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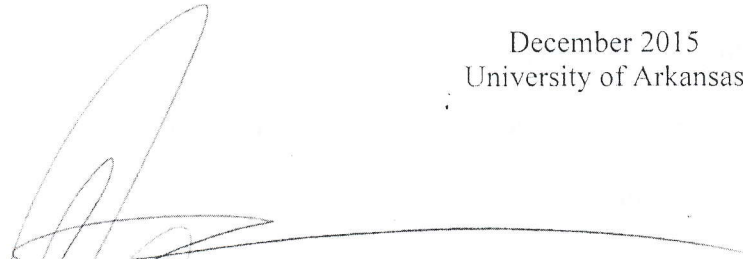
Evaporometry: An Effective Analytical Technique for
Membrane Pore Size Characterization of Hollow Fiber
Membranes

A thesis submitted in partial fulfillment
of the requirements for the degree of
Bachelors of Science in Chemical Engineering

by

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University of Arkansas



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Evaporimetry: An Effective Analytical Technique for Membrane Pore Size Characterization of Hollow Fiber Membranes

Abstract

A new analytical technique called evaporimetry has shown to be an effective and inexpensive method for membrane pore size characterization. This technique is based on the correlation between vapor pressure and pore size as described by the Kelvin equation. Evaporimetry has many advantages over traditional pore size characterization techniques. This technique allows for large sample sizes, uses minimal equipment, is capable of analyzing membranes within a wide range of pore sizes, and provides a highly descriptive representation of the pore distribution. This research looks at the application of evaporimetry as a technique for characterization of hollow fiber membranes. Using the theory for evaporimetry of flat sheet membranes and a modification to the diffusion chamber, this technique was successfully applied to hollow fiber membranes.

Introduction

Since their inception for use in drinking water treatment, hollow fiber membranes have been widely adapted for many types of industries [1]. They have been expanded to be used in other water treatment processes such as waste water treatment and desalination [2]. Recently, a more common use of hollow fiber membranes has been their use in gas separation technologies due to the capability to flow a gas through the membrane with lateral separation through the pores [3]. Hollow fiber membranes have also shown promise for application as a gas delivery

device. Application of these membranes for this purpose have looked at using the membranes to diffuse oxygen into water without the formation of bubbles [4]. In addition, investigations have looked at using hollow fiber membranes as a carbon dioxide gas delivery device to algae-growth raceways as well as a gas exchange device that could act as an artificial lung [5-6].

Proper characterization is important in the fabrication and use of hollow fiber membranes. Much research has used characterization techniques to determine how fabrication process conditions affect the pore size, wall thickness, and other properties of the membranes [7]. Characterization is also important before and after the use of hollow fiber membranes in many experimental studies. Fouling of hollow fiber membranes poses a major challenge to the use of the membranes in systems containing organics. Biomedical applications of hollow fiber membranes is an area of research dominated by this challenge of fouling. Many researches are looking at using inherently hydrophilic materials to resist foiling [8]. Other researchers have looked at the application of hydrophilic coatings such as peptoids, dopamine, and other biocompatible compounds to the surface of the membranes [9-13]. Both fouling and application of coatings can have reducing effects on the pore size and distribution of hollow fiber membranes, making characterization after their modification and use very important.

Many hollow fiber membrane pore size characterization techniques have been developed including bubble gas transport, permoporometry, and mercury intrusion porosity [7]. A new technique has recently been developed by Krantz,

called evapoporometry, for use on flat sheet membranes [14]. This investigation looked at applying this technique to hollow fiber membranes.

Theory

Flat Sheet Membranes

Evapoporometry is a technique developed by Krantz as a method for determining the pore size distribution of flat sheet membranes, showing the percentage of total pores at various pore sizes. This is currently the most effective technique for analyzing pore sizes ranging from the nanometer scale to the micron scale. In addition, this technique not only allows for an average pore size to be determined, but also expresses the uniformity of the membrane, revealing macrovoids. The technique operates on the principle that the vapor pressure of a volatile liquid varies with the size of the pore in which the liquid is saturated. Therefore, the evaporation rate of the liquid from a pore is dependent on the pore diameter. The Kelvin Equation describes this relationship between vapor pressure and pore size,

$$\ln \frac{P'}{P} = - \frac{2\sigma V}{RT r \cos\theta} \quad (1)$$

where P' represents the instantaneous vapor pressure, P the normal vapor pressure of the volatile liquid at the environmental conditions, σ the surface tension, V the liquid molar volume, R the universal gas constant, T the absolute temperature, r the radius of the pore, and θ the contact angle. In addition, the Irving-Langmuir evaporation equation demonstrates the proportional relationship between the vapor pressure and the evaporation rate of a liquid,

$$W = (P_v - P_p) \sqrt{\frac{m}{2\pi RT}} \quad (2)$$

where W represents the evaporation rate, P_v the vapor pressure of the liquid, P_p the partial pressure of the vapor in the gas, and m the mass of each vapor molecule. It is assumed that the temperature remains constant and the partial pressure of the vapor is negligible. Due to the proportionality between vapor pressure and the evaporation rate of the liquid, **Equation 1** can be written as

$$r = -\frac{2\sigma V}{RT \cos\theta \ln\left(\frac{W'}{W^o}\right)} \quad (3)$$

where W' is the instantaneous evaporation rate and W^o is the normal evaporation rate of the free-standing volatile liquid above the membrane surface.

Hollow Fiber Membranes

Once Krantz's method for evapoporometry was replicated for flat sheet membranes, it was of interest to see if the same technique could be applied to hollow fiber membranes. The theory makes no assumptions that would not allow for this technique to be applied to hollow fibers, however, major reconstruction of the experimental methods was necessary to overcome the physical differences in the two membrane types. Flat sheet membranes are much thinner than hollow fiber membranes. This means that flat sheets saturate with the volatile liquid much quicker than hollow fibers, needing to be soaked for almost ten times longer. Another major obstacle with using hollow fiber membranes is the prevention of lateral leakage of the volatile liquid out of the membrane. Flat sheet membranes can be easily sealed at the sides and have no internal spaces where the volatile liquid can leak out of the pores. In order to have a relatively large sample size of hollow

fibers, multiple strands of fibers must be used and the gaps between these fibers pose the problem of lateral leakage from the pores.

Method

A 1.5 in. in diameter cylindrical screw-top container was obtained to act as a diffusion chamber for flat sheet membranes. A commercial Nuclepore flat sheet membrane with a nominal pore size of 100 nm was placed in the cap of the container. The body of the container was flipped and the bottom was bored out to allow for a path of diffusion. By screwing the cap containing the membrane to the body, a seal was formed around the membrane to prevent lateral leakage of the volatile liquid.



Figure 1 Flat sheet membrane diffusion chamber for evaporometry.

A very different diffusion chamber had to be constructed for this technique to be applied to hollow fiber membranes. A 7/8" by 7/8" square Plexiglas container, open at the top, was used as the diffusion chamber. A layer of Conathane epoxy was placed at the bottom of the container to hold the hollow fibers and help to prevent lateral leakage of the volatile liquid. Hollow fibers were then cut to the length of the container and carefully placed in a row along the bottom of the container. The fibers

were then pushed slightly into the epoxy so that the epoxy only covered halfway up the side of the fibers. Additional epoxy was added to the ends of the fibers to prevent leaking from the open ends.



Figure 2 Hollow fiber membrane diffusion chamber for evapoporometry.

Isopropanol, 100%, was chosen as the volatile liquid due to its very low vapor pressure and chemical stability with the polymer membranes. Enough isopropanol was added to sufficiently wet the membrane, while allowing for a small layer above the membrane. This layer was used to determine the normal evaporation rate of the isopropanol at the environmental conditions of the laboratory. Due to the thickness of the hollow fiber membranes, it took much longer to saturate the membranes with isopropanol than it took with flat sheet membranes. Therefore, the addition of isopropanol was followed by a 24-hour period where the diffusion chamber was covered to prevent evaporation and the hollow fibers were allowed to fully saturate. The diffusion chamber was then placed on a microbalance, Mettler Toledo AB104-S/FACT. The microbalance was connected to a computer and data was logged overtime using Windmill 7 Data Acquisition Software. The mass of the diffusion chamber containing the isopropanol wetted membrane was measured every thirty seconds for approximately twenty hours.

A derivative of the recorded mass as a function of time was used to determine the evaporation rate at each reading. The data was then smoothed using a moving average of thirty data points. This developed the curve seen in **Figure 3** that shows a steady-state evaporation rate followed by a sharp drop in the evaporation rate that eventually approaches zero.

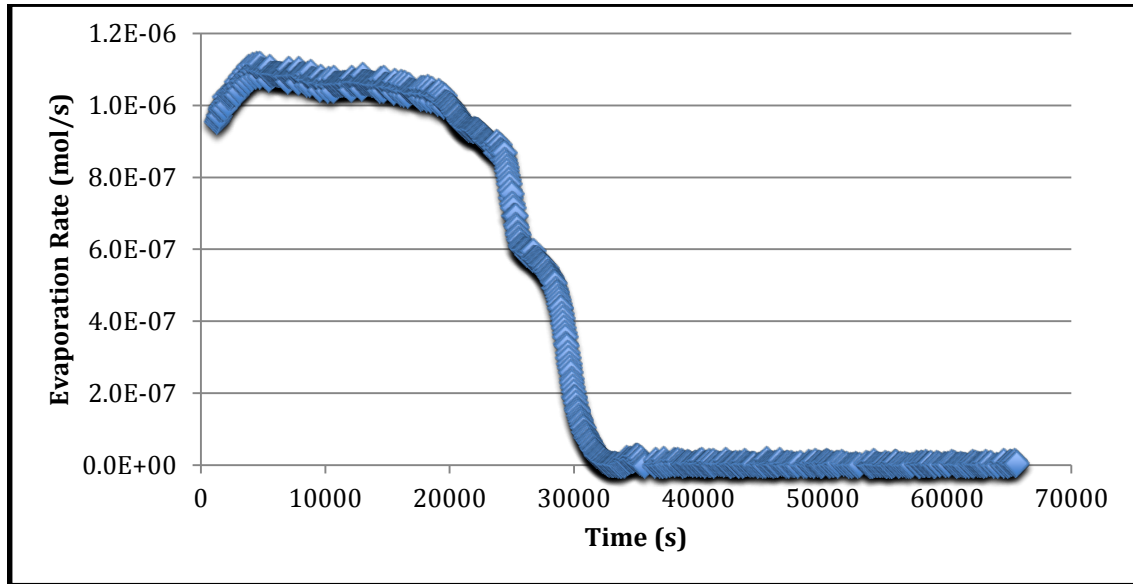


Figure 3 The evaporation rate of isopropanol from a 100 nm Nuclepore flat sheet membrane versus time.

The steady-state portion of the curve is used to determine the normal evaporation rate of the isopropanol above the membrane surface. The subsequent drop in evaporation rate occurs due to the isopropanol evaporating from the pores, progressing from the largest pores to smallest pores. The portion of the curve from the time the evaporation rate deviates significantly from the normal evaporation rate to the time that it reaches zero is used to determine the pore size distribution of the membrane. Using the properties of isopropanol, **Table 2**, and these evaporation

rates, **Equation 3** was used to determine the pore size represented by each data point along the sloped portion of the curve. By taking the average of this data, the average pores size can be determined and compared to the nominal pore size given by the membrane manufacturer as well as images produced by a scanning electron microscope (SEM). A histogram can also be constructed from this data showing the percentage of total pores as a function of pore diameter.

This method has now been used as an analytical tool for various experiments ranging from research on biofuels to biomedical applications. One such experiment involved the use of hollow fiber membranes as a carbon dioxide gas delivery mechanism to algal growth runways for biofuel production. In order to develop a mass transfer model for this gas delivery, it was important to predict the size of the bubbles produced by the hollow fibers. This was possible with the average pore diameter given by this evapoporometry method for hollow fiber membranes. Evapoporometry has also been performed on hollow fiber membranes for research involved in the development of an artificial lung. This analytical method allowed for the determination of variations in pore size distribution with the addition of enhanced-property coatings to the membrane.

Results

Flat Sheet Membrane

Before attempting to apply Krantz's evapoporometry method for flat sheet membranes to hollow fiber membranes, a commercial Nuclepore flat sheet membrane of known nominal pore diameter, 100 nm, was tested. This experiment

was performed to confirm the legitimacy of the technique and the ability to replicate the method.

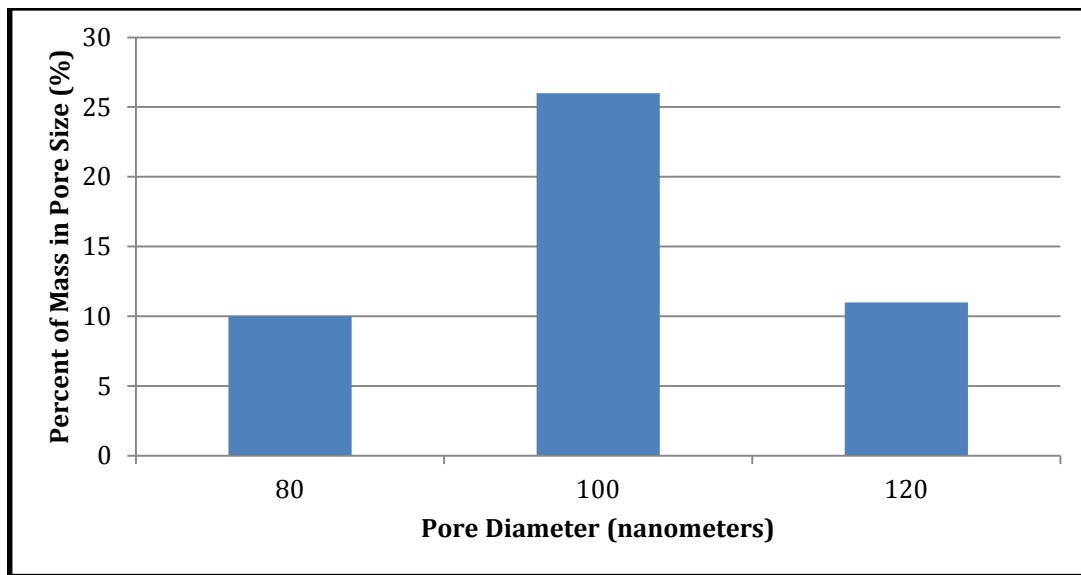


Figure 4 The pore size distribution of a 100 nm Nuclepore flat sheet membrane determined by evapoporometry.

The pore size distribution determined by evapoporometry showed an average pore diameter of 103 nm for this flat sheet membrane. Given only a three percent error from the nominal pore size given by the manufacturer, it was determined that the theory and technique were accurate and effective. The distribution also reveals the uniformity of the membrane. This membrane has a normal distribution around its average pore diameter of 103 nm with nearly equal percentages of pores above and below the average.

Hollow Fiber Membranes

Carbon Dioxide Gas Delivery for Algae-based Biofuel Production

Evapoporometry was applied to hollow fiber membranes of an unknown pore size. Since evapoporometry is a non-destructive technique, the same hollow

fiber sample was analyzed in triplicate, resulting in an average pore diameter of 27 nm with a standard deviation of 13 nm. This average pore size remains within the theoretical pore range for evapoporometry. This value was used in the calculation of the bubble size produced by the membrane to explain why hollow fiber membranes are more superior to other gas delivery mechanisms in thin film aqueous systems, such as algal raceways.

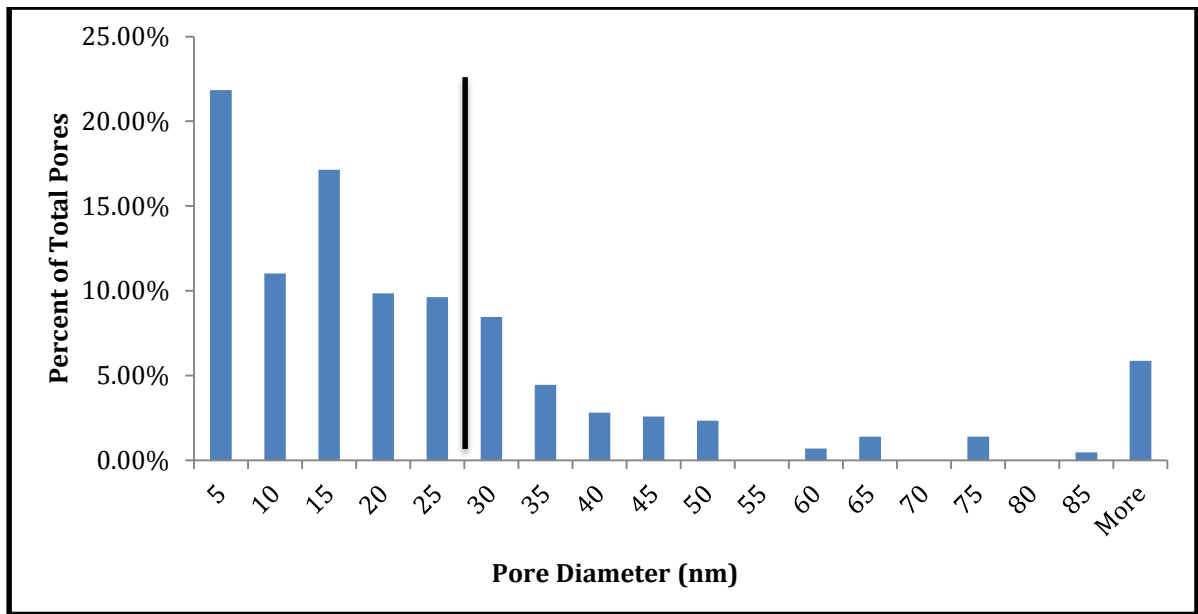


Figure 5 The pore size distribution of the hollow fiber membrane of unknown pore size as determined by evapoporometry. The solid black line depicts the average pore diameter [2].

The pore size distribution in **Figure 5** shows the uniformity of the pores by relating the pore diameter to the percent of total pores at a given diameter. The distribution for the hollow fiber membrane of unknown pore size shows a majority of the pores ranging from 5 nm to 50 nm in diameter. However, it also shows a small

percentage of the pores having a pore diameter greater than 50 nm. This is representative of possible macrovoids and defects in the membrane. The accuracy of evapoporometry as applied to hollow fiber membranes was checked using a scanning electron microscope.

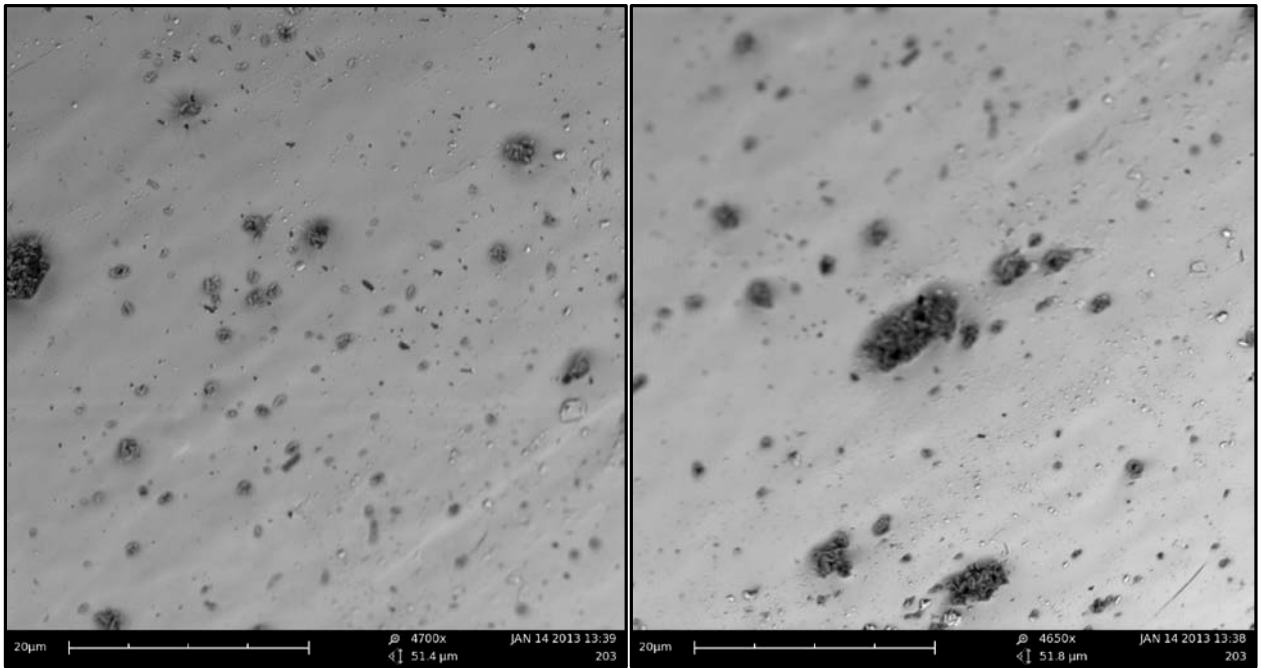


Figure 6 SEM images of the hollow fiber membrane of unknown pore size.

The SEM images represent a much smaller sample size than that which was used in evapoporometry. However, these images helped to confirm that the membrane tested contains pore sizes near the 27 nm average that was determined by evapoporometry. The images in **Figure 6** show pores with diameters between 5 nm and 30 nm. This comparison demonstrates that the use of evapoporometry on hollow fiber membranes provides highly accurate pore diameter measurement on a large sample size.

Hollow Fiber Membranes as an Artificial Lung Gas Exchange Mechanism

Evaporimetry was applied to hollow fiber membranes at the various stages of membrane treatment: bare, dopamine coated, and peptoid coated. Two samples of each fiber were tested and the average pore sizes and pore size distributions were determined. It was expected that the average pore diameter would decrease and the pore size distribution would narrow with increased application of coatings. It was assumed that the larger pores would be blocked by the addition of dopamine and peptoids on the membrane surface and produce this result.

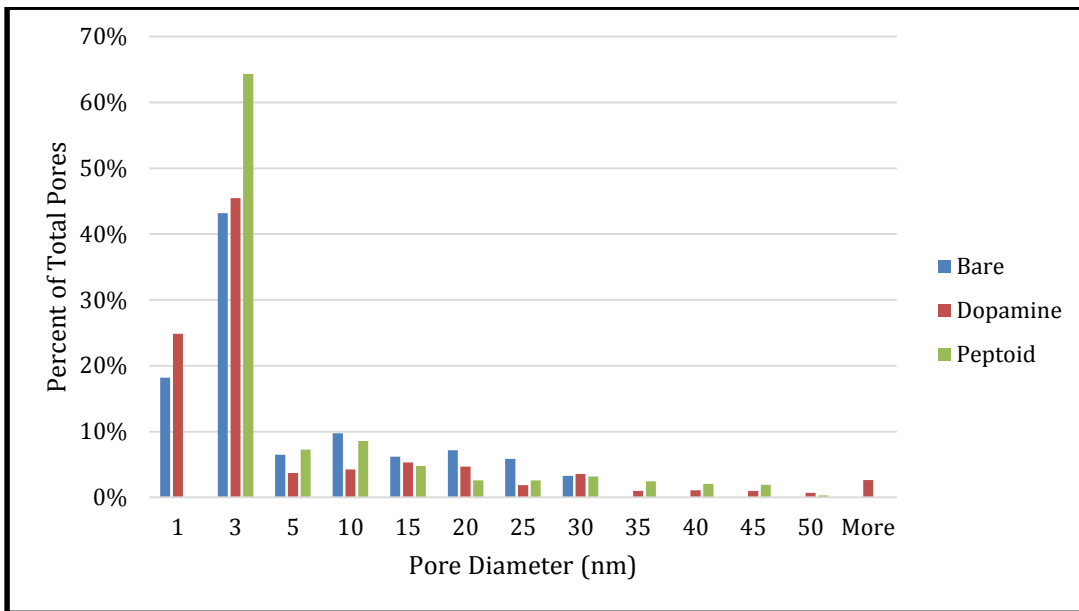


Figure 7 Comparison of the pore size distribution of bare, dopamine coated, and peptoid coated hollow fiber membranes as determined by evaporimetry.

The average pore diameters determined by evapoporometry were 6.0 nm, 7.3 nm, and 6.9 nm for bare, dopamine coated, and peptoid coated fibers, respectively. Although slight variation in average pore diameter was seen, these variations are not significantly different at a 98% confidence level. The pore size distribution seen in **Figure 7** also shows minimal variation in the three membranes tested. This means that the application of dopamine and peptoid coatings had minimal effects on the pores of the hollow fiber membranes.

Conclusions

Evaporometry, a membrane characterization technique developed by Krantz, was replicated for flat sheet membranes. This technique proved to accurately determine the average pore size of a Nuclepore flat sheet membrane with a nominal size of 100 nm, having an error of three percent. This error is likely within the manufacturer's tolerance for quality control of this membrane. The pore size distribution produced by evaporometry also showed uniformity in the membranes having a normal distribution around the average pore diameter, which is expected of commercially produced membranes.

By applying the same principles and assumptions of Krantz's model for characterization of flat sheet membranes by evaporometry, a newly designed diffusion chamber was developed and used to analyze hollow fiber membranes. Hollow fiber membranes of an unknown pore size were characterized with both evaporometry and scanning electron microscope imaging. The SEM images provided a comparison and proved that the evaporometry results were within range of the actual pore sizes of the membrane.

Evaporimetry was further used on hollow fiber membranes as an analytical technique to aid in the research of biofuel and biomedical research. This technique has shown to have key advantages over traditional membrane pore characterization techniques. It is capable of analyzing membranes within a wide range of pore sizes, provide a highly descriptive representation of the pore distribution, analyzes large sample sizes, and can be performed using minimal equipment. Additionally, evaporimetry has shown to be an effective and economical method for pore size characterization of hollow fiber membranes.

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Appendix

Variable	Definition
P'	instantaneous vapor pressure, Pa
P	vapor pressure of the liquid under normal conditions, Pa
σ	surface tension, N/m
V	liquid molar volume, m ³ /mol
R	gas constant, J/(mol·K)
T	absolute temperature, K
r	pore radius, m
θ	contact angle, degrees
W	evaporation rate, mol/s
P_v	vapor pressure of the liquid, Pa
P_p	partial pressure of the vapor in the gas, Pa
m	mass of each vapor molecule, kg
W'	instantaneous evaporation rate, mol/s
W°	normal evaporation rate, mol/s

Table 1 Definition of variables.

Property	Value
Molecular weight, g/mol	60.1
Surface tension, N/m	0.023
Liquid molar volume, m ³ /mol	7.64E-05
Contact angle, degrees	0

Table 2 Properties of isopropanol