaporation time is less than the time taken for film casting through the entire length of the casting tube. In this case, the gelation water follows the casting bob, keeping the distance between water level and the casting bob constant. For method B operation, the air-flow tube (2A) is inserted inside the air-return tube (2C) attached to the center hole in the casting bob and that in the pivot cap (2B). Air enters through 2A, is dispersed by the deflector (6), and returns through the center hole in the casting bob and the air-return tube (2C), and finally leaves the system through the opening in the pivot cap (2B), since the bottom of the casting tube is no longer open because of

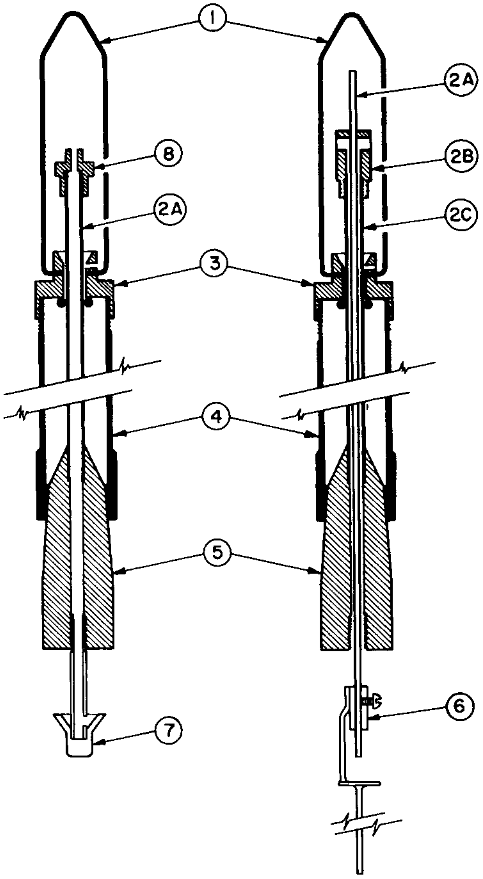

Fig. 2. Two-bob assembly for making 1-in.-diameter tubular membranes: (1) press clip; (2A) air-flow tube; (2B) pivot cap and air return; (2C) air-return tube; (3) centering cap; (4) leading bob and casting solution cylinder; (5) casting bob; (6,7) air dispersers; (8) pivot cap and air inlet tube.

water following the casting bob during film casting. Parts (6) and (7) illustrate two of the several possible designs which can be used for dispersing air.

Referring to method A in Figure 2, the sequence of operations for film casting is as follows:

The casting bob is held firm in the vertical position.

The leading bob is placed over the casting bob to make metal-to-metal seal at the bottom.

The casting solution is poured into the leading bob cylinder.

An O-ring is inserted around the air-flow tube in the casting bob.

The centering cap is screwed on the top of the leading bob cylinder pressing the O-ring down in position.

Now the casting solution is completely trapped in the two-bob assembly.

The assembly is handled by the air-flow tube attached to the casting bob, which extends at the top of the assembly.

The assembly is kept vertically in a storage chamber at the required temperature of the casting solution.

When one is ready for film casting, the assembly is removed from the storage chamber, and the air disperser is attached to the bottom of the casting bob.

The assembly is then held directly below the casting tube.

A supply of air (or any required gas), preheated or precooled (if necessary) by passage through a coil immersed in hot or cold water bath (or by similar or equivalent means), is maintained.

The air-flow rate is measured by means of a rotometer.

The air at the desired rate is passed through a flexible hose which is inserted into the pivot cap to which the air-flow tube is attached.

The two-bob assembly is held by the air disperser end and gently inserted into the casting tube.

The entire assembly is now ready for the film casting operation.

The motor is started pulling the cord and the clip at the desired casting speed.

As the clip moves up, the leading bob is pulled up, the casting bob and the leading bob are uncoupled, and the casting bob hangs by the edge of the air-flow tube resting freely on the tapered part of the centering cap, which makes the casting bob self-centering.

The uncoupling of the two bobs releases the casting solution for film casting.

As the casting bob moves up, the film is cast on the casting tube.

As the film is formed, it is also exposed to a stream of fresh air from beneath the casting bob, and the air is directed to the film surface by the air disperser.

As the bottom of the casting tube is open to the atmosphere (in method A), most of the solvent-laden air escapes into the atmosphere through the bottom of the casting tube.

After the film is cast, solvent evaporation from the membrane surface is continued for the required period of time.

The bottom of the casting tube is then closed, and cold water (gelation medium) is pumped through the casting tube at the required speed.

The film is allowed to set in cold water for the required period, after which the film is easily removed by hand.

By using different dimensions for the parts of the two-bob system and the casting tube, tubular membranes of different dimensions can be made. In particular, by increasing the length of the leading bob cylinder and that of the air-flow tube of the casting bob, tubular membranes of any desired length can be made.

Apparatus for Casting $^1/_2$-In.-Diameter Tubular Cellulose Acetate Membranes

This apparatus is similar to the one described above in all respects except for some changes (9, 10 and 11) in the two-bob assembly (Fig. 3). Part (10) is a single piece made of Teflon; it has a taper at the top, which helps to make a seal with part (4) (leading bob and casting solution cylinder), four centering fins in the middle sliding in the casting tube all the way, and the casting bob at the bottom, which is kept centered by the centering fins during film casting. Part (9) prevents the air-flow tube from falling down when the leading bob and the casting bob are uncoupled. Parts (9) and (11) take the place of part (8) in Figure 2, method A.

Membrane Assembly in Tubular Reverse Osmosis Test Cell

Design details at one end of the assembly are illustrated in Figure 4; the other end of the tubular cell is similar in design. The assembly uses an O-ring sealing technique and simple end fittings, requiring no flarings or flanges to the support tube (reverse osmosis cell) and no softening, plasticizing, flaring, bending, or folding for the membrane ends.

Referring to Figure 4, the support tube (3) (reverse osmosis cell) is any standard pipe of required material, diameter, and thickness. (Stainless steel tubes were used in this work.) The tube has suitably spaced small holes in its entire length for the withdrawal of the membrane-permeated water or solution. The tube is threaded at the ends. The

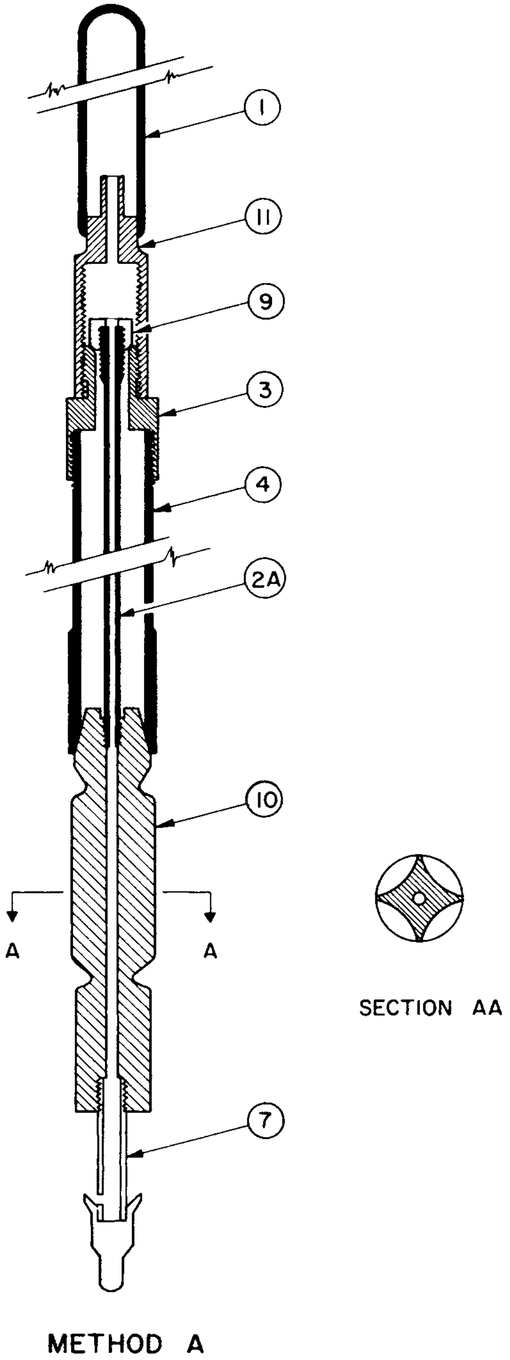

Fig. 3. Two-bob assembly for making $^1/_2$-in.-diameter tubular membranes: (1 to 8) same as for Fig. 2; (9) retainer and pivot ring; (10) centering fins and casting bob (Teflon); (11) air inlet and cap.

TABLE I
Compositions of Casting Solutions Used

	Casting solution composition, wt-%		
Casting solution	Batch 316	Batch 320	Batch 47
Cellulose acetate (E-398-3)	17	—	25
Cellulose acetate (E-400-25)	—	17	—
Acetone	69.2	69.2	45
Magnesium perchlorate	1.45	1.45	—
Water	12.35	12.35	—
Formamide	—	—	30

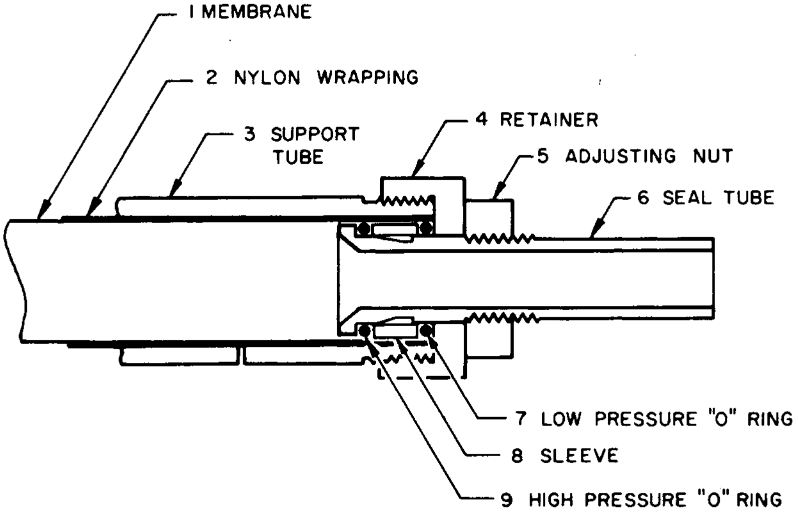

Fig. 4. Membrane assembly in tubular reverse osmosis cell.

tubular membrane (1) with backing nylon (or similar cloth) wraps is inserted into the support tube. The nylon wraps extend the entire length of the membrane, which is thus equally well supported throughout its length including the area at the ends where the O-ring seal is accomplished, as shown in Figure 4.

The end fitting consists of a seal tube (6) which has an O-ring shoulder at one end, an adjusting nut (5) on the other end, a tapered neck (for part of the way), a sleeve (8), and a retainer (4) in between, with O-rings (7 and 9) placed on each side of the sleeve, as shown in Figure 4. The diameter of the shoulder is slightly less than that of the tubular membrane. The high-pressure O-ring (9) is initially in the relaxed position in the tapered neck of the seal tube. The low-pressure O-ring (7) serves to seal the opening between the cell and the sleeve.

The seal tube, together with the high-pressure O-ring in the relaxed position and the sleeve and retainer placed in position between the O-ring and adjusting nut, is kept as a single assembly ready for use. After the membrane is loaded into the cell, the seal tube assembly is inserted freely into the tubular membrane in the cell. The sleeve is pushed toward the membrane to bring the O-rings to the required sealing position. The retainer is then tightened. Final sealing is accomplished by tightening the adjusting nut to the required extent.

The apparatus for making tubular membranes and the membrane assembly in test cell described above have been successfully tested and are in routine use in laboratory research on membrane development.

Some Experimental Results

The casting solution compositions used are given in Table I. A large number of 5-ft-long 1-in.-diameter tubular membranes were made, and tested, by the apparatus described above. A set of representative results is given in Tables II, III, and IV.

Table II gives some data on the performance of film samples taken from top, middle, and bottom part of a typical 5-ft-long tubular membrane obtained from a cellulose

TABLE II
Uniformity of Tubular Membranes[a]

Film shrinkage temp., °C	Performance of film samples taken from					
	Bottom		Middle		Top	
	Solute sepn., %	Product rate g/hr	Solute sepn., %	Product rate g/hr	Solute sepn., %	Product rate, g/hr
Unshrunk	40.1	80.8	40.1	80.9	39.9	80.8
65	85.4	27.4	85.9	26.0	86.1	26.8
70	90.7	21.3	91.7	21.1	91.6	21.1
75	95.4	14.0	95.7	12.4	96.0	12.4

[a] Casting solution composition, batch 316; temperature of casting solution, 0°C; temperature of casting atmosphere, 23–25°C; method of casting, method A; evaporation time, 3 min; air-flow rate, 0.182 ft^3/min; casting speed, 0.4 in./sec; NaCl concentration in feed, 3500 ppm; operating pressure, 250 psig; effective film area, 13.2 cm.^{2} (Data for 1-in.-diameter tubular membranes tested flat).

TABLE III
Performance of Tubular Membranes from Cellulose Acetate–Acetone–Aqueous Magnesium Perchlorate Casting Solution[a]

Method of casting	Evapn. time, min	Air-flow rate, ft^3/min	Casting speed, in./sec	Shrinkage temp., °C		Product rate, gal/day-ft^2	
				80%[b]	90%[b]	80%[b]	90%[b]
A	3	0.09	1	60	70	38	30
A	3	0.182	1		70		32.5
A	3	0.30	1	60	70	43	33
A	3	0.345	1	60	70	43	34
A	3	0.543	1	60	70	38	30
A	$2^{1}/_{2}$	0.345	1		67		30
A	3	0.345	1		70		34
A	$3^{1}/_{2}$	0.345	1		72		33
A	4	0.345	1		75		30
B	1	0.345	2	60		20	
B	1	0.345	1	71		22.5	
B	$1^{1}/_{2}$	0.182	1		70		21
B	$1^{1}/_{2}$	0.343	1		70		24
B	$1^{1}/_{2}$	0.543	1		70		22.5

[a] Casting solution composition, batch 320; temperature of casting solution, 0°C; temperature of casting atmosphere, 23–25°C; NaCl concentration in feed, 5000 ppm; operating pressure, 600 psig; data for 1-in.-diam. tubular films tested in tubular cell.

[b] Solute separation.

TABLE IV
Performance of Tubular Membranes from Cellulose Acetate–Acetone–Formamide Casting Solution[a]

Method of casting	Air-flow rate, ft^3/min	Casting speed, in./sec	Film shrinkage, temp., °C	Sclute sepn., %	Product rate, gal/day-ft^2
A	0.300	1	85	87	28.0
A	0.300	2	85	69	25.0
A	0.440	1	85	86	31.5
A	0.440	2	85	76	27.0
A	0.543	1	85	81	27.0
A	0.543	2	85	73	42.0
B	0.300	2	76	73	56.5
B	0.300	2	78	79	47.3
B	0.300	2	79	85	38.9
B	0.300	2	80	91	31.0

[a] Casting solution composition: batch 47; temperature of casting solution, 23–25°C; temperature of casting atmosphere, 23–25°C; evaporation time, 50 sec for method A and 3 sec for method B; NaCl concentration in feed, 5000 ppm; operating pressure, 600 psig; data for 1-in.-diameter tubular membranes tested in tubular cell.

acetate–acetone–aqueous magnesium perchlorate (batch 316) casting solution. Each film sample was tested in flat form. The results illustrate that the apparatus used yields tubular membranes of uniform pore structure on the surface layer of the membrane throughout its length.

Tables III and IV give the effects of evaporation time, air flow rate, and casting speed on the performance of 1-in. tubular membranes, obtained from cellulose acetate–acetone–aqueous magnesium perchlorate (batch 320) and cellulose acetate–acetone–formamide (batch 47) casting solutions. Similar data have been obtained of $^1/_2$-in.-diameter tubular membranes also. These data are not intended to show either the effects of casting conditions on the performance of resulting tubular membranes or the optimum conditions for making such membranes. The data are merely intended to illustrate that the apparatus used for making and testing tubular membranes work well, and they are suited for membrane research and development. Further, according to the literature,[1–3] only batch 47-type casting solutions have been used for making tubular membranes. The data presented in Tables II and III illustrate that successful tubular membranes can also be made from cellulose acetate–acetone–aqueous magnesium perchlorate casting solutions by the proper choice of casting conditions.

Thus, the apparatus for membrane making and the details of membrane assembly described in this paper open new areas of tubular membrane research and development for reverse osmosis.

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