Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Characterization of Ceramic Tubular Membranes by Active Pore-Size Distribution

Petr Mikulášek[a]; Petr Doleček[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF CHEMICAL TECHNOLOGY, CZECH REPUBLIC

To cite this Article Mikulášek, Petr and Doleček, Petr(1994) 'Characterization of Ceramic Tubular Membranes by Active Pore-Size Distribution', Separation Science and Technology, 29: 9, 1183 — 1192
To link to this Article: DOI: 10.1080/01496399408005624
URL: http://dx.doi.org/10.1080/01496399408005624

SEPARATION SCIENCE AND TECHNOLOGY, **29**(9), pp. 1183–1192, 1994

Characterization of Ceramic Tubular Membranes by Active Pore-Size Distribution*

PETR MIKULÁŠEK and PETR DOLEČEK
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF CHEMICAL TECHNOLOGY
NÁM. ČS. LEGIÍ 565, 532 10 PARDUBICE, CZECH REPUBLIC

ABSTRACT

A description of the use of a liquid displacement (modified bubble-point) method to characterize tubular membrane microfilters in terms of pore sizes and pore-size distributions is given. Following a theoretical analysis the method, some comments about pore-size distribution of tubular filters and experimental results for different ceramic microfilters are presented. The characterization studies reported in this paper are applicable to other ceramic membranes, and they represent a significant step in an understanding of ceramic membranes in various applications.

INTRODUCTION

Rapid progress has been made in the technology of inorganic membranes, particularly microporous membranes, to address a variety of separation problems in many industries. The interest in utilizing such membranes in separations has increased since the advent of consistent-quality, commercially available ceramic membranes with narrow pore-size distributions. Inorganic membranes exhibit unique physical and chemical properties that are only partially or not shown by polymeric membranes. For example, they can be used at significantly higher temperatures, have better structural stability without the problems of swelling or compaction, generally can withstand more harsh chemical environments, are not sub-

* Presented during the 11th CHISA Congress, Prague, Czech Republic, 1993.

jected to microbiological attack, and can be backflushed, steam sterilized, or autoclaved (1). From this point of view, membrane characterization is a very important part of membrane research and manufacturing as well as of some advanced industrial applications.

Ceramic membranes can be characterized in terms of pore size, pore-size distribution, interfacial area, void fraction, surface charge, tortuosity, etc. Various tests are carried out to obtain information on the above-mentioned characteristics of ceramic membranes. These include bubble point, water flux, SEM, mercury porosimetry, etc. However, characterization of an asymmetrical ceramic membrane is by investigation of the active pores and their distribution in the active layer. Nevertheless, among existing methods which can evaluate the pore distribution of membranes are porosimetry (BJH method, thermoporosimeter, and mercury porosimeter) and permoporometry (biliquid, liquid displacement, and "wet–dry flow" permoporometers). Above all, permoporometry can determine the active pores of membrane (2). Currently, industry uses mercury intrusion as the standard to characterize pore-size distributions of both flat and tubular membranes. Since mercury intrudes from all directions, it cannot differentiate between available pores and nonavailable pores for flow. This is because mercury not only intrudes through pores that are connected from one side of a membrane to the other, but also through pores that are blocked by skin. For a membrane manufacturer dealing with filtration, characterization of the available pores is very important. This is only possible by using the liquid displacement method. Also, this is a novel technique for tubular filters as compared to mercury intrusion because the filtration characteristics are well determined because liquid expulsion from the pores is unidirectional, thus giving an accurate representation of the state of the filter. This method does not need any special skills, is quick and easy, and the test results are clearly defined.

THEORETICAL

Active Pore Area Distribution

The permeability and separation capability of a membrane can be characterized by the *active pore area distribution* function. A typical form of the function is shown in Fig. 1.

The area of pores with radii in narrow interval $(r, r + dr)$ can be expressed as

$$dS = Sp(r)\,dr \tag{1}$$

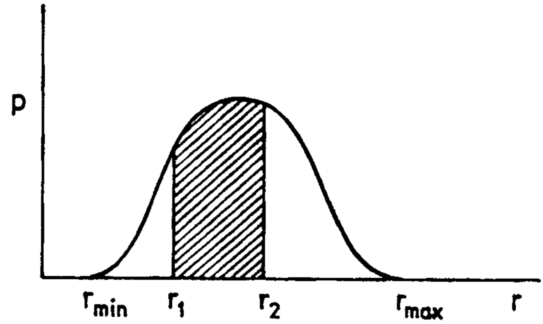

FIG. 1 Example of active pore area distribution.

where S is the active area of all pores and $p(r)$ is the distribution function. The active area of pores with radii from r_1 to r_2 is given by

$$S(r_1, r_2) = S \int_{r_1}^{r_2} p \, dr \tag{2}$$

The following condition is valid for distribution function $p(r)$:

$$\int_{r_{min}}^{r_{max}} p \, dr = 1 \tag{3}$$

where r_{min} and r_{max} are the minimum and maximum pore radii, respectively.

Fluid Flow through Wetted Membrane

The membrane is wetted with a liquid which is held in the pores by capillary forces. Another fluid (liquid or gas) acts at increased pressure on one side of the membrane and expels the former liquid from the membrane pores. The pressure difference ΔP needed to expel the former fluid from a pore with radius r is given by Laplace's equation

$$\Delta P = \frac{2\sigma \cos(\varphi)}{r} \tag{4}$$

where σ is interfacial surface tension of the system liquid–fluid and φ is contact angle of the system liquid–membrane.

When the former liquid is expelled from the pore, the other fluid begins to flow through it. We approximate the pore with capillary with a circular cross-section, and we express the volume flow rate by use of the Hagen–Poiseuille equation:

$$\dot{v} = \frac{\pi r^4 \Delta P}{8\mu L} \tag{5}$$

where μ is the fluid dynamic viscosity and L is the length of the pore.

The number of pores with radii from r to $r + dr$ is

$$dn = \frac{Sp\, dr}{\pi r^2} \tag{6}$$

and the flow rate through them (if they are open to flow) is

$$d\dot{V} = \dot{v}\, dn = \frac{S\Delta P}{8\mu L} r^2 p\, dr \tag{7}$$

The flow rate through all the open pores of the membrane can be expressed as

$$\dot{V}(\Delta P) = \int_r^{r_{max}} d\dot{V} = \frac{S\Delta P}{8\mu L} \cdot \int_r^{r_{max}} r'^2 p(r')\, dr' \tag{8}$$

where

$$r = \frac{2\sigma \cos(\varphi)}{\Delta P} \tag{9}$$

An example of the volume flow rate versus the pressure difference curve is shown in Fig. 2.

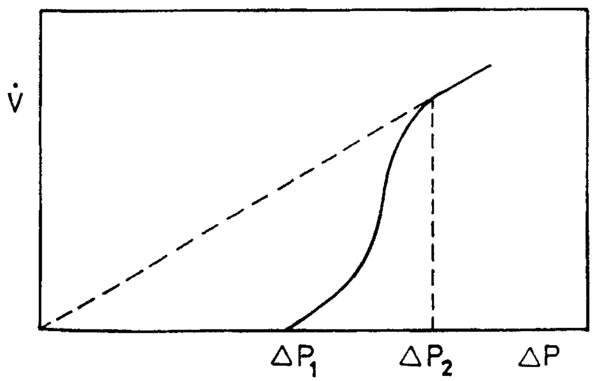

FIG. 2 Volume flow rate versus pressure difference curve.

For a pressure difference of less than $\Delta P_1 = 2\sigma \cos(\varphi)/r_{max}$, the membrane is impermeable. When the pressure difference reaches the value ΔP_1, the fluid begins to flow through the biggest pores. With increasing ΔP the liquid is expelled from smaller and smaller pores as they become open for fluid flow. For $\Delta P_2 = 2\sigma \cos(\varphi)/r_{min}$, all pores are open, and the flow rate becomes proportional to the pressure difference.

Evaluation of Active Pore Area Distribution Function

We approximate the continuous distribution function with the discrete representation shown in Fig. 3. The interval (r_{min}, r_{max}) is divided into n

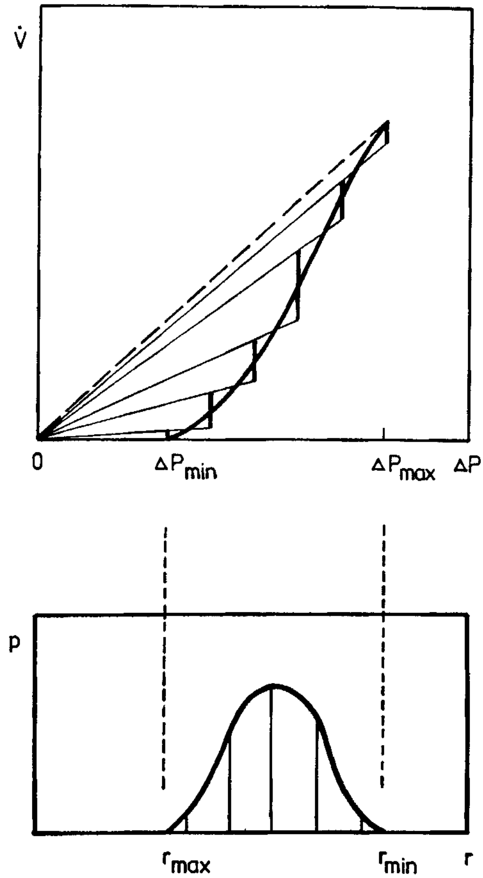

FIG. 3 Discrete type of distribution and related regression of $\dot{V}(\Delta P)$ curve.

subintervals (classes) of uniform width:

$$\Delta r = \frac{r_{\max} - r_{\min}}{n} \tag{10}$$

We assume that a pore cannot have an arbitrary radius value but must have one of a finite number of discrete values, r_j ($j = 1, \ldots, n$). Values of r_j represent the center points of the classes.

The discrete distribution is defined by

$$\text{if } r = r_j, \text{ then } p = p_j, \text{ else } p = 0$$

$$r_j = r_{\max} - \Delta r\left(j - \frac{1}{2}\right), \qquad j = 1, \ldots, n \tag{11}$$

The volume flow rate can be expressed as

$$\dot{V}(\Delta P) = \frac{S\Delta P}{8\mu L}\sum_1^i r_j^2 p_j = \sum_1^i r_j^2 c_j \tag{12}$$

where the radius r_i of the smallest open pore is given by the condition

$$\frac{(r_i - \Delta r)}{2} < \frac{2\sigma\cos(\varphi)}{\Delta P} < \frac{(r_i + \Delta r)}{2} \tag{13}$$

The parameters $c_j = (S\Delta P/8\mu L)p_j$ can be determined from experimental data on $\dot{V}(\Delta P)$ by linear regression. The principle of the regression is depicted in Fig. 3.

When we require the condition

$$\sum_1^n p_j = 1 \tag{14}$$

to be met, the parameters p_j can be evaluated from

$$p_j = c_j \Big/ \sum_1^n c_k \tag{15}$$

With p_j determined, we can calculate

$$\text{mean pore radius: } \bar{r} = \sum_1^n p_j r_j \tag{16}$$

$$\text{standard deviation: } \bar{s}_r^2 = \sum_1^n p_j(r_j - \bar{r})^2 \tag{17}$$

$$\text{relative width of distribution: } \alpha = \bar{s}_r/\bar{r} \tag{18}$$

EXPERIMENTAL

Description of the Porometer

A complete description of the porometer is given in Fig. 4. The porometer uses a widely employed liquid displacement technique that is adopted from the ASTM F-316-80 (3) procedure. This one determines pore size distribution from 0.05 to 10 μm. It uses an external air or nitrogen pressure source of up to 1 MPa. It consists of a flowmeter, a special sample holder, and a 0–1 MPa pressure sensor in conjunction with an *XY* plotter.

Description of Ceramic Filters

The ceramic membranes used for testing were alumina-based, tubular, internal-pressure-type membranes manufactured by Terronic in the Czech Republic, with an inside diameter of 6 mm, an outside diameter of 10 mm, and a length of 35 mm. In order to reduce permeate resistance, this membrane has an asymmetric structure, with the finely porous layer only on the inside of the tube. The membranes used in our characterization studies were of 0.1, 0.2, 0.35, 0.45, 0.6, 0.8, 0.9, and 1.4 μm nominal diameter.

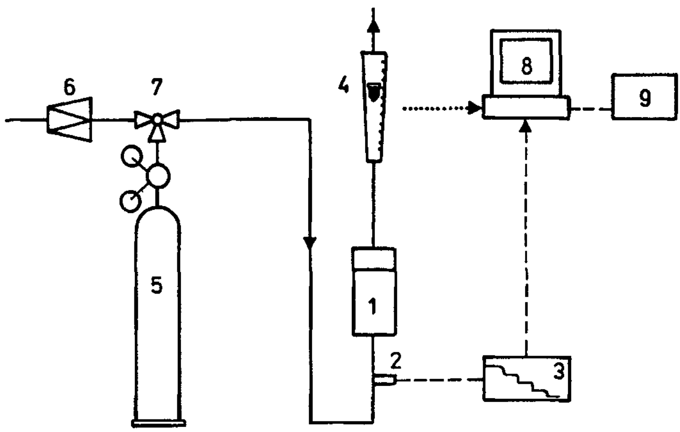

FIG. 4 Schematic drawing of the experimental system: 1, sample holder; 2, pressure transducer; 3, *XY* plotter; 4, flowmeter; 5, nitrogen pressure bottle; 6, air regulating valve; 7, three-way valve; 8, computer; 9, printer.

Analytical Method

The ceramic filter is inserted into the sample holder so that the ends of the sample are sealed. The sample holder is closed hand tight and subjected to increasing pressure and a flow of dry air or nitrogen. Then the ceramic filter is filled with a wetting liquid with low surface tension and again subjected to increasing pressure and a flow of nitrogen. Liquid is expelled from the pores of the ceramic filter when the pressure is great enough to overcome the capillary attraction of the liquid in the pores. Monitoring the initial flow of gas, i.e., the point at which gas is first seen to pass through the sample (the bubble point), allows calculation of the maximum pore size. From these two runs (dry and wet curves), the pore distributions can be calculated by a computer program. The same specimen is used for both dry and wet runs in this method, eliminating the sampling problem associated with using different specimens in two holders.

RESULTS AND DISCUSSION

The results are given as a plot of percentage pore area distribution versus pore diameter together with a table of minimum, mean, and maxi-

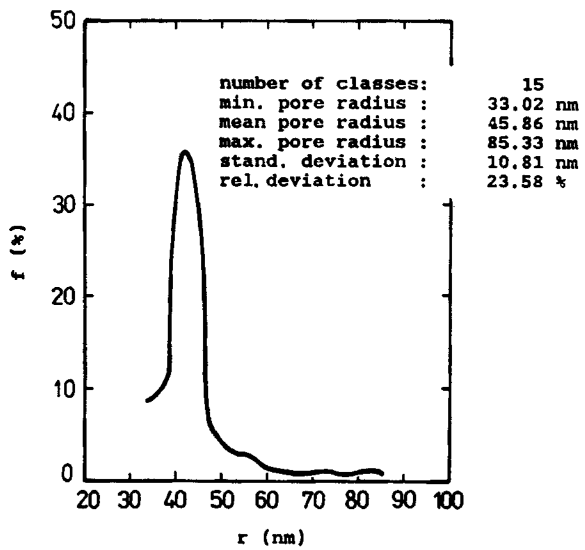

FIG. 5 Membrane pore size distribution: the exemplary results for a 0.1 μm nominal pore size ceramic membrane ($f = 100p$).

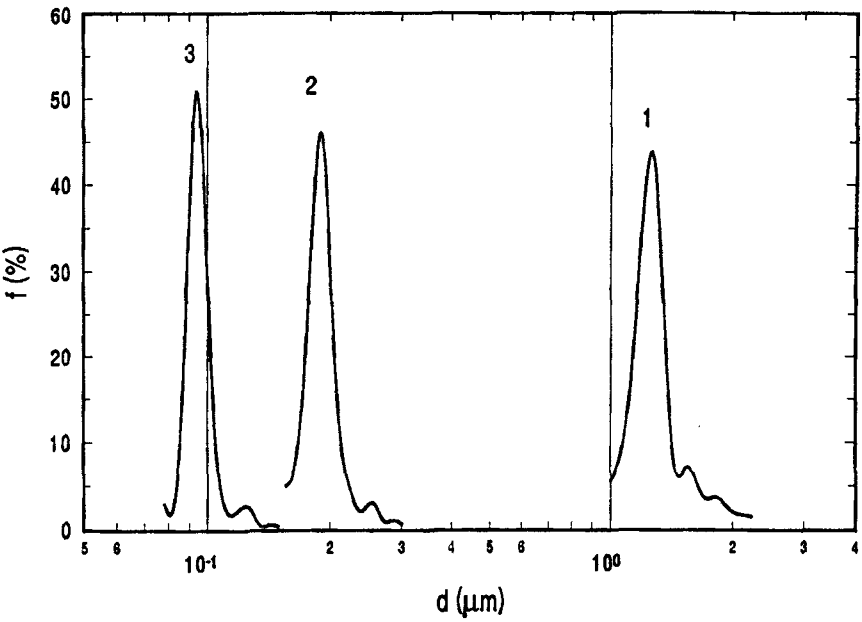

FIG. 6 Pore area distribution versus pore diameter for porous support (1), double-layer (2), and multilayer (3) Terronic ceramic membranes.

mum pore sizes. The exemplary results obtained for a 0.1 μm nominal pore size tubular ceramic membrane are presented in Fig. 5. Figure 6 shows the distribution curves for a porous support and for double-layer and multilayer Terronic ceramic membranes. The data presented in Fig. 6 indicate that the ceramic membranes used in our studies have a very narrow pore-size distribution. The narrow pore-size distribution is extremely useful in predicting the performance of tubular ceramic membranes in various applications with confidence.

CONCLUSIONS

It has been shown that tubular ceramic membranes can be well characterized by a porometer by using a nondestructive low pressure liquid displacement technique. The system allows the fast, precise, and reproducible determination of the parameters characterizing the active pore size of ceramic membranes. The narrow pore-size distribution of these ceramic membranes has enabled us to better understand their behavior in terms of the flux and rejection of different process streams.

REFERENCES

1. H. P. Hsieh et al., *J. Membr. Sci.*, *39*, 221 (1988).
2. F. P. Cuperus and C. A. Smolders, *Adv. Colloid Interface Sci.*, *34*, 135 (1991).
3. *ASTM Procedure No. ASTM F316-80*, American Society for Testing and Materials, Philadelphia, Pennsylvania, 1980.

Received by editor September 20, 1993