Micro-FTIR analysis to study the change in surface chemistry after addition of collectors and their effect on coal hydrophobicity

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Abstract: In this study, the micro-FTIR analysis was used to investigate in-situ surface properties of coal, and was directly correlated to coal hydrophobicity, as measured by the contact angle before and after the addition of collectors, to understand their suitability for flotation. Three different collectors, diesel, pine needle oil and dodecyl trimethyl ammonium bromide (DTAB) were tested. The micro-FTIR technique provided a semi-quantitative analysis of functional groups present on the coal surface exactly where the contact angle was measured and provided a visualization of collector adsorption on specific areas of coal and associated changes in coal surface properties. This analysis could lead to a smarter way of using process design in terms of reagent selection for coal flotation to obtain a product of desired petrographic composition, which would especially be useful for coking coals. This study presents a work in progress for developing a procedure for a quick pre-selection of collectors for coal flotation based on coal surface properties.

1. Introduction

Coal flotation is used for treating fines of metallurgical coal, which is used for coke production. These coals are medium to high rank and are naturally hydrophobic usually. Changes in the hydrophobicity are attributed to changes in the aromatic and aliphatic hydrocarbon coal structures, as well as the content of oxygen groups across the coal ranks (Klassen, 1953; Aplan, 1983; Onlin and Aplan, 1984; Arnold and Aplan, 1989; Holuszko and Mastalerz, 2015). The surface properties of the coal are determined by the functional groups of the organic matter, the presence of mineral matter and their quantities, pore volume, and the association between minerals and macerals, where macerals are the smallest microscopically distinguishable organic components in coal.

One of the simplest ways to establish the relationship between coal properties and hydrophobicity is by using contact angle measurements on the polished surface of coal. The contact angle techniques have been used to characterize the surface hydrophobicity for coal for many years (Hanning and Rutter, 1989). Based on contact angle measurements on a variety of coals, Gutierrez et al. (1984) concluded that the hydrophobicity of coal decreased with rank parameters such as fixed carbon and total carbon content. In another study, an alkali-extraction method was used for the determination of oxidation extent, and both contact angle technique and flotation tests were used to evaluate the influence of oxidation on coal hydrophobicity (Gutierrez et al., 1984). Arnold and Aplan (1989) investigated the hydrophobicity of microscopically identified macerals by using both captive bubble and sessile drop contact angle techniques. It was found that contact angles on vitrinite were shown to be a function of rank parameters such as carbon content, oxygen content and vitrinite reflectance. The researchers also pointed out that contact angles on heterogeneous surfaces may become misleading unless the maceral composition is known or estimated. It should be noted that in the early studies on coal hydrophobicity,

bulk properties such as total carbon content and oxygen content were usually used to correlate with hydrophobicity (Laskowski, 2001). However, the importance of the chemical composition of the coal surface should especially be emphasized when considering coal hydrophobicity.

The micro-Fourier Transform Infrared spectroscopy (micro-FTIR) procedure for coal surface analysis had been developed in the 1990s (Mastalerz and Bustin, 1993) and was found to be a unique method to investigate the in-situ chemical properties of macerals and to characterize small areas of coal (10-20 μm) in a non-destructive manner. Chen et al. (2013) suggested that a reflectance-based micro-FTIR) spectroscopy mapping method could be used to characterize the functional groups in coal macerals, and simultaneous optical imaging of the measurement area can provide high-resolution information about the chemical properties of coal macerals. Liu (2016) and Liu et al. (2017) developed an in-situ procedure for carrying out micro-FTIR analysis and contact angle measurements of the same areas and attempted to correlate the chemical composition of the coal surface, including macerals, with a corresponding contact angle to investigate the hydrophobicity of low and high-rank coals. It was concluded that for low-rank coal, an increase in aromaticity led to an increase in the contact angle whereas an increase in the aliphatic groups decreased the contact angle. For the high-rank coal, an opposite trend was observed. Also, an increase in oxygenated groups led to a decrease in the contact angle for high-rank coals. This suggested that the variation in the chemical composition of coal surface enabled the change in the hydrophobicity and this could have an impact on how different coal macerals respond to floatation since macerals exhibit variable chemical composition in terms of the content of aliphatic groups, aromatic groups, and other functional groups.

Oily collectors such as kerosene, diesel and pine oil are the most common reagents used as collectors for coal flotation. It has been proven in practice that the addition of these oily collectors increases the hydrophobicity of coal. Studying the adsorption of various collectors on the coal surface using the micro-FTIR technique is a relatively new approach to study their suitability for coal flotation, and if it was studied, it has never been reported in previous research literature. The micro-FTIR technique provides testing conditions for in-situ analysis of coal surface and correlates contact angle measurements with the chemical composition of the coal surface before and after additions of collectors, which are used to further enhance the hydrophobicity of coal.

From the previous studies, the floatability of macerals across various ranks could be stimulated by using chemical reagents that could be selected in such a way that they adsorb specifically on certain macerals (Klassen, 1953; Bujnowska, 1985; Holuszko and Mastalerz, 2015). Selection of such chemicals needs to be made in accordance with the surface properties of macerals; hence, selectivity could be induced during flotation. The possibility of finding the right collectors for each type of coal (of certain surface properties and petrographic composition) may help to reduce coal flotation problems at the industrial scale. The possibility of the selective flotation of coal to produce concentrates of a desired petrographic composition holds tremendous promise for industrial applications, especially for coking coals (Given et al. 1975; Shibaoka and Ueda, 1978; Parkash et al., 1984; Parkash et al., 1985). It is not necessary to obtain a complete separation of petrographic components if the proportion of certain components in the final product is achieved to enhance the quality of the final product.

On the other hand, there is a need for finding suitable flotation reagents for low rank and difficult-to-float coals if they are to be utilized in a sustainable way. Studying the affinity of various flotation collectors to coal surfaces of known chemistry is an important step forward in understanding the mechanisms for such affinities. It is also suggested that understanding the effects of the surface chemistry on the contact angle, as well as exploring suitable chemical reagents such as collectors to promote selectivity of certain macerals, can ultimately help to design the optimal chemical regimes to improve coal flotation.

In this study, the micro-FTIR analysis was used to investigate in-situ surface properties of selected coal spots of different petrographic composition and these were directly correlated to the coal hydrophobicity as measured by the contact angle before and after the collector addition. The micro-FTIR semi-quantitative analysis was used to quantify the changes in the surface chemistry of various coal spots after the addition of the selected collectors and was used to explain which collector worked better. In addition, micro-FTIR mapping of aliphatic and aromatic groups was used to visually provide evidence of the adsorption of the selected collector on areas with different maceral compositions.

2.   Materials and methods

2.1. Materials

Medium volatile bituminous coal from a mine in British Columbia, Canada was used in this study. This coal was a higher rank coal with an average mean vitrinite reflectance Ro of 1.6% and volatile matter content *V.M.$_{dmmf}$* of 25.2%. Two samples (H1 and H2) were selected and cut to form small coal blocks with approximate dimensions of 40 mm × 20 mm × 15 mm. Each block was polished using 200, 600, 800 and 1200 grit sandpapers followed by 6 μm and 1 μm fine diamond suspension and 0.05 μm colloidal silica to produce a smooth surface for measurements. On each block of coal, several areas (4 mm × 4 mm) were marked off for analysis. Sample H1 had two areas while sample H2 had four areas.

Three reagents: diesel (non-ionic), pine needle oil (non-ionic) and dodecyl trimethyl ammonium bromide (DTAB, cationic), were used as collectors to treat the sample surface. The sample was immersed in an emulsion/solution of the reagent. The concentration for each emulsion/solution of the reagent was kept constant at 30 mg/L. Each sample was conditioned for three minutes in the reagent before the measurement. The coal block was then washed with mild soap and dried at 45°C after measurement to prevent contamination. A low temperature of 45°C was used to minimize the probability of coal oxidation.

2.2. Contact angle measurement

A modified captive bubble method was adopted to perform the contact angle measurements using an FTA 1000 Drop Shape Analyzer according to an established procedure (Liu, 2016). In this method, the solid sample was immersed in water and sat on the top of a plastic stool in the cuvette. A small air bubble was produced at the tip of the U-shaped needle using the micro-syringe and placed in contact with the sample surface. To place the airdrop exactly on the predetermined area, a dental mirror was used to improve the view of the sample from below. A 100 μL syringe with 0.152 mm needle diameter at an automatic pump in and pump out rate of 0.08 μL/s was used for all measurements. The contact angle value after reaching stability (usually after 100 sec) was used to characterize the hydrophobicity of the predetermined spots. The measurements were conducted on the marked areas before and after being conditioned by the reagents.
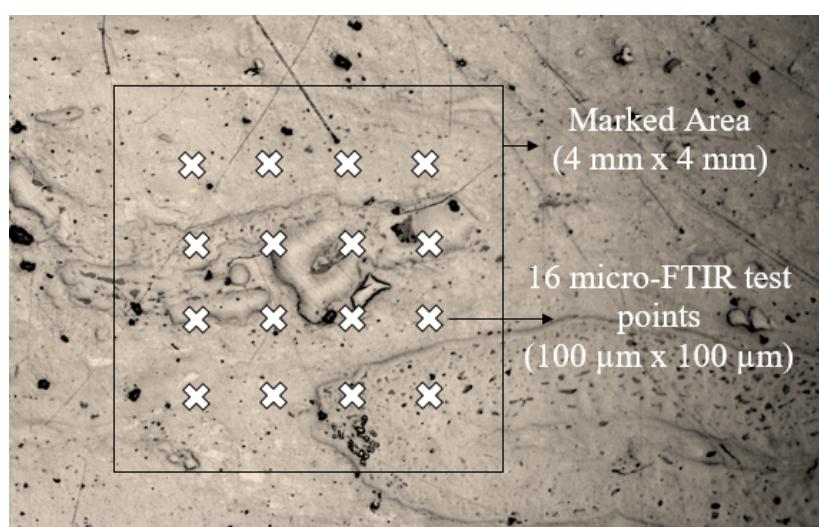
Fig. 1. Schematic of micro-FTIR test points on the polished coal sample surface

2.3. Micro-FTIR spectroscopy

A Nicolet 6700 spectrometer paired with a Nicolet Continuum microscope was used to perform the micro-FTIR measurements. The micro-FTIR was operated in a reflected light mode with a resolution of 4 cm^{-1} with a gold plate as background. The Nicolet Continuum microscope consists of a video camera, a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector and a motorized mapping stage. Reflectance micro-FTIR spectra were collected within the 4000-700 cm^{-1} wavenumber range. 500 scans

were used, and the obtained spectra were subjected to the Kramers-Krönig transformation. Band assignments followed published sources (Painter et al., 1981 and 1985; Wang and Griffiths, 1985; Mastalerz and Bustin, 1996; Chen et al., 2012). The OMNIC software was used for peak area integration.

An infrared objective with 15x magnification and an aperture size of 100 μm × 100 μm was employed to generate the spectrum of the selected areas of the samples. 16 test points, evenly distributed on each marked area, as illustrated in Fig. 1 were selected for micro-FTIR measurements. The measurements were performed before and after the conditioning by diesel, pine needle oil, and DTAB. Micro-FTIR mapping was also conducted on selected areas before and after the treatment using diesel oil. Fig. 1 illustrates the schematic of the selection of the micro-FTIR tests points while the process is described in more details in Section 2.1.

A Perkin Elmer Spectrum 100 FT-IR Spectrometer was used to obtain bulk FTIR spectra on the three reagents. The spectra were obtained between 4000 cm^{-1} and 350 cm^{-1} at a resolution of 1 cm^{-1}.

3. Results and discussion

3.1. Contact angle

The contact angle values on the high-rank coal sample were found to be variable depending on the area/spot where the measurements were taken, as listed in Table 1. For the original surface (without the reagents), the contact angle values varied between 43° to 52°. All the collectors improved hydrophobicity of the coal since contact angle values rose after using reagents as compared to the original surface. The highest contact angle values were recorded for the coal surface treated with diesel whereas the lowest increase in contact angle value was noted for the coal surface treated with DTAB. Generally, the reproducibility of the captive bubble technique was shown to be about ±0.50° with an average standard deviation of ±0.28°. Similar standard deviations have been reported by other researchers who have used these techniques (Ofori et al., 2006 and 2010; Liu, 2016). The difference in measured contact angle values could have resulted from (a) the local petrographic and chemical heterogeneity on the chosen spots; (b) the cracks; (c) the roughness and porosity of the coal surface; and (d) the presence of invisible small amounts of minerals, even though the areas were chosen to minimize these effects.

Different areas were affected differently depending on their composition. The standard deviation for the contact angle measured on the original coal surface was found to be 0.13°-1.22°, 0.42°-2.81° for diesel, 0.06° to 0.56° for pine oil and 0.08° to 0.80° for DTAB. The greatest reduction in the standard deviation was observed for the coal surface treated with diesel, compared to pine oil and DTAB, indicating more stability of the surface after treatment with diesel.

Table 1. Contact angle for different spots on coal specimen (95% confidence level)

Coal/reagent	H1 area 1	H1 area 2	H2 area 1	H2 area 2	H2 area 3	H2 area 4
Original	52°±0.04°	45°±0.07°	47°±0.05°	44°±0.32°	44°±0.09°	43°±0.23°
Diesel	59°±0.04°	66°±0.11°	56°±0.31°	54°±0.26°	62°±0.05°	63°±0.47°
Pine needle oil	53°±0.02°	52°±0.02°	54°±0.07°	52°±0.30°	55°±0.02°	52°±0.35°
DTAB	52°±0.04°	52°±0.07°	50°±0.03°	46°±0.05°	48°±0.10°	51°±0.02°

3.2. Semi-quantitative analysis of functional groups

Micro-FTIR spectra were collected in the same spots where contact angles were measured. Each spectrum represents the average FTIR spectrum of all 16 points in the selected areas. A semi-quantitative aspect of the FTIR analysis is presented as ratios of the integrated areas of individual functional groups, as shown in Table 2. These ratios have been chosen to represent chemical characteristics that influence coal hydrophobicity, followed by results obtained from work by Liu (2016).

The aromaticity (AR) is very low because of the low intensity of the aromatic CH_{ar} stretching vibration band (3083-3002 cm^{-1}). Another ratio shows a large spread in values within the same rank of coal, reflecting the chemical heterogeneity of the coal surface. The averaged values of the semi-quantitative ratio for each of the functional groups are plotted in Figs. 2 and. 3. It is noticeable that the aromaticity of coal surface is reduced when diesel and pine oil are used, while no reduction is noticed

when DTAB is used to treat the coal surfaces. On the other hand, the aliphatic character of studied coal surfaces, as represented by the aliphaticity is significantly changed after treatment with either DTAB or pine oil, but not when diesel is used. This may be attributed to the way each of the reagents is interacting with the specific coal surface.

Table 2. Semi-quantitative ratios on different spots on coal specimen

Area	Aromaticity	Oxygenated	Aliphaticity	Contact angle
H1 area 1 (original)	0.207	0.042	13.72	51.75°
H1 area 1 (pine needle oil)	0.156	0.060	3.61	52.65°
H1 area 1 (diesel)	0.074	0.079	12.83	58.86°
H1 area 2 (original)	0.179	0.032	19.54	45.07°
H1 area 2 (pine needle oil)	0.086	0.051	5.44	51.66°
H1 area 2 (diesel)	0.174	0.030	20.73	65.87°
H2 area 1 (original)	0.200	0.030	18.19	46.67°
H2 area 1 (pine needle oil)	0.224	0.060	4.95	54.28°
H2 area 1 (diesel)	0.146	0.074	6.64	55.78°
H2 area 1 (DTAB)	0.182	0.053	5.27	50.20°
H2 area 2 (original)	0.256	0.031	14.84	44.21°
H2 area 2 (pine needle oil)	0.145	0.067	3.43	52.44°
H2 area 2 (diesel)	0.115	0.071	7.77	54.41°
H2 area 2 (DTAB)	0.481	0.070	3.41	46.48°
H2 area 3 (original)	0.254	0.053	10.53	44.49°
H2 area 3 (pine needle oil)	0.252	0.033	7.07	55.29°
H2 area 3 (diesel)	0.172	0.032	18.97	62.17°
H2 area 3 (DTAB)	0.095	0.035	7.16	47.70°
H2 area 4 (original)	0.289	0.112	5.01	43.45°
H2 area 4 (pine needle oil)	0.142	0.055	4.52	52.23°
H2 area 4 (diesel)	0.151	0.048	12.63	62.50°
H2 area 4 (DTAB)	0.457	0.055	6.12	50.89°

Aromaticity defined as C-H$_{aromatic}$ stretch/C-H$_{aliphatic}$ stretch (AR); Oxygenated groups/C=C$_{aromatic}$ and Aliphaticity (CH$_{aliphatic}$/CO)
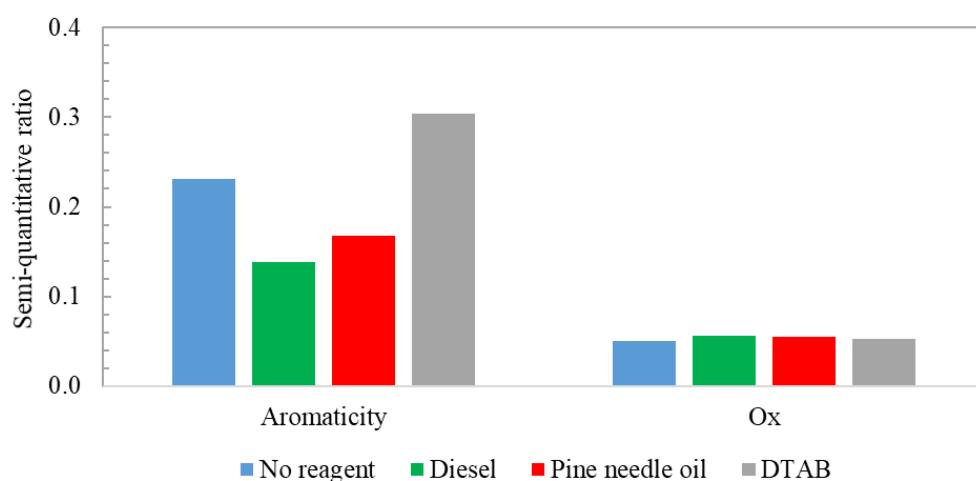
Fig. 2. Semi-quantitative ratio for averaged aromaticity (AR) and oxygenated groups on coal before and after reagent treatment

3.3. Aromaticity and contact angle

There is a linear relationship between aromaticity and contact angles, as derived from the captive bubble techniques. In the coal studied, the contact angle increases as the aromaticity decreases and this is

consistent with the previous results by Liu (2016). The higher rank coal used in this study is of medium volatile bituminous rank, and it is possible that the decrease in hydrophobicity of this coal is due to the increase in aromaticity, as suggested by Klassen (1953), which is caused by the increase in aromatic groups while these groups interact with polar water molecules through the π-electrons, thus resulting in decreasing contact angle values.

The trend between AR and contact angle shows that an increase in aromaticity causes a decrease in contact angle for the original coal surface as shown in Fig. 4. Adding diesel as a reagent leads to the decrease of the overall aromaticity of the coal surface and this, in turn, makes the coal surface more hydrophobic, as evidenced by increased contact angle values. While both pine needle oil and DTAB fail to reduce the aromaticity of this high-rank coal to the same extent as diesel, this results in making coal less hydrophobic, as evidenced by the contact angle.
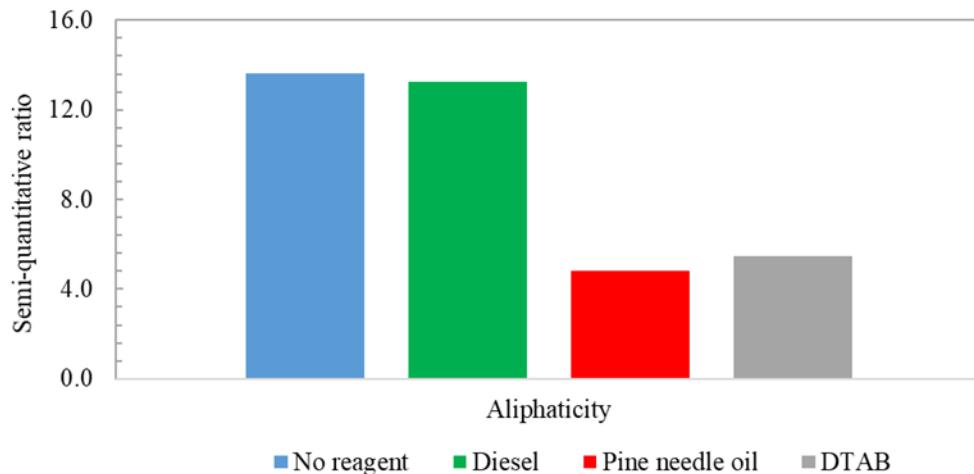
Fig. 3. Semi-quantitative ratio for averaged aliphaticity (AL) on coal before and after reagent treatment
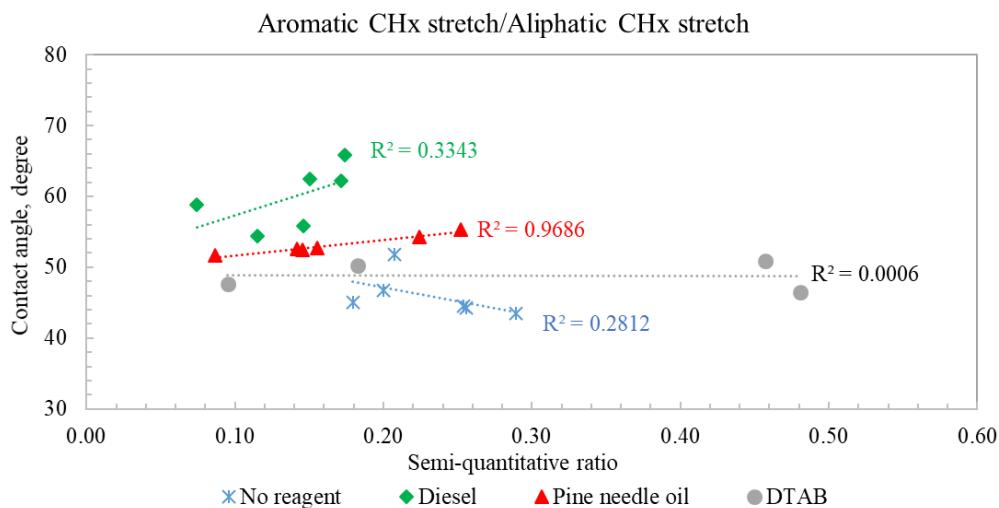
Fig. 4. Effect of aromaticity on the contact angle with and without reagents

3.4. Presence of oxygenated groups and their effect on contact angle

The amount of oxygen functional groups is a major factor that affects the hydrophobicity of a coal surface (Klassen, 1953; Laskowski, 2001). Hydrogen bonding, dipole-dipole, and even electrostatic interactions between water molecules and oxygen functional groups on the coal surface would increase the overall work of adhesion of water to coal. The ratio of $CH_{al}/C=O$ at 1832-1677 cm^{-1} is used here to demonstrate the relative contents of aliphatic and oxygenated groups and to assess their effect on contact angle values, as shown in Fig. 5.

The CH$_{al}$/C=O ratios vary significantly for the tested areas on coal, but there is only a slight effect on the contact angle on the original surface (without reagents), which could be the result of competing effects of aromaticity and the oxygen functional groups content on the measured areas, representing specific spots. The wide-spread of the oxygenated group's ratio indicates a wide variation in the chemical composition of various spots on the coal surface, which is due to its petrographic composition. Generally, the addition of reagents improves the hydrophobicity of coal surface, with the greatest effect being attributed to the treatment by diesel.
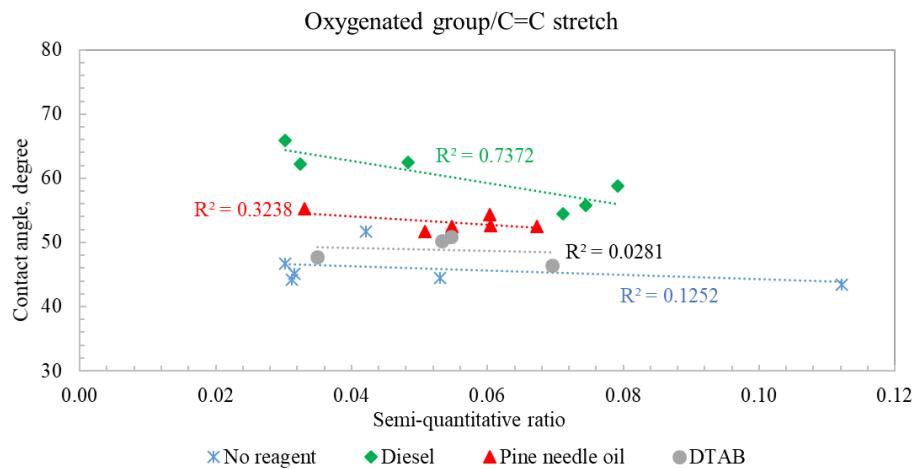
Fig. 5. Effect of oxygenated groups on the contact angle with and without reagents

3.5. Aliphaticity and contact angle

The increase in the abundance of aliphatic groups is significant, as shown in Fig. 6, especially for coal surfaces that were treated with the collectors, and the effect is the greatest for surfaces treated with diesel. Both pine needle oil and DTAB contribute very little to the increase of hydrophobicity for the studied coal surfaces. If anything, they reduce the aliphaticity of the coal surface and this does not help to significantly increase contact angle values.
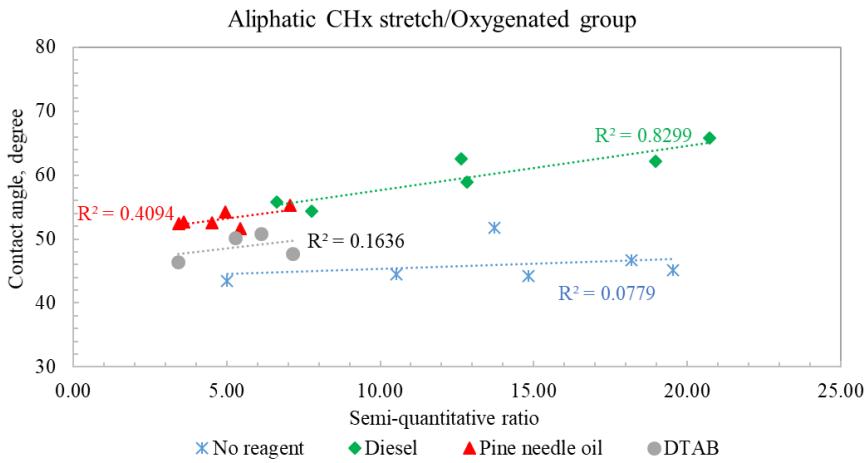
Fig. 6. Effect of aliphatic groups on the contact angle with and without reagents

3.6. FTIR mapping of coal surface

For the tested coal samples, the aromaticity and aliphaticity of different areas provide evidence that the chemical composition of each of these spots contributes to the hydrophobicity of coal, and at the same time, general trends are observed on coal hydrophobicity when all the data is plotted collectively.

The heterogeneity of coal surface arises from the petrographic composition since different coal macerals represent a great diversity in terms of their chemical composition, hence they can also influence the action of the reagents. Micro-FTIR mapping on two areas is performed to find out how the

collector is distributed on the coal surface given its petrographic make-up or how the chemical composition of the surface is changed after the treatment. Since diesel oil shows the best performance as a collecting reagent, increasing the hydrophobicity for this coal, the mapping was performed on the tracking aromaticity and aliphaticity of coal areas before and after the treatment with diesel Fig. 7 and Fig. 8 present mapping of H1 area1 while Figs. 9 and 10 provide mapping information on H2 area4 with respect to the aliphatic stretching region and aromaticity ratio at 3000-3100/2800-3000 cm^{-1}.
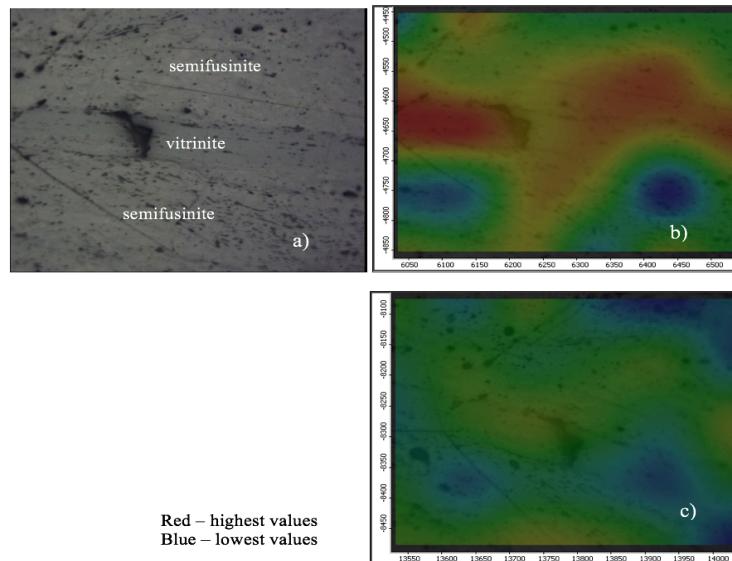
Fig. 7. Micro-FTIR mapping of an aliphatic stretching region on H1 area1; a) image of the mapped area; b) before treatment; c) after treatment with diesel
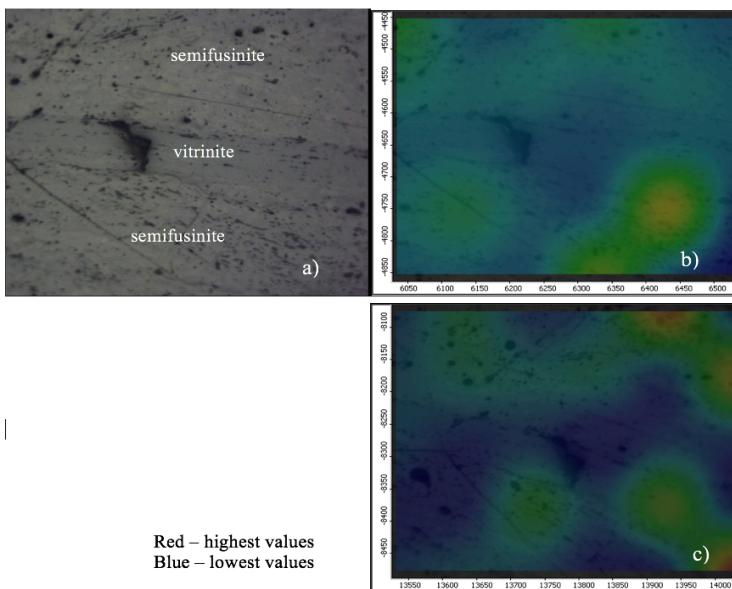
Fig. 8. Micro-FTIR mapping of aromaticity ratio at 3000-3100/2800-3000 cm-1 region on H1 area 1; a) image of the mapped area; b) before treatment; c) after treatment with diesel

Mapping of H1 area1 resulted in the following observations. The intensity of aliphatic stretching bands follows maceral composition to some extent, being higher in vitrinite than in inertinite. Some semifusinites also show a relatively high intensity (Fig. 7b).

Diesel treatment slightly rearranged this distribution of the intensity of aliphatic stretching bands; the zones of highest intensities in the untreated area do not correspond to the zones of highest intensity in the treated area (Fig. 7c).

Aromaticity (3000-3100/2800-3000 cm^{-1}) roughly follows maceral composition, with lower aromaticity in vitrinite and higher in inertinite zones in the b) before treatment. This is also the case c) after diesel addition, although there is a slight shift in the highest aromaticity zones. In addition, vitrinite becomes even less aromatic after diesel treatment, and the inertinite becomes relatively more aromatic, compared to the original aromaticity distribution. This could suggest that diesel got adsorbed to vitrinite better than to inertinite (Fig. 8c).
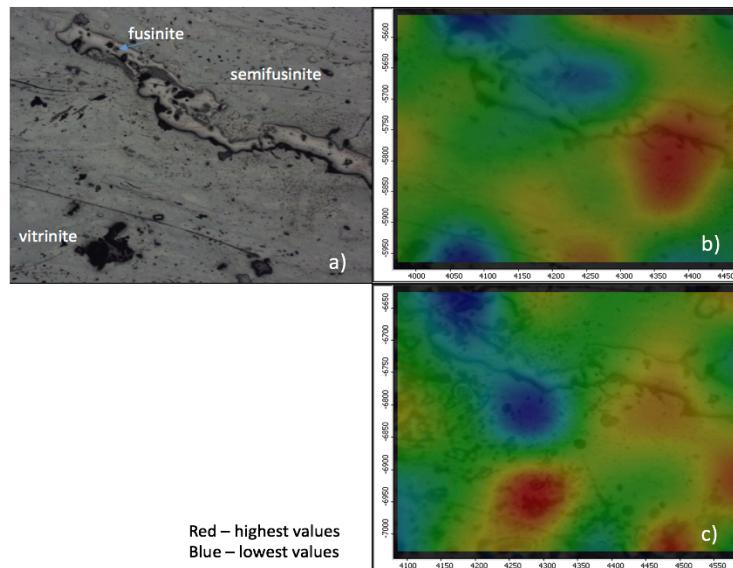
Fig. 9. Micro-FTIR mapping of an aliphatic stretching region on H2 area 4; a) image of the mapped area; b) before treatment; c) after treatment with diesel
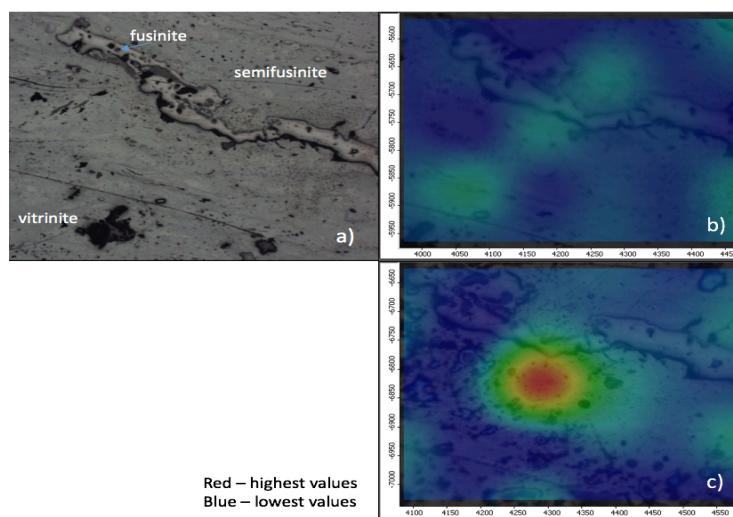
Fig. 10. Micro-FTIR mapping of aromaticity ratio at 3000-3100/2800-3000 cm-1 region on H2 area 4; a) image of the mapped area; b) before treatment; c) after treatment with diesel

Mapping of H2 area 4 resulted in the following observations. Diesel also rearranged the distribution of the intensity of aliphatic stretching bands. In this area, dependence on maceral composition is not so obvious. However, this is also an area with the predominance of inertinite type of macerals (semifusinite, fusinite), so relatively similar maceral composition in terms of chemical composition. Generally, aromaticity does not follow maceral arrangement, and diesel causes a shift in maximum aromaticity. However, surprisingly, for H2 area 4, where the effects of diesel were shown to be quite effective in increasing contact angle after treatment (Table 1), diesel action cannot be easily explained.

The effects of diesel addition clearly indicate that while diesel (as a chemical compound) is highly aliphatic, it was adsorbed onto the areas that were only slightly aromatic (vitrinite) and by doing so, improved the hydrophobicity of coal surface. It could be assumed that the affinity of diesel to the vitrinite will result in selectivity towards this maceral when using this reagent for the flotation of this coal.

4.   Conclusions

In this study, the micro-FTIR semi-quantitative analysis of chemical functional groups on the surface of high-rank coal was performed on the areas that were subjected to the contact angle measurements, serving as a proxy for the evaluation of the hydrophobicity of coal, as hydrophobicity is a prerequisite for successful flotation. It was shown that for this high-rank coal, an increase in aromaticity led to the reduction of hydrophobicity, and an increased presence of aliphatic groups improved it. Results with different reagents showed that some optimal ratio of aromatic and aliphatic groups is required to provide a desired coal surface hydrophobicity. The micro-FTIR mapping provided valuable insight into the adsorption of diesel on the coal surface. It was concluded that it adsorbed onto less aromatic vitrinite and resulted in an improved hydrophobicity of coal surface. It is possible that diesel adsorbed preferentially on the vitrinite and this could result in selectivity towards vitrinite if this reagent is used for flotation of this coal.

This study should still be considered as a work-in-progress in developing a procedure to find suitable collectors for the flotation of coals of different ranks and petrographic compositions. The outcomes of this work will eventually provide a fundamental understanding of why some reagents are better for some coals than for others, and it may lead to finding a way for better selectivity in coal flotation and achieving better quality coal product as a result.

Acknowledgments

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