Capillary Flow Porometry

The Capillary Flow Porometry technique (CFP, or gas-liquid displacement method) relies on imposing a trans-sample pressure at which a suitable liquid is displaced from the pores of the examined sample. The displacement is detected by registering the permeating flow of a non-reactive gas through the media. In CFP tests, the sample is filled with a wetting liquid, assuming the filling of its entire accessible porosity. Pressure is applied to one side, while the other is kept at atmospheric pressure. This trans-sample pressure difference forces the wetting liquid out of the pores resulting in a permeating flow. Increasing the trans-sample pressure will promote pore clearance, increasing the permeating flow until the sample is fully cleared from the wetting liquid (Figure S1). Young-Laplace equation is then used to correlate the capillary pressure in the media with its pore diameter. If the capillary is assumed of cylindrical shape, Washburn equation can be applied, which is a typical assumption for indirect method CFP measurements [1][2]:

$$d = -\frac{4\gamma cos\vartheta}{\Delta P} \tag{1}$$

where ΔP is the applied trans-sample pressure, d is the narrowest diameter of the capillary, γ is the surface tension of the chosen wetting liquid, and ϑ is the contact angle between the wetting liquid and the wet surface. Assuming that the chosen liquid can guarantee full wettability of the porous media, the contact angle can be assumed as 0°, leading to further simplification:

$$d = -\frac{4\gamma}{\Delta P} \tag{2}$$

Given that the listed geometrical assumptions are to be applied to a complex porous media, it is important to remark that this technique is able to give information on an average geometry [3][4]. This averaging summarizes the main flow characteristics of the media, rather than a precise pore shape. Moreover, the flow distribution proves dependent on the wetting liquid choice, the scanning speed, and the ramping method [5]. Nevertheless, given that the scope of this work is to evaluate if there is any influence of support pre-treatments on the gas permeance and flow distribution through the media, this level of accuracy is considered sufficient for quality comparisons between samples of the same nature.

By measuring the permeating gas flow for each applied trans-sample pressure, the flow distribution with respect to the dry media can be used to retrieve information about its average geometry. In particular, the cumulative flow distribution through the porous tube is:

$$C_{flow} = \frac{Q_{wet}}{Q_{dry}} \quad (3)$$

where Q_{wet} represents the permeating flow through the wet media and Q_{dry} is the permeating flow through the dry media at the applied trans-sample pressure. From the cumulative flow distribution C_{flow}, it is then possible to retrieve the differential flow for each pore diameter D as:

$$Diff_{flow} = \frac{dC_{flow}}{dD} \quad (4)$$

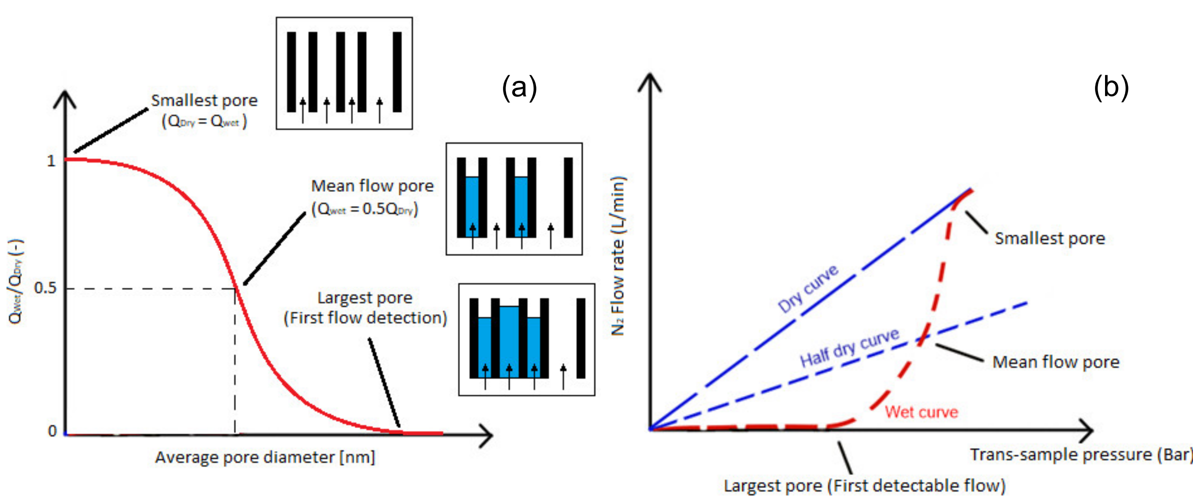

Figure S1. Graphical representation of (a) Cumulative Flow Distribution, (b) CFP curves.

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