Contact angles on heterogeneous coal surface: The effect of mineral matter

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Abstract—Coal is an organic sedimentary rock of complex structure, composed of both organic matter as well as inorganic matter. It is demonstrated in this study that the discrete mineralogical nature of coal largely influences the wetting of the coal surface by water. Both advancing and receding contact angles were measured using captive-bubble and sessile-drop techniques with an automatic image analysis system. The distribution of mineral inclusions on the coal surface was examined by scanning electron microscopy. The coal surface region, on which the contact angles were measured, was separated from the bulk part by micro-slicing the coal samples, and the amount and size distribution of mineral grains in the coal surface region were determined through low-temperature ashing, followed by mass balance and particle size analyses. A significant scatter in contact angle values (up to ±15 degrees) is reported for samples of the same coal, indicating poor reproducibility of heterogeneous structures of coal at a microscopic level. Further, it was found that the increasing amount of mineral matter in coal samples reduced the contact angle value, although the scattered data clearly indicate that there are some other factors responsible for the contact angle variation. The results reveal that an important factor in analysis of contact angle variation on coal surfaces is the size of the hydrophilic mineral inclusions. Both the advancing and receding contact angles decrease with increasing size of the mineral grains and this effect is more pronounced for receding contact angles.

Keywords: Coal; coal wettability; contact angle; contact angle hysteresis; mineral matter; surface heterogeneity.

1. INTRODUCTION

Coal is made of organic macerals and inorganic minerals. Three different groups of macerals can be distinguished in coal: vitrinite, exinite and inertinite [1]. In this paper we do not take into consideration the behavior of particular macerals, but instead consider them all together as a group.

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Coal macerals have vegetal origin and are composed of a mixture of combustible metamorphosed plant remains, which vary both in chemical and physical compositions [2, 3]. The major elements of coal macerals are carbon, hydrogen, oxygen, and nitrogen. A broad variety of minerals form inorganic inclusions in the coal. The mineral matter represents several forms of inorganic material including optically identifiable mineral phases [2, 3]. Common minerals present in coal are silicates (quartz), and alumino-silicates (kaolinite, illite), carbonates (dolomite, calcite), and sulfides (pyrite) [2].

The term wettability describes interaction between a liquid and a solid and is often determined by contact angle measurements. The knowledge and understanding of wettability play a very important role in coal preparation and utilization processes including froth flotation, oil agglomeration, dust abatement, and preparation of coal-water slurries [4, 5, 6]. The major differences in wetting properties have been noted between hydrophobic organic macerals and hydrophilic inorganic mineral inclusions [4]. The contact angle for water on coal organic matter has been estimated to be as high as 100 degrees [6]. In practice, lower contact angle values (usually of a broad distribution) have been reported during examination of the coal samples [4, 6-14]. Irreproducibility of heterogeneous structure of coal, at both macroscopic and microscopic levels, is the main reason that wetting of coal varies from sample to sample. It is thus often more informative to report the wetting of coal, from a particular source, as the distribution of contact angles rather than describe this property as one averaged contact angle value [15]. Additionally, the use of different experimental techniques and different experimental conditions in many laboratories make the comparison of wetting characteristic among coals almost impossible to perform.

Factors affecting the coal wettability are coal rank [8, 14, 16, 17], mineral matter content [18, 19], moisture level [20], porosity [7, 11], and degree of oxidation [14, 17, 21].

It was reported by many researchers ([18, 19] and references therein) that the contact angle decreased with increasing mineral matter content in the coal sample. The mineral matter occurs in the form of distinguishable mineralogical grains. Ionic or polar sites of mineral matter present on the coal surface may become heavily hydrated in water. When the ratio of polar to non-polar sites is high, the contact angles are small over a broad range of pH values.

A systematic examination of the effect of microscopic heterogeneity on contact angles was initiated a few years ago [7, 22]. The recent contribution has improved the procedure for coal surface preparation [22]. This procedure involves polishing with abrasive paper, alumina powder, and a cloth, followed by ultrasonic cleaning and washing. Further, the captive-bubble measuring technique has been compared with the sessile-drop technique and the former has been recommended for the examination of the wetting properties of polished coal specimens [7].

The aim of this project was to study the effects of the amount, size and distribution of mineral matter inclusions present in coal on measured contact angles. Both advancing and receding contact angles were measured using a goniometer
equipped with an automatic image analysis system. The distribution of inorganic inclusions on the coal surface was examined by scanning electron microscopy. The coal surface region was separated from the bulk part by micro-slicing the coal samples. The micro-slices of coal samples were ashed in a low-temperature plasma asher and the amount of mineral matter was determined from mass balance. Finally, the size of mineral particles left in the ash was determined by using a particle size analyzer. The extended characterization of coal surface composition with regard to the mineral matter amount, size and distribution is critical for the success of this research program. A traditional proximate analysis of the tested coals, intended to test the coal bulk, cannot provide such detailed characterization of the coal surface.

2. MATERIALS AND METHODS

2.1. Coal samples

The coal samples, along with their mineralogical and chemical characterizations, were received from the Penn State Coal Bank. The coal samples used in this study were mined in different regions of the United States as specified in Table 1. Proximate analyses of the coals are given in Table 1. Ultimate analyses, calorific value, maceral composition, caking, and ash fusion temperatures for the same coals can be received from the authors or from the Penn State Coal Bank.

More than one specimen of each coal sample were usually used in the experiments. Letters following the sample number indicate each individual specimen.

2.2. Sample preparation

The experimental procedure for coal sample preparation, use, and characterization is schematically shown in Figure 1. The lumps of coal were cut into small pieces using a diamond saw. Then, they were polished according to the developed methodology [7, 22]. The wet polishing was done using a series of abrasive papers with a grit from 60 to 1200. This was followed by polishing with 0.5 μm alumina powder. Final polishing was done on a fibrous cloth (Chemomet from Buehler). Water washing and ultrasonic cleaning of coal specimens followed each step of the polishing procedure as previously described [7, 22]. The coal samples were stored in a refrigerator in plastic bags at the temperature of 4°C, and freshly repolished on a fibrous cloth before contact angle measurements.

2.3. Contact angle measurements

The contact angles were measured using a G10 Krüss goniometer equipped with a CCD camera. The system consists of a source of light with a diffuser; a microscope to which the CCD camera is connected; and a computer with DSA (Drop Shape Analysis) software designed for calculating the values of contact angles. See Figure 2 for a simplified schematic of the instrumentation.
Table 1.
Data on proximate analysis provided by Penn State Coal Bank

<table>
<thead>
<tr>
<th>Coal sample</th>
<th>Deposit location</th>
<th>Rank of coal</th>
<th>Ash [%]</th>
<th>Moisture [%]</th>
<th>Volatile matter [%]</th>
<th>Fixed carbon [%]</th>
<th>Number of samples used</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECS 25</td>
<td>Montana</td>
<td>Lignite A</td>
<td>7.71</td>
<td>34.91</td>
<td>27.32</td>
<td>30.05</td>
<td>2 (B and C)</td>
</tr>
<tr>
<td>DECS 26</td>
<td>Wyoming</td>
<td>Sub-bituminous B</td>
<td>5.58</td>
<td>26.30</td>
<td>33.06</td>
<td>35.06</td>
<td>1 (A)</td>
</tr>
<tr>
<td>DECS 30</td>
<td>Virginia</td>
<td>Medium Volatile Bituminous</td>
<td>3.81</td>
<td>2.06</td>
<td>29.51</td>
<td>64.62</td>
<td>8 (A to H)</td>
</tr>
<tr>
<td>DECS 32</td>
<td>West Virginia</td>
<td>High Volatile A Bituminous</td>
<td>19.76</td>
<td>2.64</td>
<td>30.74</td>
<td>46.86</td>
<td>4 (A to D)</td>
</tr>
<tr>
<td>DECS 33</td>
<td>Ohio</td>
<td>High Volatile B Bituminous</td>
<td>11.30</td>
<td>5.97</td>
<td>40.49</td>
<td>42.24</td>
<td>8 (A to H)</td>
</tr>
</tbody>
</table>

* – Corresponds to number of samples used during the experiments.
** – Corresponds to alphabetical identification of the samples.
Figure 1. A schematic of the experimental procedure used in this study.

Figure 2. A schematic of the experimental set-up for contact angle measurements.
The DSA program calculates the contact angle for a drop or a bubble placed on the substrate. The contour of the drop or the bubble is mathematically described by adapting the Young-Laplace equation for a curved interface. The contact angle corresponds to the angle at which the drop contour line meets the surface.

The majority of contact angle measurements in this study were carried out using the captive-bubble technique because this technique provides contact angles that are less sensitive to imperfections of the coal specimen surface [7]. Also, humidity is maintained constant in the captive-bubble method.

In a rectangular glass chamber the coal sample, a few centimeters in size, was placed with the flat surface facing downward. The chamber was filled with de-ionized water of pH 5.8-6.0. A small air bubble was produced at the tip of the U-shaped needle using a microsyringe and placed in contact with the coal surface from below. The volume of the air bubble was increased or decreased in order to produce the movement of the three-phase contact line. The water advancing and receding contact angles were measured in 10-15 seconds after the volume of the bubble was increased or decreased, respectively. The contact angles were measured for varying gas bubble volume from 5-8 µl to 40-50 µl. The measurements were repeated several times for different positions on the coal surface.

In selected experiments the sessile drop technique was also used. In this regard, a small water drop (3-5 µl volume) was placed onto a coal sample surface in air using a microsyringe. Adding more water increased the drop size. The advancing contact angle was measured in 10-20 seconds after the increase of the drop volume. Also, the receding contact angle was measured in 10-20 seconds after the volume of the drop was reduced to cause the retreat of the three-phase contact line.

After contact angle measurements, the top surface layer 1-3 mm thick was separated from the rest of the sample. The top slice layer of the coal was cut into three pieces and subjected to mineralogical analysis using scanning electron microscopy and low temperature ashing followed by particle size analysis of the mineral particles, as schematically shown in Figure 1.

2.4. Scanning electron microscopy

Inorganic inclusions on the surface of coal specimens were mapped using a Philips scanning electron microscope equipped with IMIX (Integrated Microanalyzer for Images and X-rays). The SEM with IMIX microanalyzer stores complete spectra at every pixel while scanning the beam at full electron-imaging speed. It also simultaneously collects the maps for all elements, the spectra from specific regions, and high-resolution digital images. In this study, the system was working at the following conditions: K_{α} detection, 10 ~ 10.2 mm working distance, 15 keV accelerating voltage, 1000x magnification, and data were collected over a 600 s time interval. Coal specimens were carbon coated before the SEM analysis.
The specimens were scanned, while the processor (Digital Pulse Processor) measured the energy of each x-ray photon. The photon was detected and tagged with the image location from which it came. Digital signal processing provides extraordinary enhancement of x-ray spectra and gives clean, well-resolved peaks with improved precision and optimum light element sensitivity. The peaks indicated that several chemical elements were present in coal samples. Only the highest peaks of ten chemical elements (S, Fe, C, O, Al, Si, K, Ca, Mg, and Na) were considered during the experiment. The x-rays were then sorted dynamically into a 3-D structure, which was later computer analyzed and x-ray maps were created. The images were taken from compositional contrast using a backscattered electron detector.

2.5. Low temperature ashing

A Low Temperature Asher (LTA) was used to obtain the mineral matter by removing the organic matter. Organic matter was burned and removed at 50-100°C under oxygen for 10 hours. The LTA worked under the following conditions: flow of oxygen – 250-350 cm³/min, and vacuum – 1.0-1.5 mm Hg.

For ashing, the slices of coal samples were dried and placed on a clean glass. The dried samples were placed into the LTA and ashed under oxygen. Only the surface of the coal was ashed, so that the recovered mineral particles would be representative of the minerals exposed during contact angle measurements. The mineral matter obtained by ashing was examined to determine the particle size distribution as described in the next section.

2.6. Particle size distribution of mineral matter

The Elzone PC 280 analyzer was used to determine the particle size distribution for the mineral particles obtained by low-temperature ashing of coal. Tubes with pinholes of 300 and 48 μm in diameter were used in this study. Using these tubes, the size of particles with a diameter from 11 to 300 μm could be determined. The particle size distribution analysis was carried out at low concentration of particles (approximately 0.01%) dispersed in an electrolyte solution (1-4% NaCl). Only the particles that were obtained from the sliced top surface (on which previously the contact angles were measured) were analyzed.

2.7. Mineral matter content

One-third of the coal specimen surface layer, on which the contact angles were measured, was ground into a fine powder, 160 μm or less in diameter. The grinding was performed in a clean agate mortar. The sample was then ashed in LTA at 50-100°C for 10-25 hours. After low temperature ashing, the content of mineral matter was determined from the mass balance.
3. RESULTS AND DISCUSSION

3.1. Characterization of mineral matter

3.1.1. Distribution and identification of mineral matter on coal surface

As a crude approximation the coal surface can be treated as a uniform hydrophobic (organic) solid contaminated with hydrophilic inorganic mineral inclusions. In this regard, the amount, size and distribution of hydrophilic inclusions should have a profound effect on wetting characteristics of coal surface. In this section, the nature and distribution of inorganic inclusions present on the surface of examined coal samples are briefly discussed.

By using the scanning electron microscope, the digital compositional maps of coal sample surfaces were prepared. Figure 3 presents the SEM images for the DECS 33C sample. The map of this sample showed significant presence of aluminum, silicon, iron and sulfur elements. The map shows the presence of aluminum and silicon around similar points and this indicates that clay minerals are characteristic inorganic inclusions on the surface of DECS 33C sample. Also, characteristic areas of the presence of iron and sulfur match together indicating the occurrence of pyrite (FeS₂), or other iron-sulfides. The area of iron also matches with carbon and oxygen showing that siderite (FeCO₃) might be present in the DECS 33C sample. Carbon also might come from the carbon coating, to some extent, and in this case instead of siderite, iron sulfate (FeSO₄) will be present for sample DECS 33C because the iron, sulphur and oxygen phases match together well, too.

From images in Figure 3, it appears that pyrite is present in smaller quantities than clay minerals, siderite or iron sulfate, and other minerals. Further, it was found from images in Figure 3 that calcium, potassium, oxygen and carbon were not distributed uniformly over the surface of the DECS 33C sample. Small inclusions were found for these elements on the DECS 33C coal surface. On the other hand, magnesium and sodium were relatively uniformly distributed on the surface.

The results from SEM mapping were compared with the inorganic elemental analysis data provided by the Penn State Coal Bank. For the DECS 33 coal, the major inorganic elements in the form of oxides are presented in Table 2. These data from the Penn State Coal Bank support the mineralogical characterization of coal surface obtained using scanning electron microscopy. They showed that major chemical elements like silica, aluminium and iron are present in this coal.

Figure 4 presents the SEM images for the DECS 25C sample. In this case, maps of iron and sulfur match very well showing the significant amount of pyrite. Pyrite is distributed in the form of small inclusions over the entire surface of the coal sample. Additionally the areas of calcium/carbon/oxygen and calcium/sulfur/oxygen matched very well indicating that respectively calcite (CaCO₃) and gypsum (CaSO₄·2H₂O) are present in sample 25C. They were found in a very small amount. The remaining chemical elements such as magnesium and sodium were distributed on the surface uniformly.
The results were also compared with the data from The Penn State Coal Bank. The major oxides for sample 25 are presented in Table 2.

Compositional maps were also prepared for other coal samples used in contact angle measurements in this study (images not shown). A few similarities between different samples were found. First, all samples showed characteristic macerals contaminated with grains of minerals. Further, the mineral grains were randomly distributed over the surfaces of coal samples. However, the majority of the min-
Table 2.
Major inorganic elements present in coal. Data provided by Penn State Coal Bank

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECS 21</td>
<td>55.1</td>
<td>30.7</td>
<td>4.24</td>
<td>0.88</td>
<td>0.56</td>
<td>0.22</td>
<td>4.93</td>
<td>0.04</td>
<td>0.20</td>
<td>2.9</td>
<td>1.8</td>
<td>0.33</td>
<td>0.06</td>
<td>0.04</td>
<td>0.02</td>
<td>0.46</td>
<td>0.002</td>
</tr>
<tr>
<td>DECS 25</td>
<td>25.7</td>
<td>16.1</td>
<td>5.26</td>
<td>8.20</td>
<td>23.3</td>
<td>0.31</td>
<td>0.28</td>
<td>0.41</td>
<td>17.4</td>
<td>1.3</td>
<td>1.0</td>
<td>0.41</td>
<td>0.55</td>
<td>1.9</td>
<td>0.03</td>
<td>0.03</td>
<td>0.020</td>
</tr>
<tr>
<td>DECS 26</td>
<td>31.7</td>
<td>16.1</td>
<td>4.84</td>
<td>4.64</td>
<td>23.5</td>
<td>1.80</td>
<td>0.40</td>
<td>0.89</td>
<td>12.7</td>
<td>1.0</td>
<td>0.6</td>
<td>0.23</td>
<td>0.19</td>
<td>1.1</td>
<td>0.09</td>
<td>0.02</td>
<td>0.026</td>
</tr>
<tr>
<td>DECS 30</td>
<td>46.8</td>
<td>28.8</td>
<td>13.9</td>
<td>0.90</td>
<td>1.94</td>
<td>2.15</td>
<td>1.52</td>
<td>0.52</td>
<td>0.20</td>
<td>0.9</td>
<td>0.6</td>
<td>0.4</td>
<td>0.02</td>
<td>0.05</td>
<td>0.06</td>
<td>0.05</td>
<td>0.009</td>
</tr>
<tr>
<td>DECS 32</td>
<td>51.0</td>
<td>34.3</td>
<td>3.15</td>
<td>1.02</td>
<td>1.89</td>
<td>0.30</td>
<td>3.84</td>
<td>0.40</td>
<td>0.90</td>
<td>4.8</td>
<td>3.7</td>
<td>0.45</td>
<td>0.12</td>
<td>0.27</td>
<td>0.05</td>
<td>0.65</td>
<td>0.035</td>
</tr>
<tr>
<td>DECS 33</td>
<td>41.5</td>
<td>22.0</td>
<td>19.2</td>
<td>0.85</td>
<td>6.46</td>
<td>0.52</td>
<td>1.70</td>
<td>0.07</td>
<td>5.60</td>
<td>2.4</td>
<td>1.4</td>
<td>1.6</td>
<td>0.06</td>
<td>0.56</td>
<td>0.05</td>
<td>0.17</td>
<td>0.004</td>
</tr>
</tbody>
</table>
eral grains was separated from each other and the grain aggregation over small areas was rare for the samples selected for this study. Also, no significant difference in the distribution of the mineral grains over the surface was noted between different samples.

3.1.2. Mineral matter content
Table 3 shows a comparison between the ash content in the coal as determined by Penn State Coal Bank through proximate analysis of representative coal samples (second column in the table) and ash content of the surface region determined for
Table 3.
Contact angle measured on DECS 33 and DECS 25 coal specimens of varying mineral matter content in the surface region

<table>
<thead>
<tr>
<th>Coal sample</th>
<th>Ash%</th>
<th>Contact angle [deg]</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk*</td>
<td>Surface</td>
<td>Advancing</td>
<td>Receding</td>
</tr>
<tr>
<td>DECS 33A</td>
<td>12.02</td>
<td>9.06</td>
<td>77 – 91 (81)**</td>
<td>44 – 64 (51)**</td>
</tr>
<tr>
<td>DECS 33B</td>
<td>12.02</td>
<td>15.33</td>
<td>74 – 88 (82)**</td>
<td>43 – 64 (52)**</td>
</tr>
<tr>
<td>DECS 33C</td>
<td>12.02</td>
<td>3.20</td>
<td>77 – 90 (83)**</td>
<td>41 – 56 (50)**</td>
</tr>
<tr>
<td>DECS 33D</td>
<td>12.02</td>
<td>4.34</td>
<td>76 – 90 (85)**</td>
<td>47 – 59 (54)**</td>
</tr>
<tr>
<td>DECS 33E</td>
<td>12.02</td>
<td>2.83</td>
<td>76 – 84 (79)**</td>
<td>43 – 61 (53)**</td>
</tr>
<tr>
<td>DECS 33F</td>
<td>12.02</td>
<td>11.66</td>
<td>77 – 87 (82)**</td>
<td>30 – 62 (48)**</td>
</tr>
<tr>
<td>DECS 33G</td>
<td>12.02</td>
<td>11.71</td>
<td>62 – 66 (65)**</td>
<td>28 – 45 (35)**</td>
</tr>
<tr>
<td>DECS 33H</td>
<td>12.02</td>
<td>9.07</td>
<td>79 – 86 (82)**</td>
<td>41 – 55 (51)**</td>
</tr>
<tr>
<td>DECS 25C</td>
<td>11.85</td>
<td>51.55</td>
<td>32 – 65 (40)**</td>
<td>19 – 46 (36)**</td>
</tr>
</tbody>
</table>

*as specified by Penn State Coal Bank; ** Θ₅₀ is the average value of contact angle determined from the cumulative frequency versus contact angle curve at 50% (see Figures 7 and 8).

Specimens used in this study (third column in the table). The results of low temperature ashing and mineral matter analysis performed in this study indicate a substantial difference in mineral matter content in the surface region for majority of the samples. For example, the mineral matter content in the 1-3 mm surface region of the DECS 33C sample was about 3 wt%, which is 9 wt% less than average ash amount in this coal. Also, the ash content was 51.6 wt% in the surface region of the DECS 25C sample as compared to 11.9 wt% that is typical for this coal.

As the result of this research, it can be concluded that a traditional proximate analysis of coals cannot provide detailed characterization of the coal surface. The contact angle data discussed later in this paper are related to the mineral matter content determined for the coal specimen surface region.

3.1.3. Distribution of mineral grain size
Figure 5 shows the distribution of mineral grain size recovered from the coal surface region of the following samples: DECS 25 (sample B) – lignite A; DECS 30 (sample F) – medium volatile bituminous; DECS 32 (sample B) – high volatile bituminous A; and DECS 33 (sample A) – high volatile bituminous B. Each coal is of different rank and, consequently, represents a different chemical composition (Table 1).

The d₅₀ average grain size of mineral matter is shown in Table 4. The d₅₀ value is the size of particle taken at 50% of the cumulative frequency versus particle size curves. From the data two main groups can be distinguished: the mineral particles for which the d₅₀ values are in the range of a few micrometers (samples: DECS 30F (1.5 μm), DECS 33A (2.5 μm) and DECS 32B (3.3 μm)), and the DECS 25B sample for which the average size of mineral particles is approximately 15 μm. It
was already shown in this paper that lower rank coals contain significant amount of mineral matter (Table 3), and it appears from the data in Table 4 that the size of the mineral particles has a direct relation with the mineral matter content.

3.2. Water contact angles measured on coal

3.2.1. Distribution of contact angles

Coal, with a great deal of variation in its petrographic composition and mineral matter content, varies profoundly in wetting properties at both microscopic and

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**Table 4.**
The $d_{50}$ average particle sizes for mineral particles separated from coal samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_{50}$ [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECS 25B</td>
<td>15</td>
</tr>
<tr>
<td>DECS 30F</td>
<td>1.5</td>
</tr>
<tr>
<td>DECS 32B</td>
<td>3.3</td>
</tr>
<tr>
<td>DECS 33A</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$d_{50}$ – the average grain size of mineral matter taken at 50% of the cumulative frequency versus particle size curve.
macroscopic levels [7, 15, 18]. Coal macerals are hydrophobic components of the coal, whereas the mineral matter forms hydrophilic inclusions [11, 18]. Since partitioning, content, and size of minerals grains vary from seam to seam and from sample to sample, it is quite typical that a distribution of contact angles for coal is often reported instead of a single value [4, 6, 15].

Figure 6 presents the advancing and receding contact angles measured for fourteen DECS 33 samples using the captive-bubble method. The measurements were performed for air bubble volume varying from about 5 to 90 μL. A small effect of the bubble volume on contact angles is hidden under the experimental results (Figure 6) but it is a minor effect for significantly scattered data and thus, the contact angle versus bubble size relationships are not discussed here. The effect of bubble (drop) size on advancing and receding contact angles was previously discussed for solids of varying surface quality [23-25].

As shown in Figure 6, a significant scatter in both advancing and receding contact angle values is observed for the DECS 33A-H specimens, all cut from the same coal lump. The advancing and receding contact angles varied from about 50 degrees to 91 degrees and from 28 to 45 degrees, respectively. The scatter in contact angle values is sometimes smaller for individual samples (Figure 6 and Table 3). The variation of contact angles and average values, along with a characterization of the surface mineral matter content in a coal sample, are shown in Table 3 for several samples.

It is expected that the observed scatter in contact angles is associated with the heterogeneity of the coal surface. For any surface with randomly distributed heterogeneities, as it is in the case of coal, a scatter in contact angle values will always be observed, irrespective of coal surface smoothness and precision of the
measurements. Nevertheless, the coal surface roughness could also influence the variation of contact angles shown in Figure 6. Although the coal samples used in this study were polished according to the advanced methodology, the coal surface was still rough at sub-microscopic dimensions [22].

The contact angle values measured in this study were used to prepare the frequency distribution graphs that seem to be more informative in analysing the wettability of solids with heterogeneous surfaces [15]. Examples of such graphs are shown in Figures 7 and 8 for two different samples: DECS 33C and DECS 25B. Figures 7 and 8 present cumulative frequency for both advancing and receding contact angles. The DECS 33C and DECS 25B coal samples differ in rank and mineral matter contents (Table 3). The DECS 33 coal is classified as a bituminous, whereas the DECS 25 coal is a lignite. The results of low temperature ashing and mineral matter analysis also indicate a substantial difference in mineral matter content in the surface region of these two samples as compared to the results of proximate analysis (for bulk material). The mineral matter content in the 1-3 mm surface region of the DECS 33C sample was about 3 wt% and it was 15 wt% in the DECS 25B sample.

As shown in Figures 7 and 8, wettability of the DECS 33C and DECS 25B samples differed. The advancing and receding contact angles varied from 77 to 90 degrees and from 41 to 56 degrees respectively, for the DECS 33C sample. The contact angles varied from 44 to 58 degrees and from 13 to 32 degrees for

![Figure 7. Distribution of advancing and receding water contact angles for the DECS 33C coal.](image-url)
advancing and receding contact angles, respectively, for the DECS 25B sample. In this study, the cumulative frequency versus contact angle relationships, such as in Figures 7 and 8, were used to determine the $\theta_{50}$ contact angle value. This value is assumed to be the representative average contact angle value and corresponds to the value taken at 50% cumulative frequency of all results (Figures 7 and 8). For example, the $\theta_{50}$ values for the advancing ($\theta_{A50}$) and receding ($\theta_{R50}$) contact angles measured on the DECS 33C sample are 83 and 50 degrees, respectively. Thus, the contact angle hysteresis $\Delta \theta_{50} = \theta_{A50} - \theta_{R50}$ is 33 degrees for this sample. In the case of the DECS 25B sample, the $\theta_{50}$ values for advancing contact angles, receding contact angles, and contact angle hysteresis are 50, 24, and 26 degrees, respectively. Surprisingly, as these results indicate, the average values of advancing and receding contact angles are significantly different for the two samples (DECS 33C and DECS 25B) whereas the contact angle hysteresis values are very close to each other. However, this result might be misleading in the analysis of heterogeneous surface. The Young equation (1) clearly indicates that a cosine of a contact angle should be used in the analysis of energy barriers producing contact angle hysteresis.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$$

where $\gamma_{SV}$, $\gamma_{SL}$, $\gamma_{LV}$ are the solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, respectively, and $\theta$ is the contact angle.
For example, although the contact angle hysteresis is similar for both DECS 33C and DECS 25B coal specimens (33 and 26 degrees, respectively), the energy barriers calculated based on the values of the cosine of contact angles and surface tension of liquid, $\Delta G = \gamma_{LV} (\cos \theta_{A50} - \cos \theta_{R50})$, are 37.9 mJ/m² and 19.7 mJ/m², respectively. Such a significant difference in the value (37.9-19.7=18.2 mJ/m²) suggests that DECS 33C and DECS 25B specimens had significantly different surface heterogeneity patterns.

As discussed in Section 3.1.1, the mineral grains were randomly distributed over the surfaces of coal samples used in this study. The majority of the mineral grains, however, was separated from each other and the grain aggregation over small areas was rare for the coal samples. Also, no significant difference in the distribution of the mineral grains over the surface was noted between different samples. It is, therefore, unlikely that the distribution of mineral matter is the major reason for the differences in the wetting of coals of different ranks used in this research and thus, this factor was not studied in details.

3.2.2. The effect of mineral matter content on contact angles

Several researchers have shown that there exists a correlation between the mineral matter content and the wetting characteristic of coal [18, 19, 26, 27]. The effect of mineral matter content on contact angles was also analyzed in this study. Figures 9 and 10 present the relationships between the $\theta_50$ values, for advancing and receding contact angles respectively, and the amount of the mineral matter determined in the surface layers of coal samples studied in this program.

As Figures 9 and 10 indicate, increasing amount of mineral matter in the coal causes a decrease of both advancing and receding contact angle values. This correlation, however, is not very clear as the contact angle values are considerably scattered. The receding contact angles seem to correlate better with the amount of mineral matter than advancing contact angles.

The wettability of a heterogeneous solid surface can be described by Cassie's model that predicts a correlation between the contact angle (2) and composition of the surface [28, 29]. For a two-component surface, the Cassie equation is as follows [28, 29]:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

(2)

where $f_1$ is the fractional area of the surface with a contact angle $\theta_1$, and $f_2$ is the fractional area of the surface with a contact angle $\theta_2$.

In a very simplified model, the coal can be considered as a two-component heterogeneous material composed of hydrophobic macerals and hydrophilic mineral inclusions. The contact angle for water on organic macerals can be as high as 100 degrees [6]. Many inorganic inclusions are hydrophilic with water contact angle close to zero. As discussed in Section 3.1.1, the majority of inorganic inclusions are made of silicates, oxides, and carbonates that exhibit high affinity to water. It is well known that the high-energy solids such as inorganic minerals can be easily
Figure 9. The effect of mineral matter on the $\theta_{A50}$ advancing water contact angle. The solid line in figure A is shown as a guide to the eye. The solid line in figure B represents a prediction from the Cassie equation (2) assuming that $\theta_2 = 0$. 
Figure 10. The effect of mineral matter on the $\theta_{R50}$ receding water contact angle. The solid line in figure A is shown as a guide to the eye. The solid line in figure B represents a prediction from the Cassie equation (2) assuming that $\theta_2 = 0$. 
contaminated with air-borne organic contaminants when exposed to the laboratory environment, making the surface only partially wetted by water. The contamination of mineral surface by air-borne impurities can be avoided if the surface is freshly polished under water (as in this study).

It follows from equation (2) that the correlation between cosine of contact angle and amount of mineral matter should be linear if the contact angle results fit to Cassie's model. Figures 9B and 10B demonstrate that the correlation between \( \cos \theta \) and the amount of mineral matter deviate from a linear relationship for both advancing and receding contact angles. A scatter in the results suggests that the amount of the mineral matter is not the only factor influencing the measured contact angles.

3.2.3. The effect of size of mineral inclusions on contact angles

Early modeling of the contact angles on heterogeneous surfaces by an Johnson and Dettre [30] and continued by others [31] indicate that the size of heterogeneity features should have a profound effect on contact angles. Unfortunately, the experimental work on the effect of the heterogeneity dimension on advancing and receding contact angles has been very limited. Only recently the measurements of contact angles on surfaces with model heterogeneous structures have been initiated [32-35], but the literature is still short of experimental results and thus, the theoretical models have not been sufficiently justified. In this study, the size of mineral grains distributed in the macerals of examined coal samples was determined (Section 3.1.3) and correlated with the measured contact angles with the mineral matter content.

The correlations between average contact angles \((\theta_{A50} \text{ and } \theta_{R50})\) and the average cross-sectional area of mineral particles are shown in Figures 11 and 12. As these figures indicate, both average advancing and receding contact angles decrease with increasing size of mineral grain (average value) contaminating the coal organic matrix in the surface region. This effect is more pronounced for receding (Figure 12) than for advancing contact angles (Figure 11). As Figure 11 shows, the average advancing contact angle was only slightly affected by the presence of mineral inclusions having an average cross-sectional area \((A)\) from about 0.1 \(\mu m^2\) (hypothetical diameter of the circular grain is \(d=(4A/\pi)^{1/2}=0.36 \mu m\)) to 10 \(\mu m^2\) (\(d=3.6 \mu m\)). The influence of mineral grains on advancing contact angle increased for particles with an average area larger than 10 \(\mu m^2\) (\(d=3.6 \mu m\)).

The significance of the size of the hydrophilic mineral grains on wettability of coal specimens seems even more obvious in the analysis of receding contact angles (Figure 12). As shown in Figure 12, the increasing size of mineral inclusions causes a decrease in the receding contact angle. This effect is observed for the entire range of area occupied by the inorganic grains, from about 0.02 \(\mu m^2\) (\(d=0.16 \mu m\)) to 100 \(\mu m^2\) (\(d=11.3 \mu m\)).

Several researchers have correlated the value of contact angles with heterogeneity of solid surfaces for model systems in the past [28-35]. The results presented in Figures 11 and 12 provide probably the first experimental evidence sup-
Figure 11. The effect of average cross-sectional area per ash particle on average advancing water contact angle. Markers indicate experimental points and the line indicates possible trends.

Figure 12. The effect of average cross-sectional area per ash particle on average receding water contact angle. Markers indicate experimental points and the line indicates possible trends.
porting the significance of the size of heterogeneous features obtained for complex solids having random surface heterogeneity.

In order to evaluate the effect of mineral matter on coal surface wettability it was implicitly assumed that coal was composed of a hydrophobic organic matrix with some hydrophilic mineral inclusions. However, since coals varying in ranks were used in the experiments the wettability of coal organic matrix varied as well. It can be expected that while such a matrix for low volatile bituminous coal is very hydrophobic, it is more hydrophilic for lignite. As a matter of fact, nothing is known about the wetting of the organic matter of different coals since all the measurements are carried out on coal which always contains some amount of mineral matter.

4. SUMMARY

In agreement with current knowledge on wettability of heterogeneous surfaces, the microscopic heterogeneity of coal surface causes significant scatter in both advancing and receding contact angles, reaching about ±15 degrees in this study. Also, large contact angle hysteresis for water drops and gas bubbles on heterogeneous coal surfaces, up to 35 degrees, was observed for the coal specimens.

The proximate analyses of bulk coal are not representative for coal specimens used in contact angle measurements, and a detailed surface characterization of coal samples should compliment the contact angle measurements. This was accomplished in this study through mineralogical mapping of coal surface using scanning electron microscopy with the IMIX microanalyser, followed by low-temperature ashing of coal surface region, and particle size analysis of mineral matter present in ashed slices of coal samples. It was found that the mineral matter content in the coal surface region had an impact on measured advancing and receding contact angles. Both contact angles decrease with increasing amount of mineral matter in the coal samples, although correlation is not as straightforward as is usually discussed in the literature. The size of the mineral matter grains forming inclusions in the coal surface has profound effect on wetting characteristics of coal sample. It was found that both advancing and receding contact angles decreased with increasing dimensions of mineral grains. It is especially interesting that these correlations are quite consistent in spite of the use of coal samples with different mineral matter contents and different ranks.

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