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# A pycnometric method to estimate the porosity of hydrophobic hollow fiber membranes ☆

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ABSTRACT

The porosity of hollow fiber membranes is an important property in the design of processes implementing membrane contactors as it is directly related to the effective surface available for mass transfer. Nevertheless, measuring the porosity requires most of the time complex experimental setup and some of the existing methods are questionable when applied to polymeric membrane materials. In this work, we adapted a method originally proposed to estimate the porosity of flat membranes, in order to estimate the porosity of hollow fiber membranes.

- Some hydrophobic hollow fibers are put in contact with a non-wetting solvent inside a pycnometer. The mass of the system is measured.
- The process is repeated using a wetting solvent.
- The porosity is deduced from the difference between the weighing data.

## Specifications table

| | |
|---|---|
| Subject area: | Chemical Engineering |
| More specific subject area: | Membrane processes |
| Name of your method: | Pycnometric porosity |
| Name and reference of original method: | This article presents a modification of the method of Smolders and Franken [1] originally proposed for measuring the porosity of flat membranes.<br>K. Smolders, A.C.M. Franken, Terminology for membrane distillation, Desalination. 72 (1989) 249–262. https://doi.org/10.1016/0011–9164(89)80010–4. |
| Resource availability: | N.A |

## Background

Membrane contactors are widely used in many mass transfer applications involving two immiscible fluid phases, either liquid-liquid [2] or gas-liquid [3]. Membrane contactors offer multiple advantages compared to other contacting devices, such as improved interfacial area, non-dispersive contact, scalability, among others [4]. Membrane contactors implement capillary microporous hollow fibers that act as interface between the two fluids, which circulate on opposite sides of these fibers. Given that the interfaces are formed at the mouth of the pores, the porosity is directly linked to the effective surface available for mass transfer. As such, knowing the porosity is essential for process design.

☆ **Related research article** None.

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Several methods can be used to measure the porosity of hollow fibers, some of them are extensively reviewed in [5]. Nevertheless, most of these methods require complex experimental devices and some of them are not completely adapted to polymeric membrane materials due to pressure-induced deformation (e.g., mercury porosimetry). In this work, we adapted a pycnometric method originally proposed by Smolders and Franken [1], which only requires common laboratory equipment, to estimate the porosity of hollow fiber membranes.

## Method details

The porosity of a membrane represents the void fraction of the total volume of the membrane [6]. In order to estimate the void volume, the method proposed by Smolders and Franken [1] consists in performing two sets of weighings after putting the membranes in contact with two solvents with different physical properties (hydrophobic and hydrophilic). In order to keep constant the total volume of the system composed of the membrane and the solvent, Smolders and Franken [1] proposed the use of a pycnometer.

This method relies on two main assumptions: (*i*) the solvent with more affinity towards the membrane completely fills the internal lumen volume and the pores (wetting solvent) whereas the solvent with less affinity is not capable of penetrating (non-wetting solvent); and (*ii*) there is no volume changes during the contact (no swelling phenomena). Considering these assumptions, if a weighing is done after prior contact with each solvent, the difference between the two weighings corresponds to the mass of solvent trapped inside the fibers (lumen and pore volume). If the lumen volume of the fibers is known, the volume of the pores can thus be deduced.

The original method was designed to estimate the porosity of flat membranes. However, several adaptations are necessary when dealing with hollow fibers because the apparent external volume of the fiber ($V_1$) also includes the internal volume of the channel ($V_2$) which should not be counted in porosity measurements. The geometry of a hollow fiber is illustrated in Fig. 1A. The total volume of a membrane fiber wall ($V_m$) includes a volume related to the polymer constituting the membrane material ($V_p$: polymer) and the pores ($V_v$: void). The porosity is defined as the void fraction of the total membrane volume, as expressed in Eq. (1). For illustration purposes, the different volumes needed to determine porosity are presented as projections in Fig. 1B.

$$\varepsilon = \frac{V_v}{V_m} \tag{1}$$

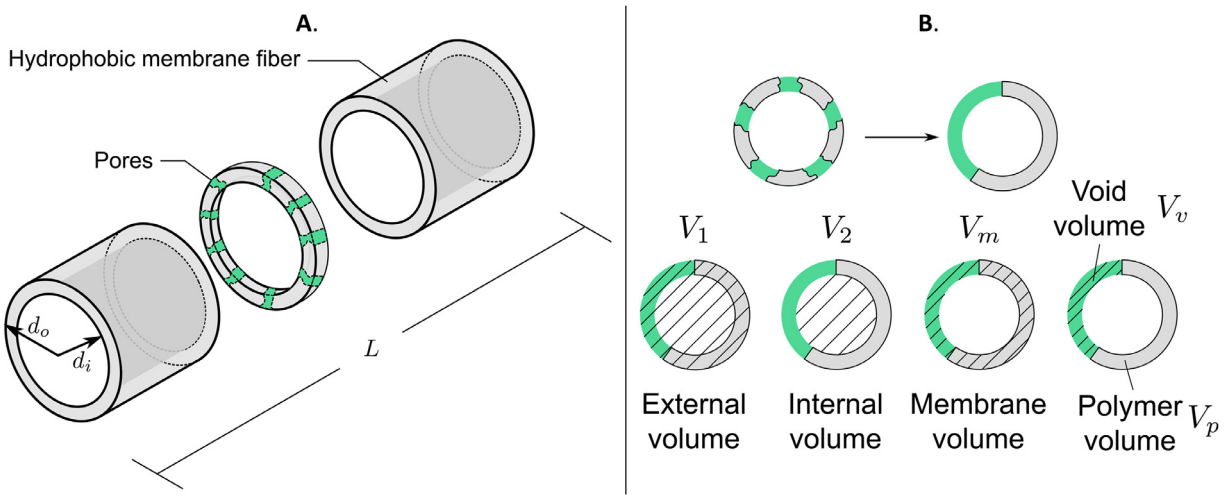


**Fig. 1.** Schematic view of a porous hollow fiber A) Isometric scheme of a hollow fiber with a transversal cut, B) projections of the volumes needed to estimate the porosity, represented as hatched areas.

### *Required materials and equipment*

- Ultrapure Milli-Q water
- 2-propanol
- 10 mL pycnometer
- Ultrasonic water bath
- Precision scale (±0.0001 g)

### *Formation of membrane bundles*

In this work, weighings were carried out using about 50 hollow fibers as illustrated in Fig. 2. This number of fibers was found to be appropriate to fit into the pycnometer and to represent a significant pore volume. The proposed method was tested to estimate the porosity of polypropylene Liqui-Cel™ X-50 fibers (3 M, MN, USA). The average length, internal and external diameter of the hollow

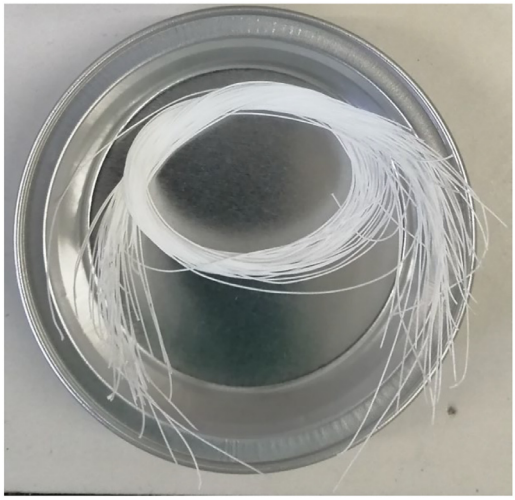

**Fig. 2.** Fibers forming a bundle.

**Table 1**
Specifications of Liqui-Cel™ X-50 fibers used in this work.

| | |
|---|---|
| Average length ($L$) (mm) | 225 |
| Internal diameter ($d_i$) (μm) | 220 |
| External diameter ($d_o$) (μm) | 300 |

membrane fibers are presented in Table 1. Some SEM images of Liqui-Cel™ X-50 hollow fiber membranes are available in literature [7,8].

*Hydrophobicity regeneration*

To ensure the hydrophobicity of the membranes, the fibers were put in contact with 2-propanol. The fiber bundles were put in a Branson 5510 ultrasonic bath (Danbury, CT, USA) for 15 min at a frequency of 40 kHz. The sonication step facilitates the penetration of the solvent in the lumen and in the pores. Subsequently, the membranes were kept in the solvent at 25 °C for 24 h. The fibers were then dried at 30 °C for 72 h. In the literature, drying the membranes for several hours has been reported to reestablish their hydrophobicity [9]. From preliminary tests (data not shown), after 5 h of drying, no further change of the mass of the fibers was observed.

The dried fibers were carefully weighted using a precision scale (±0.0001 g) before being put in contact with the first solvent. The mass of the fibers was named $m_m$.

*Contact with the solvents and weighings*

Water was selected as the first solvent (non-wetting solvent). A first weighing ($m_1$) of the pycnometer filled with water was performed. In this study, the volume of the pycnometer was 10.279 $cm^3$. Subsequently, the dried fibers were put in the pycnometer paying attention to eliminate the air bubbles trapped in the vicinity of the surface of the membranes by shaking the pycnometer carefully by hand. The system was let settle at 25 °C for 10 min before performing the second weighing named $m_2$. An illustration of the fiber bundle in the pycnometer is presented in Fig. 3.

Considering that the total volume inside the pycnometer is constant between the two weighings, the external volume of the fibers ($V_1$) was defined as Eq. (2).

$$V_1 = \frac{m_1 - (m_2 - m_m)}{\rho_w} \tag{2}$$

where $\rho_w$ is the density of water.

The hydrophobic solvent selected was 2-propanol (wetting solvent). Before the contact with 2-propanol, the fiber bundle was dried for 24 h at 30 °C. Their mass ($m_m$) was checked at the end of the drying step to confirm that no water remained either on the surface or inside the fibers.

In the case of the contact with 2-propanol, a first weighing of the pycnometer filled with the solvent was performed ($\tilde{m}_1$). Subsequently, the dried fibers were put into a flask containing 2-propanol and put in an ultrasonic bath under the same conditions as described in the regeneration step. This step was done twice with a pause of 30 min between the two sonication steps. Subsequently,


**Fig. 3.** Fiber bundle in the pycnometer.

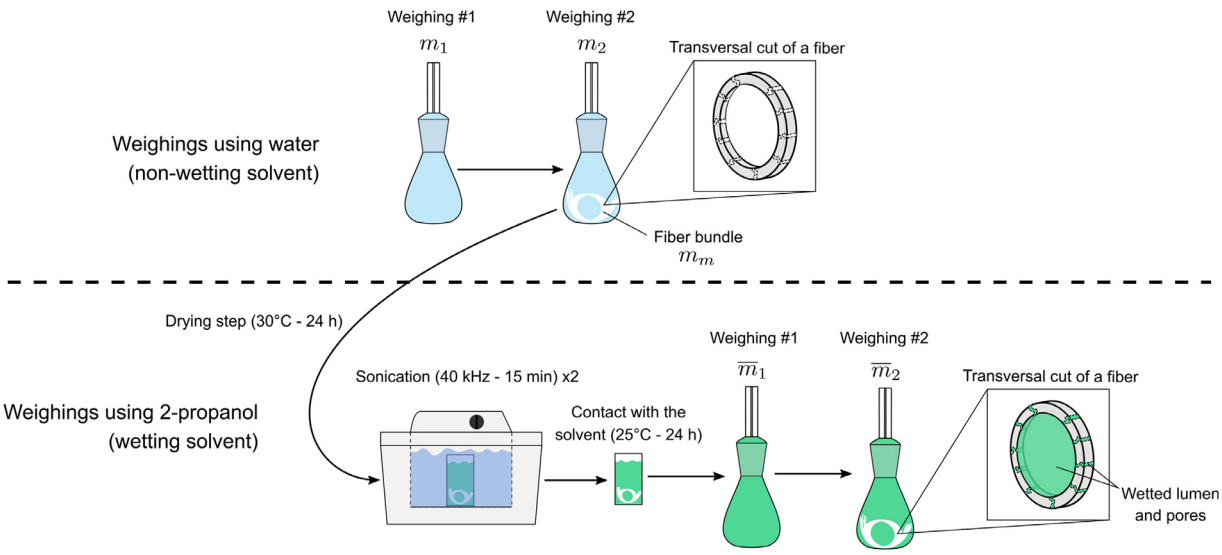


**Fig. 4.** Set of weighings of the porosimetry method adapted for hollow fiber membranes.

the fiber bundle was kept for 24 h at 25 °C in the solvent before putting it into the pycnometer previously filled with the solvent for the second weighing ($\bar{m}_2$). A graphical summary of the experimental procedure is provided in Fig. 4.

The internal volume of the fibers was estimated using the geometry as expressed in Eq. (3).

$$V_2 = n_{fib}\frac{\pi}{4}\, d_i^2\, L \tag{3}$$

Where $n_{fib}$ is the number of fibers forming the bundle, $d_i$ and $L$ represent respectively the internal diameter of the fibers their length.

**Table 2**
Estimated porosity of Liqui-Cel™ X-50 fibers.

| Membrane bundle | $V_1$ (mL) | $V_2$ (mL) | $V_p$ (mL) | $\varepsilon$ (-) |
|---|---|---|---|---|
| 1 | 0.777 | 0.427 | 0.256 | 0.27 |
| 2 | 0.765 | 0.388 | 0.247 | 0.35 |
| 3 | 0.736 | 0.404 | 0.230 | 0.31 |
| 4 | 0.776 | 0.427 | 0.252 | 0.28 |
| 5 | 0.795 | 0.416 | 0.249 | 0.34 |
| 6 | 0.734 | 0.393 | 0.227 | 0.33 |
| 7 | 0.777 | 0.419 | 0.244 | 0.32 |
| 8 | 0.803 | 0.436 | 0.259 | 0.29 |
| 9 | 0.872 | 0.472 | 0.271 | 0.32 |
| 10 | 0.813 | 0.418 | 0.237 | 0.40 |

As the volume inside the pycnometer is constant, the volume occupied by the membrane material (the polymer volume $V_p$) corresponds to the volume that the wetting solvent is unable to occupy as described in Eq. (4):

$$V_p = \frac{\bar{m}_1 - (\bar{m}_2 - m_m)}{\rho_{solv}} \tag{4}$$

Considering the external volume of the fibers obtained from the weighings using water, the void volume in the membrane ($V_v$) can be calculated as Eq. (5).

$$V_v = V_1 - V_2 - V_p \tag{5}$$

Finally, the porosity can be expressed as Eq. (6):

$$\varepsilon = \frac{V_v}{V_m} = \frac{V_1 - V_2 - V_p}{V_1 - V_2} \tag{6}$$

## Method validation

The experimental measurement was replicated using 10 different membrane bundles. The obtained results are presented in Table 2.

The mean estimated porosity was 0.32 with a standard deviation of 0.04, which represents a coefficient of variation of 11.75 %. In the light of these results, the obtained dispersion seemed reasonable considering the simplicity of the method. This variation can also be in part attributed to the intrinsic heterogeneity of the membranes. According to the manufacturer, the porosity of X-50 hollow fiber membranes is equal to 0.4. However, no data are provided regarding the method used to determine this value. Fougerit [7] (section 2.2.2.1) measured the porosity of Liqui-Cel™ X-50 hollow fibers using mercury porosimetry and reported a value of 0.29. The same author performed image analysis based on SEM-FEG, allowing to estimate a pore size distribution (section 2.2.2.2).

Liang et al. [10] reported a simple method to estimate the porosity knowing the density of the polymer, which is not available in the literature for the specific X-50 polypropylene studied in this paper. The polymer density depends on its crystallinity level, which belongs to the confidential domain of the supplier. Considering a range of density values from the literature [11,12] between 0.85 and 0.94 g.cm$^{-3}$ the method of Liang et al. [10] gives for our fibers a porosity range between 0.33 and 0.39.

The porosity obtained with our method seems consistent with these values. Our method has the advantage of being easy to implement with simple equipment and without requiring data about polymer density.

### *Limitations*

The method presented in this work is destructive and requires the use of multiple fibers in order for the pore volume to be significant. Furthermore, it is not suitable to determine the pore size distribution.

This method was developed for a hydrophobic membrane. Nevertheless, as it is based on the use of a wetting and a non-wetting solvent, it can also be adapted to estimate the porosity of hydrophilic membranes.

One can also mention that, in case of using other membrane materials, the conditions in which the fibers are in contact with the wetting solvent must be verified to ensure that the solvent completely fills the fiber lumen and pores. In the case of propylene fibers, the proposed sonication steps combined with the prolonged contact with the solvent were considered as sufficient.

## Ethics statements

N.A.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**Pedro Arana-Agudelo:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Ioan-Cristian Trelea:** Conceptualization, Methodology, Writing – review & editing, Supervision. **Kevin Lachin:** Conceptualization, Writing – review & editing, Supervision. **Violaine Athès:** Conceptualization, Writing – review & editing, Supervision. **Marwen Moussa:** Conceptualization, Writing – review & editing, Supervision.

## Data availability

No data was used for the research described in the article.

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