

Effect of temperature in the characterization of macroporous hydrophobic membranes.

Felipe Varela-Corredor, Mohamed Fawzy, Serena Bandini

Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Bologna, Italy *Corresponding author: felipe.varela2@unibo.it

Highlights

- New method Liquid entry Pressure at high temperatures
- The Liquid Entry Pressure dependence on temperature and solid material is obtained
- The "wetting temperature" parameter is defined.

1. Introduction

In membrane contactor (MC) processes, as membrane distillation, an efficient operation requires the membrane to keep the non-wettability condition satisfied. The non-wetting fluid should not pass through the pores, neither partially nor completely, to avoid bubbling, flooding and fouling. Hydrophobic membranes and operative transmembrane pressure values (ΔP) lower than the liquid entry pressure (LEP) are used to avoid flooding of the membrane pores.

LEP is the key parameter that measures the transmembrane pressure at which the membrane loses the nonwettability condition. The phenomenon is generally described by modifications of the Laplace-Young equation, originally developed for a cylindrical pore geometry; LEP can be described as a function of the surface tension (γ), of the contact angle (θ) of the geometry of the pore-channel and of the pore size distribution.

Some studies reported the use of MC at elevated temperatures with polymeric (124 °C) [1] and ceramic (80 °C) [2] membranes. However, experimentation was successfully performed only at very low ΔP , quite close to zero. In addition, theoretical studies proposed that raising the feed temperature from 80 to 180 °C, might increase the flux 9 times, in direct contact membrane distillation operated with 10-15 °C temperature difference across the membrane [3]; there is no mention about the behavior of LEP with temperature. At our best knowledge, only Saffarini et al. [4] measured the LEP up to 70 °C, in polymeric samples.

The theoretical dependence of LEP on temperature is not yet well-defined, mainly owing to the uncertainties in the measurement of θ as a function of temperature. However, some studies clearly documented an untypical behavior for contact angles of water both on polymeric [5] and on metal surfaces [6] in a range of temperature up to 180 °C.

Aim of this work is to develop a new method of measurement of the liquid breakthrough at high temperatures, in order to identify the limiting operative parameters for the applicability of this technology.

2. Materials and methods

For this study, macroporous multilayer Titania membranes were used (prototypes were manufactured by Fraunhofer Institute for Ceramic Technologies and Systems-IKTS, Germany) in two different configurations tubular and capillaries; tubular samples were tested as single-channels whereas capillaries are arranged in an un-baffled shell & tube configuration. Membranes are coated in the top layer with a combination of fluoroalkylsilanes and a polymer (confidential materials) to provide hydrophobicity.

The breakthrough conditions were measured at different temperatures with pure water, by using an improved "flooding curve method" originally introduced by McGuire et al [7]. The method was modified to perform measurements above the normal boiling point. In order to measure LEP at high temperature, a back pressure micro valve is used to control the pressure in the permeate side. At a fixed temperature, the absolute pressures of feed and permeate are set at the highest value allowed by the apparatus; then the micro-valve is



opened to create a ΔP across the membrane, by keeping the feed pressure as a constant value. After a stabilization time, the flow across the membrane is measured, if any.

3. Results and discussion

Some flooding curves with pure water are reported in Figure 1a) for different single-channels at constant temperature. Experimental data of flux vs. ΔP are elaborated in order to obtain the "normalized flux" which allows to compare data at different temperatures. The definition of the minimum LEP at a fixed temperature can be obtained. The results are reported in Figure 1 b) for samples from two different manufacturing batches.



Figure 1. Coated 100 nm-top layer ceramic membranes. a) water flooding curves at different temperatures; b) minimum LEP vs. temperature with pure water, for single channels and bundles (black symbols) of two different manufacturing batches.

Apparently, a linear trend is obtained converging to the same temperature value independent of the batches of production, both for single channels and for capillary bundles. That experimental trend has been supported and explained by a theoretical model that accounts of basic features of Laplace-Young equation and of the experimental dependence of contact angle and of surface tensions with temperature [8].

The model indicates that a maximum temperature exists at which all pores become flooded by keeping a pressure difference across the membrane close to zero. The so-called *wetting temperature* is defined straightforwardly: it is strictly dependent of the liquid type as well as of the solid material. For the ceramic membranes under investigation, the wetting temperature has been found in the range from 120 to 130 °C, for both the manufacturing batches, thus confirming that it does not depend on the pore radius distribution.

References

- [1] Singh D. and Sirkar K. K., J. Membrane Sci, 389 (2012) 380-388.
- [2] Koonaphapdeelert S., Wu Z. and Li K., Chem Eng Sci, 64 (2009) 1-8.
- [3] Luo A. and Lior N., Desalination, 419 (2017) 88-100.
- [4] Saffarini R. B., Mansoor B., Thomas R. and Arafat H. A., J. Membrane Sci, 429 (2013) 282–294.
- [5] Petke, F. D. and B. R. Ray., J. of Colloid and Interface Sci, 31 (1969): 216-227.
- [6] Bernardin, J. D., Mudawar I. A., Walsh C. B., and Franses E. I., Int J. of Heat and Mass Transfer, 40 (1997): 1017-1033.
- [7] McGuire K. S. Lawson K. W. and Lloyd D. R., J. Membrane Sci, 99 (1995) 127-137.
- [8] Lyklema, J., Colloids and Surfaces 153 (1999) 413-421.

Keywords

Macroporous Membranes, Liquid Entry Pressure, flooding Curve, Wetting Temperature