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Surface characteristics of coal-oil agglomerates in the floc regime

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the ions generated at molecular – CH_3 and 115 atomic mass units. Very little incorporation of label was identified in naphthalene itself, so this compound must be formed by polymerization of two C_5 units of pyridine. Firm conclusions as to whether methyl is incorporated into alkanes could not be drawn since the molecular ions were so weak. No label was identified as lower molecular weight homologous alkane fragments of the molecular ions, suggesting no incorporation, but some unexplainable differences were observed in other ion fragments.

The ^{13}C NMR spectra (Figure 2a,b) of the volatile products showed clear evidence for selective incorporation to certain CH_3 groups at 14, 19.9, 21.3, and 22.6 ppm. These assignments were confirmed by GASPE spectral editing experiments.[5]

After labeling, the less volatile products (Figure 2c,d) also showed more prominent resonances at 14, 15.7, 19.5, 22.1, 36, 37.8, 115, 126, and 128 ppm. The 115 ppm resonance could be assigned to an aromatic carbon ortho to amines,[12] which strongly suggests that the incorporation of label into pyridine occurs ortho. Through this mechanism nitrogen is removed from aromatic rings and eventually lost, with the production of ammonia.

Appendix. Corrigenda to Part 1[2]

Page 547. Sentences 3 and 4 of the Appendix should read as follows:

The moles of $^{13}C + ^{12}C$ added in the labeled experiment are approximately equal to the number of moles of $^{13}C + ^{12}C$ added in the unlabeled experiment; i.e., moles of $^{13}C + ^{12}C$ added in the unlabeled experiment equals $100y/1.1 \times 12$. Similarly, moles of $^{13}C + ^{12}C$ added in the labeled experiment equals $100z/30 \times 12.3$.

$$\therefore y = (1.1z/30) \times 12/12.3 \approx 1.1z/30$$

Registry No. Tetralin, 119-64-2; naphthalene, 91-20-3; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; 2,6-dimethylnaphthalene, 581-42-0; *N*-methylpyridinium iodide, 930-73-4; *cis*-decalin, 493-01-6; *trans*-decalin, 493-02-7; diphenylmethane, 101-81-5; diphenylethane, 38888-98-1; diphenyl ether, 101-84-8; pentadecane, 629-62-9; pyridine, 110-86-1; aniline, 62-53-3; benzene, 71-43-2; methylcyclohexane, 108-87-2; toluene, 108-88-3; xylene, 1330-20-7; benzylcyclohexane, 4410-75-7; hydrogen iodide, 10034-85-2; methyl iodide, 74-88-4; 1,5-dimethyltetralin, 21564-91-0; 6-methyltetralin, 1680-51-9; methylnaphthalene, 1321-94-4.

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[12] Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972.

Surface Characteristics of Coal–Oil Agglomerates in the Floc Regime[§]

K. Darcovich,*,[†] C. E. Capes,[‡] and F. D. F. Talbot[†]

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4, and Chemical Engineering Section, Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6

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Reduction of the amount of wetting phase used in the oil agglomeration process for advanced coal cleaning and utilization technologies is important to the economics of the process. This paper reports on the agglomerate surface properties and on the size enlargement characteristics and possible mechanisms of the process taking place when a few percentages of oil are used in oil agglomeration and floc-type coal agglomerates are formed. Since this product exists not as dense agglomerates but only as small aggregates of a few particles, the adhesion technique was used to determine the surface properties of agglomerates made from a high-purity coal. The surface properties closely matched those of the oil at agglomerate oil levels above 2% by weight. Particle size measurements by laser diffraction were then correlated to the surface properties as a function of the oil level and of agglomerate particle packing.

1. Introduction

Agglomeration processes bring together fine powders into larger masses in order to improve powder properties. In conventional coal mining procedure, much of the fine coal (typically–100 mesh) is rejected with tailings as it is impractical to recover it. Due to the heterogeneous nature of coal, smaller particles tend to be individually richer in either ash or carbonaceous matter compared to the overall composition of the coal. This discretization facilitates effective separation. The tailings are handled in water slurry form, and in an agglomeration/separation treatment, an immiscible oil phase (usually any liquid hydrocarbon of size C_7 or greater) is added under high-shear mixing conditions to enhance surface wetting. The oil selectively adheres to the carbonaceous surfaces and also acts as a bridging liquid to consolidate several oiled coal particles into an enlarged agglomerate. The ash is excluded and is separated via screening or by selective bubble flotation.[1–3]

[§] NRCC Contribution No. 29784.

[†] University of Ottawa.

[‡] National Research Council of Canada.

(1) Capes, C. E.; Coleman, R. D.; Croteau, S.; Jonasson, K.; Thayer, W. L. Agglomerate Recovery Methods and Yield–Impurtiy Relationships in Oil Agglomeration. Presented at the Coal Liquid and Alternative Fuel Technology Meeting, Halifax, NS, Canada, Sept 29–Oct 3, 1986.

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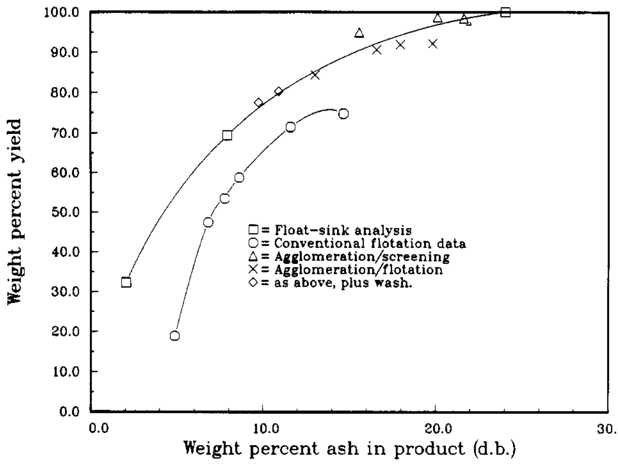

Figure 1. Yield–ash results for a minus 28 run of mine coal from Pennsylvania (wt % reagent levels based on feed solids).

Table I. Proximate Analysis of Devco Metallurgical Coal (wt %, Dry Basis)

moisture	3.23
volatiles	40.57
ash	2.09
fixed carbon	57.34

Yield–ash results are shown for the agglomeration flotation of a Pennsylvania coal in Figure 1.[4] The results compare well with other recovery methods.

The agglomerate flotation technique has been known since the turn of the century,[5] but to date, there is a considerable gap in understanding of the fundamentals involved. Since the coal–oil agglomerates in this context are a product of an upstream formation process, the material properties of the system are more or less fixed, and work has shown that such properties are favorable for flotation.[6] Flotation performance depends on both hydrodynamic and surface chemical interactions.[7,8]

Thus, it is the objective of this study to investigate the surface properties and their influence on the bonding structure for coal–oil agglomerates. These data would then be used for subsequent work on their flotation properties.

2. Experimental Section

The coal selected for this work was a high-grade metallurgical coal provided by the Cape Breton Development Co. It contains very little ash and hence can be used as is to study its agglomeration properties. The proximate analysis of the coal is given in Table I.

2.1. Agglomerate Preparation. Prior to making any surface property measurements, the procedure for agglomerate preparation was to be established.

It was found that the conventional laboratory technique for agglomeration using Waring Blendors introduces a substantial amount of air into the agglomerate structure. This complicates the study of the surface properties. This problem has been recognized[9] but has not been addressed in a surface property or flotation study. It was found that agglomeration under vacuum in a magnet-stirred baffled flask produces suitable glomerates. Hexadecane (n-$C_{16}H_{34}$) was selected as the agglomerating oil as it is a pure substance, and hence well characterized, and it is of the same boiling range of some of the fuel oils that are used industrially. n-$C_{16}H_{34}$ should contribute only dispersive surface forces.

Table II. Polymer Film Substrate Properties

substrate material	θ_c with water, deg	γ_{SV}, dyn/cm
polystyrene, Dow Chemical (T-1000)	93.7	26.5
sulfonated polystyrene, Dow Chemical (T-1101)	25.6	66.1
polyethylene, Fischer (Polygloves)	83.0	33.2
poly(ethylene terephthalate), Hoechst (Hostaphane 2000)	69.1	41.8

Table III. Suspending Liquid Composition and Surface Tension

vol % CH_3OH	γ, dyn/cm	vol % CH_3OH	γ, dyn/cm
0.0	72.5	51.0	35.0
9.0	59.8	95.0	24.2
24.0	47.0		

Agglomerates were prepared at a 10% pulp density. The coal (density = 1.3 g/cm^3) was mixed with distilled water and stirred under vacuum for about 90 min to remove any air from the system. After deairing, the required volume of hexadecane was added and the mixing continued for a further 30 min to form the agglomerates. It was found by sizing measurements that the agglomerates grow to a maximum size at a given oil level within 30 min. Agglomerates were prepared at hexadecane levels ranging from (based on weight percent of coal) 0.25% to 10.0%.

2.2. Surface Tension Measurements. The surface properties of the agglomerates were determined by the adhesion technique.[10,11]

Briefly, this technique involves measuring the extent of particle adhesion to various solid substrates as a function of the composition (surface tension) of the suspending liquid. A water–methanol system was used, since hexadecane is immiscible across their entire binary composition range.[12] Thus the agglomerate structure is not interfered with. Surface tensions of binary water–methanol mixtures span possible coal and/or oil surface tensions. For cases where the surface tension of the suspending liquid is greater than the particle surface tension, $\gamma_{LV} > \gamma_{PV}$, adhesion should decrease with substrate surface tension γ_{SV}, and when $\gamma_{LV} < \gamma_{PV}$ the opposite pattern is predicted. For the case where $\gamma_{LV} = \gamma_{PV}$ the change in free energy due to particle adhesion is zero. Adhesion occurs when a particle–solid interface forms replacing previous particle–liquid and solid–liquid interfaces. That is, eq 1 would indicate that this change would be energetically favorable. It may be helpful to think of the surface tension quantities as surface free energies that tend to a lowest energy state.

Thus, plotting extent of adhesion vs γ_{SV} with γ_{LV} as the parameter give lines of varying slope. Plotting the slopes vs the respective γ_{LV} gives γ_{PV} at slope = 0. That is, this zero sope implies that since both the particles and liquid have the same surface tension, they will have an identical affinity to form the interface with the substrate. The resulting measured adhesion is a function of other forces only.

The adhesion method surface tension measurements were carried out as described below.

Four different polymer film substrates were used to span the possible surface tensions of the coal–oil system. These polymers are detailed in Table II. θ_c is the contact angle formed with water in air. These values were measured with an optical goniometer. They closely match values reported in ref 10. Solid surfaces tensions in Table II are for the solid–air interface.

Teflon blocks of 9.5/mm ($^3/_8$ in.) thickness with holes of 10 mm diameter were used to contain the suspending liquids and

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the agglomerates. Prior to use, the polymer films were cleaned in absolute ethanol to degrease the surface, then rinsed in distilled water, and then dried in an oven at temperatures no higher than 50 °C. Subsequent handling of the films was done with Teflon-tipped tweezers. The polymer substrate films were affixed to the bottom of Teflon blocks with a medical grade silastic (Dow Corning, SILASTIC MDX-4-4210) to form a seal. This material is an inert silicone elastomer that comes with a separate curing agent since self-curing silastics typically release acetic acid, which would interfere with the surface tension measurements.[13]

The agglomerates were prepared as previously described and then added to various water–methanol mixtures to make a slurry of a constant particulate content with a prescribed suspending liquid surface tension. Owing to the fact that the agglomerates were formed in water and could not be dried without fundamentally changing their properties, the highest possible methanol content was 95% by volume. Table III shows the various suspending liquid compositions and the corresponding surface tension. Water–methanol surface tension data against air at 20 °C are taken from ref 14.

Equal volumes of each slurry were placed in the Teflon cells and the tops of the cell were sealed with silastic bonded polyethylene. The cells were left to sit for at least 3 days[10] at which point, all adhesion was considered to have taken place. The substrate films were then peeled from the Teflon blocks and gently rinsed to remove settled but unadhering particles. The surface should be dried prior to viewing under the microscope. With the sample on the microscope stage, the circular edge formed by the silastic was centered under low magnification. The magnification was then increased to 50× and the image of the adhering particles was taken from the center of the region (i.e.; without shifting the stage) since nonuniform adhesion was a source of error and was averaged out over several measurements. Consistent lighting was used from sample to sample.

The extent of agglomerate adhesion was determined by using a KONTRON image analyzer with IAS/IPL software. An image analysis program was run with a gray-level that could be specified as a cutoff which discriminated particles and background. Pixels designated as particles were summed to give a percent area of the entire frame occupied by particles. This quantity was referred to as the percent area adhesion.

2.3. Three-Phase Contact Angle Measurements. Since the coal used in this work was available only as fines, the contact angle of n-$C_{16}H_{34}$ on coal in water was estimated by measuring the contact angle of n-$C_{16}H_{34}$ in distilled water on a series of polymer substrates. The same polymers used for the adhesion experiments (Table II) were used in these experiments.

These measurements were done with an optical goniometer. In a special viewing cell, the polymer surfaces were immersed in distilled water, and then a drop of hexadecane was introduced to contact their underside.

2.4. Particle Size Measurements. The mean particle sizes for the agglomerates were obtained by using a Malvern Model 2600 laser diffraction particle size analyzer. Several measurements were made at each oil level. Laser diffraction was used for these measurements since it is an accurate and much less time-consuming method than image analysis. With mean particle diameters upwards of 30 μm, the resolution and reproducibiliy of result was more than adequate with the Malvern instrument.

Additionally, the particle size distributions of agglomerates were determined with the particles suspended in a mixture of 95% CH_3OH and 5% H_2O, at several oil levels, to see if the methanol in the suspending liquid influenced the particle size distributions. It was necessary to rezero the light scattering signal for this methanol–water mixture.

3. Results

Results were obtained for the surface tension of the agglomerate particles and the mean particle sizes at several oil levels.

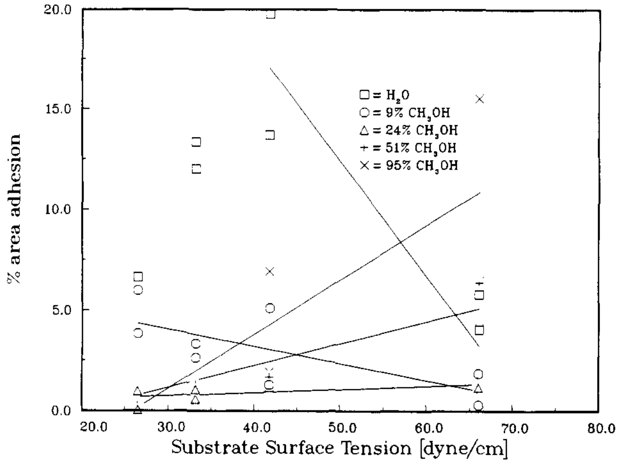

Figure 2. Agglomerate adhesion vs substrate surface tension.

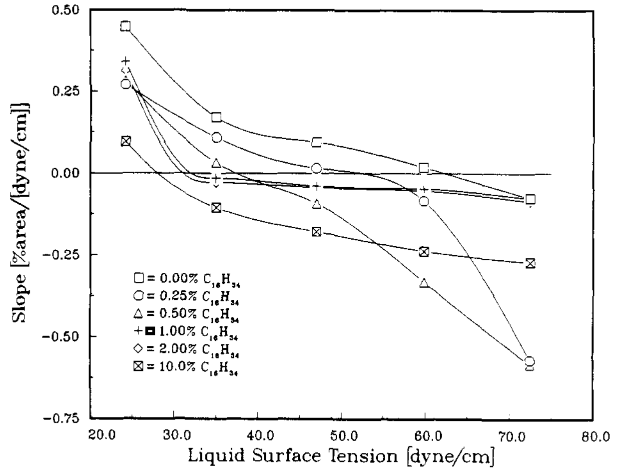

Figure 3. Adhesion slope vs liquid surface tension.

3.1. Surface Tension Results. The adhesion method was employed to determine the surface tension of hexadecane–coal agglomerates at several oil levels. Figure 2 is an example of the raw data obtained at 0.25 wt % hexadecane. Linear regressions of the points for each γ_{LV} were calculated and are shown in the figure as well. It was noticed that the slopes are negative for the case where $\gamma_{LV} > \gamma_{PV}$, as expected from the free energy of adhesion criteria.[10]

Briefly, for the particle, solid, and liquid system, the free energy of adhesion, ΔF^{adh}, is given as

$$\Delta F^{adh} = \gamma_{PS} - \gamma_{PL} - \gamma_{SL} \qquad (1)$$

where the subscripts P, S, and L respectively refer to the particle, substrate, and liquid interfaces.

Hence, for the case where $\gamma_{LV} > \gamma_{PV}$, ΔF^{adh} increases with increasing γ_{SV}, thus predicting a decreasing extent of particle adhesion with increasing substrate surface tension. When $\gamma_{LV} < \gamma_{PV}$, the opposite trend is expected.

Absolom et al.[10] reported a particle-size range of 1–20 μm for his work with the adhesion method. In this work, sample with mean particle sizes from 33 to 55 μm were used. Approximately the same degree of adhesion was found for all the samples, indicating that the change in mean size did not significantly alter the particles' capacity to adhere to the substrates in view of increased mechanical resistance for larger particles.

Figure 3 then shows the slopes of the regression fits from Figure 2 (as well as the other oil levels) plotted against γ_{LV}. γ_{PV} is determined at the point where the slope is zero. This regression and slope-plotting procedure is done at each oil

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[13] *Elastomers*, 2nd ed.; Greer, A. M., Ed.; Cordura Publishing: San Diego, CA, 1980.

[14] *CRC Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1987.

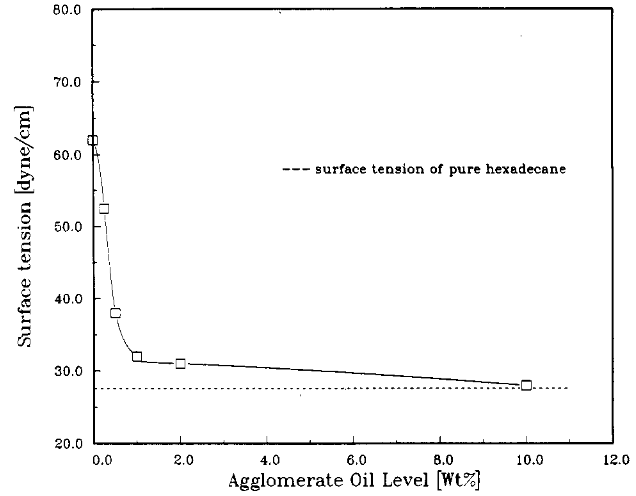

Figure 4. Agglomerate surface tension vs oil level.

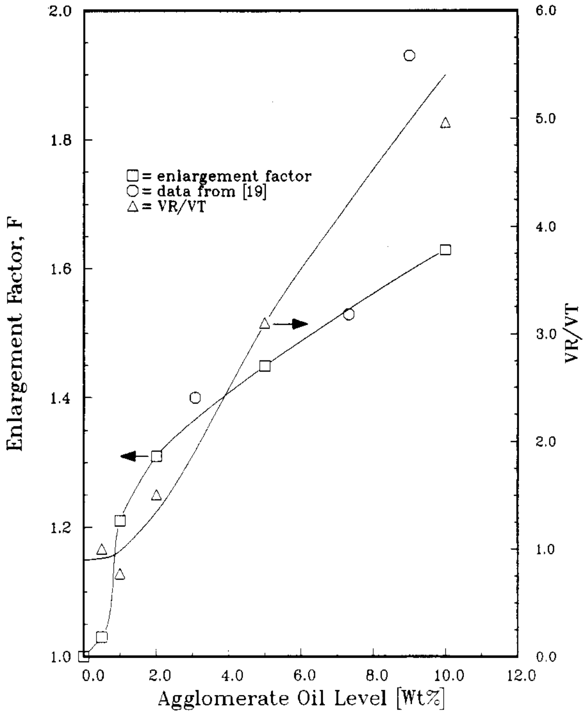

Figure 5. Enlargement factor and V_R/V_T vs oil level.

level (including zero oil) to determine γ_{PV}. Figure 4 shows the agglomerate surface tensions versus oil level. The surface tension of the unoiled coal measured by the adhesion technique was 62.0 dyn/cm, in agreement with other published results for bituminous coal.[15-17] At 10 wt % oil, the agglomerate surface tension closely approximates that of pure hexadecane.

3.2. Mean Particle Size Results. The mean particle size of the unagglomerated coal is 33 μm. As one would expect, the mean agglomerate size increases as more oil is added to the system. Figure 5 is a plot of an enlargement factor F, (discussed below) vs agglomerate oil level. Several measurements (i.e.; 10 or more) were made with each agglomerate sample, and the standard deviation of measured means was always less than 1 μm.

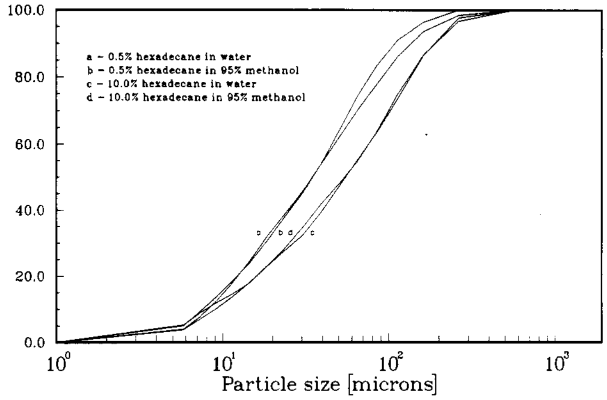

Figure 6. Size distributions in water and 95% methanol of 0 and 10 wt % oil agglomerates.

Figure 6 shows the cumulative size distribution of the agglomerates at 0.50% and 10.0% oil suspended in both water and a mixture of 95% CH_3OH and 5% H_2O. It is shown here that the methanol does not significantly degrade the agglomerate structure, and as such, the surface tension measurements should be valid.

4. Discussion

An informative way of expressing agglomeration data is with an enlargement factor, F. F can be defined as

$$F = \frac{d_p}{d_{p_0}} \tag{2}$$

where Δ_p is a mean agglomerate diameter at a given oil level and d_{p_0} is the mean diameter of the unagglomerated coal (recall Figure 5).

Assume that, at low oil levels, only single particles and doublets will contribute to the resulting enlargement factor. Now say that there are n particles plus agglomerates and one of them is double size (an agglomerate). Thus

$$F - 1 = \frac{1}{n} \quad \text{or} \quad n = \frac{1}{F - 1} \tag{3}$$

One bond will exist for every $n + 1$ particles, so the fraction of the total solid volume that is bonded in doublets, V_{SB}, is

$$V_{SB} = \frac{2}{n + 1} \tag{4}$$

Thus the bonding volume of oil, V_{OB}, relative to the volume of two bonded particles is

$$V_{OB} = \frac{V_O(n + 1)}{2} \tag{5}$$

where V_O is the total volume of oil expressed as a fraction of the total solids volume. However, for a given volume of solids, the oil will first be consumed in wetting the solid surface, and then any excess will then be used up in forming bonds. The total oil volume fraction, V_O, will be composed of two parts, a bonding volume fraction, V_B, and a wetting volume fraction, V_W. Thus

$$V_B = V_O - V_W \tag{6}$$

Thus eq 5 should be reexpressed as

$$V_{OB} = \frac{V_B(n + 1)}{2} \tag{7}$$

to account for the wetting volume.

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(15) Rumpf, H. *Agglomeration, Based on an International Symposium*; Knepper, W. A., Ed.; AIME: New York, 1961; pp 379–418.

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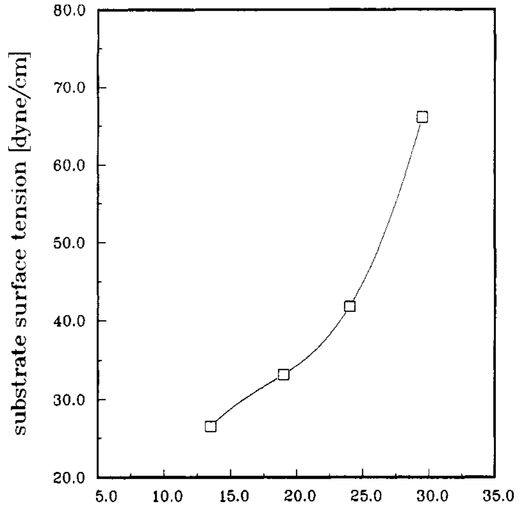

Figure 7. Contact angle of hexadecane in water vs substrate surface tension.

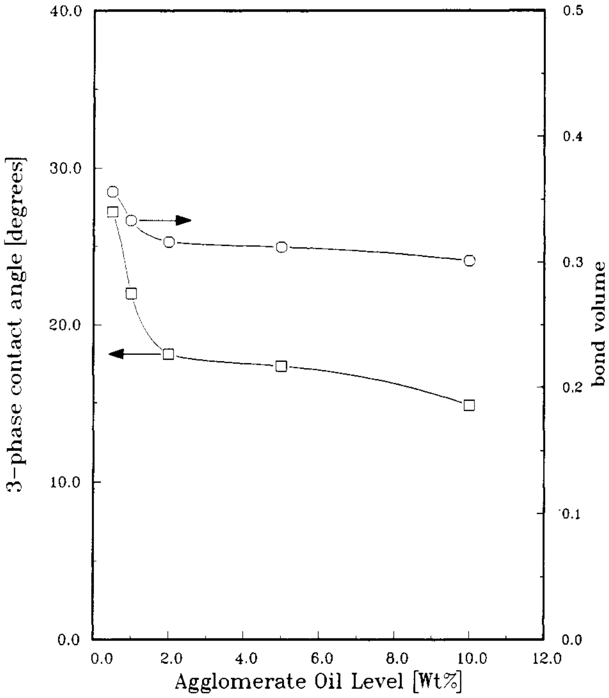

Figure 8. θ_C vs oil level (□) and bond volume vs oil level (○).

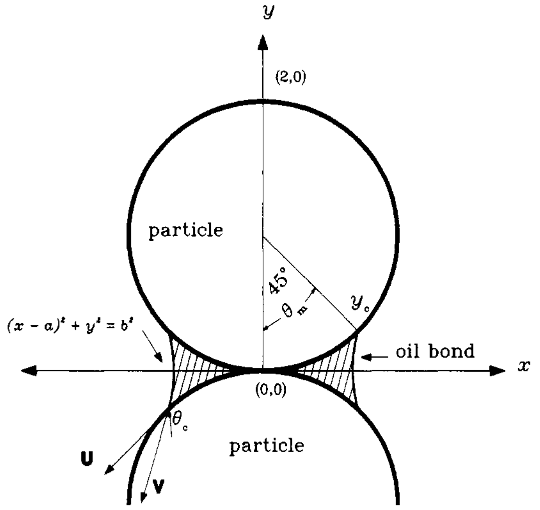

Figure 9. Schematic diagram of geometry for the bond volume in view of contact angle.

4.1. Three-Phase Contact Angle. n-$C_{16}H_{34}$ contact angles on polymer substrates in water are plotted in Figure 7. From a Lagrangian interpolation routine, hexadecane contact angles on the agglomerates at the different oil levels (surface tensions) were estimated. In Figure 8, the three-phase contact angle is plotted against the agglomerate oil level.

The addition of adsorbing oil was not found to have caused a step change in the agglomerate surface properties at low oil levels. This is because problems such as incomplete wetting and surface roughness[18] of the coal will contribute some coal character to the surface at very low oil levels. This point is further discussed in section 4.2.

4.2. Calculation of Bond Volumes. It has been shown that bonding structure of agglomerates is determined by the volume ratio of binding liquid to solid present in the system. At the binder levels considered in this work, the bonding should be exclusively pendular.[19,20] Pendular bonds are discrete lends-shaped rings at the point of contact of two particles.

Since the surface tension of the coal–oil agglomerates was found to be a function of the oil level, it is suggested that the contact angle at the three-phase junction of the oil-wetted particle, the bonding oil, and the water will also vary with the oil level. The surface tension of the agglomerates as measured represents a macroscopic or gross average of local surface properties. This was proposed by Cassie[21] and verified with many supporting citations by Crawford et al.[22]

On a microscopic scale, surface roughness, and surface heterogeneity characterize real solid surfaces. Wetting by an oil would have to exceed the dimensions of these irregularities before an essentially oil surface would be detected. Additionally, coal is a slightly porous material, oil would be withdrawn from the surface and into the pores. Further, in view of the way the agglomerates are prepared, a perfectly uniform wetting could only be the result of a perfect dispersion of the oil in the aqueous medium. At best, the coal surface is wet in a "pebbled" or "mosaic" fashion. This has been reported elsewhere.[23] Note that at agglomerate oil levels above 2% by weight, the surface that is observed is essentially an oil surface. It is in the region of 0–2 wt % of oil where incomplete wetting occurs and the existence of an intermediate coal–oil surface is postulated. This concept concurs with flotation recovery data as a function of oil level given by Capes et al.[24]

One would expect a constant contact angle only in the case of uniform wetting on smooth homogeneous surfaces. Otherwise, below a plateau oil level, the three-phase contact angle should vary with oil level.

If the effect of gravity is neglected, the binder–liquid interface will assume a profile of nearly constant curvature.[25] For our purposes, this profile can be represented

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by an arc of a circle of radius b. Figure 9 illustrates this configuration.

The meridian angle, θ_m can have a maximum size of 45° in the pendular regime, or else neighboring bonds will coalesce. Now assume the particle has a unit radius, defined by the equation $x^2 + (y-1)^2 = 1$. With θ_m equal to 45°, the three-phase junction will occur at the point $x = 1/\sqrt{2}$, $y = 1 - 1/\sqrt{2}$. The slope of the surface at this point is 1 (refer to Figure 9).

Let (u_1, u_2) and (v_1, v_2) refer respectively to the direction (slope) vectors of the particle surface and the meniscus surface at the three-phase contact point. The meniscus surface can be defined by an arc of a circle defined as

$$(x-a)^2 + y^2 = b^2 \tag{8}$$

The contact angle, θ_C is related to the two-direction vectors by

$$u_1 v_1 + u_2 v_2 = \| \vec{u} \| \, \| \vec{v} \| \cos \theta_C \tag{9}$$

With (u_1, u_2) equal to (1,1) and v_1 set equal to 1, determining v_2 gives the slope of the circle defined by eq 8 at the three-phase contact point. Thus

$$\frac{dy}{dx} = v_2 = \frac{\pm(x-a)}{\sqrt{b^2 - (x-a)^2}} \tag{10}$$

Thus eq 8 along with eq 10 determines the parameters a and b. Thus for a given contact angle, the meniscus profile is defined.

The absolute bond volume, V_{BA}, can be then taken as a volume of revolution of the meniscus area. Let the meniscus surface be $F_2(y)$ and the particles surface be $F_1(y)$. y_c is the three-phase contact point on the γ coordinate.

$$F_1(y) = 1 - (y-1)^2 \tag{11}$$

$$F_2(y) = a \pm \sqrt{b^2 - y^2} \tag{12}$$

$$V_{BA} = 2\pi \int_0^{y_c} [F_2(y)]^2 \, dy - 2\pi \int_0^{y_c} [F_1(y)]^2 \, dy \tag{13}$$

Equation 13 was integrated numerically. This was done with a 15-point Gaussian quadrature routine. The bond volume as a function of oil level is also plotted in Figure 8. Newitt and Conway-Jones[20] define the bond volume as a function of meridian angle θ as

$$V_{BA} = 2\pi r^3 (\sec\theta - 1)^2 \left[1 - \left(\frac{\pi}{2} - \theta \right) \tan\theta \right] \tag{14}$$

The V_{BA} calculated for $\theta_c = 0°$ is exactly the same result as predicted by eq 13.

The absolute bond volume is related to V_{OB} (the volume ratio of one bond to two particles) by

$$V_{OB} = \frac{V_{BA}}{8\pi/3} \tag{15}$$

for $r = 1$.

4.3. Interdependence of the Surface Tension, Oil Level, and Enlargement Factor. It has been demonstrated that the result of low-level oil agglomeration of coal is dictated by the amount of oil added to the system. It is of interest to determine how the oil distributes itself to bring about this result.

Recall eq 7. Since $1/n = F - 1$, it may be reexpressed as

$$V_{OB} = \frac{V_B F}{2(F-1)} \tag{16}$$

Assume that at low oil levels only pendular bonds will exist. By the use of V_{BA} from Figure 8 and F from Figure 5, the volume of one bond V_{OB}, is known and can be used to calculate V_B. At 0.5 wt % oil, from eq 15, $V_{OB} = 0.0425$. Thus

$$0.0425 = \frac{V_B F}{2(F-1)} = \frac{V_B(1.03)}{2(0.03)}$$

so, $V_B = 0.025$.

So from eq 6, $V_W = 0.0058$. Assuming V_W is constant for all oil levels, eq 16 may be used to determine the bond volume per particle pair. This value should be equal to the value of V_{OB} from eq 15 if the system is made up exclusively of singlets and doublets.

Denote V_{OB} from eq 16 as real volume V_R, and V_{OB} from eq 15 as a theoretical volume V_T. The ratio V_R/V_T will give a mean value of bonds per particle. If $V_R/V_T > 1$, then this implies that agglomerates larger than doublets exist. Figure 5 also shows this ratio plotted versus oil level. One may note the similarity among the two curves in Figure 5 and Figure 4. At an oil level of about 1–2 wt %, the slopes on these plots significantly change. The underlying reason for this change should be a fundamental change in the agglomerate structure. On the basis of the size data and the surface approximating that of hexadecane, it appears that beyond wt % oil, larger, more compact agglomerates are formed.

A number of factors constrain the system. The result must conform to a mass balance of solids, an oil balance, and a weighted sum of various agglomerate sizes that accounts for the observed size. A system of three linear equations may be written that determines the distribution of singlets, doublets, and triplets at each oil level based on the above criteria. They may be expressed as

$$\begin{aligned} a_{11}q_1 + a_{12}q_2 + a_{13}q_3 &= F \quad \text{(agglomerate sizes)} \\ a_{21}q_1 + a_{22}q_2 + a_{23}q_3 &= 1 \quad \text{(mass balance)} \\ a_{31}q_1 + a_{32}q_2 + a_{33}q_3 &= V_B \quad \text{(oil balance)} \end{aligned} \tag{17}$$

where the q_i's are the fraction of singlets, doublets, and triplets, the a_{1i}'s are the mean size of each type of agglomerate, the a_{2i}'s are all equal to 1 by definition of the mass balance, and the a_{3i}'s are the bond volumes per agglomerate based on the oil level. The triplets were assumed to form a triangle, which is the most stable three-body arrangement. The mean sizes were taken as an average of the maximum dimension that could be orthogonally projected against three normal planes. (i.e.; for a triplet, $a_{13} = (2 + 2 + 1.866)/3 = 1.95533$)

This system of equations was solved numerically and it gave positive element solution vectors up to 2 wt % oil. At that point, the number of doublets predicted was negative (physically impossible) thereby indicating agglomerates larger than doublets are present, which requires substantially more oil due to the increased number of bonds per agglomerate.

The system was remodeled by including a quadruple that was considered to be in tetrahedral form and to have six bonds. This required an additional linear equation, and one was formulated on the basis of the strength of the agglomerates. Consider each agglomerate in terms of the probability that it will break up, P_b. In general P_b should be proportional to the inverse of the number of bonds present. That is

$$P_b \propto \frac{1}{nb}$$

where n is the number of bonds in the agglomerate and

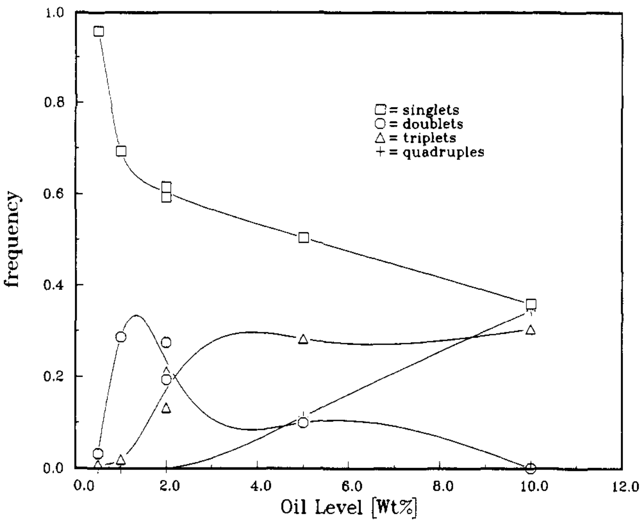

Figure 10. Agglomerate size frequency vs oil level.

b is the bond strength. The probability of break-up of the singlet may be expressed as k_0b, where k_0 is some unknown constant. k_0b may be thought of as a hypothetical quantity related to the compressive strength of the solid coal. Thus for singlets to quadruples we have

$$P_b = k_0q_1b + \frac{q_2}{b} + \frac{q_3}{3b} + \frac{q_4}{6b} \tag{18}$$

The strongest system, or minimum probability of breakup, will occur when

$$\frac{\partial P_b}{\partial b} = k_0q_1 - \frac{q_2}{b^2} - \frac{q_3}{3b^2} - \frac{q_4}{6b^2} = 0 \tag{19}$$

Rewriting eq 19, we obtain

$$k_0b^2q_1 - q_2 - \frac{q_3}{3} - \frac{q_4}{6} = 0 \tag{20}$$

In this form, the coefficient a_{41} of the new 4 × 4 matrix is indeterminate. However, in view of the agglomerate data, it can be assumed that at 1 wt % oil, the solution element q_4 will be zero and a_{41} can be calculated from the 3 × 3 system results. The 4 × 4 system was then solved and gave positive solution element vectors from 1 to 10 wt % oil. Interestingly, the 4 × 4 system predicts essentially the same distribution of sizes at 2 wt % oil as does the 3 × 3 system, indicating that the omission of quadruples from the model at very low oil levels is justified.

Figure 10 is a plot of the frequency of each agglomerate size versus oil level as calculated by the system of linear equations. Figure 11 is the same data replotted as agglomerate size distributions with oil level as a parameter. It is emphasized in this figure that the doublet is an uneconomical bonding arrangement, and from 1 wt % and upward, the number of doublets drops steadily. It can be seen from Figure 10 that the frequency of singlets as a function of oil level is a smooth curve, which supports the assumption of there being primarily only singlets, doublets, and triplets at very low oil levels. (i.e.; in Figure 10, data for 0.5–2% oil are from the 3 × 3 system, with data for 2–10% oil from the 4 × 4 system)

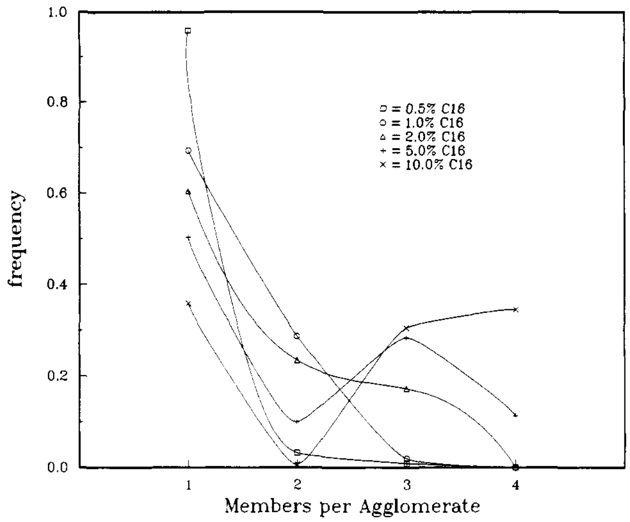

Figure 11. Agglomerate size distributions.

The above development was also calculated with the assumption of a zero contact angle at the three-phase interface, as assumed in previous papers.[15,26] The results predicted overly large agglomerates at low oil levels as the zero contact angle bond is about 65% of the volume of the finite contact angle bond. Correspondingly the wetting volume with a zero contact angle was calculated to be much larger as well.

5. Conclusions

The adhesion surface tension method and a laser diffraction particle sizer provided means of measuring respectively the surface tension and mean particle sizes of agglomerates formed from metallurgical coal and n-hexadecane in an aqueous medium. These data were then used to correlate the enlargement factor obtained at each oil level with structural features of the agglomerates.

From this study it can be said that the amount of oil introduced to a coal–water slurry for forming agglomerates determines several properties on the agglomerate surface. The net agglomerate surface tension was found to approach that of the pure oil at increased oil levels, and as such the three-phase contact angle between the agglomerate, the oil meniscus, and the suspending water decreased. Thus at oil levels below 2 wt %, the bond volumes were great enough to consume the available oil in forming agglomerates no larger than doublets and triplets. With smaller contact angles at higher oil levels, the particle bonding is more economical and larger, more compact agglomerates are seen. A constraining system of linear equations was developed to illustrate this.

A more complete analysis would involve a statistical approach encompassing the entire particle size distribution instead of the mean particle size used here.

Registry No. T-1000, 9003-53-6; T-1101, 117605-82-0; $C_{16}H_{34}$, 544-76-3; CH_3OH, 67-56-1; polyethylene, 9002-88-4; poly(ethylene terephthalate), 25038-59-9.

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