

Qualitative Analysis of Thin Films of Crude Oil Deposits on the Metallic Substrate by Fourier Transform Infrared (FTIR) Microscopy

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Thin films of crude oil samples were prepared for atomic force microscopy (AFM) analysis on the gold substrate. Sample preparation involved evaporation during a long (24 h) but mild thermal exposure (80 °C). Fourier transform infrared (FTIR) microscopy (reflectance spectroscopy) was employed to determine the quality of the thin film surface, before the morphology characterization. The surface reflectance spectra were compared to direct transmittance FTIR of liquid oil samples. The two FTIR techniques showed different spectral characteristics related to oxygenated functionalities. This clearly indicated that the surface of the thin films of the oil samples prepared for AFM is oxidized. Oil samples of different origin show different degrees of oxidation seen by the development of carboxylic acid vibrations at 1750 cm⁻¹ as well as vibrations in the 1300–1100 cm⁻¹ region. The relative degree of oxidation state was compared to surface morphology data by AFM previously reported. The reported results emphasize the advantage of complementary techniques (AFM/FTIR microscopy) in the analysis of petroleum thin films that should be considered during analysis and interpretation of this type of data.

Introduction

Heavy organic phase formation from petroleum such as asphaltene precipitation and the deposition of this material on surfaces is an area of increasing research efforts due to the large economic losses in the oil industry due to flow reduction. Many aspects remain unresolved regarding both phase behavior as well as interaction with metallic surfaces of these oil fractions as resolution often is obscured by complexity of the chemical species involved. The asphaltenes as such are defined only by the definition as *n*-heptane insolubles and toluene solubles, and hence it involves a large number of chemical species and structures fulfilling this simple solubility criterion. It is therefore composed of a distribution from high-molecular-weight–less-polar species to low-molecular-weight–more-polar species. The toluene insolubles are seldom found in reservoir fluids with normal geological history. This is, however, dependent on the history of the fluid over geological time scale, and heat impact during this time may indeed resolve in formation of toluene insolubles referred to as

carboid and carbenes or sometimes pyrobitumen when found in geological sediments.

Analysis of the interaction of these species with surfaces has mainly been focused on surfaces of mineral matter to understand reservoir wettability issues such as adsorption of asphaltenes.¹ For metal surfaces, only a few studies have been reported.² Works on interaction of asphaltenes with minerals and metals have mainly focused on measurements of adsorption isotherms, although atomic force microscopy (AFM) work has been reported mainly for adhesion and wetting studies.^{3–7} For complex mixtures such as petroleum fractions, preferential adsorption of specific compounds or compound classes is more likely than equal adsorption affinity of all components. This makes such isotherms gathered from supernatant liquid composition, that is, by UV–vis measurements, only partially representative for the

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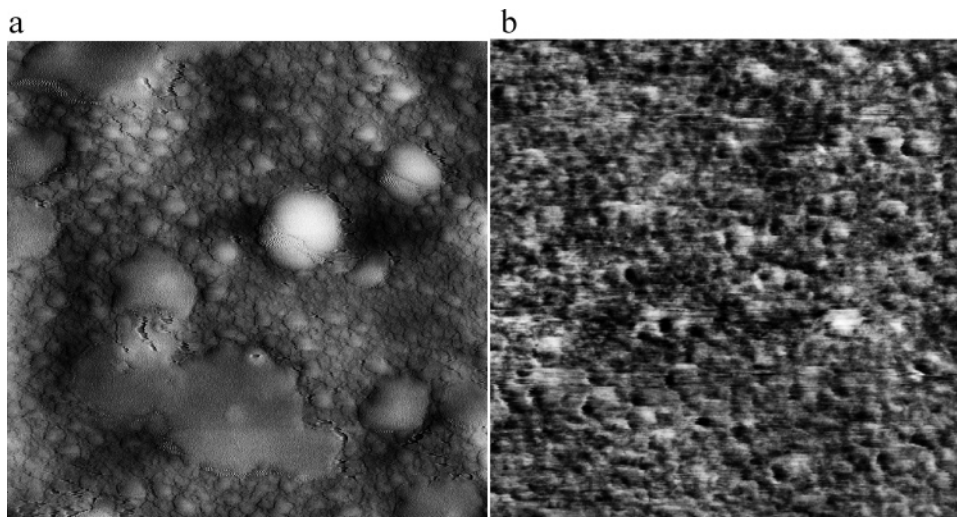


Figure 1. AFM images (size: $1.5 \times 1.5 \mu\text{m}$) of spin casting and heat-treated thin films of (a) KU and (b) SG oils. The image height range is 120 and 25 nm, respectively.

interaction. Interaction with metal surfaces and direct analysis of the species adsorbed may be achieved by a number of surface analysis techniques. Surface imaging techniques such as AFM and scanning tunneling microscopy (STM) may be used depending on the amount of adsorbed material and conductivity of the molecular film. When analyzing oil samples directly deposited, this will assume multilayer structures and hence AFM is most suitable.

In the course of developing a technique to prepare thin film oil samples suitable for the AFM analysis, FTIR microscopy based on the reflectance spectroscopy was employed to evaluate the quality of the molecular film. FTIR-microscopy and AFM are highly surface sensitive techniques giving information related to properties of either a thin film or in cases only a top surface layer. In this study, results are presented using these two complementary techniques in which AFM provides surface morphology information while FTIR microscopy describes the quality of the thin film of the spread oil. Details of the AFM study have been presented in a previous paper by the current authors.⁵

To be able to investigate crude oil with surface imaging techniques, an increase in the quality of imaging can be obtained by evaporation of light ends leaving behind concentrated samples. Indeed, this may help in analysis of light oil samples where small amounts of solid asphaltene particles are formed. In our first experiments, oil was placed directly on the gold substrate, and this was heated to 80°C for 24 h after spin coating. This led to formation of thin films of apparently solid appearance. Example AFM images of two oils are given in Figure 1. Notice the very different topography indicating a difference in the oil aggregation process. For more details, see ref 5. During an evaporation process like this, there is a high risk of oxidation of the sample. This could lead to the formation of additional asphaltene- and resin-like species, hence leading to new structuring of the petroleum molecules in the oil. Hence, new and more aggregates may form due to chemical and structural changes also known from asphalt blowing.⁸ The degree of alteration in the concentration of heavy

species is very dependent on the initial composition of the oil in terms of content of light components. Evaporation of lower alkanes up to *n*-heptane as well as aromatics such as benzene and toluene may change the dispersion forces of the oil (as a solvent for the heavy ends), which could alter the surface morphology observed. Therefore, we found it important to evaluate qualitative properties of the thin film before AFM interpretation. In the present work, we attempt to do this employing FTIR microscopy and comparing this with FTIR transmittance spectroscopy data. The latter was performed on liquid oil samples without evaporation or heat treatment.

The present findings are of importance in further developments of techniques and methodologies for surface studies of complex mixtures that may oxidize during preparation. The spreading–evaporation technique is a common technique in these studies; hence the changes and experiences reported herein may impact the interpretation of previously reported results.^{3,4,8}

Experimental Section

The metallic gold substrate used in this study was prepared and characterized as previously reported.⁵ The oil spreading and light end evaporation procedure was performed as follows: a $1 \mu\text{L}$ drop of oil was spread on the gold substrate using a rotating spin-drying device followed by placing the gold plate on a hot plate regulated to 80°C and leaving the sample for 24 h. This led to the formation of apparently solid thin films (up to few micrometers thick), suitable for the AFM analysis.

Infrared reflectance spectroscopy was made using a Nic-Plan microscope attached to a Nicolet system 800 mid-IR spectrometer ($650\text{--}4000 \text{ cm}^{-1}$). The lateral resolution was defined by a $12 \mu\text{m}$ spot. The spectra were taken on different areas of the same sample, at least at five different places, and background subtraction was performed using a representative clean gold surface reference spectrum.

Transmittance FTIR spectra were recorded on a Nicolet 710 spectrometer operated at a setting of 32 scans at a spectral resolution of 4 cm^{-1} . The crude oil samples were applied without dilution using the film casting technique on NaCl infrared windows. The film formed by this technique is liquid-like, and no evaporation is applied.

Crude oils came out of various geographic sites in Mexico. Some of these oils have known problems of asphaltenic

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Table 1. Selected Properties of Oils Investigated

| oil | density @ 25 °C | viscosity @ 25 °C (cP) | stability ^a observed |
|-----|-----------------|------------------------|---------------------------------|
| JU | 0.824 | na | unstable |
| TC | 0.831 | 5.9 | unstable |
| P | 0.836 | 4.7 | unstable |
| C1 | 0.852 | 11.2 | unstable |
| SG | 0.858 | 1.3 ^b | unstable |
| Y3 | 0.863 | 8.7 | unstable |
| B1 | 0.919 | na | stable |
| KU | 0.980 | 14 317 ^c | stable |

^a Reservoir experience: organic deposition is reported. ^b At 125 °C; na, not available. ^c KU is a heavy oil.

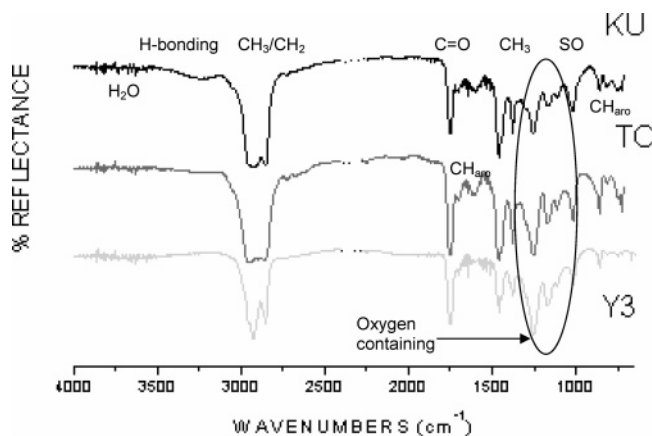


Figure 2. Surface reflectance IR spectra obtained for spin casting and heat-treated samples in group 1: KU, TC, and Y3 oil, with high level of oxidation. Assignment of peaks is indicated.

deposits during productions (termed instable oils) as described elsewhere.⁵ Oils were used as received without any pretreatment such as dewatering. Various properties of these oils are given in Table 1.

The methodology and results of AFM analysis of the same crude oil samples and preparations were reported in one of our previous papers.⁵ The abbreviation used to identify samples used in the previous paper is also applied herein.

Results and Discussion

Although conditions were the same in the preparation by heating and evaporation of volatile components, the effects were highly different in terms of the occurrence of oxygenated structures in the different oils. The discussion will concentrate on these observations.

According to the reflectance spectra of the FTIR microscopy, the samples could be placed in three groups as indicated in Figures 2–4.

In all spectra, the presence of hydrocarbon structures is seen in the C–H stretching vibration region at 3000–2800 cm^{-1} as well as by the peaks at 1460 and 1375 cm^{-1} .

Group 1 contains samples (KU, TC, Y3) of high concentrations of oxygenate functionalities after preparation. This is seen by the appearance of a large number of peaks in the range from 1800 to 900 cm^{-1} . One of these, the 1030 cm^{-1} peak, is related to the formation of sulfoxide, which has been debated to be present in virgin oils only in very small concentrations if at all.⁹ This peak is found in all of the other samples analyzed

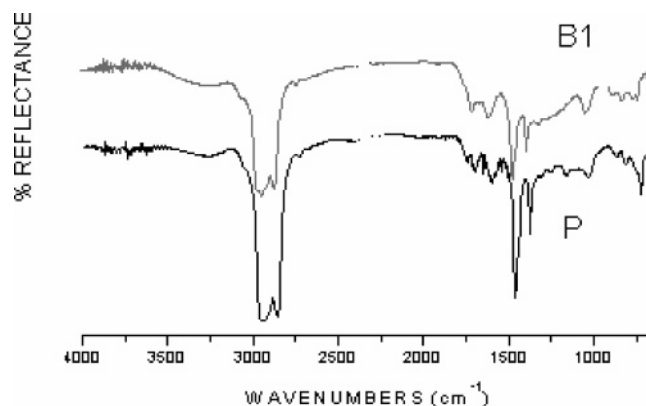


Figure 3. Surface reflectance IR spectra obtained for spin casting and heat-treated samples in group 2: B1 and P oil, with intermediate oxidation level.

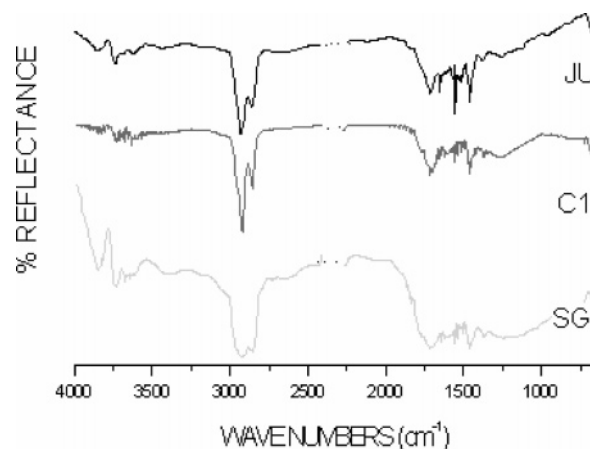


Figure 4. Surface reflectance IR spectra obtained for spin casting and heat-treated samples in group 3: JU, C1, and SG oil, with low oxidation level.

but not to the same extent. Cagniant et al.¹⁰ also assigned this peak to be related to ethers in combination with peaks at 1120 and 1061 cm^{-1} . The latter vibration is not directly observable. However, the 1120 cm^{-1} peak is pronounced and appears apparently in combination with the 1160 cm^{-1} vibration. Cagniant et al.¹⁰ assigned this to phenol by alkylation reactions, whereas both sulfones and esters have been given as possible sources for this peak. However, controversy persists in the area of esters as oxidation products of petroleum related products.¹¹ In this group, the carbonyl peaks at 1750 cm^{-1} are dominating. This vibration is related to the carboxylic C–O, which is often found in asphaltene fractions or in oxidized oils, and carbonylic ketone types are also seen at 1700 cm^{-1} . Comparison with transmission FTIR spectra of seven of the liquid oils (excluding oil TC) given in Figures 5 and 6 indicates that the commonly used technique of spin-drying preparation prior to AFM studies has a great impact on the chemistry for some oils. First, the peaks related to alkyls in the region between 1460 and 1370 cm^{-1} were seen to diminish significantly due to the evaporation of light components. Yet the main impact is the oxidation of samples. As an example, for oil KU, the peak at 1030

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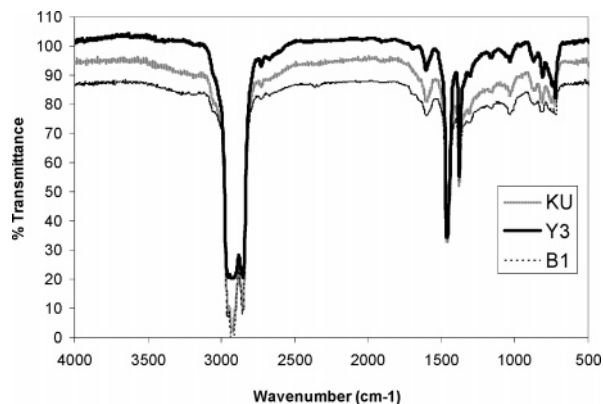


Figure 5. Transmittance IR spectra of oil samples: KU, B1, and Y3, prepared without heat treatment.

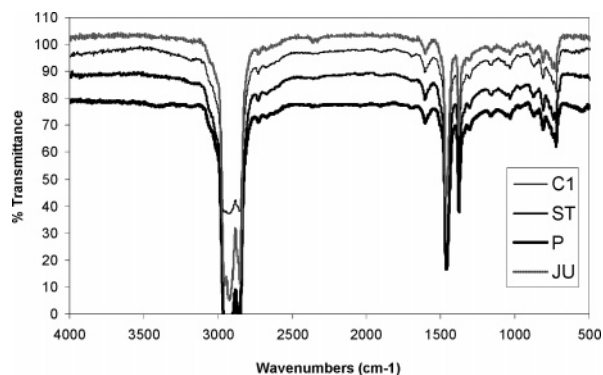


Figure 6. Transmittance IR spectra of oil samples: JU, P, C1, and SG, prepared without heat treatment.

cm^{-1} is relatively much more intense in the oil sample after spin coating. This could be related to the content of large amounts of reactive sulfur probably located in the high content of asphaltenes in KU. KU is a typical heavy oil, which is also reflected in the very high viscosity of the crude oil. In the reflectance spectra of this group, a specific peak at 1253 cm^{-1} was seen as well. This is normally assigned to dicarboxylic anhydride (C–O–C), which should be linked to peaks at 1735 and 1765 cm^{-1} . Anhydride formation is a normal reaction between carboxylic acids in asphalts at elevated temperature.¹² Comparison of the reflectance IR patterns with transmission IR clearly indicates that oxidation has taken place in this group of samples.

Group 2 consisting of oil B1 and oil P showed signs of milder oxidation. Minor peaks of sulfoxide and of carbonyl were seen. However, in the range between 1300 and 1100 cm^{-1} , the large peaks of oxygenated functionalities were only seen as smaller peaks in oil P, whereas the levels were very small in oil B1. In P, the 1160 cm^{-1} peak was observed. The transmission mode revealed quite similar spectra for these two, although B1 did show indications of higher carbonyl content. However, comparison with the reflectance spectra again points in the direction of a mild oxidation especially seen by the development of peaks at ca. 1030 cm^{-1} . Both reflectance and transmission spectra oil P (in comparison with B1) had a higher level of components related to the vibration at 1170 cm^{-1} .

Table 2. Generic Composition Obtained by Saturates, Aromatics, Resins, and Asphaltenes (SARA) Separation

| oil | Composition (wt %) | | | |
|-----|--------------------|-----------|--------|-------------|
| | saturates | aromatics | resins | asphaltenes |
| JU | 52.1 | 36.3 | 10.9 | 0.7 |
| TC | 60.5 | 32.6 | 6.3 | 0.5 |
| P | 59.3 | 30.6 | 9.4 | 6.3 |
| C1 | 54.7 | 28.9 | 13.3 | 3.08 |
| SG | na | na | na | na |
| Y3 | 55.1 | 30.8 | 9.4 | 2.7 |
| B1 | na | na | na | na |
| KU | 21.4 | 36.9 | 37.9 | 11.8 |

Group 3 consists of a number of light oils C1, SG, and JU, which did not show a large degree of oxidation after the preparation relative to the spectral characteristics of the previous two groups. JU and C1 apparently have very low aromatic contents as seen by the lack of peaks in the range from 900 to 700 cm^{-1} as well as the typical peak at 3070 cm^{-1} . However, this is not in agreement with the SARA analysis reported in Table 1, which indicates that all oils have similar aromatic content. The apparent lack of aromatic molecular structures is not confirmed by the transmission spectra as these all contain clear evidence of aromatic structures in the common vibrations at 3050 , 1600 , 880 , 815 , and 745 cm^{-1} .

For groups 2 and 3, the low levels of distinct peaks could also be due to the formation of a vast number of different oxygenated functionalities as the background level is increased in the 1300 – 1000 cm^{-1} region. This, however, remains speculative and may not be resolved for such complex fluids.

For the reflectance spectra, the vibrations in the hydrogen bonding region of –OH, –SH, and –NH species between 3500 and 3100 cm^{-1} are seen for KU, B1, and P. SG apparently shows this but not to a significant extent.

The differences in intensity of peaks in the different samples in the reflectance region between 3000 and 2800 cm^{-1} could be due to slight differences in film thickness or due to alignment of the FTIR microscope. This will, however, not affect the qualitative analysis of the spectral region affected by oxidation.

A comparison within the transmission spectra (Figures 5 and 6) reveals that the apparent main difference was observed in the content of alkyl structures seen at 3000 – 2800 , 1465 , 1375 , and 725 cm^{-1} . The alkyl level for KU and B1 was similar and relatively low as these are both heavy oils. For KU, this was in agreement with the SARA separation given in Table 2. All samples showed intensities of hydrogen bonding between 3600 and 3100 cm^{-1} except oil JU. However, when comparing the two techniques, we find that KU and Y3 obviously suffer from oxidation in the surface technique as seen by the large peaks in the 1000 – 1300 cm^{-1} range as well as the 1700 cm^{-1} vibration. This could not evolve from only evaporation.

Part of this grouping was surprising from a geochemical point of view as oils B1 and KU, JU and TC, and Y3 and C1 are from similar geographic zones and to some extent must be expected to have a similar composition,¹³ and hence one could expect a similar response to the

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oxidation. This may indicate that oxidation could be easily altered by the presence of other components in the oil.

In the AFM studies of the samples investigated,⁵ applying the preparation procedure given herein, no grouping according to either geographic source or related to the oxidation profile given herein was observed. Only the size exclusion chromatographic traces showed a good correlation with origin such that similar profiles were recorded for oils of the similar geographic origin.⁵ In the previous study, the oils C1, JU, TC, and SG were grouped together as was Y3 and P, while B1 and KU were more difficult to group based on the topographic image. However, we could see that the samples with the largest particles such as KU and Y3 also belong to the most oxidized samples. On the contrary, the samples such as SG and JU that had a characteristic morphology consisting of very small nanometric-sized spherical particles belonged to the less oxidized group. These observations directly lead to two conclusions: (1) that the size of particles could be correlated to the oxidation as more oxidized samples give bigger particles; (2) at this point, taking both factors into consideration we cannot conclude that samples with bigger particular material being more oxidized is more likely to lead to deposition during oil production, nor that material that oxidize easily lead to greater production problems. Also, the data show that reactivity toward oxidation is different in different oils. One may speculate that monitoring of ability to oxidation may give a path to understand the formation of deposit layers. The latter is important in the line of our research and in understanding if oxidation is an "inevitable" part of the formation of deposited layers on production tubing.

The findings herein especially on oxidation issues may also be of importance in other techniques where surface deposition is used followed by solvent evaporation such as casting on IR-window material and FTIR attenuated reflectance on solid powder matrixes, etc.¹⁴ Also, the effect of chemisorption between the substrate and the compounds spread may result in changes in the spectrum both in peak intensity and in position. Kahn et al.¹⁵ reported among other compounds the complete loss of peaks of phenolic OH when spread on platinum [111] using electron energy loss, IR, and Raman spectroscopy. Hence, this may be taken into account in our assumptions when analyzing surface spread materials by infrared spectroscopy.

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In the comparison of spectra obtained by the two techniques, it should be stressed that there might be differences due to the application of reflectance and transmission modes. In reflectance, there might be a dependence in thick samples on the penetration depth affecting the results. In that case, the FTIR microscopic spectra would be related to top layers and not to the entire fluid as the transmission spectra. In our case, the film thickness is small and reflection from the gold substrate may take place. Hence, we assume that a full comparison was possible in the above analysis.

Conclusions

Surface reflectance IR spectroscopy has been used to analyze the possible extent of oxidation of oils deposited and spin coated on gold surfaces under mild heating. The spin coating technique is widely used in the analysis of materials on surfaces; hence one should be careful to avoid effects of oxidation. The impact of the oxidation on the AFM derived morphologies is still not clear. In our particular study, a grouping of samples into three distinct groups was seen, which did not relate to geochemical origin, but seems to be related to affinity to oxidation. The comparison with our previously published AFM analysis did indicate that the most oxidized samples also revealed larger particular structures in the morphology seen in the AFM images. The impact of this on our understanding of the deposition of petroleum colloids on metal surfaces during oil production remains unclear.

A large difference between spectra obtained in reflectance versus transmittance mode is related to different sample preparations including oxidation during the evaporation process for FTIR microscopy. Further studies could prove that oxidation of molecular layer has an important role in formation of asphaltene deposits.

Most important, spin coating of petroleum-related products onto solid substrates for surface analysis should be performed in an inert atmosphere such as nitrogen to avoid oxidation. The results should also be applicable for casting of samples on infrared windows and KBr powder material for reflectance studies if solvent evaporation is applied.

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