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Combining the Enhanced Bubble-Point and Pressure Decay methods in characterization of micro-filtration products using the HumiPyc

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Background

The Bubble-Point Method

The bubble-point method is a commonly used technique for determination of the largest pore(s), so-called active pores, in a given filter (membrane). Experimentally, the bubble-point instrument measures the **pressure** needed to cause bulk flow of gas (formation of gas bubbles), typically air, through the liquid filled porous sample. From the theory of capillarity and using an ideal cylindrical approximation of real pores, the transitional pressure is reported as the pore diameter by employing this simple formula:

$$d = \frac{4\sigma \cos\Theta}{p} * 10^6 \qquad (1)$$

where

d - (ideal) pore diameter [μm]
σ - surface tension of the liquid [N/m]
θ - liquid-solid contact angle [degrees]
p - pressure at the first bulk flow bubble(s) appearance [Pa]

Since usually there is some amount of liquid present above the sample, the differential pressure is corrected by the pressure exerted by the liquid. When this correction is introduced, the form of the equation 1 changes to

$$d = \frac{4\sigma \cos\Theta}{p - \varsigma g h} 10^6 \qquad (2)$$

where

ς - density of the liquid [kg/m^3]
g - gravitational constant 9.81 [m/s^2]
h - height of the liquid over the sample [m]

The equation 2 is often used as presented but some standard methods, e.g. ASTM F316-86 method, stipulate that the nominator of the equation 2 needs be multiplied by a shape/tortuosity factor, which in this case has 0.715 value. It should be noted that this equation is an over-simplification of any real pore system.

The Pressure Decay Method

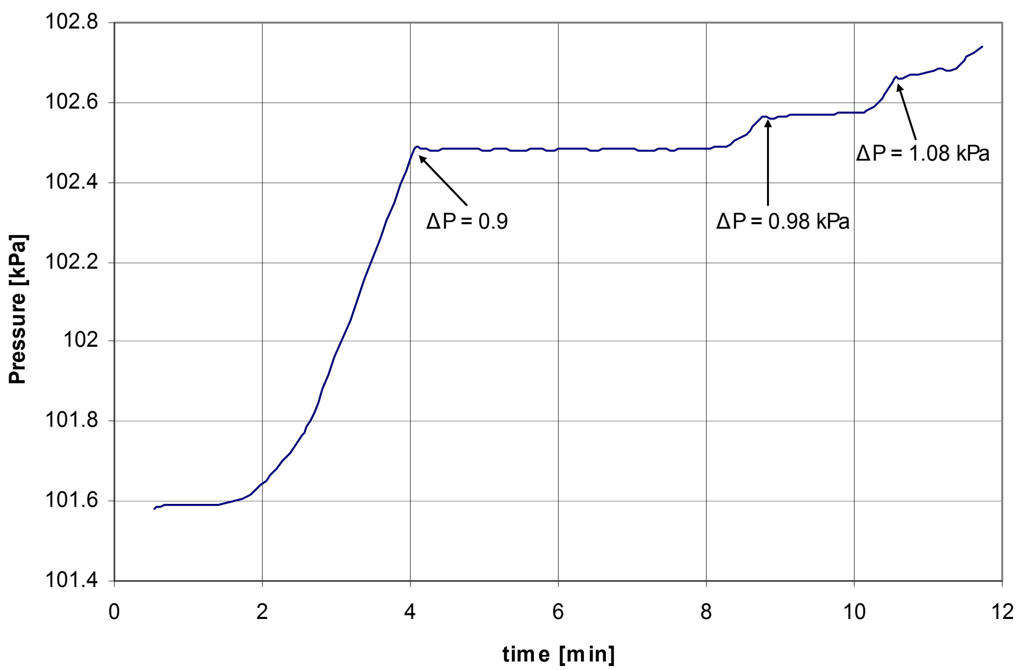
Before the bulk flow of gas appears on one side of the wetted sample in form of bubbles while the pressure is raised slowly, the diffusional mode of the gas transport takes place. In the pressure decay or pressure drop test, the pressure is raised to the vicinity of bubble point pressure and the flow of gas is cut off. From the rate of pressure drop versus time and the known initial volume of the gas, additional gas transport properties of the sample can be deduced.

Experimental considerations

It is often reported, that the bubble-point pressure value depends on the rate of the pressure increase. Other factors, like a detection method or a particular setup, the sample-wetting liquid, and temperature also play a role. However, in many practical implementation of the method, and perhaps only for marketing reasons, a quick determination of the bubble point pressure (about or under 2 minutes) is quoted. This and other issues have been more rigorously investigated using the combined setup of the HumiPyc and ancillary hardware. The sample holding hardware allows also for visual observation of the bubbles formation through the transparent closure when it is used externally to the pycnometer.

Utilizing the programmable pressure control capabilities of the HumiPyc and large spectrum of pressure increase rates, the bubble-point method can yield better results than just single pore detection for samples featuring larger pore sizes. That is, however, possible when the pressure is raised slowly and high-resolution data acquisition system is employed. An example of such experiment is presented in Fig.1. below.

Fig. 1. Bubble-Point test of a coffee filter at T = 25 ˚C, Liquid - isopropanol 91%, (10mm height)



Applying faster pressure increase rates degrades ability to resolve other than the largest pore sizes and causes variations as to the determination of the bubble point pressure. The problem of the selection of the pressure increase rate and the proper detection of the bubble-point pressure is even more interesting for samples with much smaller pore sizes. A specimen with relatively uniform porosity and bubble point pressure of about 125 kPa (visual determination) was used for testing different pressure rate increase. Several runs were carried out at the same temperature 24.5 ˚C with different pressure increase step within allotted time. Results for the 10 and 40 Pa rate are presented below in Fig. 2 and 3, respectively. Using the 10 Pa rate, the pressure of the bubble point is easy to be determined and it agrees well with visual observations of the onset of the air bubbles stream. Above the bubble-point pressure, the line contains small bumps, characteristic to appearance of new sources of the bulk flow. The time of the pressure scan, however, is quite long.

Fig. 2. Bubble Point test , 10 Pa step, T = 24.5 ˚C

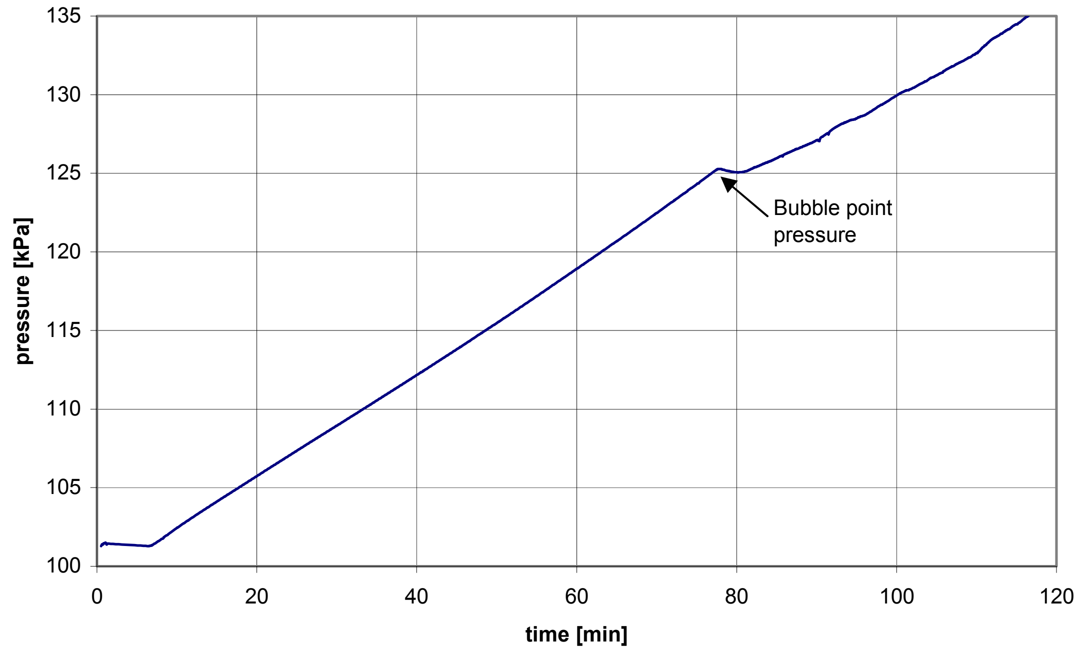
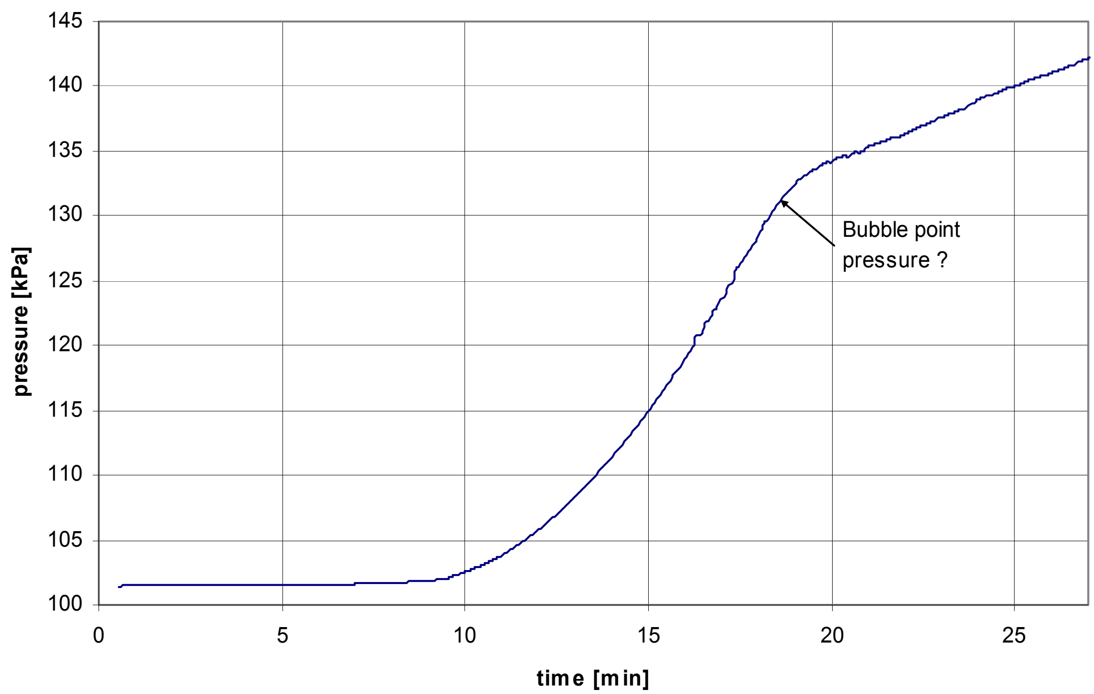


Fig. 3. Bubble Point test, 40 Pa step, T = 24.5 ˚C



The increase of the scan rate shortens the overall time but at the expense of the accuracy of the bubble-point pressure, that in this case (Fig. 3) is about seven kPa above the originally determined value. Additionally, it is harder to determine the transitional pressure. For rates of 100, 250, and 625 Pa the profiles were similar to the Fig. 3 but the detection of the bubble point pressure was harder to accomplish and its values were trending higher.

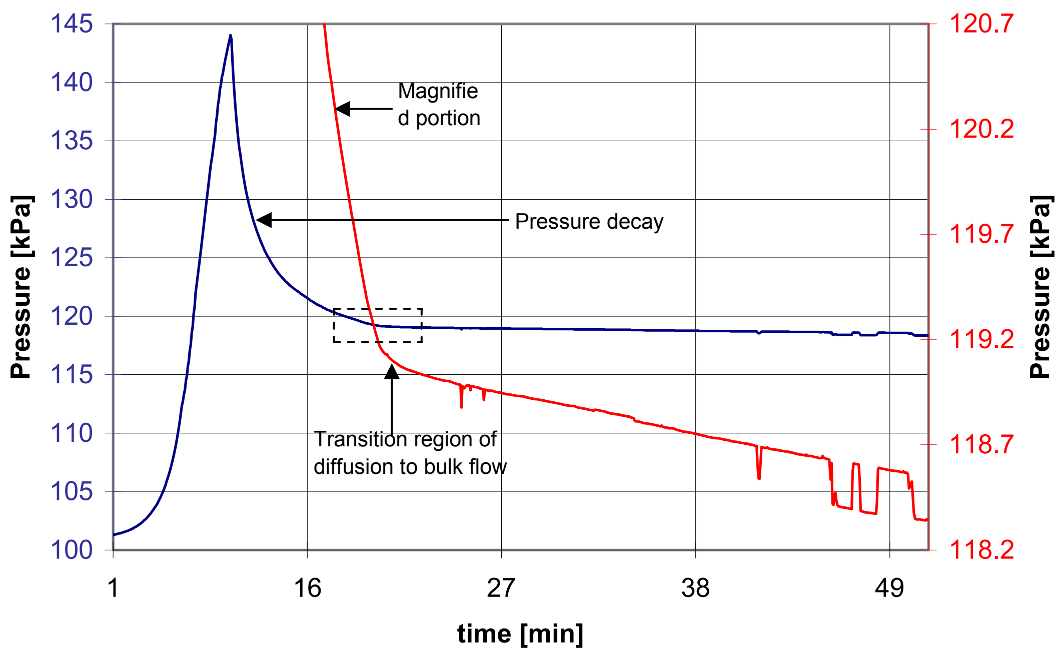
However, this outcome is to be expected, at least from the mechanistic point of view. The tiny flow of bubbles from a very thin pore does not create an appreciable amount of flow. Any aggressive pressure increase will likely attenuate the flow appearance and only when enough pores will get open at higher pressure, than the flow will be detectable. If an instrument measures the flow after it passes through the membrane, than there are at least two factors that cause variations of results due to a particular design. First, it is the amount of the dead volume between the liquid above the sample and the entry to particular detecting device. Second, it is the minimum flow detection limit (pressure that needs to be established in the dead volume before a particular detecting device begins to work). **Thus, it is very likely, that in many implementations of the bubble point method, the determined transitional pressure of the bubble-point in larger than the actual one.**

The pressure decay method

The pressure decay method seems to be under-utilized in the characterization of porous media. The reason, perhaps, is that more expensive hardware and computerized approach is needed than in some simple implementations of the bubble point method. However, from the following results and discussion, the method does provide valuable information about the sample.

Using the same specimen for the pressure decay study, several different runs were carried out at the same temperature 24.5 ˚C and the allowed step of 0.625 kPa. After bringing the pressure well above the bubble-point pressure, the gas flow was cut off. The profile of pressure drop versus time is presented on the Fig.4.

Fig. 4. Pressure Decay and magnified transition region of bulk/diffusional flow

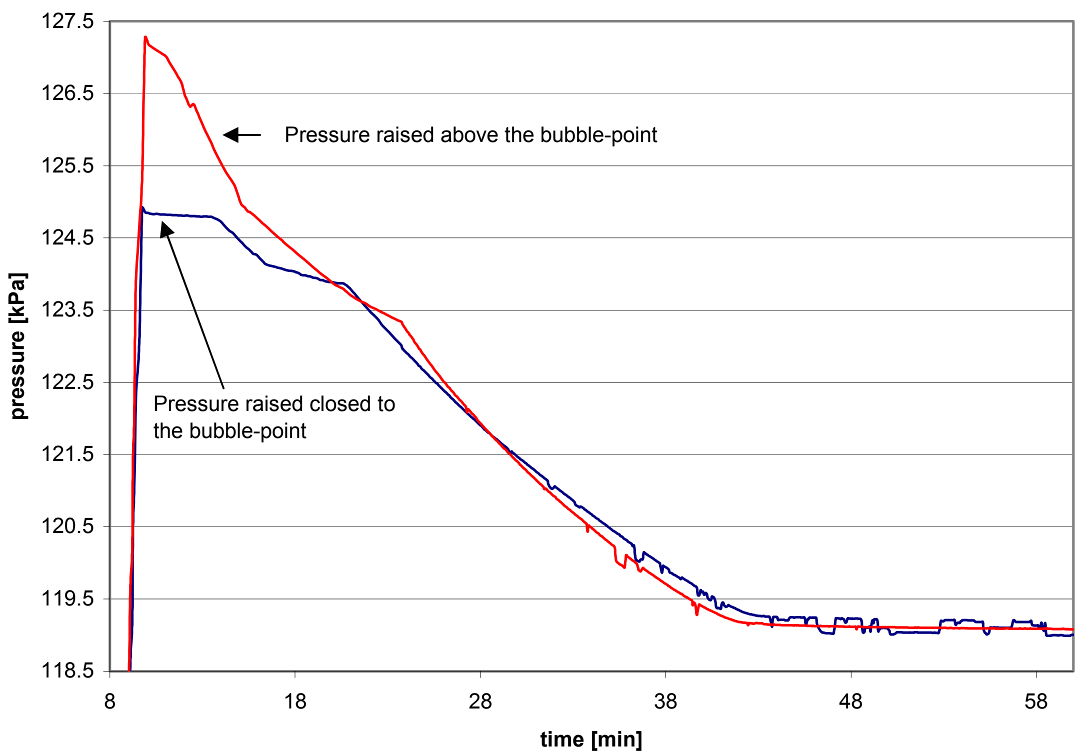


Small rectangular fragment from the pressure decay line (dark blue line) was magnified 20 times (see the secondary pressure axis). The red line show the expanded portion of the rectangle The onset of the bulk flow (large slope line) and the end of diffusional flow (small slope line) are rather confined in a small but easily identifiable region. An immediately noticeable experimental fact is that this region is well below the previously determined bubble point pressure. Despite using different rates to cross well above the bubble point pressure and subsequently stop the flow, the location of transitional region was fairly well positioned at the same pressure. **The hysteresis between the bubble point pressure and the plateau can be considered as one of the characteristics of a given liquid-sample system at a specified temperature.**

Using the HumiPyc, the volume **V** occupied by the gas between the suspended sample and the pressure transducer can be easily determined by carrying out the pycnometric measurements. Assuming applicability of the ideal gas law, the pressure changes versus time can be directly related to the number of moles of gas (and hence the volume of gas at STP) transported through the membrane. **Therefore, the rates of diffusional and bulk flow can be calculated. Relating the rates of bulk flow to a given pressure, a distribution of most active pore sizes can be attempted.**

Additional and more detailed information about the sample can be obtained by conducting a series of runs just above the bubble point pressure, in the vicinity of it, and just below it. The first two cases are presented in the Fig. 5 below. The pressure scale on the low side was truncated to show more details.

Fig. 5. Pressure decay profiles

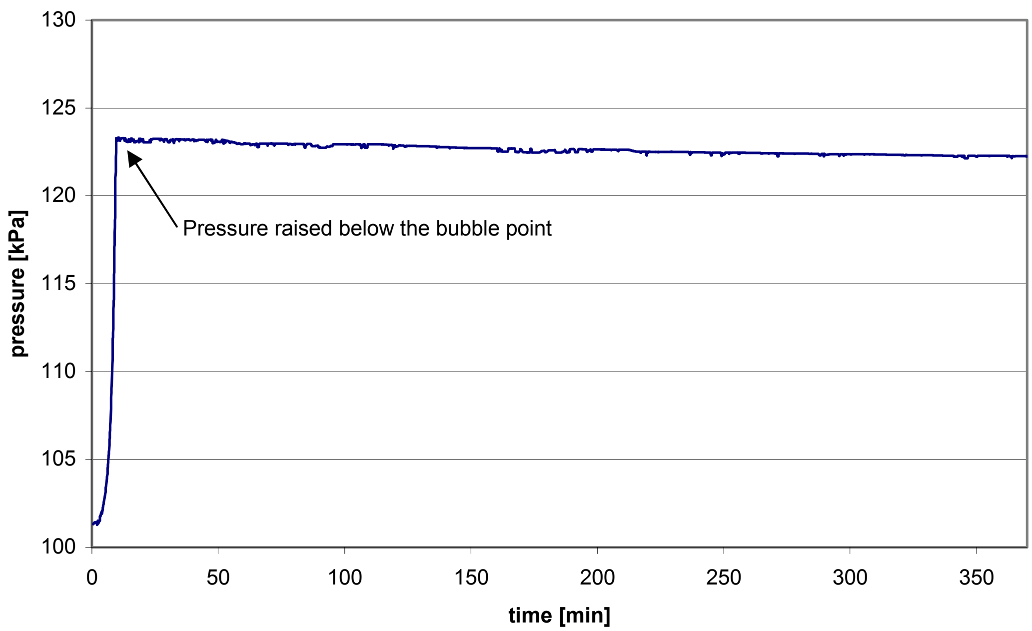


Both profiles show initially segments of straight lines where more than one bubble spots are responsible for the pressure drop. It is also interesting to observe, that while trying to get very close the bubble point pressure (dark blue line), it seems as if an incubation period is needed (or some change in experimental conditions) that triggered the bulk flow of the pressure decay. In the last stages of the bulk flow of the pressure decay where usually only one bubble spot exists, **it is possible to calculate rates of gas flow**

through the single pore size (after subtracting the contribution of the diffusional flow to the total flow). By raising the pressure above the bubble point pressure, contribution from additional pores and their bubble point pressure values can be determined. Furthermore, if the pressure is raised well above the first bubble point value, than the contributions from smaller pores can be estimated.

The final case, where the pressure was raised below the bubble point value, is shown on the Fig. 6 below. Despite the long time allotted for this run, only the diffusional flow can be seen.

Fig. 6. Pressure decay - diffusional mode



The pressure decay profiles can yield interesting details about a particular wetting liquid-porous sample system and the details are revealed in the "natural" time of the system at the selected experimental conditions. The pressure decay method seems to be more informative for studying a particular sample than the bubble point method alone with an arbitrary pressure rate increase. The analysis of the curvature of the single pore flow segment and flow rate could be valuable in developing a better pore model than just an ideal cylinder. Since the pressure decay profile shows features innate to a particular wetting liquid-pores system, it seems to be a more valuable tool in studying effects of any modifications in a product development as well as aging or contamination effects of a micro-filtration product**. In addition to carrying out experiments at a single temperature, the data can be obtained at other temperatures within the HumiPyc operational range.** Therefore, the changes of the characterization parameters versus temperature could contribute to better understanding of the porous structure of the sample and its affinity towards the wetting liquid.

From the instrumentation point of view, only some additional hardware for sample holding needs to be added to the basic HumiPyc as a gas pycnometer to accomplish the standard methods in testing micro-filtration products. Some other techniques used for filter integrity testing can be also materialized. Since one or more pores can be identified using the bubble point method, and the pressure decay method can yield flow characteristics and pores sizes of the most active pores in a more meaningful way, substantial portion of information about the active pore structure can be obtained. The ability to vary the volume V for different rates of pressure decay allows the user for studying large spectrum of samples. The data obtained from the natural decay profile are sounder than by applying any arbitrary flow rates.