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# Wettability Study of Organic-Rich Solids Separated from Athabasca Oil Sands<sup>†</sup>

K. Darcovich,\* L. S. Kotlyar, W. C. Tse, J. A. Ripmeester, C. E. Capes, and B. D. Sparks

*Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*

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Bitumen recovery from oil sands by water-displacement processes depends on the wettability of the sand particles. Some of the oil sands solids have been found to be associated with toluene-insoluble organic components. It has been demonstrated that this material is related to the humic matter normally found in soils and is tightly bound to amorphous minerals such as allophane. Three samples of solids associated with humic matter were separated, and the adhesion method of measuring particulate surface tension was employed to assess their surface properties. It was found that the humic matter coating is moderately hydrophobic in character and the degree of hydrophobicity depends on the insoluble organic carbon content.

## Introduction

In general, oil sands can be defined as sand beds saturated with viscous bitumen that cannot be recovered by conventional methods. In Canada these bituminous sands occur in layers up to 100 m thick in four large areas of Northern Alberta totalling over 40 000 km<sup>2</sup>.<sup>1</sup> With respect to their oil saturation, oil sands can be divided into three grades. Oil sand with more than 10 wt % oil saturation is considered to be rich, 8-10 wt % is moderate, and less than 8 wt % is lean.

The first schematic description of the mutual arrangement of solids, water, and bitumen in Athabasca oil sands was attempted in 1963 in Cottrell.<sup>2</sup> This schematic presentation, as improved by Takamura,<sup>3</sup> is given in Figure 1. According to this refined model, the pore space in high-grade oil sands is filled with water and bitumen. About 30% of the total water exists as pendular rings at the contact points between sand grains while the remainder forms a 10 nm thick water film connecting these rings and completely covering the sand grain surfaces. The clay minerals in the oil sands are also considered to be coated with a thin water layer. For lower grade oil sands, clusters of fine particles saturated with water exist within the framework formed by coarse sand grains. The main assumption in the Takamura model is that oil sands solids are completely water wet. It has long been recognized, however, that oil reservoirs (including oil sands) are not completely water wettable and that the surface characteristics of oil sands solids are of great importance when bitumen is recovered by hot- or cold-water displacement processes.<sup>4-8</sup> The common point of view is that the hydrophilic character of the surfaces of some oil sands solids has been modified by the deposition of so-called tightly bound organic matter. This material cannot be removed by extraction with good solvents for bitumen such as toluene or dichloromethane. The greater part of the tightly bound organic material consists of humic matter,<sup>7</sup> similar to that normally present in soils and sediments, which cannot be characterized in specific physicochemical terms (molecular weight, boiling point, and so on).

In order to improve bitumen separation a better understanding of the forces involved in the bonding between

inorganic matter, humic matter, and bitumen is needed. To this end it is necessary to liberate the solids enriched with humic matter (organic rich solids) from the rest of the oil sands solids in order to be able to analyze it further. In earlier reports,<sup>9,10</sup> it has been demonstrated that organic-rich solids could be isolated from oil sands by using a cold water agitation test (CWAT) with Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution as a separating agent. Structural characterization of the humic matter as well as inorganic minerals present in these solids has been a subject of recent papers.<sup>9-13</sup>

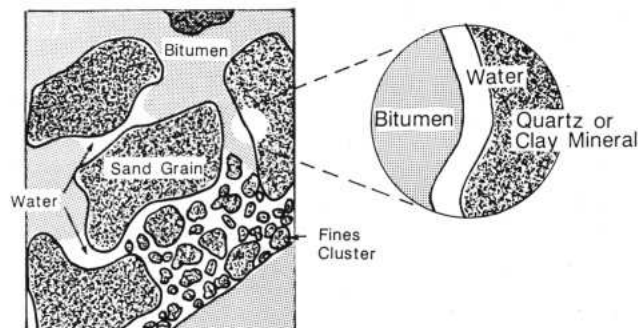
The present work is our first attempt to study surface properties of organic-rich solids isolated from oil sands. The aim of this study was 3-fold: (1) to adopt the method used in coat science<sup>14,15</sup> to examine the wettability of organic-rich solids; (2) to establish a relationship between the wettability of various organic-rich solids fractions and the amounts of humic matter present; (3) to compare wettabilities of oil sands organic-rich solids with those of clays, inorganic materials, coals, and polymers.

## Experimental Section

The work presented here was carried out on Athabasca oil sands

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<sup>†</sup>NRCC No. 30026.



**Figure 1.** Schematic presentation of Athabasca oil sands. Reproduced with permission from ref 3. Copyright 1982 Canadian Society for Chemical Engineering.

**Table I.** Solids Distribution and IOCC in the Separated Layers

layer	solids distribn by layer, <sup>a</sup> wt %	IOCC, wt % (dry, bitumen-free solids)
B	0.2	42.12
A-1	0.8	12.76
A-2	3.1	12.76
RS	95.9	0.10

<sup>a</sup> Related to the total solids in initial sample, on a bitumen-free, dry basis.

of medium grade obtained from the Syncrude quarry, Fort McMurray, Alberta, Canada. The oil sands were ground using a Comomil (Quadro Engineering Inc., Waterloo, Ontario, Canada), subsequently mixed to prepare homogenized samples, and then stored in sealed containers. The compositions of the oil sand sample, as determined by using Soxhlet extractors in conjunction with Dean and Stark separators,<sup>16</sup> was as follows: bitumen, 9.5%; water, 4.6%; solids, 85.9%.

**Separation of Organic-Rich Solids.** The organic-rich solids were isolated from oil sands by using the cold water agitation test (CWAT). The procedure is described in detail elsewhere<sup>9</sup> and is briefly summarized as follows: known amounts of 0.1%  $\text{Na}_4\text{P}_2\text{O}_7$  solutions were added to unextracted oil sand feed stocks. The samples were agitated in glass jars with a high-intensity Spex mixer. As a result of the treatment the following layers (from the bottom to top of the jar) were formed: a residue layer (R) containing the bulk of the solids, an aqueous layer (A) containing some suspended solids, and a bitumen layer (B). Layer B was separated by skimming off, while layer A was separated by decanting. Toluene was used to remove soluble organics from each layer. In the case of layer A, treatment with toluene resulted in formation of a skinlike top layer (A-1) with a very stable aqueous suspension at the bottom layer (A-2). The solids present in B, A-1 and A-2, and R layers were repeatedly washed with toluene until the supernatant toluene solution was colorless.

The solids contents of the bitumen-free layers were determined gravimetrically after the samples were dried at 110 °C. The yield and the insoluble organic carbon content (IOCC) of solids present in layer B, A-1, A-2, and R are given in Table I. It can be seen that solids associated with the bitumen layer (B) had the highest IOCC, followed by solids from A-1 and from A-2. The IOCC of solids present in the residue layer (R) was very low.

**Acid Treatment.** Samples of organic-rich solids used for carbon-13 NMR study were leached with HCl and HF to remove excess inorganic minerals. The treatment scheme is described in detail elsewhere.<sup>17</sup>

**Carbon-13 NMR Spectroscopy.** Solid-state CP/MAS  $^{13}\text{C}$  NMR spectra were recorded on a Bruker CXP 180/90 NMR spectrometer operating at either 45.2 or 22.6 MHz. Single cross-polarization contacts of 1 ms were used with rf field amplitudes of 40 kHz at 22.6 MHz and 60 kHz at 45.2 MHz.

(16) *Syncrude Analytical Methods for Oil Sand and Bitumen Processing*; Syncrude Canada Ltd.: Edmonton, Alberta, Canada, 1979; p 58.

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**Table II.** Polymer Film Substrate Properties

substrate material	$\theta_c$ with water, deg	$\gamma_{sv}$ , 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

Magic-angle spinning rates were 3 kHz for an Andrew-Beams type spinner at the lower frequency and 5.2 kHz in a Doty Scientific probe at the higher frequency.

**Analysis.** The insoluble organic carbon content (IOCC) of all solid fractions was obtained by subtracting carbonate carbon from the total carbon. The total carbon content was measured by using a Leco CR12 carbon analyzer. Carbonate carbon was determined titrimetrically after acid digestion by using a Carbon Dioxide Coulometer Model 5010 instrument.<sup>18</sup>

**Surface Characterization. Fundamental Principles.** The adhesion technique developed by Absolom et al.<sup>14,19</sup> was used to characterize the surface properties of the three samples of humic coated solids. This technique has been successfully employed to measure surface tensions of coal particles<sup>27</sup> and, more recently, coal-oil agglomerates.<sup>15</sup> The technique was developed to determine surface properties of solids that occur only in particulate form, such as erythrocytes in blood.<sup>19</sup> 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,  $F_{adh}$ , is expressed as

$$F_{adh} = \gamma_{PS} - \gamma_{PL} - \gamma_{SL} \quad (1)$$

where  $\gamma_{PS}$ ,  $\gamma_{PL}$ , and  $\gamma_{SL}$  are respectively the particle-substrate, particle-liquid, and substrate-liquid interfacial tensions. If adhesion occurs to an appreciable extent, it implies that the displacement of two interfaces (particle-liquid and substrate-liquid) by one (particle-substrate), is greatly favored.

If the surface tension of the suspending liquid is greater than the particle surface tension ( $\gamma_{LV} > \gamma_{PVL}$ ), eq 1 suggests that the extent of adhesion should decrease with increasing substrate surface tension ( $\gamma_{SV}$ ). The opposite trend is expected when  $\gamma_{LV} < \gamma_{PVL}$ . When  $\gamma_{LV} \approx \gamma_{PVL}$ , 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  $\gamma_{SV}$ .

Briefly, the following procedure was employed for the adhesion method surface tension measurements.

**Substrate Materials.** Polymer film substrates must be chosen to provide a broad range of substrate surface tensions. This allows higher resolution of the dependence of the extent of adhesion on substrate surface tension for each suspending liquid. Table II

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Table III.  $^{13}\text{C}$  NMR Chemical Shift Regions for Various Types of Carbon Present in Coal-Like Substances

region I (0–50 ppm)	region II (50–110 ppm)	region III (110–160 ppm)	region IV (160–190 ppm)	region V (190–220 ppm)
paraffinic C primary secondary tertiary terminal methyl	alcohol amines ( $\text{CNH}_2$ , $\text{CNHR}$ , $\text{CNR}_2$ ) carbohydrate ether methoxyl acetal	aromatic C olefinic C	carboxyl ester amide	aldehyde ketone

lists the polymer substrates used in this study.

**Liquid Medium.** A binary liquid system with a broad surface tension range was also necessary. Several compositions of this binary system should be prepared such that the anticipated particle surface tension falls between the extremes of the liquid surface tensions. The liquid system must not degrade the polymer substrates or react with the particles being tested. A water-methanol system was chosen for this work. This system has been used with good results in similar studies. Additionally, preliminary testing with other binary systems (water–DMSO, water–propionic acid) produced unacceptably high scatter in the data.

**Adhesion Cells.** Virgin Teflon blocks  $\frac{1}{2}$  in. 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 with the cell walls. The polymer film substrates were cut to the size of the Teflon blocks. They were soaked in absolute ethanol prior to use and then rinsed in distilled water and finally dried in an oven at 50 °C. With the use of Teflon-tipped tweezers, the substrate was affixed to the bottom of the cell with an inert medical grade silastic (Dow Corning MDX4-4210) leaving the substrate surface exposed to the opening in the Teflon block. Particulate slurries of equal concentration (1 g/L in this case) were prepared in each liquid composition. Aliquots of equal volume (1 mL) were then put in each cell. The tops of the cells were then sealed with silastic and a polyethylene film to prevent the liquid from evaporating or dust contaminating the system.

**Extent of Adhesion Measurements.** The particles were allowed to settle and adhere to the substrates for 3 days. It has been shown<sup>14</sup> that, by this time, the extent of adhesion stabilizes to a plateau value.

The polymer substrate films were carefully peeled from the blocks and gently rinsed to remove settled but unadhering particles. The samples were dry before viewing. The films were then mounted on a microscope stage (Olympus SZH). Under low magnification, the circle formed by the edge of the silastic was centered in the viewer. In this location, the magnification was then increased to 40 $\times$  and the image was recorded on videotape. The center area of the substrate was always recorded despite nonuniform adhesion, so that with several measurements, this error could be averaged out. The same backlighting was used for each sample.

**Image Analysis.** The image of adhering particles from each cell was input to an image analysis program (Kontron Image Analyzer with IBAS software) where a gray-level cutoff was determined to discriminate adhering particles from the background. Pixel regions designated as particles were integrated to give a percent area adhesion.

**Data Analysis.** For each particulate sample, a linear fit was determined for the percent area adhesion as a function of substrate surface tension for all the different liquid compositions. The slopes of these regressions were then plotted as a function of the suspending liquid surface tension. Often several repeats of the adhesion data were necessary to be able to fit the slope versus liquid surface tension data to a low-order polynomial. The point where this curve crossed the x axis was considered to be the particulate surface tension.

## Results and Discussion

**Spectral Analysis.** As mentioned previously, one of the purposes of this work was to establish a relationship between wettability of organic-rich solids and the amount of humic matter present in the respective samples. The reasoning behind this approach is that it was expected that at a certain concentration of humic matter the inorganic

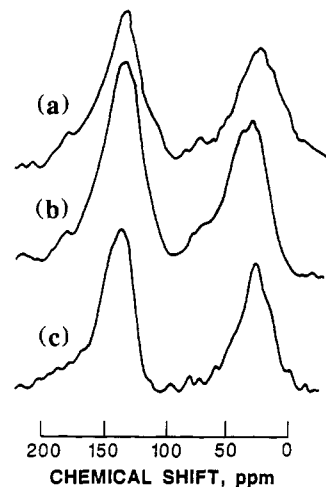


Figure 2. Solid-state  $^{13}\text{C}$  NMR spectra of demineralized organic-rich solid present in layers B (a), A-1 (b), and A-2 (c).

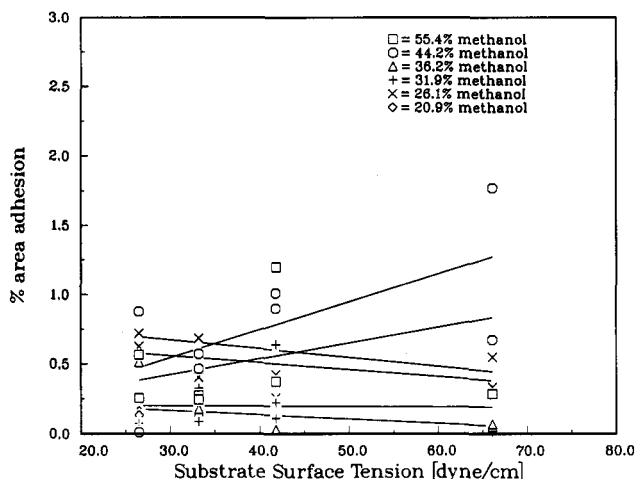
mineral surface would be mostly organically covered so any further increase in the amount of humic matter would not substantially influence the surface properties and wettability.

As the nature of humic matter was also an important parameter that could govern wettability, all three fractions of organic-rich solids were examined by solid-state carbon-13 NMR to ensure that humic matter present in these solids had similar structural parameters. The organic-rich solids studied contain substantial amounts of inorganic components (especially those separated from A-1 and A-2 layers), it was therefore necessary to concentrate humic matter by demineralization in order to obtain good NMR spectra. Demineralization was achieved by treatment with HCl and HF. Treating humic matter with these acids was potentially dangerous, as carbohydrates and proteins (if present) could be selectively removed from the sample. There was also the possibility for cyclization of carbohydrates to form aromatic groups; decarboxylation and hydrolysis of proteinaceous substances could also result.<sup>20</sup> In order to examine the effect of the HCl/HF treatment we compared spectra for A-1 solids both before and after acids leaching. Except for the signal to noise ratio there was practically no difference. Solid-state  $^{13}\text{C}$  NMR spectra of acid leached solids separated from B, A-1, and A-2 layers are given in Figure 2.

Interpretation of these spectra is based on reported data for coal-like materials.<sup>18–26</sup> All spectra could be divided into five representative regions based on chemical shift: 0–50 ppm (region I), aliphatic; 50–110 ppm (region II), N- and O-substituted alkyl carbon, including carbohydrate, ether, amine, amide, alcohol, acetal, ketal, and methoxyl functional groups; 110–160 ppm (region III), aromatic carbon. [Olefinic carbon, which is not considered to be a major constituent of humic acids, could also contribute to region III. This region can be subdivided into a band assigned to carbon bonded only to hydrogen or carbon (110–145 ppm), and a band assigned to O and N-substituted carbon (145–160 ppm).]; 160–190 ppm (region IV),

**Table IV. Aromaticities of Humic Matter Present in Organic-Rich Solids**

layer	aromaticity, %
B	46.0
A-1	44.8
A-2	45.4

**Figure 3.** Percent area adhesion vs substrate surface tension. The line shows a duplicate measurement for the A-2 sample in the narrow liquid surface tension range.

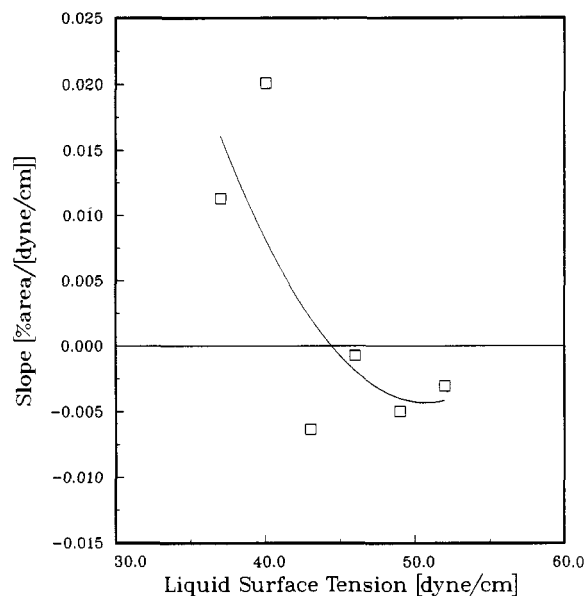
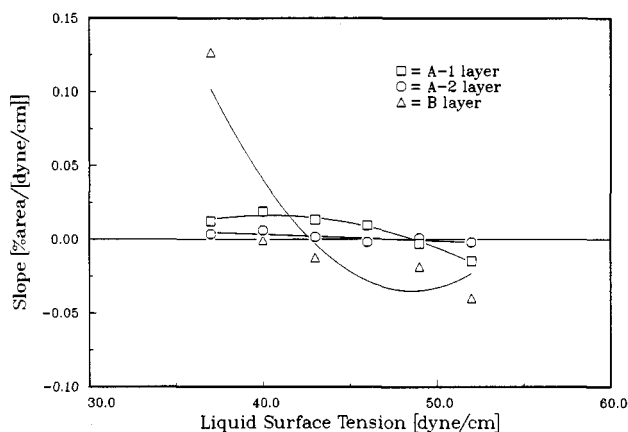
carboxyl, amide carbonyl, and ester carbonyl groups; 190–220 ppm (region V), ketones and aldehydes.

Assignments for chemical shifts in these regions<sup>21</sup> are given in Table III. It can be seen from Figure 2 that the spectra of demineralized CWAT fractions resemble each other. In all cases the dominant signal in region I was observed at ~30 ppm and was assigned to the carbon of polymethylene groups (CH<sub>2</sub>)<sub>n</sub>. The broad band of resonances present in the aliphatic region was an indication of a wide variety of carbon types (methyl, methylene, and methine groups) being present. Peaks related to methoxyl carbon (55 ppm), oxygen-substituted aromatic carbon (150 ppm), and aromatic carbons ortho or para to an oxygen-substituted aromatic carbon (120 ppm) were clearly absent in the spectra. Peaks for carbohydrates (72 and 106 ppm) were also absent indicating advanced post depositional changes in the sediment. In region III a strong broad peak was observed at 130 ppm. Such resonances could be provided by unsubstituted and bridgehead aromatic carbons or olefinic nuclei. However, olefins are known to be present in negligible amounts in geological materials. Alkylbenzenes could also resonate in the 130 ppm region. In region IV all spectra showed a small peak at 175 ppm, which was an indication of carboxyl carbon.

For comparison purposes the spectra were characterized using aromaticity (percent of carbon in the region from 160 to 110 ppm to total carbon) as a quantitative parameter (Table IV). Aromaticities for Athabasca humic matter from different samples were similar to each other, indicating an apparent similarity in the nature and origin of the humic matter present in the various fractions of the organic-rich solids.

**Surface Characterization.** Preliminary adhesion measurements were performed on all three humic matter samples with a water-methanol suspending liquid surface tension range of 25–72 dyn/cm. These tests indicated that the surface tensions of all three samples were between 35 and 50 dyn/cm.

The adhesion measurements were repeated with six liquid compositions of surface tensions between 37 and 52 dyn/cm. This smaller, more finely divided range gave

**Figure 4.** Adhesion slope vs liquid surface tension for the A-1 sample with duplicate data points. Note poor second-order fit.**Figure 5.** Adhesion slope vs liquid surface tension for the three humic matter samples.**Table V. Surface Properties of the Three Humic Matter Samples**

sample	surface tension, dyn/cm	S <sub>25 °C</sub> water	S <sub>80 °C</sub> water	S <sub>25 °C</sub> toluene	S <sub>80 °C</sub> toluene	contact angle, deg
B	42.7	-53.5	-28.4	11.2	14.0	74.8
A-1	48.6	-45.6	-19.1	14.1	16.1	68.2
A-2	47.4	-47.1	-21.0	13.6	15.7	69.5

higher resolution to the data, thereby allowing small differences in the particulate surface tensions to be determined.

As an example of the raw data, Figure 3 shows the percent area adhesion versus the substrate surface tension for a range of water-methanol surface tensions between 37 and 52 dyn/cm for the particles from the A-2 layer. The slope changes from positive to negative between the 31.9 and the 26.1 vol % methanol lines, indicating that the particle surface tension is between 46 and 49 dyn/cm. The data in Figure 3 are from a set of duplicate experiments. Plotting the slopes against  $\gamma_{LV}$  will give  $\gamma_{PV}$  at zero slope. For example, Figure 4 shows slopes vs.  $\gamma_{LV}$  for a set of duplicate experiments with sample A-1. The second-order fit of these data was poor due to scatter. When the data set was increased to include 10 repeats, the averaged slope values at each value of  $\gamma_{LV}$  produced a much improved



second-order fit. Such curves are shown in Figure 5 for all three humic matter samples.

The samples from layers A-1 and A-2 can be seen to have surface tensions similar in value. The surface tension of the particles from the B layer is significantly lower. A second-order polynomial was fit locally to the data and is shown in Figure 5. The intercept values,  $\gamma_{PV}$ , are given in Table V and have an error range of no more than  $\pm 5\%$ , based on the raw data variance. Even within this error range,  $\gamma_{PV}$  for B could not be considered equivalent to  $\gamma_{PV}$  of the other two samples. Samples A-1 and A-2 have values of  $\gamma_{PV}$  that fell into an overlapping error range and in this sense did not significantly differ. Unfortunately, no sample from the R layer was available to provide a surface tension for oil sand particles with a very low IOCC.

The humic matter surface tensions indicate a moderate degree of hydrophobicity. From Neumann's equation of state<sup>30</sup>

$$\gamma_{SL} = \frac{(\sqrt{\gamma_{SV}} - \sqrt{\gamma_{LV}})^2}{1 - 0.015 \sqrt{\gamma_{SV}\gamma_{LV}}} \quad (2)$$

and Young's equation<sup>31</sup>

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (3)$$

the theoretical contact angles formed by water on the humic matter surfaces were calculated. These values are also shown in Table V. The contact angles are in the 70° range; above 90° implies nonwettability and near 0° indicates that the liquid spontaneously spreads on the surface.

The coefficient of spreading  $S$  is given by

$$S = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \quad (4)$$

Values for  $S$  for water are shown in Table V. Since these values are negative, the spreading of water on these surfaces is unfavorable. When  $S$  is calculated for a low surface tension liquid (i.e.; toluene), it is positive and wetting of the humic matter by such a liquid would be favored.

The fact that the B layer solids were separated in a bitumen layer by skimming them from an aqueous layer confirms the surface tension measurement, showing them to be less water wettable than the two A fractions. Further when the A-1 and A-2 layers were washed in toluene, the higher surface tension A-2 layer would be preferentially wet by toluene, facilitating this separation.

Since the experiments were conducted at room temperature ( $\approx 25^\circ\text{C}$ ), it would be instructive to examine the wetting properties at the elevated temperatures of the hot-water separation processes. Values of  $\gamma_{LV}$  at 80 °C for water and toluene of 62.6 and 23.1 dyn/cm, respectively, were from the literature.<sup>32</sup>  $\gamma_{SV}$  were not expected to vary significantly with temperature provided no structural phase change was involved.<sup>33</sup> The coefficients of spreading were calculated for 80 °C by using eq 2 and 4 and are also shown in Table V. The values of  $S$  at the elevated temperatures predicted the same surface-influenced behavior as at room temperature, except that the degree of wetta-

**Table VI. Comparison of Humic Matter Surface Tensions with Data for Other Solids**

material	surface tension, dyn/cm	material	surface tension, dyn/cm
organoclays	22–26	fresh coal surfaces	35–60
bitumen	25–30	oxidized coal	60–70
polyisobutane	27	kaolinite	170–203
polyethylene	31	silica	129–259
graphite	33	bentonite	166–229
polypropylene	34	montmorillonite	179–221
polystyrenes	30–40	marble	198–205
polyesters and polysilanes	40–45	alumina	268–273
poly(oxyethylene)	43	mica	300
B humic matter	42.7	sodium chloride	305
A-2 humic matter	47.4	magnesium oxide	1090
A-1 humic matter	48.6	calcium oxide	1310

bility of the humic matter was altered. Toluene spreads more readily ( $S_{\text{toluene}}^{80^\circ\text{C}} > S_{\text{toluene}}^{25^\circ\text{C}}$ ), but the surface is also less hydrophobic ( $-\gamma_{\text{water}}^{80^\circ\text{C}} < -\gamma_{\text{water}}^{25^\circ\text{C}}$ ). Additionally, volatility and viscous effects at higher temperatures assist the separation.

Table VI shows the surface tensions for the humic matter samples compared to data for other typical solid materials.<sup>34–39</sup> These data were determined by using the contact angle or the heat of solution method. The temperatures for these data are  $20 \pm 5^\circ\text{C}$ , where typically  $d\gamma/dT$  is on the order of  $-0.1 \text{ dyn}/(\text{cm}\cdot^\circ\text{C})$ .

Hydrocarbon-based polymers all have surface tensions near 30 dyn/cm. Polymers, with functional groups containing oxygen have surface tensions in the 35–50 dyn/cm range, suggesting some basic difference. The NMR spectra suggest that low-surface-energy aliphatic and aromatic carbons are the predominant species in the IOCC; consequently, there must be some other constituent that influences the overall surface tension.

Cassie's equation<sup>40</sup> suggests that a composite surface would have a surface tension  $\gamma^c$ , characterized by a weighted sum of the surface tensions,  $\gamma_i$  of its constituents. That is,  $\gamma^c = \gamma_i \alpha_i$ , where  $\alpha_i$  is the area fraction of component  $i$  on the composite surface. Thus if some high-surface-energy material were present on the surface, the gross measured surface tension of the humic matter would be some value between that of the aliphatic/aromatic constituents and that of the inorganic mineral matter. Typical data for inorganic clays and salts given in Table VI show these materials to have much higher surface tensions ( $\gamma_{SV} > 150 \text{ dyn/cm}$ ) than the humic matter samples. Organoclay solid surface tensions in the region of 22–26 dyn/cm have been reported<sup>36</sup> where the surface was composed almost entirely of hydrocarbon functional groups. The surface tensions of the humic matter samples were in the 40–50 dyn/cm range, suggesting a composite organic/inorganic surface. The substantially higher IOCC in the B layer compared to that of A-1 and A-2 may correspond to its lower surface tension measurement. It could also be

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suggested that the oil sands have a surface layer of humic matter even at low IOCC levels, which was reflected in the small measured differences in absolute surface tension. Only this much can be said about the different compositions of the humic matter, since, with only three samples, a thorough quantitative correlation between surface tension and IOCC is inappropriate. Samples near 0% IOCC should be tested to see if their surface tension has a more inorganic character.

Also, the possibility exists that, over time, the humic matter on the surface could have become slightly oxidized, which would increase the surface tension. This has been shown to be the case for surface tension measurements on coal.<sup>27,41</sup>

## Conclusions

The adhesion surface tension method provided a means of determining the surface tensions of three humic matter samples extracted from tar sands. The sample with the highest carbon content was found to be the most hydrophobic of those tested. Given surface tensions of other solids, the surface tension data for the humic matter samples provide a basis for determining comparative wettabilities.

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# Effects of Pore Structure on Initial Catalytic Activity for Residuum Desulfurization and Coal Liquefaction

Young-Woo Rhee, James A. Guin,\* and Christine W. Curtis

*Department of Chemical Engineering, Auburn University, Auburn, Alabama 36849*

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The initial activities of a series of laboratory prepared NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts having micro- and macro-micropore size distributions were evaluated in residuum desulfurization and coal liquefaction reactions. Maxima occurring in catalytic activity as a function of catalyst extrudate micropore diameter support the presence of hindered diffusion of reactant molecules in catalyst pores. High-surface-area macroporous (bimodal) catalysts have higher intraparticle diffusion rates and thus have higher initial activities when compared to unimodal catalysts on an equal mass of catalyst basis; however, because of the lower density of the macroporous catalysts, this advantage is offset to some degree when the two types of catalysts are used on an equal volume basis.

## Introduction

Reaction rates in coal liquefaction can be limited because many of the reactant molecules involved are large enough to encounter the hindered diffusion regime in catalyst pores. The hindered diffusion regime is entered whenever the size of the diffusing molecule is appreciable compared to the catalyst pore size. Because catalysis is a surface phenomenon, it is generally desirable to utilize a catalyst with as high a surface area as possible. However, for a unimodal catalyst, this may result in pore diameters so small as to drastically reduce diffusion rates into the catalyst pellet. One possible method to circumvent this dilemma is the utilization of macroporous, e.g., bimodal, catalysts that may be used to reduce pore diffusional limitations, since the macroporosity can serve as a diffusing channel for large molecules. However, because of various tradeoffs, e.g., the catalytic surface area per unit volume being generally smaller for a less dense macroporous catalyst, and because the exact molecular size distribution of the reactants is not precisely known in complex coal liquefaction and petroleum reactions, it is difficult to predict a priori the extent to which the addition of macroporosity will contribute to better catalytic performance.

The objective of the present investigation was to determine the extent of improvement in initial catalyst activity in coal liquefaction and residuum desulfurization that could be obtained through modification of the catalyst

support pore size distribution and, in particular, through the introduction of macroporosity. The emphasis here is on the initial catalytic activity as it relates to catalyst pore structure, and the broader problem of catalyst deactivation is not addressed herein.

To accomplish this objective, several catalysts having different pore structures were prepared by using two basic methods, viz., impregnation and coextrusion. The catalyst pore structures were controlled either by sintering techniques or by introduction of combustible fibers.<sup>1</sup> Catalyst activity was measured in terms of changes in product distribution by using a relative solubility method and by the extent of desulfurization.<sup>2-5</sup>

**Previous Studies.** Considerable evidence regarding pore diffusional limitations in coal systems has been reported in the literature. Ho and Weller<sup>6</sup> observed that the conversion of coal increased as catalyst pore diameter increased from 100 to 500 Å in hydrolification of coal with

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