

## **Interfacial Engineering**

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**Lecture-11**

**Washburn approach; Tutorial**

**Washburn equation; non-ideal cases; porous solids; contact angle; capillarity**

Welcome back.

So in today's video lecture, we will look at what is known as Washburn equation. Okay. If you want to measure the contact angle of, let's say, bulk powders, especially porous material, we can use this approach, you know, to determine the contact angle, right So remember, when we derived the Young-Dupré Equation, we made several assumptions, right One of the assumptions we made was no absorbing of liquid by the surface, right So if the surface is smooth and no interwoven in nature, then we can very well apply the Young-Dupré equation. But what if we have to deal with a porous material, bulk powder, which will absorb a certain amount of liquid into it.

In such case, what kind of equation we can use, if not Young-Dupréy. So that is the question that we are addressing today. So in this equation, you can measure the dynamic contact angle of any given porous material as a function of time. Let's begin.

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### Capillary penetration method

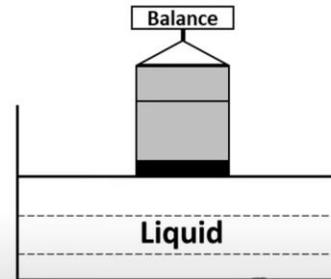
$$\frac{dV}{dt} = \frac{\pi \cdot \Delta p \cdot r^4}{8 \cdot \eta \cdot h}$$

$$dV = \pi r^2 \cdot dh$$

$$\Delta p = \frac{2 \cdot \gamma_{LG} \cdot \cos \theta}{r}$$

Capillary rise

$$h^2 = \frac{t \cdot r \cdot \gamma_{LG} \cdot \cos \theta}{2 \cdot \eta}$$



$\theta$  or wetting of solid required in granulation, pelletization, and coating in pharmaceutical i

Ulrich Teipel, Irma Mikonsaari, Part. Part. Syst. Charact. 21 (2004) 255 – 260

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So, as I mentioned, we can use this capillary penetration method if you want to understand the the contact angle measurements of porous material. The approach is going to be very simple. So one would have to plug this porous material into the capillary tube. And then this capillary tube attached with the micro balance can be carefully placed such that it touches the liquid right. So then what will happen is this liquid molecule will be penetrated inside the porous channels right.

So these porous channels will consist of several porous channels. They will be interconnected three-dimensional network channels. Okay, through these channels, these water molecules will be conducted, will be, you know, absorbed by this porous material. Right, so the approach is you can measure the mass of the uptake, the liquid uptake. Okay, mass of the liquid which is being absorbed by the solid.

right and then by knowing the measurement mass of that liquid can we measure the contact angle okay so this approach is going to be the dynamic approach in which you will have to record the contact angle as a function of time Okay, right. So this is what we are going to use and our very first equation is going to be, you know, a Darcy-Weisbach equation. So that is something we will see shortly. So you will have, you will obtain the equation of this form.

Okay. While deriving, we will have to use this relation, capillary rise, you know, using the capillary rise method, the pressure, the delta P that we developed for the capillarity, using the capillarity approach. And then we'll try to see how we can develop the simple expression as a function of time, right? Right. So, you can ask, where is this approach going to be really helpful? It is very important to know the wetting nature of the solid,

especially when you deal with the, you know, operational life granulation, pelletization. Sometime if you deal with coating of tablets in pharmaceutical industries, the wetting or three-phase contact angle or contact angle of you know the solid the dry powder with the given liquid is very important right. So one would use this approach in these applications right.

So let's try to understand the derivation part of the Washburn equation. So Washburn equation our approach starts with the simple fluid flow to the conduit or pipe. So our starting equation is going to be the Darcy Weisbach equation for any flow to the conduit or pipe. So in this equation when we look at this equation you see that there is something called the friction factor. So we are going to assume a laminar flow. Okay, because the flow is going to be inside the porous channels through the porous channels.

(Time:06:08)

So, it is safe to assume laminar flow. For laminar flow, we know the relation for the friction factor (f),

$$f = \frac{16}{Re}$$

This can also be expressed in another form. Now, when we substitute this relation into the equation, we get:

$$32\mu Lu/d^2$$

This substitution is done by replacing f (friction factor) in the equation with the given relation. For brevity, we denote L as H, because we are considering the flow of liquid

through a capillary tube. Thus, for convenience, we can replace L with H in our calculations.

So in that case, one would obtain the equation, which is popularly known as Hagen-Poiseuille equation. This is we often, you know, I mean, this equation is quite familiar to all of us, right? Right. Right. So from here, how do we depart from here? Okay. So let's write this equation.

(Time:09:08)

We know 32, I heard it,  $\Delta P$  is nothing but:

$$\Delta P = \frac{32\mu HU}{D^2}$$

We can write this equation in terms of U, which is:

$$U = \Delta P D^2 / 32\mu H$$

Now, we can express D in terms of capillary radius (r) as:

$$D^2 = (2r)^2 = 4r^2$$

Thus, substituting this in the equation:

$$U = \Delta P \cdot 4r^2 / 32\mu H$$

So, remember, we are not just talking about a single radius of a capillary tube. If we look at the capillary tube, we have a porous bed containing n number of cylindrical tubes.

Since some cylindrical tubes may be very small and some may be much larger, one must use the statistical average rather than a single capillary radius to account for the variability in porous channels.

So, in such a case, we can say that:

$$\Delta P / 32\mu H$$

All right, so we can also express this in terms of volumetric flow rate, which is very convenient for us. So, we can simply multiply both sides by area (A).

(Time: 11:04)

Washburn approach; Tutorial

$$\frac{dV}{dt} = \frac{\Delta P \times 4r^2}{32 \times \mu \times L}$$

$$dv = \frac{\Delta P \times 4r^2}{32 \times \mu \times L}$$

In that case, one would get:

$$Q = \Delta P \cdot 4r^2 A / 32\mu H$$

Okay, all right. Since this is volumetric flow rate, I can use this as:

$$dv/dt = \Delta P \cdot 4r^2 A / 32\mu H$$

So, in this way, you can see that I can connect these two equations. Now, I have dV on the left-hand side. Then, I will take this time derivative on the right-hand side, and I will simply have dt.

Now, this dV I can write as:

$$A \cdot dh$$

Okay, right. Then, I can simply write this as:

$$\Delta P \cdot 4r^2 A$$

I think when we multiply both sides by area, we have to multiply here as well, which we missed. Kindly correct that.

Right. Okay. So, you can simply have this:

$$4r^4 \pi$$

And here also, you have:

$$\pi r^2$$

Right, yeah, right. So, you will have:

$$4r^4 \pi / 32 \mu h$$

And then dt you have. So, you can cancel  $\pi r^2$ , this you can easily cancel out, so you will have  $r^2$  over there. Then, if you bring this  $h$  here, you will have:

$$h \cdot dh$$

Which is nothing but:

$$\Delta P \cdot 4r^2 t / 32 \mu$$

Okay, all right. So, this I can write as:

$$h^2 / 2 = \Delta P \cdot 4r^2 t / 32 \mu$$

So, yeah. All right. All right. So,  $h^2$ . Now, I want to expand this  $\Delta P$  for capillarity.

We know the capillary rise through a capillary tube. We can write this  $\Delta P$  as:

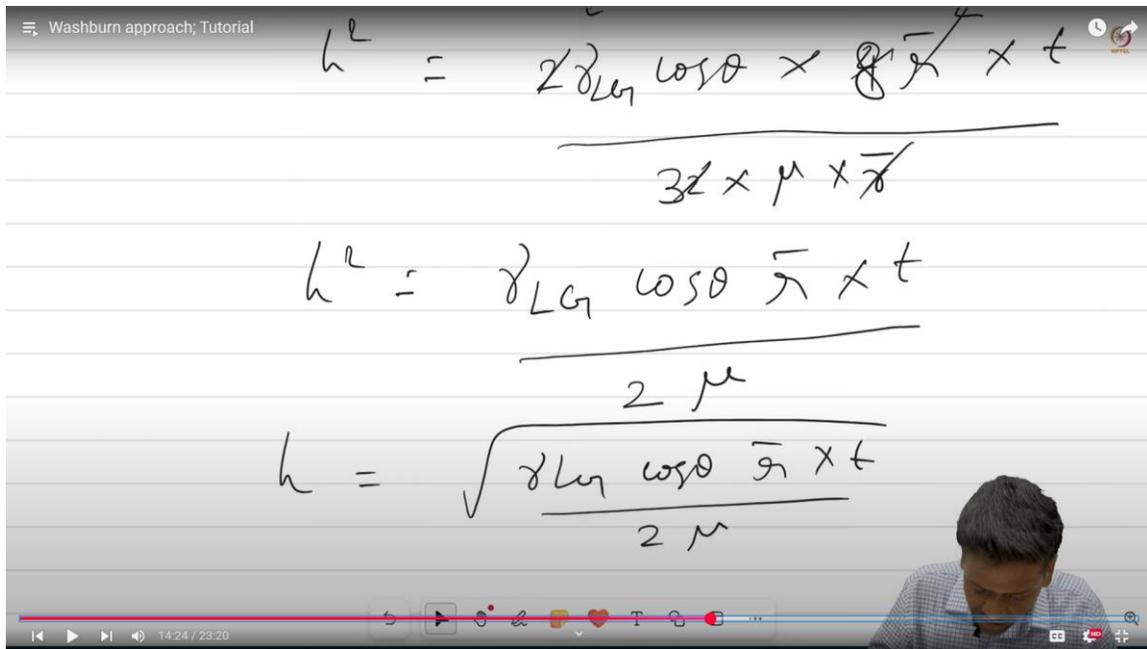
$$\Delta P = 2\gamma \cos \theta$$

Okay, into 8, right. This is going to be:

$$8r^2 t / 32 \mu r$$

Okay, so this is what we have. So, this will be 2, right.

(Time: 14:24)



So,

$$h^2 = \gamma l g \cos \theta \cdot r \cdot t / 2\mu$$

So, this is my equation in terms of h, right.

This is going to be my equation in terms of h, but what is going to be more useful for me is in terms of mass of liquid, so that I can directly calculate the mass using the microbalance, right.

So that is going to be my approach now. How I can do that is:

I know mass is nothing but:

$$m = h \cdot \rho \cdot S$$

So, I know mass squared is nothing but:

$$m^2 = \rho^2 S^2 h^2$$

Okay. So we have this equation already for  $h^2$ .

If I multiply both sides by  $\rho^2 S^2$ , then I can simply substitute that as mass squared, right? So that is what we are going to do now:

$$m^2 = \gamma l g \rho^2 S^2 \cos \theta \cdot r \cdot t / 2\mu$$

This is my new equation. All I need to do is recognize that this is going to be mass squared.

So I have:

$$\gamma l g \cos \theta \cdot \rho^2 S^2 \cdot r \cdot t$$

I'm sorry, this is not  $\bar{r}^2$ . You can correct this to:

$$m^2 \cdot 2\mu / \gamma l g \rho^2 S^2 \cdot r \cdot t$$

So you can see that this equation is in terms of  $t$ , which represents dynamic contact angle, right?

One step further, it is very useful for us to include porosity in the equation so that if you know the porosity, you can directly measure it.

Porosity is defined as:

$$\text{Porosity} = \text{Void Volume} / \text{Total Volume}$$

Or you can also say:

$$\text{Porosity} = S / A_p$$

Which is nothing but  $S$  divided by the projected area.

(Time: 17:17)

The screenshot shows a video player interface with a title bar that reads "Washburn approach; Tutorial". The main content area displays handwritten mathematical equations on a lined background. At the top right, there is a faint equation:  $\gamma L_{cr} \times (\rho S)^2 \times \bar{r} \times t$ . Below it, the following equations are written:

$$\cos \theta = f(\alpha)$$
$$\bar{\epsilon} = \frac{S}{A_p}$$
$$\cos \theta = \frac{m^2 \times 2\mu}{\gamma L_{cr} \times (\rho \bar{\epsilon} A_p)^2 \times \bar{r}}$$

The video player controls at the bottom show a progress bar at 17:17 / 23:20 and various playback icons. A small inset video of a person is visible in the bottom right corner.

If I substitute this over here, I can simply get:

$$\cos \theta = m^2 \cdot 2\mu / \gamma l g \cdot \rho^2 \cdot (\epsilon \cdot A_p)^2 \cdot r \cdot t$$

So if you look at this equation, if you know  $\bar{r}$ , which is the statistical average of capillary radius as a function of time, you can actually get the dynamic measurements of  $\cos \theta$ . This measurement is very useful whenever we deal with granulation, pelletization, and coating, especially in pharmaceutical industries, because in these applications, the measurement of  $\theta$  or the wetting behavior of a solid is very important. So this is going to be my final Washburn equation. We will now try to look at this problem: the determination of heat of immersion based on surface tension and contact angle data.

(Time:20:07)

**Determination of Heat of Immersion from Surface Tension and Contact Angle.**

Estimate the heat of immersion for the system for which  $\gamma$  and  $\theta$  are  $22 \text{ mJ m}^{-2}$  and  $30^\circ$ , respectively, at  $20^\circ\text{C}$ . The temperature variations of  $\gamma$  and  $\cos \theta$  are  $-0.10 \text{ mJ m}^{-2} \text{ K}^{-1}$  and  $0.0010 \text{ K}^{-1}$ , respectively. These values are close to those observed for liquid alkanes on Teflon.

$$\Delta H_{im} = -\gamma_{LV} \cos \theta + T \cos \theta \frac{d\gamma_{LV}}{dT} + T \gamma_{LV} \frac{d(\cos \theta)}{dT}$$

The screenshot shows a video player interface with a red progress bar at the bottom. The video title is 'Washburn approach; Tutorial' and the current time is 20:07 / 23:20. The video content includes a problem statement and a handwritten equation in red ink. The equation is  $\Delta H_{im} = -\gamma_{LV} \cos \theta + T \cos \theta \frac{d\gamma_{LV}}{dT} + T \gamma_{LV} \frac{d(\cos \theta)}{dT}$ . A small inset video of a person is visible in the bottom right corner of the video player.

So, this is based on the application of Young-Dupré, which we derived in the previous class. In this problem, some data have been given already. We know:

- The surface tension,  $\gamma_{LV}$ , is  $22 \text{ mJ/m}^2$ , contact angle  $\theta = 30^\circ$ , temperature  $T = 293 \text{ K}$
- The variation of  $\gamma_{LV}$  with temperature is  $-0.10 \text{ mJ/m}^2 \cdot \text{K}$
- The variation of  $\cos \theta$  with temperature is  $0.0010 \text{ per K}$

This is for the case of liquid alkane on Teflon.

Let's start with our governing equation for  $\Delta H_{immersion}$ :

$$\Delta H_{immersion} = \gamma_{LV} \cos \theta + T \left( \frac{d\gamma_{LV}}{dT} \cos \theta + \gamma_{LV} \frac{d(\cos \theta)}{dT} \right)$$

Now, plugging in the given values:

$$\Delta H_{\text{immersion}} = (-22 \times 10^{-3}) \cos 30^\circ + 293((-0.10 \times 10^{-3}) \cos 30^\circ + (22 \times 10^{-3} \times 0.0010))$$

Adding all terms together:

$$\Delta H_{\text{immersion}} = -19.05 - 25.374 + 6.446 = -38 \text{ mJ/m}^2$$

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Washburn approach; Tutorial

Tutorial

$$\Delta H_{im} = -\gamma_W \cos \theta + T \cos \theta \frac{d\gamma_W}{dT} + T \gamma_{LV} \frac{d \cos \theta}{dT}$$

$$= -22 \times 10^{-3} \times \cos(30) + 293 \times \cos(30) \times (-0.10) \times 10^{-3} + 293 \times 22 \times 10^{-3} \times 0.0010$$

$$= -19.05 + (-25.374) + 6.446$$

$$\Delta H_{im} = -38 \text{ mJ/m}^2 \Rightarrow \checkmark$$

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Thus, the heat of immersion for this problem is  $-38 \text{ mJ/m}^2$ . This method, based on Young-Dupré, helps in understanding heat of immersion calculations. This is particularly useful in applications like granulation, pelletization, and coating. While microcalorimetry can measure the heat released during these operations, this theoretical approach can complement the calorimetry data.

We will stop here and continue in the next lecture.

Thank you.