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# A novel method for determining surface free energy of powders using Washburn's equation without calculating capillary factor and contact angle

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ABSTRACT

Measuring surface free energy ($\gamma_s$) of powders is important. When liquids are used as test probes, two primary techniques based on Washburn's equation can be used, namely, thin layer and column wetting methods. In the two methods, contact angles of $n$-alkane are assumed to be zero to obtain geometric or capillary factor. However, several researchers believe this assumption is irrational. In this paper, to avoid calculating geometric or capillary factor, an approach for determining $\gamma^d_s$ of powders using Washburn's equation was established and confirmed by measurements for nanosized $SiO_2$, ZnO, and $TiO_2$ powders. When a series of $n$-alkanes was used, a linear relationship was found between square root of alkanes' $\gamma_l$ and measured wetting result of $\frac{w^2}{t}\frac{\eta}{\rho^2}$. This rule was deduced from Washburn's and Fowkes's equations and was supported by the wetting results. It was also found that after obtaining the equation of $n$-alkanes' line, $\gamma^d_s$ of powders could be calculated from the slope and intercept of the line or from $\gamma_l$ of an imaginary alkane. Due to the obtained $\gamma^d_s$ of the powders from the developed method and IGC measurements were almost equal, it was believed that the developed method could be used in determining $\gamma^d_s$ of powders.

## 1. Introduction

Numerous solid materials that are applied in industries can only be used as powders, such as catalysts, additives and pigments. The surface free energy of powders is an important parameter in predicting and understanding some of their properties, such as adhesion, adsorption and catalysis. The surface free energy of a material with flat and smooth surface can be obtained by measuring the contact angle of some liquid sessile drops on the surface [1–4]. However, given that powder samples with flat and smooth surfaces cannot be easily prepared, the contact angle of liquid probes cannot be obtained directly. Measurement of contact angle on compressed pellet of powders is believed to be unreliable [3,4]. To date, only two indirect techniques are commonly used to measure the surface free energy of powders. One technique is powder wetting, which is based on Washburn theory, and the other is inverse gas chromatography (IGC) [5,6].

Washburn's equation was originally used to describe the capillary penetration of liquids, and then it was extended to packed powders, in which it was used to determine the dynamic liquid contact angle by measuring the penetration rate of a liquid into the packed powders [1–3]. The original Washburn's equation is [7]:

$$x^2 = \frac{R_{\mathrm{eff}}\gamma_l\cos\theta}{2\eta}t \tag{1}$$

where $R_{\mathrm{eff}}$ is the effective radius of the interparticle capillaries in the porous packed powders, $\gamma_l$ is the surface free energy of the probe liquid, $\eta$ is the liquid viscosity, and $\theta$ is the wetting contact angle. A linear relation typically exists between the squared wetting distance $x$ in the packed powders and time $t$. Another common form of Washburn's equation is [4,8]

$$h^2 = \frac{cr\gamma_l\cos\theta}{2\eta}t \tag{2}$$

where $h$ is the wetting height, $c$ is the tortuosity factor, and $r$ is the capillary radius. Given that weighing the gained mass using automatic electronic balance is easier than observing the wetting height, Eq. (2) is often changed to the following form [3,9,10]:

$$w^2 = \frac{c\rho^2\gamma_l\cos\theta}{\eta}t \tag{3}$$

where $c$ is the geometric factor and $\rho$ is the liquid density.

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When using Washburn's equation to calculate the contact angle $\theta$ or $\cos\theta$, the first step is to decide the geometric or tortuosity factor. A total spreading liquid is generally used as probe, which can completely wet the surface of the powders. The contact angle of the liquid is taken as zero ($\cos\theta = 1$). Generally, short-chain *n*-alkanes, such as *n*-heptane to *n*-nonane, are used as total spreading liquids. For the same packed powders, when other liquids such as diiodomethane (DI) or α-bromonaphthalene (α-BR) are used as probes, the $\cos\theta$ or $\theta$ and dispersion surface free energy $\gamma^d{}_s$ of the powders can be determined [3].

The rationality of the assumption that the contact angle of *n*-alkanes is zero was discussed in detail by Chibowski [3]. In addition, the contact angles calculated from Washburn's equation are mostly believed to be higher than those measured directly (measured on the smooth surface of the same powders, if a smooth slice could be prepared), which would result in lower and erroneous surface free energy of the powders. Therefore, new theoretical and experimental approaches to solve these problems are being explored [3,8].

IGC is an important technique that is used in measuring surface free energy of powders. The main difference between common gas chromatography (GC) and IGC is that the species of interest is the stationary phase in the IGC column. When a series of *n*-alkanes are used as probes and injected in the column at infinite dilution, the dispersion surface free energy of the solid stationary phase can be calculated from the retention time of these probes [11]. Compared with the contact angle and Washburn technique, the disadvantage of IGC is that the temperature during measurement has to be above room temperature. Therefore, the surface free energy at room temperature has to be extrapolated from the results obtained at above room temperature.

In measuring surface free energy using Washburn's equation, the geometric factor is first measured using *n*-alkanes, and then the contact angles of other liquid probes are measured. The contact angles of *n*-alkanes are assumed to be zero.

To avoid the basic assumption that the contact angles of *n*-alkanes are zero, we explored an approach that determines the dispersion surface free energy of powders through Washburn's equation without calculating the geometric or capillary factor and contact angle. Given that the IGC technique can reflect the surface free energy of powders using only a series of *n*-alkanes as probes, the Washburn's equation method could also reach it with only *n*-alkanes as probes. In this study, the column wetting experiments were performed on a self-made equipment for measurement of the surface free energy of nanosized $SiO_2$, ZnO, and $TiO_2$ powders, with only some *n*-alkanes as probe liquids. IGC was also performed for the same powders to validate the results.

## 2. Method

The developed approach for determining surface free energy of powders without calculating the geometric or capillary factor and contact angle is described in this part. In the published reports about Washburn's method, we found that for the wetting liquids, the effect of gravity force or work is often considered. However, after a brief analysis, we found that the gravitational action could be ignored (see the Appendix A part). This way, for a liquid rising in a packed column, the rising force $F$ induced by the attraction between the liquid and the solid powders is equal to $\gamma_l \cos\theta$, which is also equal to $\frac{1}{c}\frac{w^2}{t}\frac{\eta}{\rho^2}$ according to Eq. (3). When the liquid rises to a height of $dh$, the work ($dw$) done by force $F$ is:

$$dw = F \cdot dh. \tag{4}$$

Because the rising process of the liquid is also the spreading process over the surface of the powders, $dw$ is also named as spreading work, $W_s$. When the gravitational work is ignored, the spreading work is equal to the difference between adhesion work $W_a$ and cohesion work $W_c$, which is $W_s = W_a - W_c$ [3]. When only dispersion surface free energy (dispersion surface tension) exists, $W_a$ is the Fowkes' adhesion work $2\sqrt{\gamma_s^d \gamma_l} \cdot dA$, where $dA$ is the interfacial area between the solid powders and the wetting liquid, $\gamma^d{}_s$ is the dispersion surface free energy of the powders, and $\gamma_l$ is the surface free energy of the liquid. For the rising liquid, because there is no phase change (the liquid doesn't change to vapor) and its volume doesn't change during the rising process, the cohesion work $W_c$ can be neglected when comparing with the adhesion work $W_a$. Therefore, the spreading work will be approximately equal to the adhesion work. Given that a direct positive ratio between $dA$ and $dh$ exists, the following equation can be obtained:

$$\frac{1}{c}\frac{w^2}{t}\frac{\eta}{\rho^2} \cdot dh = c' \cdot \sqrt{\gamma_s^d}\sqrt{\gamma_l} \cdot dA. \tag{5}$$

After taking $1/c$ in the left hand side of the above equation to the right hand side and integrating both sides of the equation, we can obtain the following equation:

$$\frac{w^2}{t}\frac{\eta}{\rho^2} = cc'c'' \cdot \sqrt{\gamma_s^d}\sqrt{\gamma_l} + C \tag{6}$$

where $c''$ is equal to the ratio of the total rising area $A$ and rising height $h$. $C$ is a constant after the integration calculation. The above equation can be simplified as:

$$\frac{w^2}{t}\frac{\eta}{\rho^2} = k \cdot \sqrt{\gamma_l} + I \tag{7}$$

where $k$ is the slope and $I$ is the intercept of an experimental *n*-alkanes' line when a series of *n*-alkanes is used as probe liquids. Fig. 1 shows the developed approach for the calculation of surface free energy of powders using Washburn's equation.

In Fig. 1, $\gamma_l^0$ is the surface free energy of an imaginary alkane, which does not rise as it goes in contact with the packed solid powder. For a real *n*-alkane (e.g. $C_6$–$C_{10}$) with surface free energy of $\gamma_l$, when it contacts with the packed solid powders having the same dispersion surface free energy ($\gamma^d{}_s = \gamma_l$), the *n*-alkane liquid will not rise because the solid is equivalent to the alkane liquid itself. After comparing Eq. (6) with Eq. (3), the parameter $k$ in Fig. 1 can be given such as a physical meaning that is a *dragging* factor of the solid, equaling to the ratio of $\gamma_s$ to $\gamma_l$. Therefore, if the *dragging* factor $k$ equals to 1, $\gamma^d{}_s$ will equal to $\gamma_l^0$. For the general case, the following equation will exist:

$$\gamma_s^d = k \cdot \gamma_l^0 \tag{8}$$

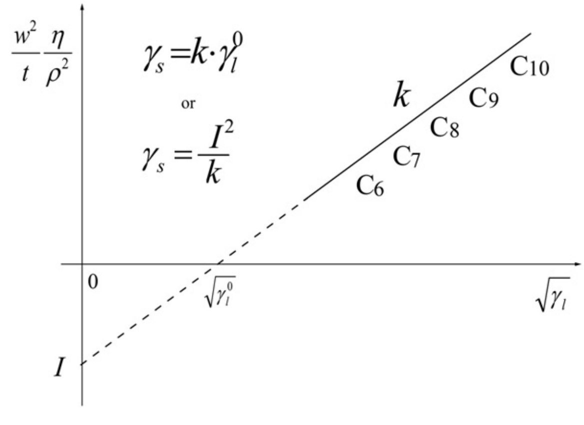

**Fig. 1.** Developed approach for the calculation of surface free energy of powders.