NRC·CNRC

NRC Publications Archive
Archives des publications du CNRC

Coal rank and surface properties of oil agglomerates

Darcovich, Kenneth; Smyth, T. J.; Capes, Charles

This publication could be one of several versions: author’s original, accepted manuscript or the publisher’s version. / La version de cette publication peut être l’une des suivantes : la version prépublication de l’auteur, la version acceptée du manuscrit ou la version de l’éditeur.

Publisher’s version / Version de l'éditeur:

Advanced Powder Technology, 4, 2, 1993

NRC Publications Record / Notice d'Archives des publications de CNRC:
https://nrc-publications.canada.ca/eng/view/object/?id=87554ab2-24de-4c8e-a490-ac46e7e15ad
https://publications-cnrc.canada.ca/fra/voir/objet/?id=87554ab2-24de-4c8e-a490-ac46e7e15ade

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L’accès à ce site Web et l’utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D’UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n’arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada
Conseil national de recherches Canada

Canada

Advanced Powder Technol., Vol. 4, No. 2, pp. 115-128 (1993)

Paper

Coal rank and surface properties of oil agglomerates

K. DARCOVICH, T. J. SMYTH and C. E. CAPES

National Research Council of Canada, Institute for Environmental Chemistry, Process Technology Section, Ottawa, Ontario, Canada, K1A OR6

Received for *APT* 15 February 1992; accepted 5 August 1992

Abstract—The wettabilities of agglomerates made from coals of several different ranks were measured by the adhesion technique. Oil levels from 0 to 10% by weight were used. As was expected, it was found that higher-rank coals are more easily oil-wetted and that the surface properties of the agglomerates correlate with agglomeration recovery and ash removal data.

1. INTRODUCTION

Agglomeration processes bring together fine powders into larger masses in order to improve powder properties. In conventional coal mining, much of the fine coal (typically −100 mesh) is rejected with tailings as it is impractical to recover. Due to the heterogeneous nature of coal, smaller particles tend to be either individually richer in ash or carbonaceous matter compared with 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 is added under high-shear mixing conditions to enhance surface properties. 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. Many authors [1-3] have researched and illustrated this process. The agglomerate flotation technique has been known since the turn of the century as shown by Froment [4]; however, to date, there is a considerable gap in understanding the fundamentals involved. Work by Brown [5] has shown that properties inherent to coal-oil agglomerates are favorable for flotation. Thus, it is the objective of this study to determine the surface properties of agglomerates formed with coals of different ranks and to compare these results with recovery data. This can provide a means to assess the effect of the nature of the agglomerate surface in relevant processing situations.

2. EXPERIMENTAL

2.1. *Sample preparation*

Five different coals were used in this study. Some of the samples arrived in very large pieces. To approximate the state of particulates in waste fines treatment, the following procedure was used to prepare the samples. The coal chunks were reduced to millimeter size by successively passing them through a roll mill, then a Wiley Mill

---

NRCC No. 34229.

Table 1.
Analysis of coal samples (as-received)

Sample	Volatile (%)	Fixed carbon (%)	Moisture (%)	Ash (%)	Sulphur (%)	Size (μm)	BTU	Classification
Devco	40.57	57.34	3.23	2.09	0.101	33.0	10 102	bituminous
Highvale	34.85	44.61	10.74	20.54	0.332	9.4	8 171	sub-bituminous
Montgomery	44.17	47.26	13.30	8.57	0.624	20.3	9 731	sub-bituminous
Bien Fait	46.69	38.59	30.57	14.72	0.584	6.0	9 726	lignite
Costello	51.08	39.79	36.32	9.13	0.823	7.4	10 299	lignite

with a 1 mm screen. The samples were then wet ground (to avoid heat and oxidation) in an attrition mill for approximately 30 min. The particle size distributions were then measured with a Malvern 2600 laser diffraction instrument. Their as-received properties are summarized in Table 1. Analysis of the coals' composition was done on a Leco Mac 400 instrument.

Each coal was agglomerated at oil levels of 0, 1, 5 and 10 wt% using hexadecane (n-$C_{16}H_{34}$, $\rho = 0.773$ g/ml). Agglomerates were prepared at a 10% pulp density. The coal 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 introduced, and the coal–oil–water system was further stirred with a magnetic bar under vacuum in a baffled flask for at least 30 min to achieve air-free agglomeration. Having only two-phase agglomerates (coal and oil) allows for a less complex material for the study of the surface properties. Normally, agglomerations carried out in high-shear mixing vessels (such as blenders) will introduce substantial amounts of air into the system from the vortices created by the stirring as well as by cavitation in the water from the mixing blades moving at extremely high speeds. At present, very little research has addressed the topic of agglomerates formed as a three-phase (coal–oil–air) material. A paper by Dryzmala *et al.* [6] discussed the presence of air in agglomerated systems.

2.2. *Surface tension measurements*

The adhesion technique developed by Absolom [7, 8] was used to characterize the surface properties of the coal–oil agglomerates. This technique has been successfully employed by Absolom *et al.* [7] to measure surface tensions of coal particles, as well as by Darcovich *et al.* [8] for coal–oil agglomerates. It was originally developed to measure surface properties of solid materials that occur only in particulate form, such as erythrocytes in blood, as shown by Absolom *et al.* [9]. The adhesion method involves measuring the extent of particulate adhesion on various substrates as a function of the composition (surface tension) of the suspending liquid.

The free energy of adhesion, ΔF^{adh}, is expressed as,

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

where γ_{PS}, γ_{PL} and γ_{SL} are, respectively, the particle–substrate, particle–liquid and substrate–liquid interfacial tensions.

If the surface tension of the suspending liquid is greater than the particle surface tension ($\gamma_{\mathrm{LV}} > \gamma_{\mathrm{PV}}$), equation (1) suggests that the extent of adhesion should decrease with increasing substrate surface tension (γ_{SV}). The opposite trend is expected when $\gamma_{\mathrm{LV}} < \gamma_{\mathrm{PV}}$. When $\gamma_{\mathrm{LV}} \simeq \gamma_{\mathrm{PV}}$, neither the particle nor the liquid will be energetically favored to form an interface with the substrate and the extent of adhesion should be independent of γ_{SV}. The terms 'surface tension' (dyne/cm) and 'surface free energy' (erg/cm^2) can be used to represent the same quantity. The latter is of use to associate thermodynamic properties with interfacial systems.

Virgin teflon blocks 12.7 cm thick with 1 cm diameter holes were used to contain the particulate slurry. The low surface energy of this material minimized interaction of the particulates and suspending liquid with the cell walls. The polymer film substrates were cut to the size of the teflon blocks, cleaned and affixed to the blocks with an inert medical grade silastic (Dow Corning MDX4-4210), leaving the substrate surface exposed to the opening in the teflon block.

Table 2.
Polymer film substrate properties

Substrate material	θ_c with water (deg)	γ_{SV}
Polystyrene Dow Chemical (T-1000)	93.7	26.5
Sulfonated polystyrene Dow Chemical (T-1101)	25.6	66.1
Polyethylene Fischer	83.0	33.2
Polyethyleneterephthalate Hoechst (Hostaphane 2000)	69.1	41.8

Four different polymer film substrates were used to span the possible surface tensions of the coal–oil system. These polymers are detailed in Table 2. θ_c is the contact angle formed with water in air. These values were measured with an optical goniometer. They closely match values reported by Absolom *et al.* [7], calculated by Neumann's surface tension equation of state. This equation is fully detailed in Absolom *et al.*'s paper [7]. Solid surfaces tensions in Table 2 are for the solid–air interface.

After the attritor grinding, the moisture in the coal–water mixture was determined by extraction with toluene. The coal–water mixtures were kept well sealed to prevent evaporation of water.

Particulate slurries were prepared in each of five water–methanol compositions. These coal slurries contained a solids weight fraction of 0.01. Equal aliquots were put in each cell which were then sealed on top with a silastic bonded plastic film to prevent evaporation of the liquid. Two cells were prepared for each case. The water–methanol suspending liquid compositions are summarized in Table 3 below. The water–methanol system was selected, since as shown by Stephen and Stephen [10], hexadecane is essentially immiscible across their entire binary composition range. Thus the agglomerate structure was not interfered with. This data for water–methanol solution surface tensions against air at 20°C was given by Weast [11].

The particles were allowed to settle and adhere to the substrates for 3 days. It has been shown by Absolom *et al.* [7] that, by this time, the extent of adhesion stabilizes to a plateau value.

Table 3.
Suspending liquid composition and surface tension

Volume % CH_3OH	γ (erg/cm^2)
0.0	72.5
9.0	59.8
24.0	47.0
51.0	35.0
95.0	24.2

The polymer substrate films were carefully peeled from the blocks and gently rinsed to remove settled but non-adhering particles. The samples were dry before viewing. The films were then mounted and centered on a microscopic stage (Olympus SZH) and a video image of each sample was taken.

The image of adhering particles from each cell was input to an image analysis program (Kontron Image Analyzer) where a grey-level cut-off was determined to discriminate adhering particles from the background. Pixel regions designated as particles were integrated to give a percent area adhesion.

For each sample, a linear fit was determined for the percent area adhesion as a function of substrate surface tension for each different suspending liquid composition. Figure 1 shows such a plot, this data from the Highvale coal at 0 wt% oil. The slopes of these regressions were then plotted as a function of the suspending liquid surface tension, with an interpolated curve put to the data (i.e. Fig. 2, also for Highvale coal at 0 wt% oil). The point where this curve crossed the *x*-axis was considered to be the particulate surface tension. A more detailed description of this procedure is given by Darcovich *et al.* [12].

2.3. *Agglomeration tests*

Agglomerations were run on each of the coals at 1, 5 and 10 wt% oil using hexadecane. Coal (50 g) was mixed with 500 ml of distilled water in a Waring Blendor with the appropriate amount of oil added. The coal was thus agglomerated at 10% pulp density, undergoing high-shear mixing for 30 s and low-shear mixing for 1 min. For the flotation tests, a Denver laboratory flotation cell was used. The 10% pulp density sample was floated in 1500 ml of water. The skimmed product was washed in 500 ml of water for 2 min and then re-floated in the same cell. This

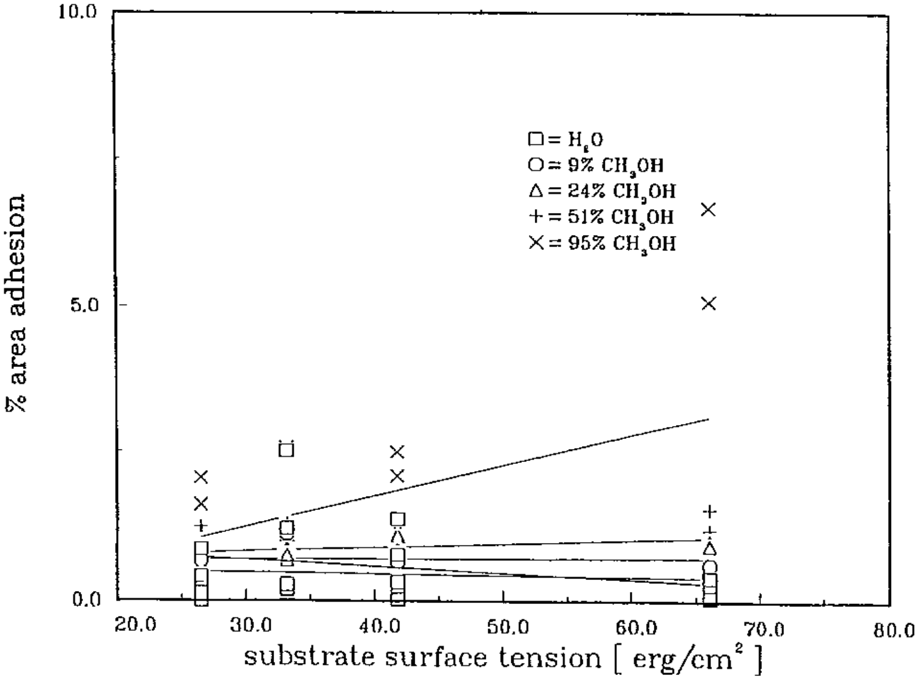

Figure 1. Percentage area adhesion versus substrate surface tension (Highvale 0% oil).

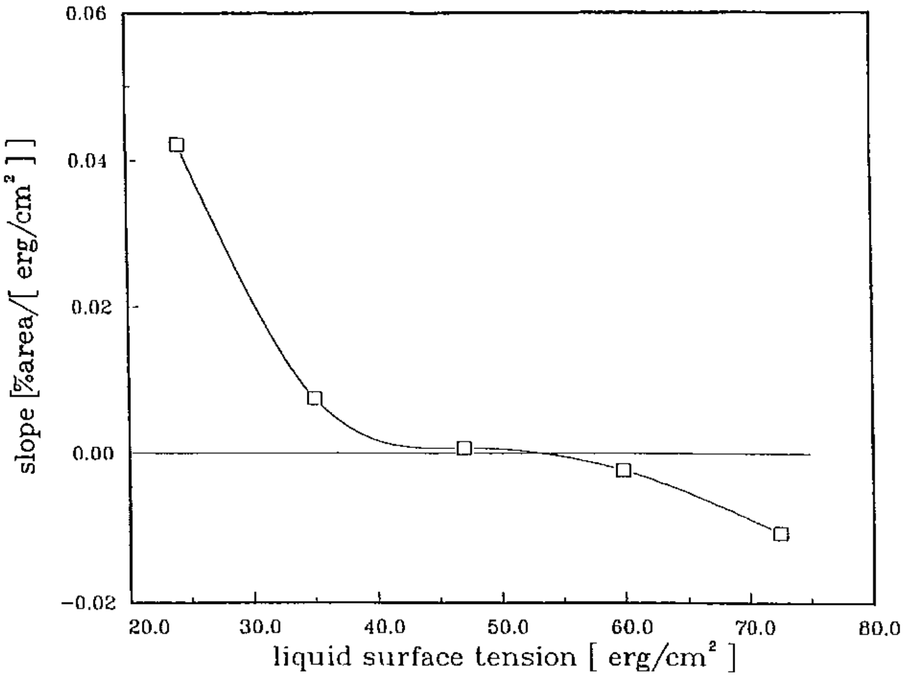

Figure 2. Slope versus suspending liquid surface tension (Highvale 0% oil).

product, along with the tailings from the first and second floating, was dried in an oven at 300°C overnight. The masses of the products and the tailings were recorded, and then these samples were analyzed for ash content. The same procedure as above was also carried out with No. 4 fuel oil.

3. RESULTS

3.1. Agglomerate surface tensions

Interpreting the data from the area of adhesion measurements as detailed above, the surface properties of the agglomerates across the range of oil levels tested are shown in Fig. 3. This data pertains only to agglomerates formed with hexadecane. The surface tensions of the unoiled coals fall in the range of 54.0–64.0 erg/cm^2, in agreement with the previous findings of Varga-Butler *et al.* [13] and Sablik [14]. At 10 wt% oil, the surface tensions of the bituminous and sub-bituminous coals closely approximate that of pure hexadecane. The two lignite samples show a more gradual wetting curve and a surface, which even at 10 wt% oil, does not exhibit a hexadecane character.

3.2. Agglomerate recovery and ash removal

The agglomerate flotation recovery and ash rejection data are shown in Figs 4 and 5. The percentage ash rejection is defined as {([% ash in feed] − [% ash in cleaned product]) × 100/[% ash in feed]}. Two oils were used in this work, i.e. hexadecane and No. 4 fuel oil. The fuel oil was used primarily to show the recovery properties of the lignite samples. They simply did not agglomerate sufficiently to be recovered with hexadecane; however, some recovery, illustrative of their wettability, was achieved with the heavier, more viscous, No. 4 fuel oil. As reported by Capes and

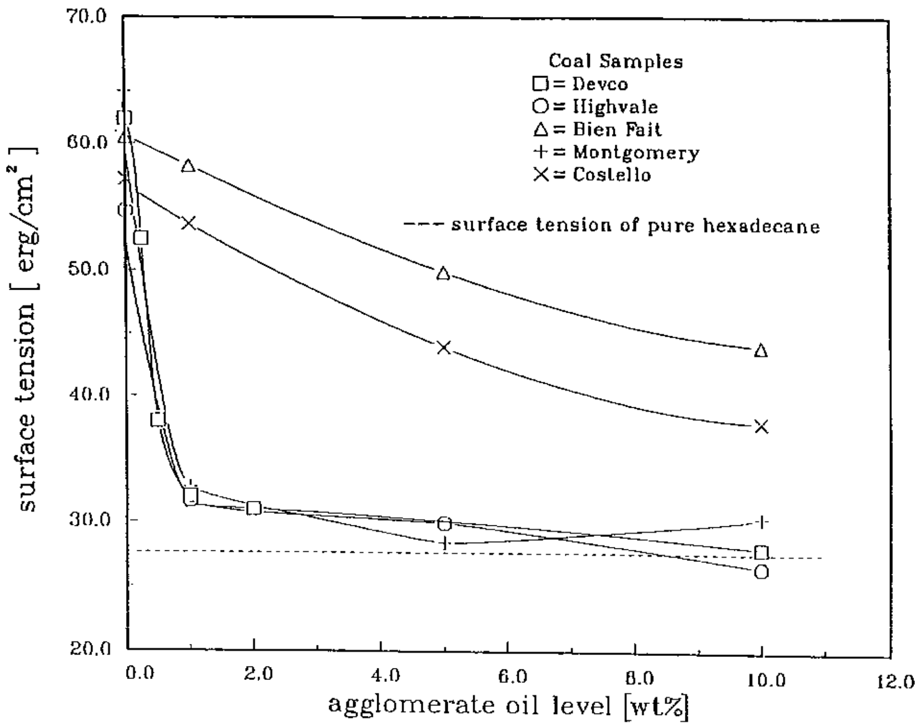

Figure 3. Agglomerate surface free energy versus wt% oil.

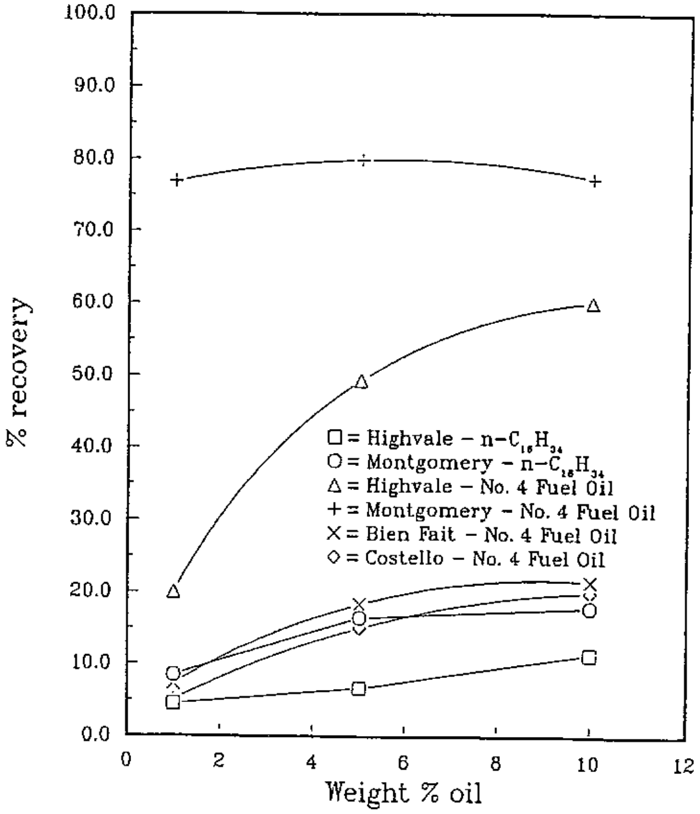

Figure 4. Percentage recovery versus wt% oil.

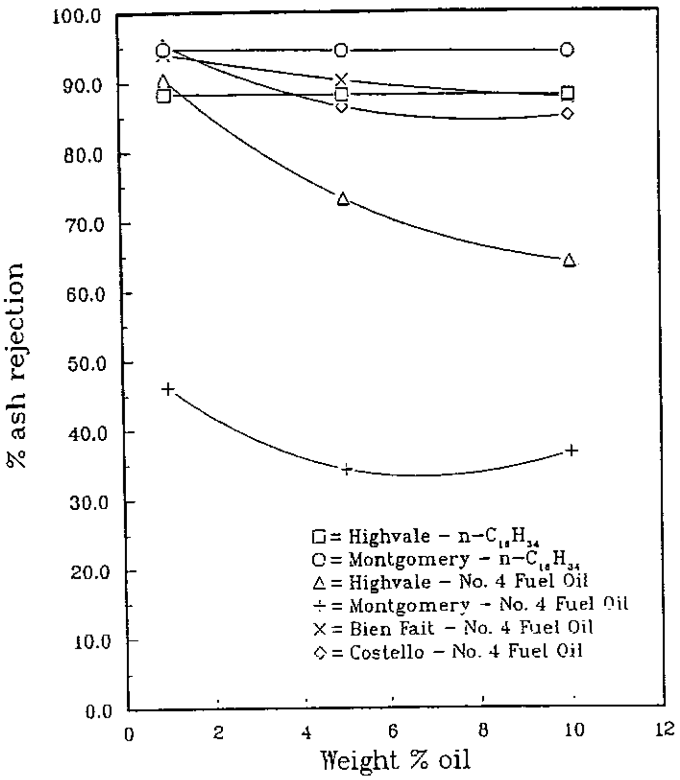

Figure 5. Percentage ash rejection versus wt% oil.

Germain [15], more complex oils contain some inorganic polar species such as nitrogen, oxygen and sulfur. These functional groups impart a greater oil wettability to a lower rank, more hydrophilic coal surface such as lignite.

4. DISCUSSION

The data in Fig. 3 show how the amount of oil used to form coal–oil agglomerates produces a net surface free energy for that agglomerate. As was discussed by Darcovich *et al.* [16], the surface free energies at intermediate oil levels (from 0 to 1 wt% oil) reflect a heterogeneous surface composed of both coal and oil components. These intermediate surface free energy values can be attributed to imperfect wetting of the surface arising from surface heterogeneities, surface roughness and discretized dispersion of the oil through the aqueous medium in which the agglomeration takes place. Further, the wetting occurs with a non-zero contact angle, so that the wetting and spreading will not be spontaneous and complete, rather the oil will coat the surface in patches and spread as it can locally. A monolayer coverage of oil on the coal would only be achieved if the surface was very smooth and the oil was perfectly dispersed in the aqueous phase. The monolayer coverage is more related to model systems, rather than with impure, irregular real surfaces. It can be seen that for the Devco, Highvale and Montgomery coals (subbituminous and higher in rank), the surface free energy drops very sharply at low oil levels, to a value near the surface free energy of pure hexadecane. Thus the surface of these agglomerates has essentially an oil character at low oil levels.

At 10 wt% oil, the data for the Highvale coal shows a surface free energy less than that of hexadecane. This difference is slight and should be understood to be within the range of experimental error for this measurement. The adhesion method is subject to several sources of error. The prescence of ash in the adhesion cells with the agglomerates may have interfered with the settling and adhesion. It was assumed that because of their inorganic, mineral nature, the ash is of sufficiently high surface free energy that it was unlikely to adhere to the polymer substrate surfaces. Further, the surface tensions of the water–methanol suspending liquid mixtures were very sensitive to composition. Any amount of evaporation or even small volumetric inaccuracies in their preparation could make substantial errors. Great care was taken in the experimental work to ensure sound and reasonable data.

In the case of the Bien Fait and Costello lignite samples, the surface free energy does not decrease sharply with oil level and, even at 10 wt%, has a value at least 10 erg/cm^2 greater than that of hexadecane. Typically, lignites have a high moisture content and contain many polar groups that inhibit oil wetting. This has been confirmed by Jin *et al.* [17] showing poor flotation results and long contact time, as well as by Naka and Nishida [18], who showed lignites to be much more water wettable than other coal ranks. Similarly, Rosenbaum and Fuerstenau [19] noted that coal surfaces contain an increasing amount of hydrophilic functional groups as rank is lowered.

A comparison between the two lignites can also reveal mechanistic reasons for the observed results. The Costello sample was found to be more wettable by hexadecane than the Bien Fait sample, as shown by the data in Fig. 3. The most marked composition difference between the two lignites is that the Bien Fait sample contains relatively 50% more ash, contributing to hydrophilic behavior suppressing oil wetting.

It has been reported by Wójcik *et al.* [20], Good *et al.* [21] and others, that the surface free energies are similar for a wide variety of coals, independent of rank. This is confirmed by the small range of surface free energy values obtained for the five coal samples in this study, shown in Fig. 3 for the case of 0 wt% oil. However, it is well known that recovery processes based on surface wetting are very rank dependent.

Figure 4 shows the flotation recovery data and Fig. 5 shows the ash rejection data for the sub-bituminous and the lignite samples. The oil-wettable sub-bituminous samples are far more easily recovered than the lignite samples. The flotation tests done with hexadecane as the agglomerating oil show poor recovery results; however, they do uphold the trend of increased recovery with increased oil wettability. Hexadecane has been found by Jańczuk *et al.* [22] to have a weak bonding ability between coal particles and air bubbles in dynamic systems. However, it is not intended to use hexadecane for commercial recovery processes; rather, it is simply a well characterized pure hydrocarbon suitable for this wettability study. As a practical point, hexadecane is much less viscous than No. 4 fuel oil, so it is more amenable to wetting the coal in the low-shear vacuum flask agglomeration procedure. The agglomeration in the case of the flotation measurements was done in a high-shear blender, capable of more thoroughly dispersing heavier oils.

No. 4 fuel oil was also used to conduct flotation recovery tests. The recovery of the sub-bituminous coals was markedly improved compared with the hexadecane results and, further, a small amount of recovery was achieved with the lignite samples. Tampy *et al.* [23] have attributed this to the presence of aromatics in the fuel oil which interact more favorably with the coal surface to form some hydrogen bonds with polar groups. This phenomenon in turn, will hold the oil-bubble interface more securely in a flotation situation. This concept is confirmed by the data showing the lignite samples which have a much higher composition of polar groups, responding favorably to the fuel oil as an agglomeration/flotation agent, while essentially failing to be recovered by the purely dispersive hexadecane oil. If size data were available for the hexadecane-lignite agglomerates, it would likely show little or no enlargement, which would be a process to enhance the probability of successful flotation.

The surface free energies of the unoiled lignites were 60.5 erg/cm^2 for the Bien Fait sample and 57.3 erg/cm^2 for the Costello sample. Across the entire range of oil levels tested, the Costello sample agglomerates maintained a lower surface free energy. If we consider $d\gamma_{PV}/dwt\%$ oil, there appears to be no substantially different thermodynamic driving force to promote the oil wetting of these coals. In this sense, the recovery data, which show the Bien Fait sample to be slightly superior, can be explained by suggesting that the absolute *extent* of wetting may be the same. The lower (lyophobic) volatile content and the lower (hydrophilic) moisture content of the Bien Fait sample could then account for its slightly greater recovery between the two lignites, in the sense that it would have a more favorable interaction with the No. 4 fuel oil. A macroscopic surface free energy model for heterogeneous surfaces has been proposed by Cassie [24]. It is stated as $\gamma_H = \Sigma c_i \gamma_i$, where γ_H is the macroscopic surface free energy of the heterogeneous solid and γ_i is the surface free energy of the ith component which comprises the fraction c_i of the entire surface. In general, ash content will contribute to a higher surface free energy, while volatiles and fixed carbon would tend to reduce it. If the volatile fraction is assumed to have a surface free energy value similar to that of hydrocarbon oils, then the addition of such oils as a wetting agent would be preferentially attracted to the carbonaceous portion of the coal since the ash content is significantly more hydrophilic than the rest of the surface, and the wetting of an oil over an already oil-like (volatiles) surface is not very thermodynamically favorable. Thus with fixed carbon contents of 38.59 and 39.79%, respectively, for the Bien Fait and Costello samples, the extent of wetting ($d\gamma_{PV}/dwt\%$ oil) could be considered to be very similar.

It is of interest to compare the differences in agglomeration/flotation recovery shown in Fig. 4 for the Highvale and Montgomery sub-bituminous samples, in view of their apparently similar wettability. Consider the surface free energy values for their unoiled surfaces. The Montgomery sample result was 64.2 erg/cm^2, while the Highvale coal value was 54.6 erg/cm^2. While both coals can be considered recoverable by the agglomeration/flotation method, the Montgomery sample showed a markedly superior recovery (see Fig. 4), especially with the No. 4 fuel oil, and notably with the No. 4 fuel oil at low oil levels. The Montgomery sample had a higher recovery with hexadecane as well. The lower ash content of the Montgomery sample, coupled with its higher unoiled surface free energy, could indicate more of a fixed carbon fraction at the surface which would lend itself to a more complete wetted state. That is, if the surface free energy of a solid is higher, but not as high as say the ash fraction so to be hydrophilic, the thermodynamic driving force for oil wetting will be greater. Further, if a larger fraction of the surface is oil wettable, this will enhance probabilities of both agglomeration and the subsequent flotation. If the quantity ($d\gamma_{PV}/dwt\%$ oil) is considered, the Montgomery sample exceeds the Highvale sample by about 10 erg/cm^2 wt% oil. This is another way of saying that for the same amount of oil present, the surface character of the Montgomery sample has been subject to far more modification by wetting that improves its agglomeration/flotation performance. If it can be supposed that with a smaller area available for wetting, the Highvale sample may have a thicker covering of oil on its wettable regions. It has been shown by Jańczuk *et al.* [22] that the detachment force for air bubbles on oiled coal surfaces is lower when the oil layer is thicker. This finding is thus consistent with the idea of a restricted wetting area and hence a thicker wetting layer. At higher oil levels, when the wetting becomes less selective, this effect is less pronounced both in terms of the quantity ($d\gamma_{PV}$/dwt% oil) as well as the difference in the agglomeration/flotation recovery obtained.

Figure 5 shows the ash rejection as a function of agglomerate oil level. The Montgomery coal, which is recovered in to a greater degree, is at the same time less efficiently deashed. This was the case with the No. 4 fuel oil. The lower unoiled surface free energy of the Highvale coal would make the wetting more selective and, further, at a particle size much smaller than the Montgomery coal, there is a higher probability to have a cleared discretization between ash and carbonaceous matter.

One point which has not been given too much consideration in this discussion is that of the mean particle size. The Highvale sample had a mean size of 9.4 μm, while the Montgomery coal was larger, with a mean size of 20.3 μm. The data in Fig. 3 suggest that the oil character given to the agglomerate surface is roughly the same at oil levels from 1 to 10 wt%. Even at 1 wt% oil, there is still more than sufficient oil present to fully wet the entire surface area of both samples of coal. If particle size (or surface area) were to have an effect, it would likely be at an oil level such as 0.50 wt% or below, where the larger coal would be expected to show a comparatively more oil-like surface character. Where this factor does make a difference is with the agglomeration/flotation recovery data. It was shown by Darcovich *et al.* [16] that excess oil on a coal surface contributes to improved inter-particle bonds for the formation of agglomerates. Well wetted, larger agglomerates would improve flotation recovery, as larger particles offer more inertia to counter hydrodynamic resistance in the bubble–particle collisions necessary for attachment. Thus for a less easily oil wetted coal, such as the Highvale sample, the choice of agglomerating oil becomes more crucial for achieving good recovery.

The data in Fig. 3 show the difference between the sub-bituminous and bituminous coals that are easily oil wetted, and the lignites which do not readily acquire an oil character to their surfaces. The oil-wetted coals have a sharp drop in surface free energy at low oil levels and have a surface character essentially of the wetting oil itself at higher oil levels. This characteristic of the curve indicates that it is reasonable to expect successful recovery and upgrading of the coal by the agglomeration/flotation procedure, but it does not really predict what extent of recovery can be expected. The success of recovery depends on the components of the coal matrix itself and how these components interact with whatever agglomerating oil is selected to bind them.

In view of the above discussion, consider a definition of hydrophobicity index h, for the as-received coal, formulated as:

$$h = \frac{\text{wt\% fixed carbon} + \text{wt\% volatiles}}{\text{wt\% ash} + \text{wt\% moisture}}\,. \tag{2}$$

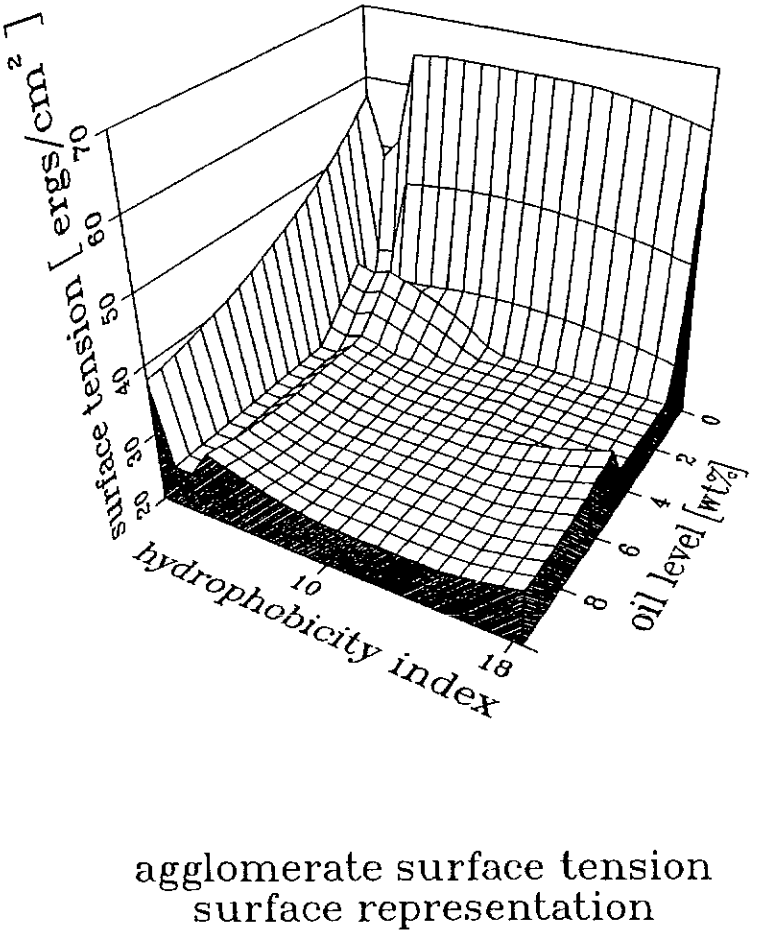

Figure 6. Agglomerate surface tension versus *h* and oil level.

This parameter *h* is essentially the ratio of the amount of the components of the coal that will be hydrophobic and oil wettable (carbon and volatiles), to the amount of components (ash and moisture) that are comparatively much more hydrophilic. Figure 6 shows a three-dimensional surface where the surface tension of the agglomerate is mapped out as a function of the oil level used in making the agglomerate and the value of *h* determined for the five coal samples used. The surface was generated from the data with a two-variable constrained quadratic interpolation routine. In Fig. 6, it can be seen that if the coal is not overly hydrophobic ($h \gtrsim 2$), only a small amount of oil is required to make an agglomerate with a surface that can be considered to be the same as that of the agglomerating oil. The ridges on the surface can be attributed to the scatter in the data.

With a properly chosen oil for flotation, agglomerates can be recovered with high yields at oil levels below 2 wt%. The low oil requirement is an attractive feature of the agglomeration/flotation process.

5. CONCLUSIONS

From the work carried out, it can be said that there is a direct correlation between the measured surface free energy of coal-oil agglomerates in aqueous media and the agglomeration/flotation recovery results. Coals of sub-bituminous and bituminous rank will acquire an oil-like surface at oil levels as low as 1 wt%. Lower ranked lignites show a decrease in surface free energy as the oil level is increased, but their ability to be agglomerated and floated is limited. For the two sub-bituminous coals, despite showing similar wetting curves, the agglomeration/flotation recovery was markedly different and this difference has been attributed to how their composition contributes to their macroscopic surface behavior. Coals high in ash are more likely to have restricted wetting on the surface and this in turn depresses the agglomeration/flotation recovery. Further, smaller particles and smaller agglomerates will encounter more hydrodynamic resistance to successful flotation, and even collisions leading to agglomeration and wetting.

Ash rejection among the coals tested was high, no matter what oil level used. It was found to be most selective at low oil levels where the hydrophobic and hydrophilic properties of microscopic regions on the coal surface are more pronounced. In this case, there is not an excessive amount of oil present to wet less thermodynamically favored regions such as ash, when the fuel bearing portions have already been oil wetted. Provided that the hydrophobicity index h is greater than about 2, small amounts of oil are required to give the agglomerate surface an oil character, which promotes agglomeration and recovery.

Lignites do not show good recovery and agglomeration at low oil levels. They would require some sort of surface conditioner to modify polar and hydrophilic sites to allow low oil level agglomeration and flotation.

REFERENCES

1. C. E. Capes and K. Jonasson, Application of oil-water wetting of coals in beneficiation. In: *Interfacial Phenomena in Coal Technology*. G. D. Botsaris and Y. M. Glazman (eds.). New York: Marcel Dekker Inc., 1989, pp. 115–155.
2. T. Hirajima, E. Chan, S. Whiteway, M. Stefanski and I. Stewart, Beneficiation of char, from a pyrolyzed eastern Canadian coal, by aggregative flotation. *Coal Prep.* **5**, 85–108, 1987.
3. W. Wójcik and A. M. Al Taweel, Beneficiation of coal fines by aggregative flotation. *Powder Technol.* **40**, 179–185, 1984.
4. A. Froment, Improvements relating to the concentration of ores. *UK Patent, No. 12,778*, June 4, 1902.
5. D. J. Brown, Particle trajectories, collision and attachment in froth flotation. In: *Aerodynamic Capture of Particles*, E. G. Richardson (ed.). London: Pergamon Press, 1960, pp. 35–43.
6. J. Dryzmala, R. Markuszewski and T. D. Wheelock, Influence of air on oil agglomeration of carbonaceous solids in aqueous suspension. *Int. J. Miner. Process.* **18**, 277–286, 1986.
7. D. R. Absolom, K. Eom, E. I. Vargha-Butler, H. A. Hamza and A. W. Neumann, Surface properties of coal particles in aqueous media. II. Adhesion of coal particles to polymeric substrates. *Coll. Surf.* **17**, 143–157, 1986.
8. K. Darcovich, C. E. Capes and F. D. F. Talbot, Surface properties of coal-oil agglomerates in the floc regime. *Preprints 196th ACS Natl. Meeting* **33**, 765–776, 1988.
9. D. R. Absolom, W. Zingg, C. Thomson, Z. Policova, C. J. Van Oss and A. W. Neumann, Erythrocyte adhesion to polymer surfaces. *J. Coll. Interface Sci.* **104**, 51–59, 1985.
10. H. Stephen and T. Stephen, *Solubilities of Inorganic and Organic Compounds, Vol. 2: Ternary and Multicomponent Systems*. New York: Pergamon Press, 1964, Part 2, No. 5160, 1740.
11. R. C. Weast (ed.), *CRC Handbook of Chemistry and Physics*. Boca Raton, FL: CRC Press Inc., 1987.
12. K. Darcovich, L. S. Kotlyar, W. C. Tse, J. A. Ripmeester, C. E. Capes and B. D. Sparks, Wettability study of organic-rich solids separated from Athabasca oil sands. *Energy and Fuels* 3, 386–391, 1989.
13. E. I. Vargha-Butler, M. Kashi, H. A. Hamza and A. W. Neumann, Direct contact angle measurements on polished sections of coal. *Coal Prep.* 3, 53–75, 1986.
14. J. Sablik, Free surface energy of coals of highest hydrophobicity. *Pol. J. Chem.* **59**, 433–438, 1985.

15. C. E. Capes and R. J. Germain, Selective oil agglomeration in fine coal beneficiation. In: *Physical Cleaning of Coal*, Y. A. Liu (ed.). New York: Marcel Dekker Inc., 1982, pp. 293–352.
16. K. Darcovich, C. E. Capes and F. D. F. Talbot, Surface characteristics of coal-oil agglomerates in the floc regime. *Energy and Fuels* **3**, 64–70, 1989.
17. R. Jin, Y. Ye, J. D. Miller and J. S. Hu, Characterization of coal hydrophobicity by contact angle, bubble attachment time, and FTIR spectroscopy. In: *116th AIME Annual Meeting*. Preprint no. 87-146, 19 pp. Denver, CO, 1987.
18. N. Naka and Y. Nishida, Water wettabilities of foreign coals. *Yukagaku* **33**, 80–87, 1984.
19. M. Rosenbaum and D. W. Fuerstenau, On the variation of contact angles with coal rank. *Int. J. Miner. Process.* **12**, 313–316, 1984.
20. W. Wójcik, T. Bialopiotrowicz and B. Jańczuk, The critical surface tension of Polish coals and their surface free energy components. *Fuel* **67**, 688–692, 1988.
21. R. J. Good, N. R. Srivasta, M. Islam, H. T. L. Huang and C. J. Van Oss, Theory of the acid–base hydrogen bonding interactions, contact angles, and the hysteresis of wetting: application to coal and graphite surfaces. *J. Adhesion Sci. Technol.* **4**, 607–617, 1990.
22. B. Jańczuk, W. Wójcik and T. Bialopiotrowicz, Studies on contact angle and work of adhesion in the system coal/*n*-alkane film–air bubble–water. *Powder Technol.* **61**, 211–216, 1990.
23. G. K. Tampy, M. E. Prudish, R. L. Savage and R. R. Williams, Free energy changes and hydrogen bonding in the wetting of coal. *Energy and Fuels* **2**, 787–793, 1988.
24. A. B. D. Cassie, Contact angles. *Discuss. Faraday Soc.* **3**, 11–16, 1948.