

Trong Dang-Vu*, Jan HUPKA*

CHARACTERIZATION OF POROUS MATERIALS BY CAPILLARY RISE METHOD

Received March 15, 2005; reviewed; accepted May 15, 2005

Capillary rise method is widely used for contact angle determination using Washburn equation. Penetration kinetics of porous media comprised from particles of varying size distribution was investigated. It was found that the penetration kinetics and the validation of Washburn's theory depend not only on the particle size but also on the pore size distribution. The effect of particle size on contact angles was not observed. In case of bed consisting of wide size distribution particles, the smallest fraction plays a significant role creating the smallest capillaries and allowing for more even porous bed penetration. This increases precision of contact angle measurement. A difference of time between fluid flow through a porous bed and its complete saturation (Δt_{sf}) was proposed as a new parameter describing capillary size distribution in porous media. It allows for fast estimation of both capillary size distribution in a porous bed and precision of contact angle determination.

Key words: capillary rise, penetration kinetics, Washburn's equation, porous media.

INTRODUCTION

Capillary rise is a fundamental phenomenon existing in many natural processes and human activities [1]. Knowledge of capillarity laws is important in chemical, metallurgy, and ceramic industry, in oil recovery and civil engineering, in dyeing of textile fabrics, ink printing, and a variety of other fields. This explains the continuous interest in the subject from the side of industry and fundamental science.

Experimental method based on capillary rise is widely used for porous media characterization (i.e. pore radius, contact angle, free surface energy). Among them measurement of height penetration and mass gain of wetting liquids in time are most commonly employed. In both approaches Washburn's equation is a basic instrument for analysis of obtained results. For along time of using this equation, many modifications have been applied and although critics, Washburn's equation presents useful model for evaluation of porous media observed in industrial practice.

* Department of Chemical Technology, Gdansk University of Technology, 80-952 Gdansk, Poland,
jhupka@chem.pg.gda.pl

Capillary rise method is used broadly for characterization of porous materials. However, it does not or not sufficiently study the effect of particle size of porous materials on the contact angles and penetration kinetics. The aim of this paper is to characterize the porous materials using capillary rise method and to study the effect of particle size on penetration kinetics and contact angles.

WASHBURN'S EQUATION AND CAPILLARY RISE METHOD

Capillary rise method allows determination of the radius of the porous media and contact angles of liquid on the solid surface [2-5]. It also enables to calculate the surface free energy, which is very important in flotation, particles aggregation, and stability of colloid system [4, 6-11]. Measurements of penetration distance [12-16] and liquid mass gain [7, 17, 18] are two main experimental methods, in which Washburn equation is a basic instrument to analyze the obtained results.

By assuming the steady-state flow and according to Poiseuille's law expressing the balance between viscous forces and capillary and hydrostatics forces (neglecting inertial effects), the rate of liquid penetration is given as follows:

$$dV = \frac{r^4 \Delta P \pi}{8\eta h} dt \quad (1)$$

The relationship between the liquid volume and height is given by:

$$dV = r^2 \pi dh \quad (2)$$

The difference between capillary P_k (Eq. 3)) and hydrostatic pressure P_h (Eq.4)) allows calculating the pressure drop, ΔP (Eq. 5)):

$$P_k = \frac{2\gamma}{r} \cos \theta \quad (3)$$

$$P_h = g\rho h \quad (4)$$

$$\Delta P = \frac{2\gamma}{r} \cos \theta - g\rho h \quad (5)$$

By substitution of Eq. (2) and (5) to Eq. (1) the penetration rate is transformed into:

$$\frac{dh}{dt} = \frac{r^2}{8\eta h} \left(\frac{2\gamma}{r} \cos \theta - g\rho h \right) \quad (6)$$

Assuming that the hydrostatic pressure can be neglected in case of flow under capillary pressure, Eq. (6) can be rewritten as:

$$h \frac{dh}{dt} = \frac{r\gamma \cos \theta}{4\eta} \quad (7)$$

The Washburn's equation is obtained after the integration of Eq. (7) with the initial condition ($h = 0$ at $t = 0$) [19]:

$$h^2 = \frac{r\gamma \cos \theta}{2\eta} t \quad (8)$$

Washburn's equation presents linear dependence of square of height penetration of penetrating liquid in the tube versus time. In case of porous media, Washburn's theory assumes the model as a bundle of cylindrical capillaries. Capillary radius r is equal to mean or equivalent pore radius.

Several restrictions are applied to this relationship: (a) steady-state laminar flow, (b) zero velocity of the liquid at solid/liquid interface, it means lack of slip (slip coefficient $\varepsilon = 0$), (c) no external pressure, and (d) negligible gravitation differences.

The modified Washburn's equation is also used as dependence between wetting liquid mass and time [17]. The relation between liquid mass and height in the column is linear as given by Eq. (9):

$$m = \pi R_k^2 h \rho \varepsilon \quad (9)$$

Substitution into Eq. (8) gives:

$$m^2 = \left[\frac{r(\pi R_k^2)^2 \varepsilon^2}{2} \right] \frac{\rho^2 \gamma \cos \theta}{\eta} t \quad (10)$$

Which leads to

$$m^2 = \frac{C \rho^2 \gamma \cos \theta}{\eta} t \quad (11)$$

where

$$C = \frac{r(\pi R_k^2)^2 \varepsilon^2}{2} \quad (12)$$

Washburn's equation (Eq. (8)) and its modified form (Eq. (11)) present linear dependence of square of height penetration and square of liquid mass versus time, which is observed by many researchers [2, 5, 20-23]. However, the deviation from

linearity is also observed [1, 17, 24-26]. As a reason the change of contact angles during capillary rise [27], non-uniform pore size distribution in porous media [1], or the change of start line of penetrating liquid into bed (the choice of the coordinate system (h,t)) [26] are proposed.

Hypothesis of non-uniform pore size distribution is cited in literature [1]. However, author did not study the bed with different pore size distribution, so this shows lack of strong fundamentals of hypothesis.

THE EFFECT OF PARTICLE SIZE ON PENETRATION KINETICS AND CONTACT ANGLES

The large number of particle size and type is used to study the effect of particle properties on the penetration kinetics and wettability by capillary rise method, see Table 1. It results that the influence of particle size on the penetration kinetics was observed. In case of contact angles, the effect of particle size is not observed, and this is not discussed in literature.

Table 1. Type and size of particle bed used for capillary rise investigation

Type of bed	Particle size [μm]	The effect of particles	Literature
Silica flour	0 – 123	The larger particle size distribution the higher penetration rate	[2, 17]
Alkyl-silane treated silica flour	0 – 123	The larger particle size distribution the higher penetration rate	[17]
Glass	< 106 106 – 300 300 – 425	The effect of particle size on the contact angles is not observed	[28]
Quartz particle	37 46	The effect of particle size on the contact angles is not observed	[29]
Hydrophilic and hydrophobized quartz crystals	5 – 10 44 – 53 204 – 208	The effect of particle size on the contact angles is not observed	[13]
Siliconized beads	105 – 125 125 – 149 149 – 177 250 – 297 297 – 350	The larger particle size distribution the higher penetration rate	[30]
Glass beads	100 – 120 450 – 520	The larger particle size distribution the higher penetration rate [2]	[18] [2]
Limestone	0 – 500	The larger particle size distribution the higher penetration rate	[17]
Sphalerite particles	7.22 9.8 15.0 21.5 28.6 38 – 75 75 – 150	The effect of particle size on the contact angles is not observed	[5]

Variable results were presented by Nishi et al. [31]. For carbonized fir fibers and carbon fiber felts penetration rate of heavy oil increases with increasing in porous materials porosity. However, for exfoliated graphite the situation is opposite, penetration rate decreases with increasing in porous materials porosity.

EXPERIMENTAL

The investigation was carried out for glass beads containing: 70-73 % SiO₂, 13-15% Na₂O, 7-11 % CaO and max. 0.1 % Fe₂O₃, and making up amorphous 2410 kg/m³ density glassy phase. The characteristics of particle bed are presented in Table 2.

Table 2. Characteristics of bed of particles

Symbol	Pore size, [μm]	Porosity, [m^3/m^3]	Bulk density, [kg/m^3]
A	60 – 110	0.34	1589
B	150 – 250	0.33	1619
C	60 – 250	0.30	1678

Capillary rise experiments were carried out using liquids for which properties were readily available, see Table 3.

Table 3. Characteristics of liquids used for capillary rise experiments (20°C)

Wetting liquid	Density [kg/m^3]	Viscosity [$\text{mPa}\cdot\text{s}$]	Surface tension [mJ/m^2]	Dielectric constant
Water	997	1.01	72.3	78.5
Toluene	862	0.55	27.8	2.3
Ethanol	785	1.20	22.0	24
Heptane	684	0.41	20.3	1.9
Octane	703	0.55	21.8	1.9
Decane	730	0.92	23.9	2.0

The apparatus for the capillary rise experiments is shown in Fig. 1. The particles were manually placed in small, glass columns (0.7 cm inner diameter and 20 cm long) which were closed at the bottom by nonwoven fabric to support the bed. The decrease in mass of the container with the wetting liquid was recorded every second using an electronic balance, attached to a computer. The time $t = 0$ approximately corresponded to the moment of column submersion in the wetting liquid.

The procedure and repeatability of the packing play a key role in capillary rise method, therefore a great care was taken when preparing the packed bed. The assumption of the present study is that packed beds with a comparable bulk density have similar spatial packing. In order to obtain repeatable packing density, the packing procedure was run as follows: the particles with known mass were manually

introduced to the column, which then was tapped many times from the height of 2 cm until the particle height reached the given value. Porous materials with the same ratio of mass vs. height of packing in the column have the same bulk density.

In the procedure use in this work the whole particle mass is put to the column once, not several times. This leads to even packing of bed along the column. Adding particles as weight increments results in uneven packing because the lower layer has higher bulk density due to more tapping time.

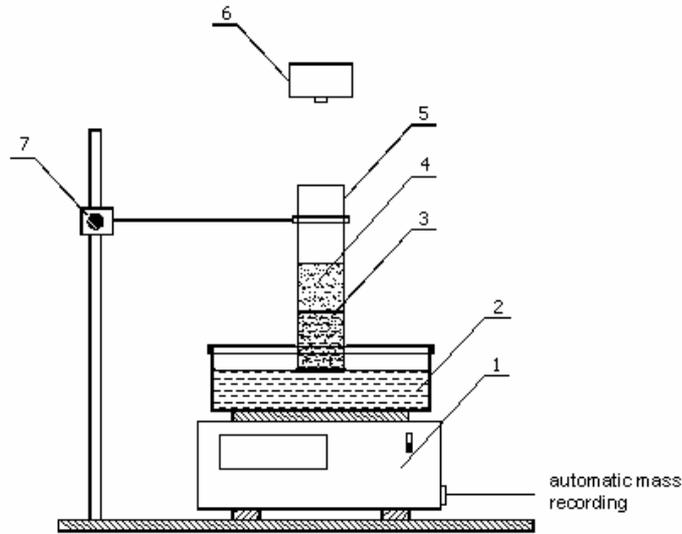


Fig. 1. Laboratory set-up used for measurements: 1-electronic balance, 2-covered container with wetting liquid, 3-liquid front, 4-particle bed, 5-column, 6-camera, 7-micrometric screw

Evaluation of repeatability of bed packing is based on the assertion that if the mass of liquid penetrating into different bed packing at the same interval time is comparable, then the bed packing is repeatable. For this purpose the difference between the liquid mass for two bed packing after the same time is evaluated using F-Snedecor and t-Student test.

The standard deviation of values of liquid mass for different bed packing is given by:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (13)$$

where:

- x_i - liquid mass in given time,
- \bar{x} - the arithmetic mean of liquid mass,
- n - the number of values of liquid mass.

Parameter F of F-Snedecor test is defined as follows:

$$F = \frac{s_1^2}{s_2^2} \quad (14)$$

where s_1^2 or s_2^2 , whichever is the larger, is put in the numerator and the smaller value in the denominator, so that $F > 1$.

From a comparison between F calculated using Eq. (14) and critical value F_{critic} (from the table of F) with significance level α and number of degrees of freedom f_1 and f_2 (where $f_1 = n_1 - 1$ and $f_2 = n_2 - 1$), the following conclusions can be drawn: if $F < F_{\text{critic}}$ then values of standard deviation are not different regarding precision, otherwise the statistical difference is occurred.

Parameter t of t-Student test is defined as follows:

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2 + s_2^2}} \cdot \sqrt{n} \quad (15)$$

From a comparison between t calculated using Eq. 15 and critical value t_{critic} (from the table of t) with significance level α and number of degrees of freedom $f = n_1 + n_2 - 2$, the following conclusions can be drawn: if $t < t_{\text{critic}}$ then values of standard deviation are not different regarding accuracy, otherwise the statistical difference is occurred.

RESULTS AND DISCUSSION

REPEATABILITY OF BED PACKING

The dependence of heptane mass increase vs. time for capillary tubes with 40, 50, and 60 mm packing height is shown in Fig. 2. The overlapping of curves in the plot indicates good repeatability of bed packing. For the remaining experimental system of wetting liquids and particle beds similar results are obtained.

In order to evaluate the repeatability of bed packing, the increase of liquid mass for packing height of 40 and 50 mm after 5, 10, 20, and 30 seconds are compared by means of the F-Snedecor and t-Student test. The same procedure is repeated for packing height of 40 and 50 mm after 5, 10, 20, 30, and 40 seconds. The obtained results for penetration of heptane into bed A are presented in Table 4.

With significance level of $\alpha = 0.05$, critical values $F_{\text{critic}} = 19$ and $t_{\text{critic}} = 2.776$. From Table 4 it results that for bed heights of 40, 50, and 60 mm the conditions $F < F_{\text{critic}}$ and $t < t_{\text{critic}}$ are satisfied. Hence, the bed packing for these three heights is not statistically different regarding precision and accuracy.

Similar results were obtained for other wetting liquids as well as remaining beds. Hence, the proposed method satisfies the repeatable conditions of packed bed for the capillary rise method.

Table 4. F-test results of bed packing for heptane

Time [s]	Height of bed [mm]			Calculated F for two heights of bed [mm]		Calculated t for two heights of bed [mm]	
	40	50	60	40 i 50	50 i 60	40 i 50	50 i 60
5	n = 3 $\bar{x} = 0.205$ s = 0.0123	n = 3 $\bar{x} = 0.210$ s = 0.0098	n = 3 $\bar{x} = 0.206$ s = 0.0131	1.25	1.33	0.449	0.346
10	n = 3 $\bar{x} = 0.279$ s = 0.0119	n = 3 $\bar{x} = 0.279$ s = 0.0096	n = 3 $\bar{x} = 0.276$ s = 0.0098	1.24	1.02	0.031	0.308
20	n = 3 $\bar{x} = 0.382$ s = 0.0118	n = 3 $\bar{x} = 0.379$ s = 0.0070	n = 3 $\bar{x} = 0.379$ s = 0.0116	1.67	1.64	0.360	0.087
30	n = 3 $\bar{x} = 0.456$ s = 0.0105	n = 3 $\bar{x} = 0.454$ s = 0.0067	n = 3 $\bar{x} = 0.457$ s = 0.0153	1.56	2.28	0.246	0.324
40		n = 3 $\bar{x} = 0.517$ s = 0.0101	n = 3 $\bar{x} = 0.523$ s = 0.0167		1.64		0.411

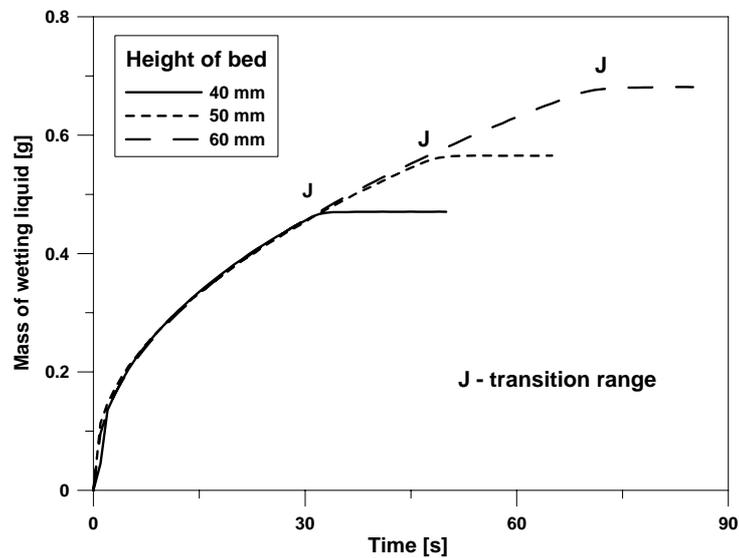


Fig. 2. Mass of liquid penetrating particle bed A vs. penetration time

KINETICS OF LIQUID PENETRATION. A DIFFERENCE OF TIME Δt_{SF} AS A NEW PARAMETER DESCRIBING CAPILLARY SIZE DISTRIBUTION IN POROUS MATERIALS

Fig. 3 shows stages of water penetration into bed A. The liquid front rises uniformly until saturation, so liquid flow through the bed A is even. In order to better observation of liquid penetration into the bed, wetting liquid was dyed by potassium permanganate with concentration of 0.5 g/l.

Particles of bed A are small and have narrow pore size distribution (see Table 2). Therefore, they create the similar space in the column, through which the liquid flow is even.

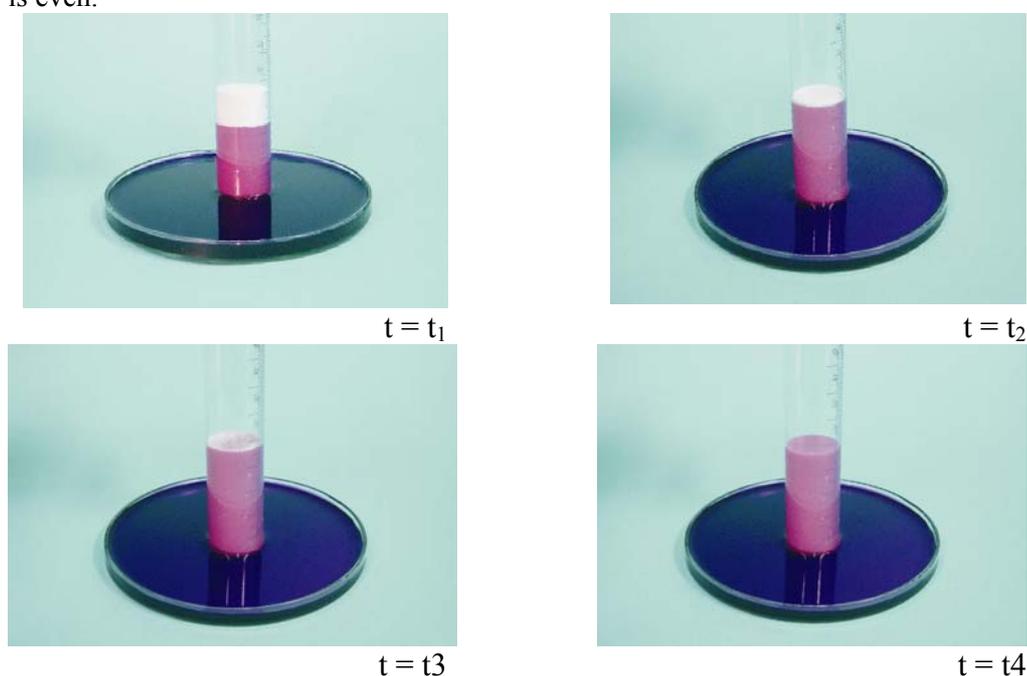


Fig. 3. Gradual penetration of wetting liquid into bed A; t is penetration time, $t_4 > t_3 > t_2 > t_1$

The curve of dependence between liquid mass and penetration time (Fig. 2) is distinguished two stages: penetration and saturation. In the first stage, the liquid mass increases gradually until it reaches a more or less constant value, and in the second one, the liquid mass does not change due to saturation of the bed. In case of bed A, the transition range (J) is short and clear due to even liquid penetration. When liquid rises to the top of the packed bed, it is saturated immediately.

The liquid penetration into bed B was presented in Fig. 4. It can be seen that penetration is uneven. Particles of bed B are larger than A (see Table 2), the spaces in the bed B are uneven, therefore, liquid penetrates capillaries in the bed at different

rates. At the beginning liquid penetrates all of capillaries, then relatively fills quick some and continues to penetrate remaining capillaries. When all of capillaries are filled, the saturation is taken place.

Fig. 5 shows the dependence between heptane mass and penetration time for bed B. It can be seen that transition range between penetration and saturation stages is long, and in case of height of 60 mm, the transition range is gentle and gradual. Particles of bed B are large, so they create diversified capillaries, as a consequence the difference between flow and saturation time is large (for heptane the difference of time Δt_{sf} for bed B for height of 60 mm is equal 25 s, but for bed A – 7 s). The transition range of bed B is long, so in Fig. 5 it can be seen the gentle section. It is in agreement with results of Nishi et al. [31], which prove that the transition range is clearer for higher bulk density of bed, i.e. for smaller and more homogeneous. In case of carbonized fir fibers for bulk density of 31 kg/m^3 transition range is very sharp, while for bulk density of 6 kg/m^3 transition range is not almost observable.

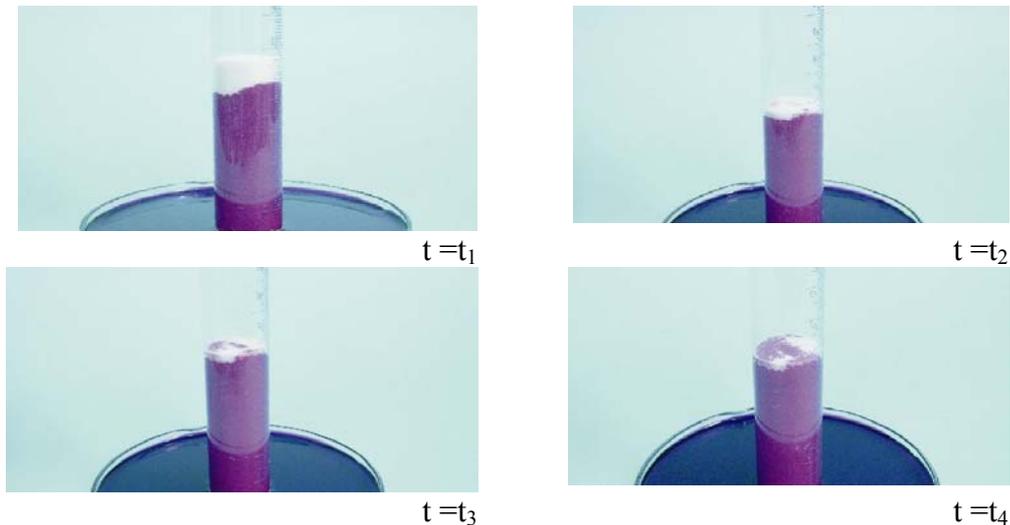


Fig. 4. Gradual penetration of wetting liquid into bed B; t is penetration time, $t_4 > t_3 > t_2 > t_1$

The dependence of heptane mass vs. penetration time for bed C is presented in Fig 6. It results that dependence have an intermediate character between the bed A and B. The bed C is mixture of 50 % bed A and 50 % bed B. Despite of concluding larger particles, transition range for bed C is clearer than that for bed B. In bed C the smaller pore size distribution of $60 - 110 \mu\text{m}$ fills the large space created by larger pore size distribution of $150 - 250 \mu\text{m}$, so created capillaries in bed C are more homogeneous regarding the size than that in bed B.

The difference between flow and penetration time Δt_{sf} is proposed as a new parameter characterizing porous materials. When the kinetic of liquid penetration into bed A, B, and C is analyzed, the following conclusions are made:

1. In case of small particles, the difference of time Δt_{sf} is small. For heptane penetration into bed A with height of 60 mm, Δt_{sf} is equal 7 s. Capillaries, created by small particles, are small and homogeneous regarding the size. To describe this bed, the model of parallel capillaries with the same radius can be used.
2. The large value of Δt_{sf} responses to large particles of bed, for example bed B. Coarse particles create the diversified capillaries regarding the size. The model of parallel capillaries with different radii is used to describe the bed. Liquid penetrates these capillaries at different rates. This causes large Δt_{sf} . For example, the bed B at bed height of 60 mm, $\Delta t_{sf} = 27$ s.
3. The bed with large and small particles characterizes small value of Δt_{sf} . Small particles fill large pores created by large particles, so the pores in this bed are small. These pores are smaller than pores created by large particles only, for example bed C.

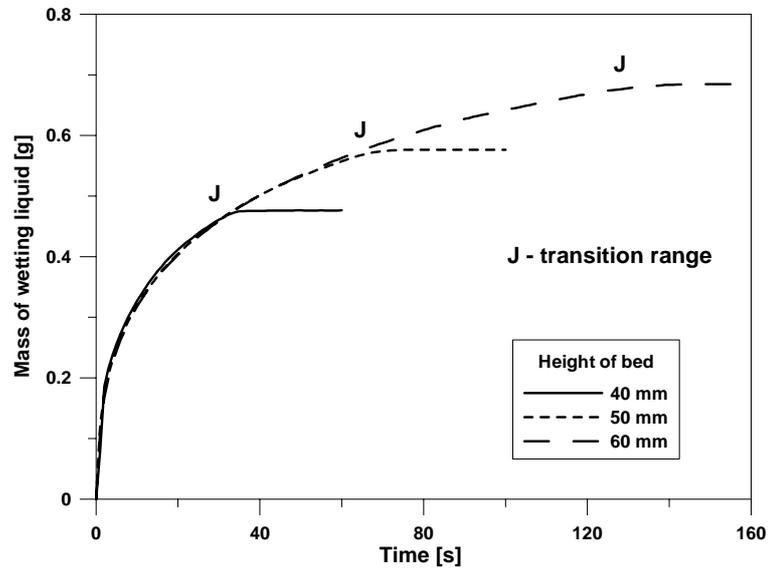


Fig. 5. Mass of liquid penetrating particle bed B vs. penetration time

These observations can be interpreted using Washburn's theory. Considering the liquid penetration into the bed with flow time t_f and saturation time t_s , the Washburn's equation can be rewritten as follows:

$$\frac{h^2}{t_f} = \frac{r_f \gamma \cos \theta_f}{\eta} \quad (16)$$

$$\frac{h^2}{t_s} = \frac{r_s \gamma \cos \theta_s}{\eta} \quad (17)$$

where subscript f and s correspond to the liquid flow to the top of given bed height and its saturation.

Combination of Eq. (16) and (17) leads to:

$$\frac{t_s - t_f}{h^2} = \frac{\eta}{\gamma} \cdot \left(\frac{1}{r_s \cos \theta_s} - \frac{1}{r_f \cos \theta_f} \right) \quad (18)$$

$$\Delta t = h^2 \cdot \frac{\eta}{\gamma} \cdot \left(\frac{1}{r_s \cos \theta_s} - \frac{1}{r_f \cos \theta_f} \right) \quad (19)$$

Assumption of $\cos \theta_s = \cos \theta_f = \cos \theta$, Eq. (19) becomes:

$$\Delta t = h^2 \cdot \frac{\eta}{\gamma \cos \theta} \cdot \left(\frac{1}{r_s} - \frac{1}{r_f} \right) \quad (20)$$

where r_f is radius of quick penetrating capillaries created in the bed, and time needed to fill these capillaries corresponds to flow time t_f , while r_s is radius of slow penetrating capillaries and time needed to fill these capillaries corresponds to saturation time t_s .

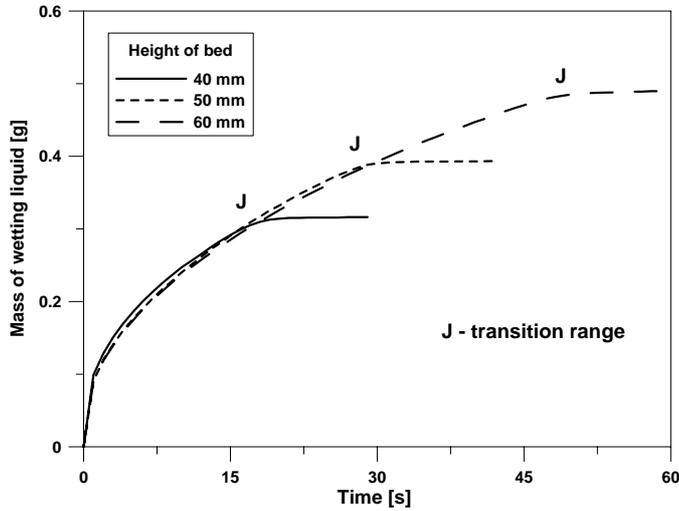


Fig. 6. Mass of liquid penetrating particle bed C vs. penetration time

Particles of bed A are small with narrow pore size distribution, create small and homogeneous capillaries, $r_f \approx r_s$ so $t_f \approx t_s$, as the consequence the difference of flow and saturation time is small.

The lower the bed height, the smaller the Δt_{sf} and the clearer the transition range. In case of bed B, particles are large, created capillaries are heterogeneous and the value of Δt_{sf} is large.

CONTACT ANGLES AND PORE RADIUS

Wettability determination by capillary rise method is based on measurement of mass increasing of capillary tubes filled glass beads, and on plot of dependence of square of mass increasing vs. time. Contact angle values are calculated by means of Eq. (11).

Fig. 7 shows the dependence between square of liquid mass and penetration time for bed A. For all wetting liquids the dependences are linear and in agreement with Washburn's equation.

It is seen from Fig. 7 that water is the fastest penetrating liquid, ethanol – the slowest. Although water faster penetrates than toluene, however toluene was assumed as the reference liquid according to its largest product $\frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma}$. This means that the penetration rate is not proportional (correlational) with wettability of solid due to the complexity effect of viscosity, surface tension, and density of liquid. The slope for toluene was calculated and used to determine C. This value allowed calculating of the contact angles for other liquids according to Eq.(11). Contact angles obtained for other liquids are presented in Table 5.

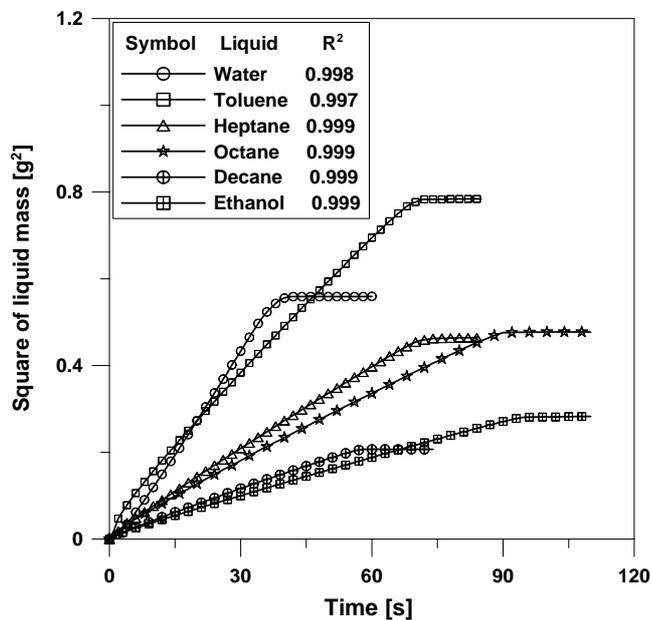


Fig. 7. Dependence of square of liquid mass vs. time for bed A

As show in Table 5, water contact angle on the surface of bed A is smaller than 90°, therefore most researchers agree that the surface is hydrophilic. On the other hand, contact angles for strongly polar water are larger than that for the investigated hydrocarbons which are hydrophobic liquids. Since hydrocarbons even better wet the bed than water. The bed surface represents amphipatic (hydrophobic - hydrophilic) properties.

It also results that the correlation between wettability, surface tension, viscosity, and density of liquid are not observed. The decreasing order of contact angles values: toluene > heptane > ethanol > water is in agreement with findings of Bruil and van Aartsen [12], who studied wettability of aluminium powder. In case of hydrocarbon, it is shown that penetration rate increases and contact angle decreases as a function of the alkane length (number of carbon atoms). This is in agreement with results obtained by other researchers [2, 3, 32-34].

Table 5. Slope and contact angles for bed A

Wetting liquid	Slope	C·cosθ x10 ¹⁶	C	θ [deg]
Water	0.0152	2.1x		44
Toluene	0.0110	3.0	3.0x10 ⁻¹⁶	*
Heptaen	0.0065	2.8		20
Octane	0.0053	2.7		25
Decane	0.0036	2.6		29
Ethanol	0.0030	2.7		27

* Toluene was assumed as reference liquid.

The values of C enables to determine the pore mean radius of bed A. Eq. (12) can be rewritten:

$$r = \frac{2C}{(\pi R_k^2)^2 \varepsilon^2} \quad (21)$$

hence, $r_a = 3.5 \mu\text{m}$

THE EFFECT OF PARTICLE SIZE ON PENETRATION KINETICS AND WETTABILITY

The relationship between liquid mass squared and time for beds B and C is presented in Fig. 8 and Fig. 9, respectively. In case of bed B, which contains coarser glass beads than bed A, the function of heptane and decane is no longer linear. Such influence of the particle size on the kinetics of liquid flow was previously reported by Siebold et al. [17]. This also can be clearly shown in Table 6: the coefficient of determination of heptane and decane for bed B is equal 0.961 and 0.916, respectively.

In case of bed C (see Fig 9) the curves of relationship between square of liquid mass and time for all studied liquids are linear and in agreement with Washburn's

equation. Liquid penetrates bed C more uniformly than bed B, because in bed C small particles of pore size distribution of 60 – 110 μm fill large pores created by larger particle of pore size distribution of 150 – 250 μm, so the pores in bed C are small, and create small capillaries with comparable radii.

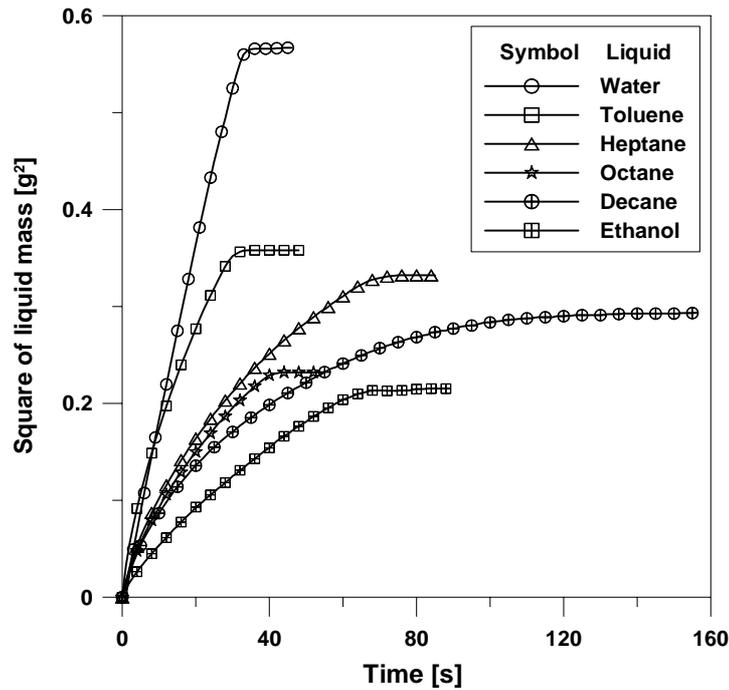


Fig. 8. Square of mass of wetting liquid vs. penetration time for bed B

A mean radius of pore of bed B and C was calculated according to Eq (11), and the results are $r_b = 3.9 \mu\text{m}$ and $r_c = 3.4 \mu\text{m}$. It is shown that $r_b > r_a > r_c$.

Table 6. Slope, coefficient of determination, and contact angles for bed B and C

Wetting liquid	Bed B			Bed C		
	Slope	Coefficient of determination	θ [deg]	Slope	Coefficient of determination	θ [deg]
Water	0.0178	0.9988	38	0.0096	0.9982	54
Toluene	0.0117	0.9776	*	0.0085	0.9989	*
Heptane	0.0047	0.9616	50	0.0050	0.9990	21
Octane	0.0056	0.9765	26	0.0041	0.9938	25
Decane	0.0027	0.9164	52	0.0028	0.9972	28
Ethanol	0.0032	0.9872	27	0.0024	0.9940	23

* Toluene was assumed as reference liquid.

Analogously to case of bed A, for bed B and C toluene has largest product $\frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \gamma}$ and was assumed as the reference wetting liquid. The slope for toluene was calculated and used to determine the constant C for bed B and C. This value allowed calculating of the contact angles of other liquids by means of Eq. (11) and obtained results are presented in Table 6.

The slope of curves and contact angles regarding wetting liquid for bed A and C are identical. The similar results are observed for bed B in spite of heptane and decane. The coefficient of determination of heptane and decane for bed B is very smaller than one, their curves are better described by parabolas. Water fastest penetrates and worst wets bed A and C. In comparing of three beds, the slope for bed B is the largest, and for bed C – smallest, see Table 5 and Table 6.

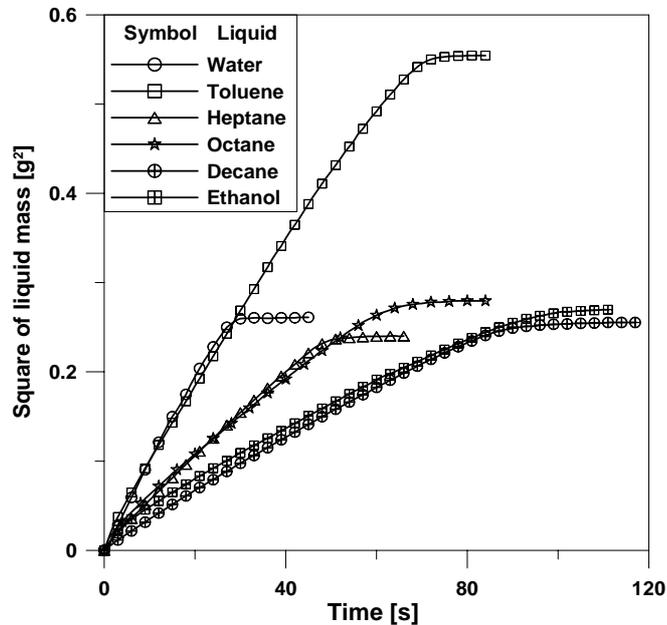


Fig. 9. Square of mass of wetting liquid vs. penetration time for bed C

The radius of bed C, which is mixture of bed A and B, is comparable with radius of bed A. This indicates that in case of mixing of two different pore size distributions of bed, a smaller one plays a key role creating mean radius of the porous bed.

It is seen from Table 5 and Table 6 that the contact angles are changed slightly with the particle size variation. Except water, contact angle of liquids for all beds is comparable within measurement error limits. Therefore, the particle size does not influence on the contact angles. This is in agreement with data presented in literature [5, 13, 28, 29].

It can be seen that studied particle size influences on the penetration rate but not on contact angles. Capillary rise is a comparative method. Contact angles of studied liquids are calculated basing on the contact angle of reference liquid and it depends on penetration rate. Therefore, variation of particle size causes variation of penetration rate of all liquids, including reference liquid.

Labajos et al. [26] interpreted deviation from linearity by choice of coordinate system. When coordinate $h(0), t(0)$ is transferred to other one h', t' , then the new equation rise will be obtained, by means of which the relationship between square of liquid mass and time will be linear. However, these arguments are still discussed and were used only by author et al. [26, 35, 36].

CONCLUSIONS

The Washburn's equation is the useful tool for characterization of porous materials in case of small particles of bed. For the larger particles the application of Washburn's equation is restricted due to uneven liquid rise in the bed and the deviation from linearity of dependence between square of liquid mass and penetration time is observed.

From present study it results that penetration kinetics as well as validation of Washburn's equation depend not only on the particle size but also on the pore size distribution. Addition of fine particles to the bed increases the penetration rate of liquid and improves precision of the measurement. On the other hand, the particle size as well as pores size distribution do not influence on the values of contact angles due to the fundament (comparative) of capillary rise method using Washburn's equation.

A simple procedure of preparing a packed bed was proposed for capillary rise method. It is the first time that the statistics test is used to evaluate the repeatability of packed bed and the obtained results confirm the accuracy of the proposed procedure.

ACKNOWLEDGEMENTS

The investigations were financed by the Polish Committee for Scientific Research within the framework of grant No. and by the Gdansk University of Technology.

REFERENCES

1. Marmur A., Penetration and displacement in capillary systems of limited size, *Adv. Colloid Interface Sci.*, **39** (1992) 13 – 33.
2. Siebold A., Nardin M., Schultz J., Walliser A., Oppliger M., Effect of dynamic contact angles on capillary rise phenomena, *Colloid Surf. A*, **161** (2000) 81 – 87.
3. Kalogianni E. P., Savopoulos T., Karapantsios T. D., Raphaelides S. N., A dynamic wicking technique for determining the effective pore radius of pregelatinized starch sheets, *Colloid Surf. B*, **35** (2004) 159 – 167.
4. van Oss C. J., Giese R. F., Li Z., Murphy K., Norris J., Chaudhury M. K., Good R. J., Determination of contact angles and pore sizes of porous media by column and thin layer wicking, *J. Adhesion Sci. Technol.*, **6** (1992) 413 – 428.

5. Subrahmanyam T. V., Prestidge C. A., Ralston J, Contact angle and surface analysis studies of sphalerite particles, *Miner. Eng.*, **9** (1996) 727 – 741.
6. van Oss C. J., Wu W., Giese R. F., Naim J. O., Interaction between proteins and inorganic oxides – adsorption of albumin and its desorption with a complexing agent, *Colloid Surf.B*, **4**(1995) 185- 189.
7. Wolfrom R. L., Chander S., Hogg R., Evaluation of capillary rise methods for determining wettability of powders, *Miner. Metallurg. Process.*, **19** (2002) 198 – 202.
8. Troger J., Lunkwitz K., Grundke K., Burger W., Determination of the surface tension of microporous membranes using wetting kinetics measurements, *Colloid Surf. A*, **134** (1998) 299 – 304.
9. Desai T. R., Li D., Finlay W. H., Wong J. P., Determination of surface free energy of interactive dry powder liposome formulations using capillary penetration technique, *Colloids Surf. B*, **22** (2001) 107 – 113.
10. Grundke K., Bogumil T., Gietzelt T., Jacobasch H. J., Kwok D. Y., Neumann A. W., Wetting measurements on smooth, rough and porous solid surfaces, *Progr. Colloid Polym. Sci.*, **101** (1996) 58 – 68.
11. Grundke K., Augsburg A., On the determination of the surface energetics of porous polymer materials, *J. Adhesion Sci. Technol.*, **14** (2000) 765 – 775.
12. Bruil H. G., van Aartsen J. J., The determination of contact angles of aqueous surfactant solutions on powders, *Colloid Polym. Sci.*, **252** (1974) 32 – 38.
13. Subrahmanyam T. V., Monte M. B., Middea A., Valdiviezo E., Lins F. F., Contact angles of quarts by capillary penetration of liquids and captive bubble techniques, *Miner. Eng.*, **12** (1999) 1347 – 1357.
14. Prestidge C. A., Tsatouhas G., Wettability studies of morphine sulfate powders, *Int. J. Pharm.*, **198** (2000) 201 – 212.
15. Stuebaker M. L., Snow C. W., The influence of ultimate composition upon the wettability of carbon blacks, *Wettability of Carbon Blacks*, **59** (1955) 973 – 976.
16. Popovich L. L., Feke D. L., Manas-Zloczower I., Influence of physical and interfacial characteristics on the wetting and spreading of fluid on powders, *Powder Technol.*, **104** (1999) 68 – 74.
17. Siebold A., Walliser A., Nardin M., Oppliger M., Schultz J., Capillary rise for thermodynamic characterization of solid particle surface, *J. Colloid Interface Sci.*, **186** (1997) 60 – 70.
18. Wawrzacz B., rozprawa doktorska, Politechnika Gdanska, 1998.
19. Washburn E. W., The dynamics of capillary flow, *Phys. Rev.*, **17** (1921) 273 – 283.
20. Chibowski E., J. Solid surface free energy components determination by the thin-layer wicking technique, *J. Adhesion Sci. Technol.*, **6**, (1992) 1069 – 1090.
21. Chibowski E., Hołysz L., Use of the Washburn equation for surface free energy determination, *Langmuir*, **8** (1992) 710 – 716.
22. Hołysz L., Chibowski E., Surface free energy components of α -alumina from thin layer wicking, *Langmuir*, **8** (1992) 717 – 721.
23. Hołysz L., Surface free energy components of silica gel determined by the thin layer wicking method for different layer thicknesses of gel, *J. Mater. Sci.*, **33** (1998) 445 – 452.
24. Varadaraj R., Bock J., Brons N., Zushma S., Influence of surfactant structure on wettability modification of hydrophobic granular surfaces, *J. Colloid Interface Sci.*, **167** (1994) 207 – 210.
25. Van Brakel J., Heertjes P. M., Capillary rise in porous media. Part I: a problem, *Powder Technol.*, **16** (1977) 75 – 81.
Van Brakel J., Heertjes P. M., Capillary rise in porous media. Part II: secondary phenomena, *Powder Technol.*, **16** (1977) 83 – 90.
Van Brakel J., Heertjes P. M., Capillary rise in porous media. Part III: role of the contact angle, *Powder Technol.*, **16** (1977) 91 – 96.

26. Labajos-Broncano L., Gronzalez-Martin M., Janczuk B., Bruque J. M., Gronzalez-Garcia C. M., Distance-time measurements in capillary penetration: choice of the coordinate system, *J. Colloid Interface Sci.*, **211** (1999) 175 – 177.
27. Hamraoui A., Thuresson K., Nylander T., Yaminski V., Can a dynamic contact angle be understood in terms of friction coefficient? *J. Colloid Interface Sci.*, **226** (2000) 199 – 204.
28. Brown S. C., Oliveira R. C. G., Moudgil B. M., ‘Method for characterizing the wettability of filler particles’ in J. J. Kellar, M. A. Herpefr, B. M. Moudgil, ‘Functional Fillers and Nanoscale Minerals’, Society for Mining, Metallurgy and Exploration, Inc., Colorado USA, 2003, 105 –112.
29. R. Crawford, L. K. Koopal, J. Ralston, Contact angles on particles and plates, *Colloid Surf. A* **27** (1987) 57-64.
30. Yang Y. W., Zografi G., Miller E. E, Capillary flow phenomena and wettability in porous media, II. Dynamic flow studies, *J. Colloid Interface Sci.*, **122** (1988) 35 – 46.
31. Nishi Y., Iwashita N., Sawada Y., Inagaki M., Sorption kinetics of heavy oil into porous carbons, *Water Research*, **36** (2002) 5029 – 5036.
32. Dang-Vu T., Hupka J., Nalaskowski J., (2002) “Important of time evaluation in capillary rise method”, *Materiały The Third International Conference Environmental Technology for Oil Pollution*, 08-11.09.2002, Gdańsk, **2**, 139 – 145.
33. Hupka J., Dang-Vu T., Wersocki S., Badanie osadu czynnego jako sorbentu oleju, *Inżynieria Ekologiczna*, **9** (2003) 145 – 153.
34. Gonzalez-Martin M. L., Janczuk B., Labajos-Broncano L., Bruque J. M., Gonz C. M., Analysis of the Silica Surface Free Energy by the Imbibition, *J. Colloid Interface Sci.*, **240** (2001) 467 – 472.
35. Labajos-Broncano L., Gronzalez-Martin M. L., Bruque J. M., Gronzalez-Garcia C. M., Comparison of the use of Washburn’s equation in the distancOn the use of Washburn’s equ-time and weight-time imbibition technique, *J. Colloid Interface Sci.*, **233** (2001) 356 – 360.
36. Labajos-Broncano L., Gronzalez-Martin M. L., Bruque J. M., Washburn’a equation facing Galileo’s transformation: some remarks, *J. Colloid Interface Sci.*, **253** (2002) 472 – 474.

Dang-Vu T., Hupka J., *Charakterystyka materiałów porowatych za pomocy metody wzniesienia kapilarnego*, *Physicochemical Problems of Mineral Processing*, 39 (2005) 47-65 (w jęz. ang).

Metoda wzniesienia kapilarnego jest szeroko używana dla określenia kąta zwilżania przy wykorzystaniu równania Washburna. Badane były kinetyki penetracji ciał porowatych złożonych z cząstek o różnych wymiarach. Na podstawie przeprowadzonych badań okazało się, że kinetyki penetracji i ważność prawa Washburna zależą nie tylko od wielkości cząstek ale także od dystrybucji wielkości porów. Nie zaobserwowano wpływu wielkości dystrybucji cząstek na zmianę wielkości kąta zwilżania. W przypadku gdy placek składał się z cząstek o szerokiej dystrybucji wielkości, część najdrobniejszych cząstek odgrywa istotną rolę w powstaniu najmniejszych kapilar, które odgrywają istotną rolę w penetracji cieczy. To zjawisko ma wpływ na dokładność w dokładności mierzenia kąta zwilżania. Różnica w czasie jaka wynika z przepływu cieczy przez ośrodek porowaty i je do całkowite nasyceniu cieczą (Δt_{sf}) została zaproponowana jako mowy parametr opisujący rozkład wielkości porów w ciele porowatym. Parametr ten pozwala na szybkie określenie rozkładu wielkości porów oraz dokładne wyznaczenie kąta zwilżania.