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Determination of Contact Angle Measurement of Sub-bituminous and bituminous Coal Particles through Capillary Rise Method Using Washburn Equation for Surface Free Energy and Interfacial Energy

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Abstract
This study presents Determination of Contact Angle Measurement of Sub-bituminous and Bituminous Coal Particles through Capillary Rise Method Using Washburn Equation for Surface Free Energy and Interfacial Energy. This study aided in determination of Contact Angles of Sub-bituminous and bituminous Coal. The Lucas-Washburn equation was used to determine the contact angles θ = 64.8˚ for sub-bituminous coal and θ = 68.66˚ for bituminous coal. The coals were ground dry with a milling machine into powder form and sieved with seven standard sieves of size ranges 75µm - 850µm. The sieved coal powders and 50% ethanol/water concentrate were used for capillary rise experiment. Washburn equation was adopted for measurement of contact angle; the slope (m) of the graph between the height (H_d^2) of liquid rise and the time (t) taken for the liquid to rise, the viscosity of the liquid (η), the capillary radius (r), and the surface tension of the liquid (γ_{lv}) were used for the determination of contact angles. The values of the contact angle shows that the two materials are nonpolar materials and hydrophobic solids that are characterised by covalent and weak molecular bonds.

Keywords: free energy; capillary; contact angle

1. Introduction
Engineers do not have enough information on the surface free energy in coal. Binding agents agglomerate fine loose particles by adhesion. In most cases, hydrophobic condition is preferable because they form material bridge between the particles. Depending on the application, binders can increase the energy content of the agglomerates/briquette. Though the increase in energy might be desirable, binders should be cost effective and readily available. The optimum binder combination for mechanical properties, operational cost and availability are molasses, ethanol and line. Nevertheless, any of these binders can be used to achieve effective agglomeration. In this work, ethanol of 50% concentrations was used as binder.
Agglomeration improves some mechanical properties of coal and enhances its handling. The phenomenon of agglomeration usually involves wetting, spreading, nucleation, consolidation and coalescence. The moist agglomeration process is realized through a series of four states of pendular, funicular, capillary and droplet.
As world energy crises deepen, efficient management of energy resource is imperative. This work will investigate the Investigation into the Surface Free Energy (interfacial energy) of Sub-bituminous and bituminous Coal using Ethanol/Water Mixture

1.1 Viscosity (μ) of Ethanol/Water mixture
Ostwald viscometer was used to determine the viscosity of the liquid used in this experiment. This, essentially, consists of a capillary tube down which a known volume of ethanol solution was allowed to flow under gravity. The time taken for this flow was measured (t_1) and also that of the solvent (t_0); the relative is then given by:

$$\mu_{rel} = \mu_1 / \mu_0 = (t_1/t_0) * (\rho_1 / \rho_0) \quad (1)$$

Fig 1: Oswald viscometer

1.2 Characterization of Solid Surface
Measurements of surface tension yield data which directly reflect thermodynamic characteristics of the liquid tested. Measurement of contact angles yield data which reflect the thermodynamics of a liquid/solid interaction. To characterize the wetting behavior of the coal particles the contact angle need to be reported. The solid is tested against a 50% of ethanol-water mixture and contact angles were measured.

1.3 Contact Angle Techniques
Two different approaches are commonly used to measure contact angles of non-porous solids. They are goniometry

and tensiometry. Goniometry involves the observation of a sessile drop of test liquid on a solid substrate. Tensiometry involves measuring the forces of interaction as a solid is contacted with a liquid.

The primary focus of contact angle studies is in assessing the wetting characteristics of solid/liquid interactions. Contact angle is commonly used as the most direct measure of wetting. Other experimental parameters may be derived directly from contact angle and surface tension results.

2. Experimental

2.1 Materials

The coal particles used in this work are from Sub-bituminous and bituminous coal. They were obtained from Enugu State and Lafia-Obi, Nasarawa State, Nigeria, respectively. The fact that cost, handling, supply reliability and accessibility are location dependent; 50% ethanol-water mixture was selected as a good binder and for use in this capillary experiment because of its properties [1, 2] and criteria [3, 4] for binder's selection.

2.2 Methods

The Sub-bituminous and bituminous coal were ground dry with a milling machine into powder form and the size distribution was carried out with standard mechanical shaker Octagon 2000. The shaker comprises size range of 75µm, 150, 212µm, 300µm, 425µm and 850µm meshes.

2.3 Oswald viscometer Experimental Method

1. Ostwald viscometer
2. Water bath at 25 ˚C Seven concentrates of ethanol
3. Stop watch accurate to at least 0.1s.

The viscometer was rinsed with distilled water and the solution and it was placed in position in the water bath by carefully clamping one limb. It was checked with plumb line to ensure that it was vertical and exactly 35cm^{3}of ethanol was introduced (or the volume marked on the viscometer) at 29.6 ˚C into the right opening with a syringe or pipette. Left for about 5 minutes to equilibrate, then positive pressure was applied to the right opening or gently suction from the left opening until the meniscus rises above the upper graduation mark left opening. The experiment was repeated until the flow times agree within 0.2s; the average flow time was then calculated. The experiment was repeated with water as a standard solvent alone t_o and then with the ethanol solution (t_1). The relative viscosities were calculated from the flow time.

Table 1: Experimental Data

S/N	Items	Values	Source
1	Quantity of liquid	35cm^3	-
2	Atmospheric temp.	25˚C	-
3	t_o is standard time of flow of water	23.72 s	-
4	Surface tension of water at 25ºC	71.97mNm^{-1}	[5]
5	Surface tension of ethanol at 20ºC	22.52mNm^{-1}	[6]
6	Viscosity of water at 25ºC	8.94mPa-s	[7]
7	Viscosity of ethanol at 25ºC	1.074mPa-s	[8]

Table 2: Ethanol/Liquid Viscosity and Surface Tension Test Result

S/N	Liquid/Ethanol Concentrate %	Density (ρ) g/cm^3	Viscosity (μ) at 25^{0}C mPa-s	Mass of % Liquid/ Ethanol Mixture (g)	Volume of % Liquid/ Ethanol Mixture (cm^3)	Surface Tension at 20^{0}C (N/m)
1	50% Ethanol – water	0.920	0.984	32.21	35	47.635

2.4 Test Procedure of Measuring Contact Angle using capillary rise Technique

For powdered samples, capillary rise technique is widely used [9, 10].

- A known volume (10ml) of liquid (50% Ethanol) was poured into a cylindrical beaker
- A capillary tube was closed with a filter paper at the bottom of the tube and parked with different sizes of coal particle samples to be examined.
- The bottom of the parked capillary tube was then immersed in the liquid and at the time starting the stop-watch.
- The liquid rises to maximum height of the tube as a result of some capillary effects between the particles within the tubing and the stop-watch reading was taken.
- The distance; H_d, travelled by the liquid as a function of time t was measured.
- If one knows the mean radius r of the capillaries present in the tubing, he can calculate the contact angle using the Washburn equation [11, 12].
- The Lucas-Washburn equation for the permeation of liquid in a horizontal cylindrical capillary is given as:

$$H_d^{\ 2} = \frac{r\gamma_{lv}\,Cos\theta}{2\eta}\ t \quad (2)$$

Where; H_d = distance penetrated by the liquid in cm

r = the capillary radius in mm

γ_{lv} = the surface tension of the liquid in mJ/m^2

t = time of liquid rise in seconds s

θ = the contact angle between the liquid and the capillary surface in º

η = the viscosity of the liquid

Note: From the experiment carried out, a graph of $H_d{}^2$ against t was plotted to determine the value of contact angle θ:

Where;

$$\frac{r\gamma_{lv}Cos\theta}{2\eta} = slope\ (m)$$

Making $Cos\theta$ the subject of the formula,

$$r\gamma_{lv}Cos\theta = 2\eta m$$

$$Cos\theta = \frac{2\eta m}{r\gamma_{lv}}$$

To calculate θ;

$$\theta = Cos^{-1}\frac{2\eta m}{r\gamma_{lv}}$$

This implies that; $r = 2.43mm = 0.00243m$

$$\gamma_{lv} = 47.64\ mJm^2$$

$$\eta = 0.984\text{mPa} - \text{s}$$

Note: density and γ_{lv} are not constant for all concentrates. They are with respect to the respective liquid concentrations as the case may be, as can be seen in table 2. And because the 50% concentrate of ethanol-water mixture was only used for the capillary rise experiment because of its binding strength, all the related values are applied in this Lucas-Washburn equation.

Table 3: Contact Angle Measurement result for sub-bituminous coal

S/N	Particle size (μm)	Height of Material (cm)	Volume of Material in Beaker (ml)	Height of Liquid in Beaker (cm)	Volume of Liquid in Beaker (ml)	Height of Liquid Rise H^2 (m)	Time of Rise (s)
1	75	6.7	1.63	1.5	10.0	0.00	0.0
2	150	11.1	2.7	1.5	10.0	0.20	2.0
3	212	9.3	2.3	1.5	10.0	0.45	12.0
4	300	8.8	2.17	1.5	10.0	0.55	20.0
5	425	9.0	2.2	1.5	10.0	0.65	90.0
6	600	9.0	2.2	1.5	10.0	0.65	95.0
7	850	10.5	2.6	1.5	10.0	0.65	100

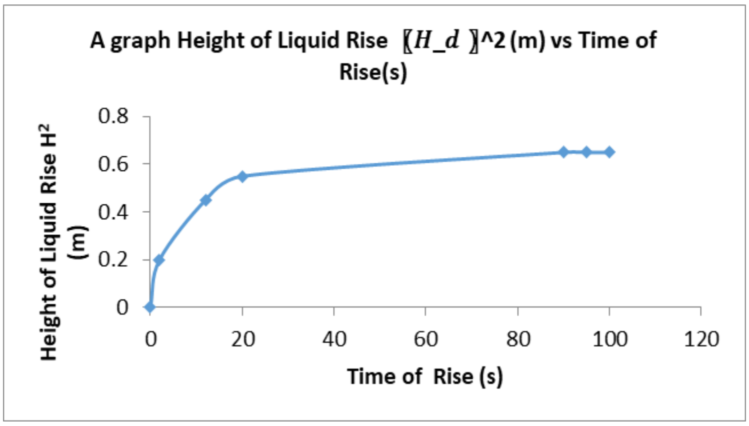

Fig 2: A graph of height of liquid rise ($H_d{}^2$) vs time of rise (s) of sub- bituminous coal

Slope (m) for sub-bituminous coal = 0.025

$$Cos\theta = \frac{2x0.984x0.025}{0.00243x47.64}$$

$$Cos\theta = 0.4249$$

$$\theta = 64.8^{\circ}$$

Table 4: Contact Angle Measurement result for bituminous coal

S/N	Particle Size (μm)	Height of Material (cm)	Volume of Material in Beaker (ml)	Height of Liquid in Beaker (cm)	Volume of Liquid in Beaker (ml)	Height of Liquid Rise H^2 (m)	Time of Rise (s)
1	75	4.4	1.1	1.5	10.0	0.00	0.0
2	150	8.8	2.2	1.5	10.0	0.25	2.0
3	212	9.3	3.25	1.5	10.0	0.55	15.0
4	300	6.5	1.6	1.5	10.0	0.65	20.0
5	425	12.5	2.0	1.5	10.0	0.75	30.0
6	600	13.0	3.15	1.5	10.0	0.85	90.0
7	850	10.5	2.6	1.5	10.0	0.85	90.0

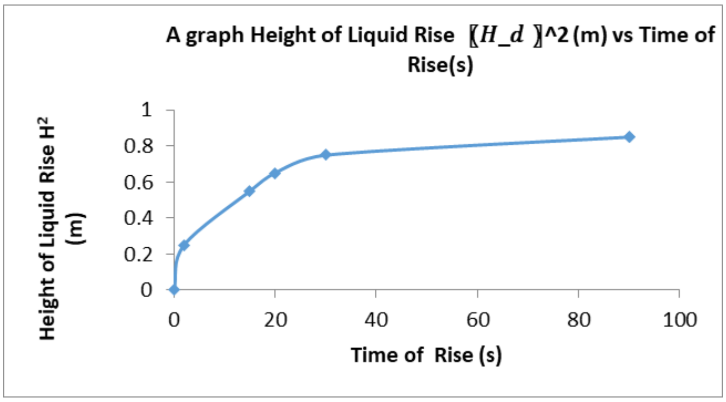

Fig 3: A graph of height of liquid rise (H_d^2) vs time of rise (s) of bituminous coal

Slope (m) for bituminous coal = 0.0214

$$Cos\theta = \frac{2x0.984x0.0214}{0.00243x47.64}$$

$$Cos\theta = 0.3637$$

$$\theta = 68.66^{\circ}$$

a) Pictures of Capillary Rise Experiment of sub-Bituminous coal

Fig 4: Height of liquid rise in 75µm

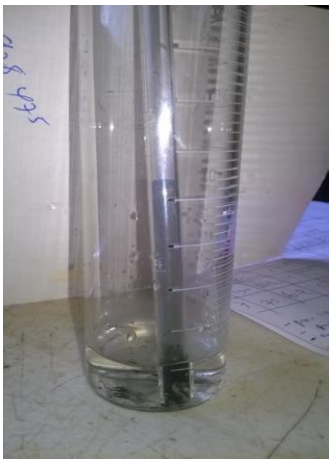

Fig 5: Capillary experiment of 75µm

b) Pictures of Capillary Rise Experiment of Bituminous coal

Fig 6: Height of liquid rise in 75µm

Fig 7: Capillary experiment of 75µm

3. Results and Discussions

The measured contact angles are $\theta = 64.8^{\circ}$ for sub-bituminous coal and $\theta = 68.66.74^{\circ}$ for bituminous coal. These values show that the liquid did not completely wet the solid because according to literature [14], in the case of complete wetting (spreading) the contact angle is 0º. Between 0º and 90º, the solid is wet table and above 90º it is not wet table. Surface of coal contains lots of impurities like sulphur, carbon, hydrogen, oxygen and some other minerals, etc.

With these, one could expect coal to be of a high energy solid. However, if carbon contents are greater than the supposed impurities, one would probably have portions that are of low energy. Therefore, these values of θ using ethanol-water mixture on coal powder show that surface free energy of the both coal for high energy solid surfaces does exist. Hence, carbon contents are presumed to be greater than the supposed impurities.

3.1 Effect of Contact Angle

The angle of contact between a liquid and a solid is a measure of the tendency for the liquid to spread over or wet the solid surface. The higher the contact angle, the tendency for the liquid not to wet the solid completely and the lower the contact angle, the greater the tendency for the liquid to wet the solid, until complete wetting occurs at an angle of zero degrees. In all cases the contact angles θ for sub-bituminous coal ≈ 64.8º and 68.66º for bituminous coal. These higher values indicate that complete wetting of the powder did not take place.

During the determination of surface tension of concentrates of ethanol/water mixture, it was observed that as the percentage of the concentrates increases, the surface tension of the resulting liquid decreases tending towards that of the particle material and may eventually become less than that of the particle [15]. At high ethanol concentration (and hence low liquid surface tension) the resulting liquid spreads very easily over the particle and may therefore wet the particle the more which may lead to an increase in pore saturation. The results of the contact angle show that coal is known to absorb moisture partially. This is another indication that the absorption of the bridging liquid into the particles may subsequently lead to swelling softening of the particles during agglomerate formation [15].

According to [16], Solids that have a surface energy higher than water are called hydrophilic solids, whereas those having surface free energy lower than water are called hydrophobic solids. Low surface free energy solids are not readily wetted by water. Minerals can be classified into nonpolar and polar types based on their surface hydrophobic properties. Nonpolar minerals such as talc, sulfur, coal, graphite, diamond, and molybdenite are hydrophobic solids that are characterized by covalent and weak molecular bonds. Nonpolar minerals are the group that possesses poor wettability by water and high hydrophobicity. The contact angles of water on these solids surfaces ranges from 60° to 90°; consequently, they possess natural floatability.

4. Conclusion

The contact angles $\theta = 64.8^\circ$ for sub-bituminous coal and $\theta = 68.66^\circ$ for bituminous coal measured with the Lucas-Washburn equation using ethanol-water mixture and coal powder on capillary rise experiment shows that surface free energy of the both coal for high energy solid surfaces does exist.

Hence, the contact angles measured for the both coal show that sub-bituminous and bituminous coal are high energy solids surfaces.

This research concludes that sub-bituminous and bituminous coal are high energy solid surfaces. The contact angles of water on these solids surfaces ranges from 64.8° to 68.66°. Hence, carbon contents are presumed to be greater than the supposed impurities.

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