

## A FOURIER-TRANSFORM INFRARED (FTIR) STUDY FOR ALGERIAN ASPHALTENES

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### ABSTRACT

despite that the Algerian light oil contain a few quantity of asphaltenes (under to 0.7 wt %) but The problem of their deposition during the oil production and transportation is strongly suggested, this deposition of asphaltenes does not depend on the percentage of asphaltenes in the oil but depends on their chemical composition which affects the behavior of asphaltenes. Functional Groups of Algerian Asphaltenes was investigated using A Fourier-Transform Infrared (FTIR), This study characterizes a Six samples of asphaltenes were collected from Hassi Messaoud's oil field at different locations, all samples were extracted using n-heptene with with 1:40 (g/ml) (oil to solvent ratio), the obtained results indicated the existence of aliphatic, aromatic and sulfoxide groups with different intensities. This study confirmed that the asphaltenes precipitation was occurs in all Hassi Messaoud's oil field locations.

**Keywords:** Asphaltenes; Extraction; Characterization; A Fourier-Transform Infrared (FTIR); Algerian Light oil.

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## 1. INTRODUCTION

A crude oil is composed of a complex mixture of saturated hydrocarbons such as alkanes, aromatic compounds, resins and asphaltenes [1,3]. The crude oil is the first source of energy in the world [4]. Asphaltenes content in crude oil matrix are one of the most problems that affect the oil recovery and its transportation processes [5]. Asphaltenes are the heavy and polar fraction content in crude oil or vacuum residue which insoluble in n-pentane or n-heptane and soluble in toluene [6-9]. Asphaltenes can precipitate at different stages during oil recovery and transportation; porous media, production tubing, valves and pipelines [5,3,10]. The oil of Hassi Messaoud in Algeria is low in asphaltenes content, however asphaltenes precipitation was recorded during the oil recovery [7,11]. So the asphaltenes precipitation does not depend on its content in the oil, but they rely with the asphaltenes stability [7]. In recent years, the problem of asphaltenes deposition was generalized on all the Algerian oil fields, where many wells so much reduced and some of them had to be closed [12]. The various factors which influence the asphaltenes stability in crude oil, the composition and chemical structure plays a key role in this stability. The remediation of the problems associated with the presence of asphaltenes in crude oil, requires a better knowledge of their structures [13]. Many techniques were employed for the characterization of asphaltenes, such as Fourier-Transform Infrared (FTIR), FTIR Spectroscopy is a well-known technique that utilizes infrared electromagnetic radiation to determine the functional groups that are present in molecules [14,15]. The FTIR is one of the most used techniques in characterization of asphaltenes [16]. The Studies about Algerian asphaltenes are very limited, we mention the FTIR study that investigated by Daaou et al for three samples from Hassi Messoud oil field that extracted on oil well, storage tank deposits and the vacuum residuum. For the three samples, the aliphatic chain, aromatic rings, OH/NH bands, esters, carboxylic acids and sulfoxide group were recorded in all samples but with different intensities, the peak area under aliphatic aromatic C=C and carbonyl C=O confirmed that the asphaltenes extracted from the storage tank deposits have a lower aromatic character and contain a higher concentration of carbonyl in comparison with two remaining samples. Other FTIR analysis for two samples was investigated by Asma larbi et al [17]; The first was extracted from the

storage tank deposit and the second was derived from a Hassi-Messaoud oil well, they obtained the same functional group that indicated in the previous study. Additional techniques such as nuclear magnetic resonance NMR, Elemental analysis and X-ray diffraction were used to determination of Hassi Messaoud asphaltenes aromaticity, polarity and stability, the results were displayed in the references [18-22]. In this study, six samples of asphaltenes have been characterized by FTIR, these samples were extracted in different location from Hassi Messaoud's oil field that is located 800 km to the south east of Algeria and to 80 km in the South-East of Ouargla.

## **2. EXPERIMENTAL SECTION**

### **2.1 Materials and Methods**

#### **2.1.1 Extraction of Asphaltenes Samples**

Six samples of asphaltenes were collected from Hassi Messaoud's oil field at different locations. The extraction process was performed by addition of n-heptane into the oil with 1:40 (g/ml) (oil to solvent ratio). The resulting mixture was allowed to boil for 2 h and then cooled down to room temperature in a dark place for 2 h. The stable solution was then filtered without agitation. Finally, the filter paper was washed with 150 ml of n-heptane, until the eluting solvent became transparent. After washing, the asphaltenes were stored in a scintillation vial and then were dissolved in 60 ml of toluene and passed to a reflux heater (soxhlet) until dissolution of all these asphaltenes. The resulting solution was sent to a round-bottom flask already washed, dried and weighed. The toluene was removed from the flask by evaporation using a rotary evaporator at atmospheric pressure and then in an oven at 100 ° C for 30 min. The flask was placed in a desiccator until constant weight [12].

#### **2.1.2 Fourier-Transform infrared spectroscopy (FTIR)**

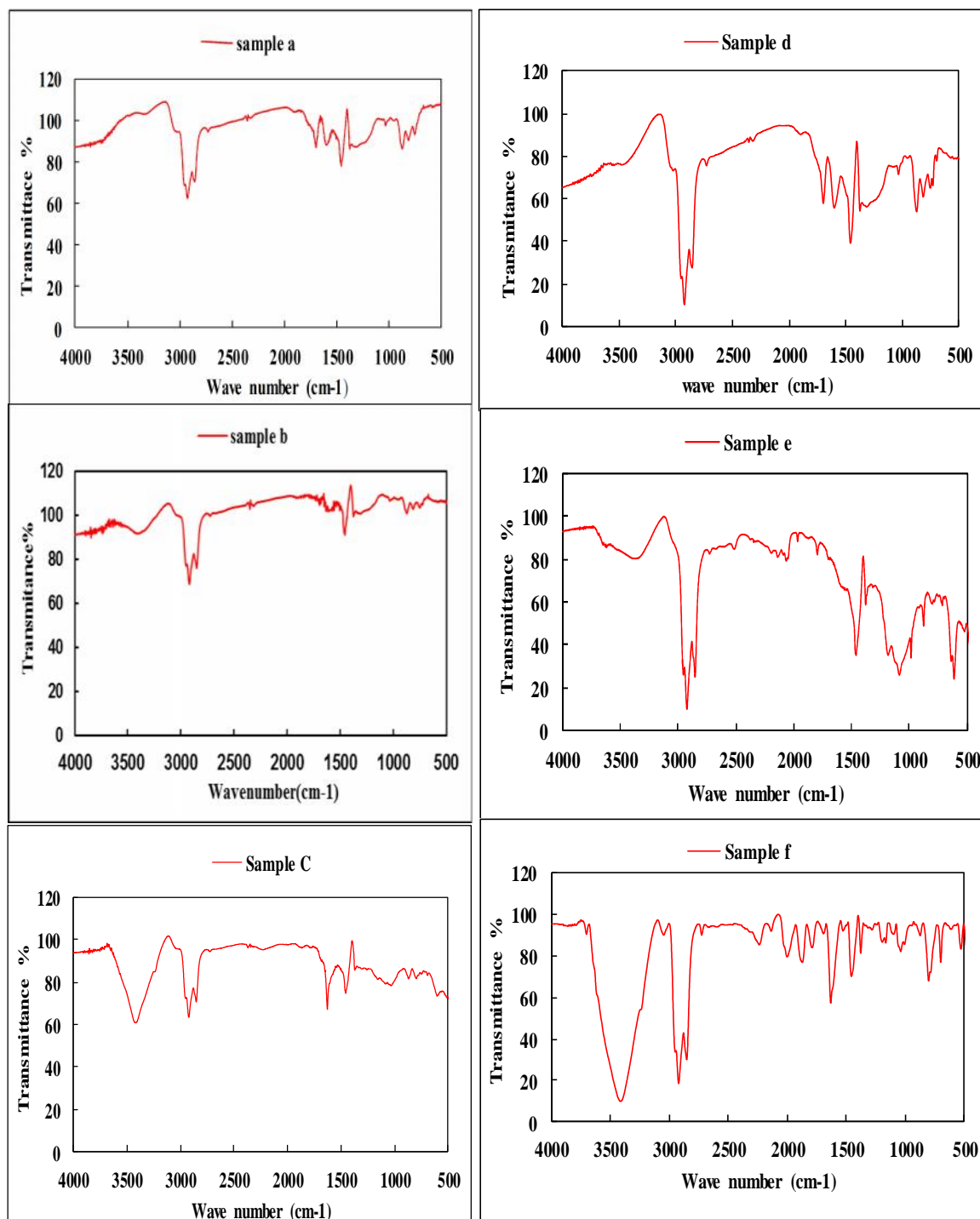
The asphaltenes samples were characterized with a Shimadzu IR Affinity-1S FTIR (Mandel, USA) thermo. Around 5 mg of the sample was mixed with 500 mg of KBr and the entire mixture was mounted in the DRIFTS sample holder. The spectra were recorded from 400 to 4000 cm<sup>-1</sup> after 50 scans. During FTIR operation, the electrons will gain energy and jump to excited states, molecules can also transition to higher energy levels if they gain enough

energy. The bounds in molecules can be imagined to vibrate with a certain frequency (and energy) that is specific to that bond energy. It is impossible to find two bonds having the same vibrational frequency. FTIR can give a fingerprint of the Sample to be studied. . In order to compare the results, all spectra should be normalized [23,24].

### 3. RESULTS AND DISCUSSION

Figure 1 shows a comparison between the infrared spectra of our asphaltenes which were extracted from Algerian light oil. The peaks of samples a, b and c showed medium and weak intensities, while in the other samples (d, e and f) are strong and weak. In addition, a special broad shape was presented in samples c and f. the spectra of a,b and d samples are similar to the spectra described in the literature [5,17,18].The sample f is very different in comparison of all samples. It is clear from the figures that the aliphatic and aromatic are presented with other functional groups like carboxyl and sulfoxide. The aliphatic stretching bonds is expected to attend in the region between 2852 to 2935  $\text{cm}^{-1}$  like a strong intensity for the samples d,e and f while it was medium in the remaining samples.. The deformation bonds were identified between 1370 and 1375  $\text{cm}^{-1}$  [5,17]. In the aromatic region the deformation of C-H Bending in all samples was assigned between 717 to 873  $\text{cm}^{-1}$  where the aromatic C-H stretching presented in the weak bands at 3040  $\text{cm}^{-1}$ .

Broad band was recorded for the samples c and f at 3404  $\text{cm}^{-1}$ , indicating an important presence of N–H and O–H groups. Amine N-H stretching and O–H are also identified at 3392 and 3332  $\text{cm}^{-1}$  for samples **b** and **e**. The presence of C=O carbonyl stretching between 1685 and 1791  $\text{cm}^{-1}$  for all samples, however, it is hard visible in sample **c** , in Addition, the C=C aromatic stretching at 1590 and 1597  $\text{cm}^{-1}$  was assigned in sample a and d respectively , while It was not recorded in other samples. The special presence of C-O aliphatic ethers at 1178  $\text{cm}^{-1}$  was evidenced in samples **e** and **f**. finally, a sulfoxide group is assigned at 1030  $\text{cm}^{-1}$  for all samples, except the sulfonyl group in the sample **e**.



**Fig.1.** FT-IR spectra of a, b, c, d, e, and f asphaltenes samples.

#### 4. CONCLUSION

In this work, the FTIR study of asphaltenes samples extracted from Algerian light oil were investigated. This study confirmed that the problem of asphaltenes deposition generalized in all Hassi Messaoud oil field and not just in zones 1 (1A, 1B, 1C) and 23 that located in the western part of the field. The results indicate that the asphaltenes would contain aliphatic, aromatic, carboxyl and sulfoxide groups with different intensities. There was significant difference between the studied samples, special presence of C-O aliphatic ethers at  $1178\text{ cm}^{-1}$  in samples e and f, the Broad band in samples c and f corresponding important presence of N-H and O-H groups. Sulfoxide group is assigned for all samples, except the sulfonyl group in the sample.

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