

1 **Investigation of microwave radiation in conjugate with acidizing as a novel**  
2 **hybrid method of oil well stimulation**

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10

11 **Abstract**

12 In this research, the effect of microwave radiation simultaneous with acidizing on the  
13 carbonate rock surface has been investigated. Saturated rock sections were first immersed in  
14 the acid solution, and then, exposed to the microwave at 1300 W and 780 W for 1, 2, and 3  
15 min. The surface wettability and hydrocarbon desorption from the rock surface were  
16 respectively investigated by the contact angle measurement and Attenuated Total  
17 Reflectance-Fourier Transform Infra-Red (ATR-FTIR) spectroscopy. It was observed that the  
18 angle under the microwave in the vicinity of the acidic solution improves toward water-  
19 wetness and becomes oil-wet. The reduction of the contact angle in the combined mode is  
20 tenser due to the simultaneous effect of acid and microwave radiation. According to the  
21 ATR-FTIR spectrums, the microwave radiation of the sections during the acid treatment led  
22 to desorption of aromatic compounds, long alkanes, polar bonds (O-H and N-H), and the  
23 compounds with C=O functional groups. The electrically polar hydrocarbons have more

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1 affinity for separation from section during microwave radiation. As a result, microwave  
2 radiation could improve wettability alteration through asphaltene desorption during oil well  
3 acidizing.

4 **Keywords:** Microwaves radiation; Acidizing; Wettability alteration; ATR-FTIR spectroscopy; oil  
5 well

## 6 **Introduction**

7 Acidizing of oil wells is conducted to create new pathways for hydrocarbon production  
8 (wormhole) and open blocked passages. The purpose of acidizing oil and gas wells includes  
9 reviving the well, opening pores, production improvement, and increasing permeability [1-  
10 3]. Wettability stands as a fundamental parameter crucial to oil fluid dynamics, significantly  
11 impacting production flow within reservoirs. Its influence extends to key factors like  
12 capillary pressure and relative permeability [4].

13 In the acidification of carbonate formations, acidizing is considered to open a new path for  
14 production, but in the acidification of sandstone formations, it leads to the reopening of  
15 passages that have been damaged and blocked. The difference between the acidification of  
16 these two formations is that in the sandstone formation, the dissolution of the damage that  
17 blocked the pores takes place, while in carbonate acidification, in addition to the damage, the  
18 reservoir rock is also dissolved by the acid . Precipitation of salts and generating asphaltene  
19 sludge are some challenges that most acidizing processes face . Hence, engineering the  
20 acidizing process to minimize the risks is always recommended[5].

21 Hong et al. applied formation microwave heat treatment (FMHT) to enhance oil production  
22 through fracturing the formation. The findings indicate a notable escalation in fractures  
23 induced by microwave energy as the heating time prolongs. These fractures, along with  
24 newly formed pore sizes due to microwave treatment, led to a reduction in wave speed (S

1 Pand) within the coal core. Additionally, the frequency spectrum range of the coal core  
2 decreased following exposure to microwave energy. Microwave radiation also influenced the  
3 frequency distribution range within the cores' frequency spectrum. Furthermore, the coal's  
4 density, bulk modulus, and shear modulus exhibited a decrease consequent to the microwave  
5 energy treatment. Notably, the rate of decrease in bulk and shear moduli surpassed that of  
6 coal density [6-10].

7 Yoo et al. 2018 explored the reaction kinetics of dolomite in carbonate acidification using  
8 both fresh and spent acid. Spent acid, characterized as a partially-reacted acid containing  
9 calcium and magnesium ions from the acid-rock reaction, was investigated. The findings  
10 revealed the dissolution of dolomite mineral within the acid. Moreover, a comparison  
11 between spent and fresh acid indicated higher kinematic viscosity and lower pH in the spent  
12 acid. The reported results suggested that the dissolution rate and diffusion coefficient of the  
13 used acid were greater than those of the fresh acid due to the higher kinematic viscosity and  
14 lower pH of the spent acid. These outcomes highlight an unusual ion effect from impurities  
15 like iron oxide and aluminum oxide in clay, unrelated to the hydrochloride-dolomite reaction,  
16 leading to increased reaction [11].

17 One of the important applications of electromagnetic waves is heating oil wells. Among the  
18 general advantages of this method of heating the wellbore region are the possible asphaltene  
19 cracking, and oil upgrading. The three employed methods are resistance heating, induction  
20 heating, and microwave heating[12]. Heating with microwaves has more advantages than  
21 other methods, such as less energy loss and not depending on the heat conduction of the  
22 environment. In this method, the microwave generating antenna is placed in a well, this well  
23 is drilled close to the production well[12]. The fluid in the reservoir that moves towards the  
24 production well is heated by microwave energy, in this way, the surrounding area of the well  
25 is uniformly heated to a large extent, and this can compensate for the pressure drop around

1 the well area to a large extent. Reducing the viscosity of heavy and extra-heavy oils in this  
2 method greatly improves the performance of the reservoir and recovery [13].

3 In their 2018 study, Taheri-Shakib et al. explored the impact of microwaves on the wettability  
4 of carbonate reservoir rock. Through an analysis of alterations in the rock's surface charge  
5 and contact angle measurements, their findings suggested that prolonged exposure to  
6 microwave irradiation led to an increased water-wet nature of the rock samples [14].

7 In their 2021 findings, Karami et al. highlighted that the enhancement of rock wettability  
8 through microwave utilization isn't solely attributed to temperature-induced alterations. They  
9 observed that microwaves contributed to the breakdown of organic compounds on the rock  
10 surface, resulting in the weakening of van der Waals forces and subsequent changes in  
11 wettability [15]. Hui Shang et al. 2018 investigated the impact of microwaves on crude oil  
12 viscosity and determined that variations in viscosity are contingent upon the specific  
13 compounds present within the oil [16]. Karami et al. 2020 conducted a study on mitigating  
14 condensate blockage using both microwave and ultrasonic methods. Their findings indicated  
15 that ultrasonic waves and microwaves exhibited a more pronounced impact on eliminating  
16 lighter oil compounds compared to heavier ones. Additionally, they inferred that the  
17 effectiveness of these methods—microwave and ultrasonic—was contingent upon the  
18 dielectric constant and acoustic properties of the respective compounds present within the oil  
19 [17]. In their 2023 study, Karami et al. compared the impact of ultrasonic and microwave  
20 treatments on asphaltene structure. Their findings indicated that both forms of radiation  
21 facilitated the cleavage of covalent bonds within asphaltene molecules. This breakdown  
22 resulted in a reduction in asphaltene size and contributed to enhancing its rheological  
23 behavior[18].

24 In this research, the effect of microwaves on the wettability of carbonate rock has been  
25 investigated. After the aging of the rock, they were exposed to microwaves and acid solution

1 for 1-3 minutes with two powers of 780 W and 1300 W. Contact angle analysis has been used  
2 to investigate changes in wettability caused by wave radiation . Regarding the fact that  
3 asphaltene sludge generated during acidizing leads to wettability alteration of the rock  
4 surface, additional treatment is required to prohibit oil-wetness of the near-wellbore region.  
5 Because microwave radiation has been proven to be feasible for improving the water-wetness  
6 of the rock surface, it was employed to modify the wettability of the rock surface treated by  
7 the asphaltene sludge. The wettability of the aged carbonate rock sections was investigated  
8 after the acidizing and microwave radiation. The desorption of hydrocarbons from rock  
9 surfaces was studied using the Attenuated Total Reflectance-Fourier Transform Infra-Red  
10 (ATR-FTIR) spectroscopy.

11

## 12 **2. Materials and method**

### 13 **2.1 Materials**

#### 14 **2.1.1 Rock sample**

15 A carbonate rock sample was used to investigate the effect of microwaves during  
16 acidification on surface wettability. The results of the X-ray fluorescence (XRF) of the rock  
17 samples are given in Table 1. Based on the XRF analysis, 94.50% of the employed rock  
18 sample is comprised of  $\text{CaCO}_3$ . X-ray diffraction (XRD) analysis of employed rock sections  
19 confirms the rock sections are mainly composed of  $\text{CaCO}_3$ . Based on the XRD spectrum, the  
20 mineral contents of the employed rock sections are calcium carbonate, gypsum, microcline,  
21 and muscovite. It should be mentioned that the rock sections used in this study had a similar  
22 origin to carbonate rock sections employed by Yazdani et al. 2023[19]. The XRD spectrum of  
23 the pulverized carbonate rock section is shown in Fig 1.

24

Table 1

25

Fig 1

1

## 2 **2.1.2 Oil sample**

3 The oil sample was sourced from a southern oil field in Iran. Table 2 displays the API  
4 gravity, viscosity, acid number, and asphaltene content of this oil sample. In addition, the  
5 composition of oil sample employed to conduct the tests is shown in Table 3.

6 Table 2

7 Table 3

8

## 9 **2.1.3 Acid solution**

10 The acid solutions were prepared at a concentration of 15% to mimic the rock-acid  
11 interaction at the beginning of injection. Three base water of distilled water, seawater, and  
12 formation water were used to synthesize the acid solutions. The composition of seawater,  
13 which is shown in Table 4, was adopted from the Persian Gulf seawater. Besides, the  
14 formation water was designed according to the produced water chemistry originated from the  
15 same field where crude oil was sampled.

16 Table 4

17

## 18 **2.2 Methods**

### 19 **2.2.1 Microwave treatment**

20 A conventional microwave oven was provided to conduct microwave treatments. The  
21 frequency of the device is 2.45GHz and its radiation power could be adjusted in the range of  
22 260-1300 W. The internal dimensions of the microwave are 10×17×20 cm. Similar to other  
23 conventional microwaves bearing a magnetron, the one used in this study could only radiate  
24 waves with a single wave frequency. After, immersing the aged rock sections in the provided  
25 acid solutions, they were treated by microwave radiation with the radiation powers of 780

1 and 1300 W for 1-3 min. To investigate the effect of microwave radiation, similar rock  
2 sections were also treated with an acidic solution without microwave radiation.

### 3 **2.2.2 Temperature changes**

4 The temperature of the rock sections was recorded by a digital laser thermometer (GM-320,  
5 Benetech) with an accuracy of  $\pm 1^\circ\text{C}$ . Regarding the fact that a digital thermometer measures  
6 the material's temperature based on the reflected beam from the surface, it is not possible to  
7 measure the temperature continuously. To measure the temperature of treated rock in the  
8 middle of the microwave radiation, it was needed to halt the radiation every 30 seconds.  
9 Considering the short treatment time (3 min), stopping the treatment for even a short time  
10 disturbs the treatment. To avoid this problem, another batch of rock sections was prepared to  
11 capture the temperature profile. For instance, to obtain a temperature curve with six data  
12 points, six rock sections were treated in six duration times. It should be mentioned that to  
13 compare the temperature increase between the oil and rock, the oil samples with a weight  
14 equal to the rock section were also treated. The weight of the oil sample and rock section was  
15 40 gr. The rock sections were cut to be in a rectangular cube form with the dimensions of 15  
16  $\text{cm} \times 10 \text{ cm} \times 5 \text{ cm}$ .

### 17 **2.2.3 Contact Angle Analysis**

18 One of the most important effective parameters for fluid displacement in the porous medium  
19 is wettability . The contact angle test was used to study the wettability alteration of carbonate  
20 rock sections before and after the treatments. The rock sections, which were cut from the rock  
21 sample described previously, were washed with methanol (two days) and toluene (ten days)  
22 to remove petroleum-based and salt-based contamination. The soxhlet device was employed  
23 to wash the rock sections. Then, the clean rock sections were saturated with formation water  
24 and kept at  $90^\circ\text{C}$  for two days. The formation water-saturated rock sections were injected with  
25 crude oil, and then, kept in crude oil at  $90^\circ\text{C}$  for 35 days. In the end, the wettability of the aged

1 rock sections was restored to the reservoir condition. The rock sections were treated with the  
2 acidic solutions for 1hr at 70°C. Afterward, they were treated by microwave radiation for 1, 2,  
3 and 3 min at radiation powers of 780 and 1300 W. At the end of the treatments, the  
4 wettability of the rock sections was investigated by using the pendant drop technique. It  
5 should be mentioned that the contact angle measurements were conducted 3 times and the  
6 median point was reported. Based on the obtained data, the accuracy of the contact angle data  
7 was  $\pm 0.6^\circ$ .

#### 8 **2.2.4 ATR-FTIR spectrums**

9 Investigating the wettability alteration by using the pendant drop method gives no  
10 information about the chemistry of the desorbed hydrocarbons. The ATR-FTIR of the treated  
11 rock sections was investigated by a refractometer (PerkinElmer, USA). The spectrums were  
12 obtained from 600-4000  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ . To obtain the computational data  
13 from the ATR-FTIR spectrums, the integral area of the hydrocarbon-related peaks was  
14 calculated. By implementing the calculated integral areas, the computational characteristic  
15 indexes were obtained through equations suggested by Karami et al. 2022[20]. Based on the  
16 characteristic indexes, given by ATR-FTIR spectrums, the polar, carbonyl, aliphatic, and  
17 aromatic content of the rock sections were addressed.

### 18 **3. Results and Discussions**

#### 19 **3.1 Temperature Changes**

20 The temperature changes of rock samples under microwave radiation are shown in Fig 2. The  
21 temperature of the oil samples increased to 55°C and 75°C after microwave radiation for 3  
22 min at radiation powers of 780 W and 1300 W, respectively. Besides, the temperature of the  
23 rock sections increased to 94°C and 120°C after microwave radiation for 3 min at radiation  
24 powers of 780W and 1300 W, respectively. The reason for temperature increase could be



1 explained by basic laws of physics. Changing the direction of electric dipoles of polar  
2 compounds, when it's exposed to the microwaves, leads to thermal energy. The kinetic  
3 energy of compounds with high dielectric constants are more absorbent to the microwave,  
4 making them good candidate for microwave thermal heating [21,22]. Therefore, higher  
5 temperature of the rock sections, respect to the adsorbed hydrocarbon, is explainable based  
6 on the higher dielectric constants of the rock sections. An increase in temperature may cause  
7 physical and chemical changes to the adsorbed hydrocarbons, leading to cracking and  
8 desorption of the polar compounds, such as asphaltenes [23,24].

9 At first glance, the range of temperature rise is not considerable; regarding other heating  
10 methods, higher temperature rise is expected for improving wetting conditions. To explain  
11 this issue, the treating condition and heating mechanism of the microwave must be  
12 considered. The rock sections were immersed in the solution to mimic the reservoir  
13 condition. There is a heat transfer between the rock section and the immersing solution,  
14 forcing the rock section to be in thermal equilibrium with the immersing solution. Although  
15 the solutions have a much higher dielectric constant with respect to the rock sections, their  
16 temperature cannot exceed its boiling point during microwave radiation.

17 At identical microwave power radiation, exposure time, and wave frequency, the temperature  
18 of the materials, including rock sections and oil samples, strongly depends on dielectric  
19 constants. The dielectric constant of oil samples, depending on their hydrocarbon content, lies  
20 in the range of 1-4.5[25-28]. In addition, the dielectric constant of the CaCO<sub>3</sub> is 9.2[29]. A  
21 higher temperature increase, which was observed for rock sections, confirmed the fact  
22 materials with a higher dielectric constant are a better absorbent to microwaves. It should be  
23 mentioned that the temperature, which was recorded by the laser thermometer, reports the  
24 macroscopic temperature. Crude oil is generally comprised of various hydrocarbons having a  
25 wide range of polarity/dielectric constants. The dielectric constant of asphaltene compounds

1 is overall four times of the aliphatic ones, leading to the creation of regions with higher  
2 temperatures on a molecular scale. Hence, the temperature of asphaltene molecules is almost  
3 four times of the bulk oil sample. As a result, if the oil sample temperature reaches 70°C after  
4 3 minutes of radiation at 850 W, the temperature of asphaltene aggregates reaches 280°C.

5 In addition, the lower temperature of the oil sample/rock sections, respect to other thermal  
6 methods could also be explained by lower radiation time (3 minutes). After 3 minutes of  
7 radiation, the contact angle of some of the rock sections reduced to 62°, while the others were  
8 still oil-wet. Increasing the radiation time leads to converging all the contact angles toward  
9 the most possible hydrophilic condition, making it impossible to investigate the effect of the  
10 microwave radiation and imbibition water composition. Hence, to capture the difference  
11 between the various acidizing conditions, the exposure time of 3 min was appropriate.

1 Fig 2

## 2 **3.2 Contact Angle**

3 According to the reduction of the contact angle in both radiation powers (780 and 1300 W),  
4 microwave radiation in conjugate with acid solutions treatment improves hydrophilicity. In  
5 the vicinity of an acid solution under a constant temperature of 70°C, the contact angle will  
6 decrease due to the loss of light components under the temperature. Due to the polarity of the  
7 acidic solution, some of the polar components of the crude oil will react and dissolve with the  
8 acidic solution, and as a result, the polar components spread on the surface of the rock will  
9 increase slightly, and as a result, the effect of reducing the contact angle due to constant  
10 temperature will not intensify. The lowest contact angle related to an acidic solution  
11 containing distilled water is 57.1° due to less polarity and the highest contact angle related to  
12 an acidic solution containing distilled water is 108.2° due to polarity. The reduction will be

13 severe, and the greatest reduction of acid solution and water formation will be near the  
14 microwave, because high salinity improves the heating power of the microwave.

15 In the vicinity of acid solution and microwave waves for different periods and different  
16 powers, the contact angle will decrease initially due to the loss of light components. By  
17 increasing the exposure time, polar compounds will be removed from the section. As a result,  
18 the contact angle increases. The lowest contact angle related to the acid solution including  
19 seawater and power of 780 W is  $55.9^\circ$  and the highest contact angle ( $114.1^\circ$ ) is related to the  
20 acid solution with a base of sea water and microwave power of 780 W.

21 The reduction of the contact angle of distilled water, seawater, and formation water will be  
22 almost equal in the initial time. The acid solutions with the base of formation water reduces  
23 the contact angle to  $55^\circ$  compared to distilled water and seawater base solutions. Also, the  
24 high polarity of formation water and seawater causes polar components to dissolve in polar  
25 solution (formation water and sea water) and therefore heavy components such as asphaltene  
26 and resin are easily separated from crude oil compounds.

27 Fig 3

28

29 Fig 4

30

31 Fig 5

32 According to the contact angles of the sections treated by acid solution, without microwave  
33 radiation, the distilled water base acid solution is more feasible for wettability alteration.  
34 Besides, a higher hydrophobicity was observed in the sections treated by the formation water  
35 base acid solution. Hence, it could be concluded that the presence of the dissolved ion

36 prohibits desorption of hydrocarbon, reducing the ability of acid solution for improving rock  
37 surface hydrophilicity.

38 In Figure 3, the contact angles are shown without the influence of microwaves and only in the  
39 vicinity of acid, and it can be seen that the contact angles undergo decreasing changes. Based  
40 on the contact angles, shown in Figure 5-4, the base water composition and irradiation power  
41 and exposure time affect the wettability of the treated rock. The wettability of the rock  
42 sections treated by radiation power 1300 W reduces to almost 60 °after 2 min, and then,  
43 increases again at higher exposure times. The reduction of contact angle, indicating rock  
44 hydrophilicity improvement, could be desorption of non-polar hydrocarbons from the rock  
45 surface. Further microwave radiation could desorb or crack the polar hydrocarbons, such as  
46 asphaltenes, leading to increasing the rock hydrophobicity. The composition of base water  
47 did not influence the rock wettability at high radiation power (1300 W).

48 Despite the sections treated by high-power radiation, the base water chemistry influenced the  
49 sections treated by microwave power of 780 W. The lowest contact angle was observed in the  
50 section treated by the formation water. More salinity of the formation water, representing  
51 higher ion concentration, makes microwave radiation more feasible for wettability alteration.  
52 The dissolved ions, which are electrically charged, are highly influenced by alternating  
53 electric and magnetic fields.

### 54 **3.3 ATR-FTIR spectroscopy:**

55 The contact angles, obtained by the sessile drop technique, addressed the wettability status of  
56 treated rock sections. But, no information was provided regarding desorption of hydrocarbons  
57 from the rock surface. The ATR-FTIR spectrums of the Acid-treated rock sections are shown

58 in Fig 6. Besides, Fig 7-8 are indicating the ATR-FTIR spectrums of the rock section treated  
59 by simultaneous acid solution and microwave radiation with 780 W and 1300 W,  
60 respectively.

61 Fig 6

62 Fig 7

63 Fig 8

64 The peaks in the ATR-FTIR spectrums depict both the adsorbed hydrocarbons and rock  
65 minerals. The observed in the ATR-FTIR spectrums could be subdivided into three groups  
66 rock-assigned, hydrocarbon-assigned, and common peaks. Regarding the fact that the ATR-  
67 FTIR spectrums were employed to address the hydrocarbon chemistry, the peaks that are only  
68 assigned to hydrocarbons were taken into calculation. As shown in Table 5, the aliphatic C-H  
69 bonds are represented by peaks in the range of 2755-3000  $\text{cm}^{-1}$ . Besides, the ranges of 3000-  
70 3100 and 1566-1668  $\text{cm}^{-1}$  are respectively standing for C-H and C=C bonds in the aromatic  
71 rings. Ketone-based functional groups, such as carboxylic acids groups, are vibrating in the  
72 range of 1668-1800  $\text{cm}^{-1}$ . In addition, the amine and alcoholic functional groups are seen in  
73 the range of 3100-3500  $\text{cm}^{-1}$ . More information regarding the chemistry of hydrocarbons  
74 could be found in Table 5. As mentioned before, to extract numerical data from ATR-FTIR  
75 spectrums, the characteristic indexes given by Karami et al 2022 were employed[30]. The  
76 Aromatic/Aliphatic, Aliphatic length, C=O/Aliphatic, C=O/Aromatic, Polar/Aliphatic, and  
77 Polar/Aromatic indexes were calculated regarding the integral areas of the corresponding  
78 peaks. Table 6 shows the characteristic indexes obtained from the ATR-FTIR spectrums [30-  
79 33].

81 To investigate the chemistry of the hydrocarbons, which have a greater tendency for  
 82 desorption from the rock surface, the ATR-FTIR spectrums were analyzed from an analytical  
 83 point of view. In this regard, the integral area of each hydrocarbon-assigned peak was  
 84 employed to be used in the characteristic equations given by Karami et al .2022 [30-35].  
 85 Equations 1-6 show the ratios used to characterize the chemistry of hydrocarbons adsorbed  
 86 on the rock surface. In Equations 1-6, the ‘A<sub>i</sub>’ stands with the integral area below the peak in  
 87 the range of ‘i’.

$$C=O/A_{\text{Aliphatic}} = \frac{A_{1668-1800}}{A_{2881-2946}} \quad (1)$$

$$C=O/A_{\text{Aromatic}} = \frac{A_{1668-1800}}{A_{1566-1668}} \quad (2)$$

$$A_{\text{Aromatic}}/A_{\text{Aliphatic}} = \frac{A_{1566-1668}}{A_{2881-2946}} \quad (3)$$

$$A_{\text{Aliphatic length}} = \frac{A_{2946-3000}}{A_{2881-2946}} \quad (4)$$

$$Polar/A_{\text{Aliphatic}} = \frac{A_{3100-3500}}{A_{2881-2946}} \quad (5)$$

$$Polar/A_{\text{Aliphatic}} = \frac{A_{3100-3500}}{A_{2881-2946}} \quad (6)$$

89 As shown in Table 6, except for the seawater-based acid solution, the Aromatic/Aliphatic  
90 index of the acid-treated section is increased. The decrease of the Aromatic/Aliphatic index in  
91 the seawater-based acid solution represents more affinity of the aromatic compound to be  
92 desorbed from the rock surface due to the presence of determining ions. Aliphatic length,  
93 which is lower in the longer aliphatic hydrocarbons, is drastically decreased in the formation  
94 of water-based acid solution. Hence, it could be concluded that the high salinity brine water  
95 reduces desorption of the long-chain alkanes. Based on the aliphatic length index, the  
96 seawater-based solution desorbed the long-chain alkanes with more efficiency. As shown in  
97 Table 6, both indexes of the Polar/Aliphatic and Polar/Aromatic only increased in the  
98 seawater-based acid solution, representing less potential of the polar functional group (O-H  
99 and N-H) for desorption respect to the aromatic and aliphatic hydrocarbons. The lower  
100 Aromatic/ Aliphatic index of the section, which was treated with a seawater-based acid  
101 solution, indicates that the aromatic hydrocarbon was tenser. Hence, the drastic increase of  
102 the Polar/Aromatic index in seawater-based acid solution could be understood by the severe  
103 desorption of aromatic hydrocarbons. Both indexes of C=O/Aliphatic and C=O/Aromatic are  
104 the least in the seawater-based acid solution, indicating more severe desorption of carbonyl-  
105 based functional groups. Based on the characteristic indexes, given by ATR-FTIR spectrums,  
106 the chemistry of the hydrocarbons on the rock surface is influenced by the composition of  
107 base water.

108 Table 7

109 The characteristic indexes calculated from the ATR-FTIR spectrums of the crude and acid-  
110 treated rock section, which were radiated by microwave, are shown in Table 7. The  
111 Aromatic/Aliphatic index of the microwave-treated sections is generally lower than the crude  
112 aged section, representing that the microwave radiation leads to more efficient desorption of

113 the aromatic compounds, such as asphaltenes. It should be mentioned that the sections, which  
114 were not treated by microwave radiation (Table 6). The Aliphatic length indexes of  
115 microwave-treated rock sections are higher than the crude rock section. Hence, microwave  
116 radiation leads to desorption of longer alkanes from the rock surface. Based on the aliphatic  
117 length index, desorption of longer alkanes is more severe in the sections treated with distilled  
118 water. The Polar/Aliphatic index is commonly lower in the microwave-treated rock sections,  
119 indicating the feasibility of microwave radiation for desorption of polar functional groups (O-  
120 H and N-H). Despite the Polar/Aliphatic index, the Polar/Aromatic index does not show a  
121 consistent trend in the microwave-radiated sections. This irregular trend for Polar/Aromatic  
122 could be explained by tense desorption of both aromatic compounds (according to the  
123 Aromatic/Aliphatic index) and polar functional groups (observed from the Polar/Aliphatic  
124 index). Except for the sections, which were treated by distilled water-based acid solution, the  
125 C=O/Aliphatic index of the microwave-treated sections was lower than the crude one. Hence,  
126 it could be deduced that desorption of C=O-based functional groups is less efficient without  
127 the presence of other ions. Besides, the C=O/Aliphatic index is generally lower in the  
128 sections radiated by the power of 1300 W, representing an increase of the C=O bond  
129 desorption at higher radiation powers. The C=O/Aromatic index of the microwave-treated  
130 sections does not follow a regular trend, which might be due to the tense desorption of  
131 aromatic compounds.

132 By comparing the characteristic indexes, given by the ATR-FTIR spectrums, the microwave  
133 radiation of the rock sections during the acid treatment leads to more efficient desorption of  
134 aromatic compounds, longer alkanes, polar bonds (O-H and N-H), and C=O Based functional  
135 group. Hence, simultaneous microwave radiation could be employed to remove the  
136 precipitated asphaltene sludge generated by acid treatment. More affinity of the aromatic,  
137 polar, and long-chain alkanes for desorption during simultaneous microwave radiation and



138 acid treatment could be explained by the fundamental laws of electromagnetic. The  
139 microwave energy absorption of the material is directly proportional to the electric polarity of  
140 the material. The material with higher dielectric constants is more absorbent respect to  
141 electromagnetic waves, such as microwaves. The hydrocarbons in the crude oil and ones  
142 adsorbed on the rock surface lies in a wide range of electric properties. According to the  
143 literature review, the dielectric constant of the asphaltenes could also be 3-4 times of the  
144 other hydrocarbons, such as alkanes[36-40]. Hence, the energy absorbed by asphaltene  
145 molecules could lie in the range of 3-4 times of the other hydrocarbons. The asphaltenes are  
146 widely accepted as polycyclic aromatic compounds, attached by aliphatic chains and polar  
147 functional groups[41-45]. Hence, the reduction of the mentioned indexes indicates the  
148 asphaltene molecule desorption during simultaneous microwave radiation and acid treatment.

#### 149 **4. Conclusion**

150 In this research, the effect of acid solution treatment in conjugate with microwave radiation  
151 on the rock-fluid interaction was investigated. Using the contact angle measurement and  
152 ATR-FTIR spectroscopy, the following statements were concluded.

153 1. According to the contact angles, the composition of base water and radiation power and  
154 exposure time affects the rock wettability. When there is no microwave radiation applied to  
155 the rock section, the addition of dissolving ions prohibits the wettability alteration. In  
156 contrast, the saline water (formation water) showed lower oil-wetness when the microwave  
157 radiation was combined. Besides, while increasing the radiation power leads to a lower  
158 contact angle, increasing the exposure time could either increase or decrease it.

159 2. By comparing the characteristic indexes, given by the ATR-FTIR spectrums, the  
160 microwave radiation of the rock sections during the acid treatment leads to more efficient  
161 desorption of aromatic compounds, longer alkanes, polar bonds (O-H and N-H), and C=O

162 Based functional group. Hence, simultaneous microwave radiation could be employed to  
163 remove the precipitated asphaltene sludge generated by acid treatment.

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317 radiation power of 1300 W for 3 min.

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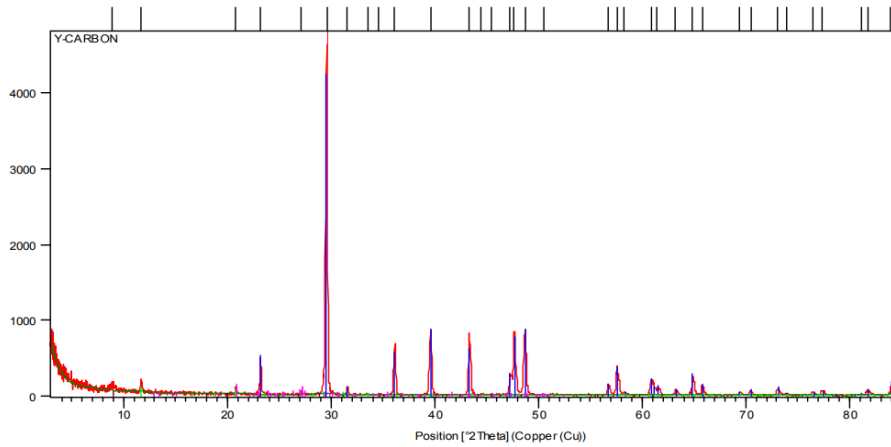
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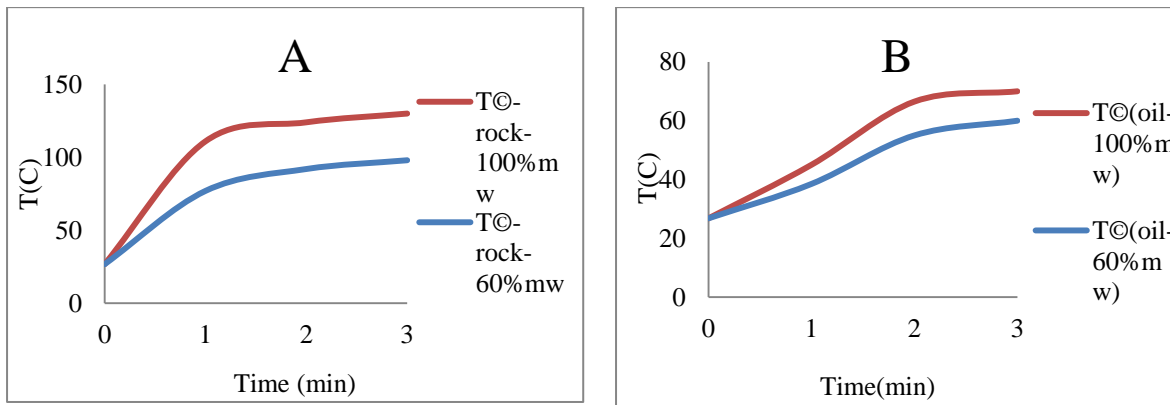




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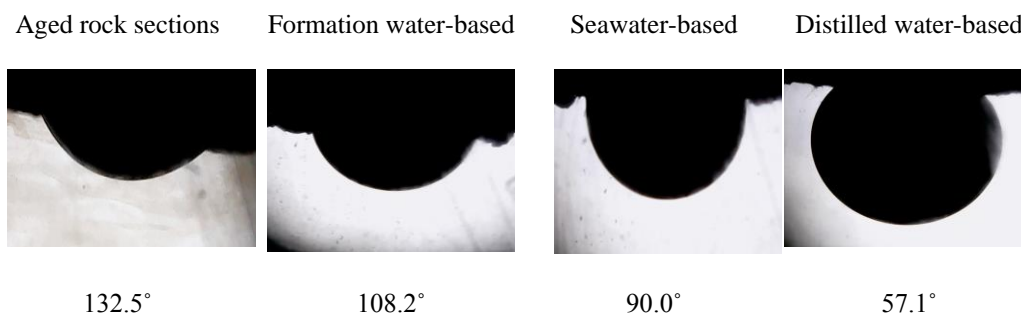
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335 microwave irradiation time

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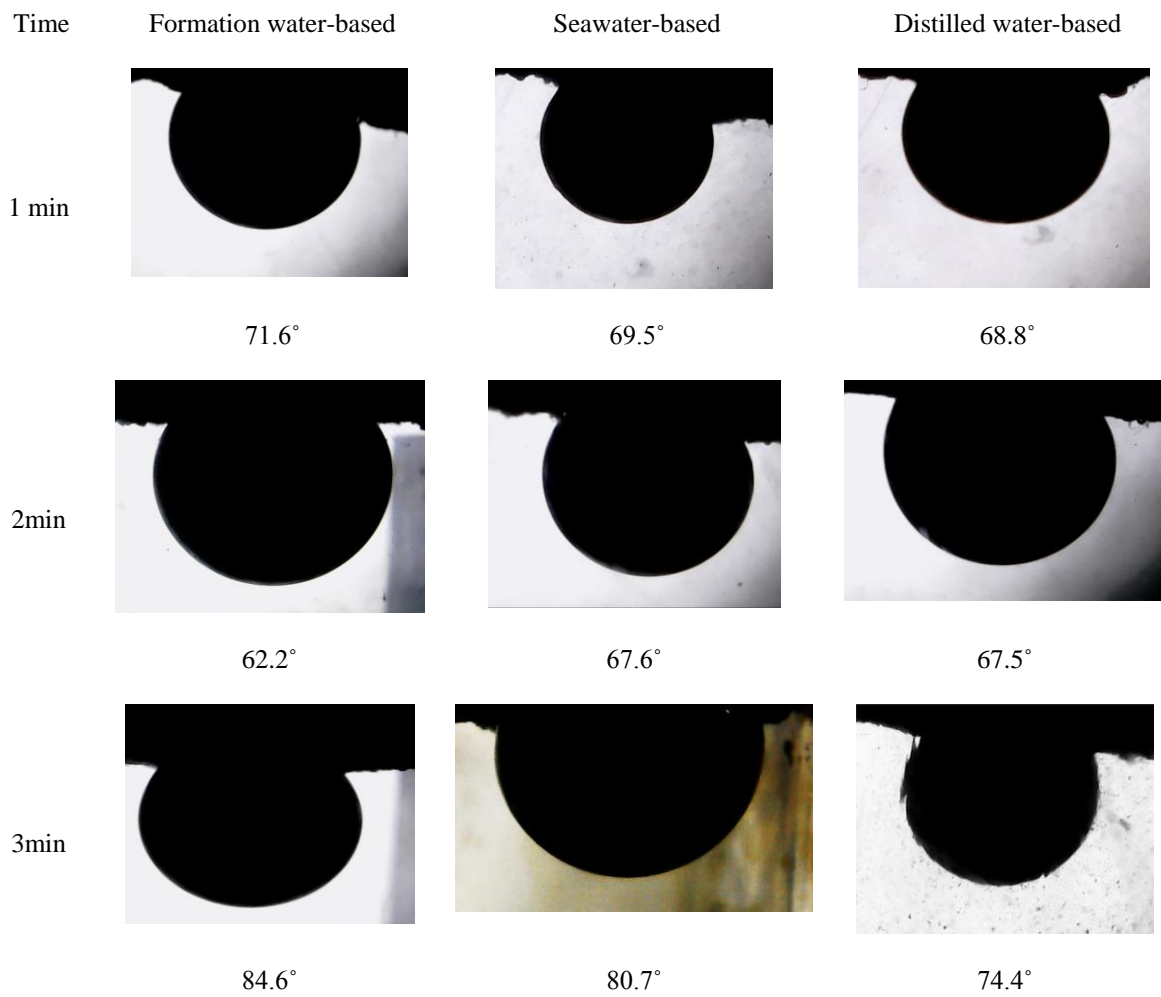


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339 without microwave radiation

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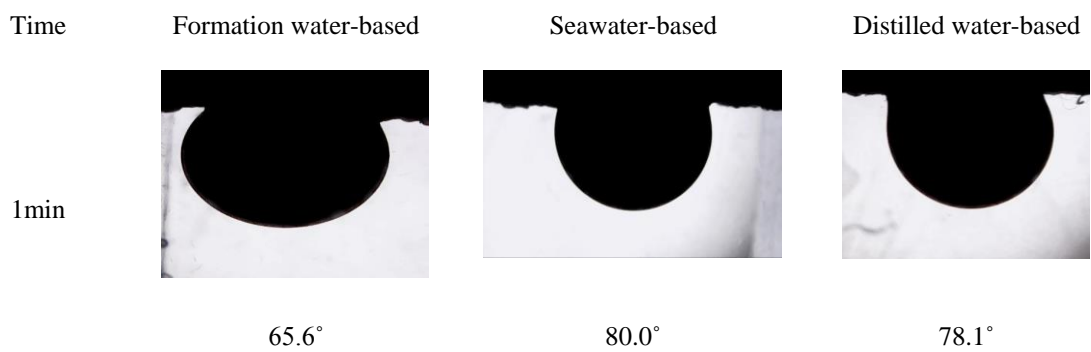


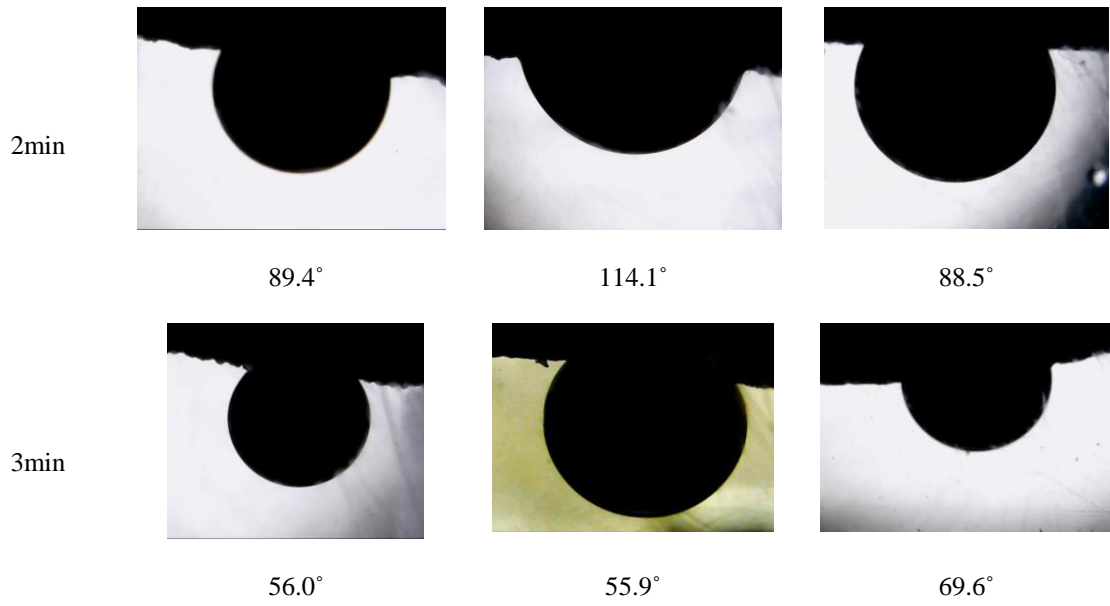
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343 Fig 4. The contact angle between rock sections and crude oil after being exposed to microwave with emission  
344 power of 1300 W and acidic solutions for 1, 2, 3 min

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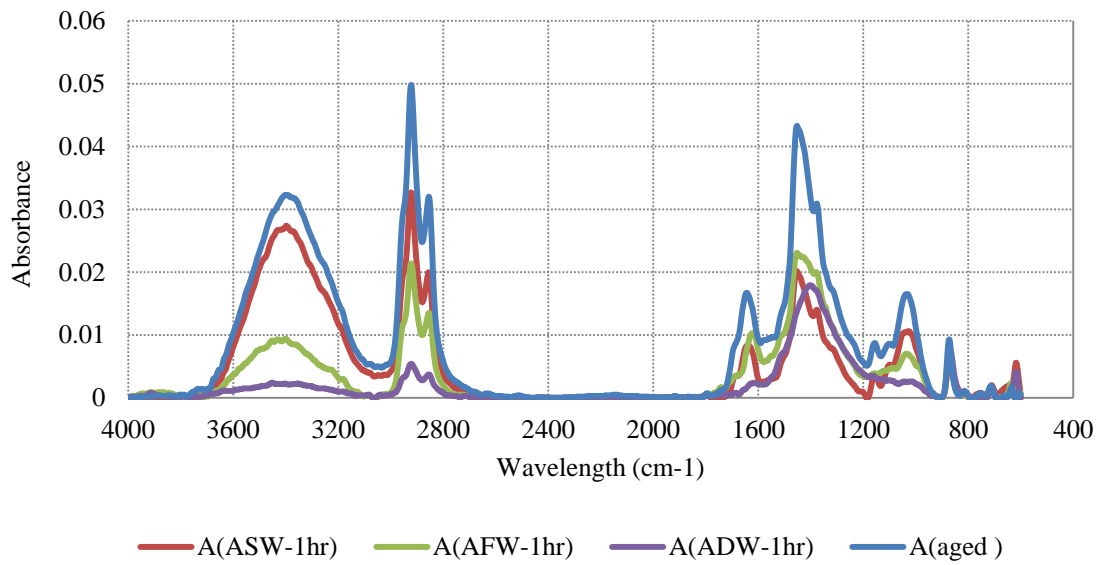




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348 Fig 5. The contact angle between rock sections and crude oil after being exposed to microwave with emission  
 349 power of 780 W and acidic solutions for 1, 2, and 3 min

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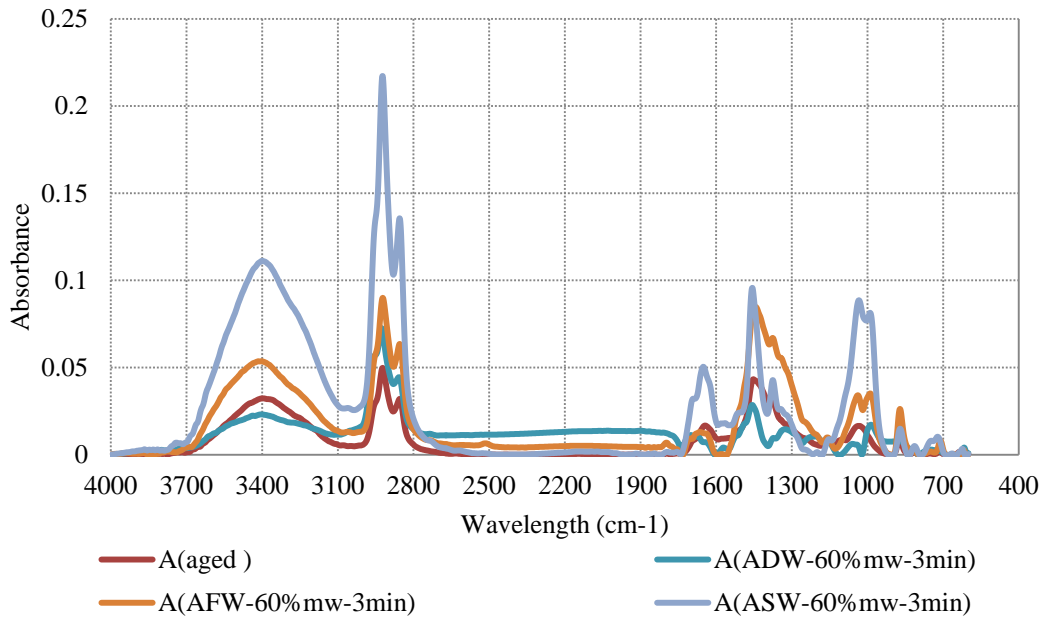


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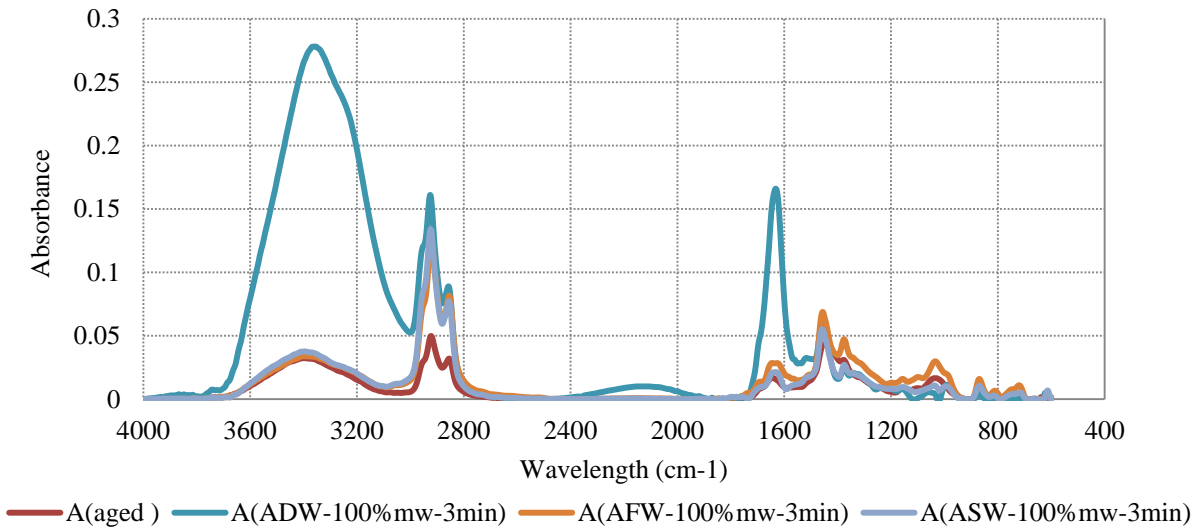
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357 Fig 7. The normalized ATR- FTIR spectra for crude section and sections treated by acid solutions and the  
358 radiation power of 780 W for 3 min



360 Fig 8. The normalized ATR- FTIR spectra for crude section and sections treated by acid solution and the  
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Table 1. The XRF analysis of the rock sample

Connie	Apparent percentage	LOI	Actual percentage
Na <sub>2</sub> O	0.035	41.09	0.059413
MgO	0.565	41.09	0.95909
Al <sub>2</sub> O <sub>3</sub>	0.178	41.09	0.302156
SiO <sub>2</sub>	0.697	41.09	1.183161
P <sub>2</sub> O <sub>5</sub>	0.081	41.09	0.137498
SO <sub>3</sub>	0.735	41.09	1.247666
Cl	0.009	41.09	0.015278
K <sub>2</sub> O	0.037	41.09	0.062808
CaO	55.675	41.09	94.50857
TiO <sub>2</sub>	0.067	41.09	0.113733
Fe <sub>2</sub> O <sub>3</sub>	0.146	41.09	0.247836
Sr	0.684	41.09	1.161093

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Table 2. API gravity, viscosity, acid number, and asphaltene content of this oil sample

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Physical properties	API	Viscosity (cP) (@ temperature 26°C)	Acid number	Asphaltene content (%)
Crude oil	20.65 °	37	0.6	16

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Table 3. The composition of oil sample used for aging the rock sections

components	Mole weight	Flashed Liquid
Nitrogen	28.01	0
Carbon Dioxide	44.01	0
Hydrogen Sulfide	34.08	0.0004
Methane	16.04	0
Ethane	30.07	0
Propane	44.1	0.139
I – Butane	58.1	0.127

N – Butane	58.12	1.318
I – Pentane	72.15	1.107
N – Pentane	72.15	3.105
Pseudo C6H14	84	6.109
Pseudo C7H16	96	9.316
Pseudo C8H18	107	9.478
Pseudo C9H20	121	8.252
Pseudo C10H22	134	7.054
Pseudo C11H24	147	6.568
Pseudo C12H26	161	5.547
Pseudo C13H28	175	4.16
Pseudo C14H30	190	3.813
Pseudo C15H32	206	3.12
Pseudo C16H34	222	2.427
Pseudo C17H36	237	2.08
Pseudo C18H38	251	1.733
Pseudo C19H40	263	1.387
Pseudo C20H42	277	1.248
Pseudo C21H44	291	1.04
Pseudo C22H46	305	0.832
Pseudo C23H48	318	0.763
Pseudo C24H50	331	0.693
Pseudo C25H52	345	0.555
Pseudo C26H54	359	0.485
Pseudo C27H56	374	0.416
Pseudo C28H58	388	0.347
Pseudo C29H60	402	0.277
C30+	935	16.666
TOTAL	-	100

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Table 4. The composition of brine water compositions (formation water and sea water)

Composition	Concentration(ppm)		
	Distilled water	Seawater	Formation water
NaCl	0	28323	177465
Na <sub>2</sub> SO <sub>4</sub>	0	4936	0
CaCl <sub>2</sub>	0	1630	28036

MgCl <sub>2</sub> . 6H <sub>2</sub> O	0	10510	6561
KCl	0	1032	3440
TDS	0	46431	215502

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Table 5. The assignments of the peaks in the ATR-FTIR spectrums [30-35].

Wavelength	Assignment
3100-3500	N-H, O-H
3000-3100	C-H stretch in aromatic
2946-3000	CH <sub>3</sub> asymmetric stretch
2881-2946	CH <sub>2</sub> asymmetric stretch
2755-2881	CH <sub>2</sub> symmetric Stretch
1668-1800	C=O stretch in ketones, aldehydes, and carboxylic acids
1566-1668	Aromatic C=C stretch

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407 Table 6. The characteristic indexes calculated from the ATR-FTIR spectrums of the crude and acid-treated rock  
408 section (HCl 15%)

Index/treatment solution	Crude	DW-based	SW-based	FW -based
C=O/Aliphatic	0.177	0.223	0.088	0.237
C=O/Aromatic	0.342	0.307	0.259	0.325



Aromatic/ Aliphatic	0.518	0.725	0.339	0.730
Aliphatic length	0.375	0.341	0.382	0.312
Polar/Aliphatic	3.648	2.298	4.640	2.256
Polar/Aromatic	7.036	3.167	13.666	3.089

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411 Table 7. The characteristic indexes calculated from the ATR-FTIR spectrums of the crude and acid-treated rock  
 412 section, which were radiated by microwave

Index	Crude	Radiation power= 780 W			Radiation power= 1300 W		
		DW	SW	FW	DW	SW	FW
C=O/Aliphatic	0.177	0.334	0.148	0.165	0.316	0.083	0.140
C=O/Aromatic	0.342	2.905	0.474	1.27	0.231	0.360	0.362
Aromatic/ Aliphatic	0.518	0.115	0.312	0.131	1.366	0.232	0.387
Aliphatic length	0.375	0.574	0.394	0.387	0.584	0.415	0.374
Polar/Aliphatic	3.648	1.943	3.043	3.272	10.980	1.678	1.649
Polar/Aromatic	7.036	16.892	9.726	24.888	8.036	7.203	4.258

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419 **Biographies**

420 **Hadi Tanhai**, Ph.D. student of Petroleum Engineering - Reservoirs at Tarbiat Modares University  
421 he MSc degree from Tarbiat Modares University in 2023. His field of research at the Ph.D is the study  
422 of the acidizing mechanism, he received his bachelor's degree in petroleum engineering from Tabriz-  
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424 it should be noted that his expertise he studied the effect of microwave in the acidizing in petroleum  
425 engineering during his postgraduate studies. Among his other work and scientific fields, we can  
426 mention cooperation with the Iran Gas Engineering Association, the Iran Nuclear Association, and  
427 the Secretary of the Oil Engineering Association, Tarbiat Modares.

428 **Dr. Amirhossein Saeedi Dehaghani** , received his Ph.D. from Tarbiat Modares University in 2013  
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437 **Saeed Karami**, the head of the Research and development of Petro Atlas Zagros Company, who  
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