Isolated Influence of Microwave Energy and Acidic solution on Wettability Alteration and Hydrocarbon Desorption in Carbonate Reservoir Rocks

Abstract

This study investigates the independent effects of microwave irradiation and acidic solutions on wettability alteration and hydrocarbon desorption in carbonate reservoir rocks. Contact angle measurements and ATR-FTIR spectroscopy were employed to analyze both surface wettability changes and molecular-scale modifications. Microwave treatment at 780 W and 1300 W reduced the contact angle from an initially oil-wet state of ~132° to 72° and 69°, respectively, indicating a pronounced shift toward water-wet conditions. FTIR analysis confirmed these observations, showing decreases in the Polar/Aliphatic and Aromatic/Aliphatic indices, which reflect the desorption of polar and aromatic compounds from the rock surface. Acidic solutions produced similar effects, although their efficiency depended on brine composition, hydrochloric acid in deionized water reduced the contact angle to ~57°, while seawater and formation water resulted in weaker changes due to ionic buffering by Ca^{2+} and Mg^{2+}. The novelty of this work lies in the separation of microwave and acid effects, demonstrating distinct mechanisms. Microwave irradiation enhances desorption through dielectric heating and bond disruption, whereas acidic solutions act primarily through chemical reactivity and ionic competition. These findings show that both methods independently promote wettability alteration, with efficiency governed by microwave power and brine chemistry. The results provide practical insights for the design of advanced Enhanced Oil Recovery (EOR) strategies, including microwave-assisted stimulation and optimized acidizing treatments in carbonate reservoirs.

Keywords: microwave irradiation, acidic solutions, wettability alteration, ATR-FTIR analysis, enhanced oil recovery

1.Introduction

Acidizing is a stimulation technique used in oil and gas wells to enhance hydrocarbon flow by dissolving formation damage and creating new channels, commonly referred to as wormholes. This

process aims to rejuvenate production by unclogging blocked pores, improving formation pfsermeability, and ultimately boosting output efficiency [1–3]. Among the key factors influencing fluid behavior in porous media, wettability plays a central role. It directly affects critical reservoir properties such as capillary pressure and relative permeability, thereby exerting a strong influence on fluid distribution and recovery performance [4].

Wettability alteration has long been recognized as a critical mechanism in enhancing oil recovery, particularly in carbonate reservoirs, which are often naturally oil-wet due to the strong affinity between rock surfaces and heavy polar components in crude oil. In such systems, shifting the wettability toward a more water-wet condition can significantly improve the efficiency of displacement processes and increase the ultimate recovery factor. Traditional acidizing techniques using hydrochloric acid (HCl) are widely employed to enhance permeability by dissolving carbonate minerals and removing formation damage. However, the effect of acidizing on wettability is often limited or inconsistent, particularly when formation brine contains divalent cations such as Ca^{2+} and Mg^{2+} that can buffer acid reactions and contribute to surface re-oiling or precipitation .To overcome these limitations, researchers have explored various additives such as surfactants, chelating agents, and nanoparticles to enhance acid-rock interactions and promote wettability alteration. Despite some success, challenges such as formation damage, acid sludge formation, and scale precipitation remain concerns in field applications[5].

In carbonate reservoirs, acidizing primarily serves to create new flow channels by dissolving both the formation rock and any existing damage, thereby enhancing hydrocarbon production. In contrast, acidizing in sandstone formations is typically aimed at restoring flow by removing damage and blockages without significantly dissolving the rock matrix itself. The key distinction lies in the mechanism: while carbonate acidizing involves the reaction of acid with the reservoir rock itself, sandstone acidizing focuses on dissolving obstructions such as fines and scale that impair permeability. However, acidizing operations in both formations are often challenged by complications such as salt precipitation and the formation of asphaltene sludge. Therefore, careful design and

engineering of the acidizing process is essential to mitigate these risks and improve treatment effectiveness [6].

Matrix acidizing is a stimulation technique used to remove formation damage or enhance permeability in zones located within a few meters of the wellbore. This technique can be applied to both sandstones and carbonates; however, the primary objectives of the operation differ between these two rock types. In carbonates, the aim is to bypass the damaged zone by creating high conductivity channels (wormholes), thereby enhancing the flow of hydrocarbons from the reservoir to the wellbore. In sandstone formations, matrix acidizing operations should primarily aim to remove or dissolve acid-soluble damage or to clear blockages in the perforations and the pore network near the wellbore. Theoretically, the acid flows through the pore system and dissolves solids and fine particles present in the cavities and pore spaces that hinder the flow of oil or gas[7].

In a 2018 study, Yoo et al. examined the dissolution behavior of dolomite in carbonate acidification, focusing on the use of both fresh and spent acids. Spent acid, which results from partial reaction and contains calcium and magnesium ions from the acid-rock interactions, was analyzed separately. The results showed that dolomite dissolved in both types of acid. When comparing the fresh acid with the spent one, it was observed that the spent acid had a higher kinematic viscosity and a lower pH. These differences were linked to a greater dissolution rate and diffusion coefficient in the spent acid, driven by its higher viscosity and lower pH. Furthermore, the study pointed out an unusual ion influence from impurities such as iron oxide and aluminum oxide present in clay, which enhanced the reaction rate, though this was not related to the specific reaction between hydrochloric acid and dolomite [8].

In reservoirs characterized by low permeability and limited heat transfer, electromagnetic (EM) techniques have shown superior performance in reducing oil viscosity and improving fluid mobility compared to conventional methods. Microwaves, a subset of EM waves with frequencies between 300 MHz and 300 GHz, generate an electromagnetic field that selectively transfers energy to materials with high dielectric constants. In petroleum applications, microwaves are most commonly utilized in oil shale and unconventional reservoirs. The heating process is typically implemented by placing a

microwave antenna near the production zone. For Enhanced Oil Recovery (EOR), this antenna is installed in a wellbore drilled adjacent to the main production well [9,10]. The presence of microwave-absorbing materials is crucial in these systems, as they significantly influence the efficiency of electromagnetic wave attenuation and energy transfer [11].

In their study, Hong et al. utilized formation microwave heat treatment (FMHT) to enhance oil recovery by fracturing the formation. The results revealed a significant increase in the number of fractures as the exposure to microwave energy was extended. These fractures, along with the changes in pore structure induced by microwave treatment, resulted in a reduction in the wave speed (S Pand) within the coal core. The exposure to microwave energy also caused a narrowing of the frequency spectrum range of the coal core. Additionally, the frequency distribution within the spectrum was altered by the microwave radiation. Moreover, a decrease in the coal's density, bulk modulus, and shear modulus was observed following microwave treatment, with the bulk and shear moduli decreasing at a faster rate than the coal's density [12].

Electromagnetic (EM) waves are widely used in the petroleum industry for thermal stimulation of oil wells, particularly for enhancing recovery in heavy oil reservoirs. Among their various applications, one of the most significant is the heating of the wellbore region to promote processes such as asphaltene breakdown and crude oil upgrading. Three primary EM-based heating techniques are employed: resistance heating, induction heating, and microwave heating [13].

Taheri-Shakib et al. (2018) investigated how microwave irradiation affects the wettability of carbonate reservoir rocks. By examining changes in surface charge and measuring contact angles, they found that extended microwave exposure enhanced the water-wet characteristics of the rock samples [13].

Karami et al. (2021) reported that the improvement in rock wettability caused by microwave application is not solely due to thermal effects. Their study revealed that microwave exposure also facilitates the decomposition of organic materials on the rock surface, which weakens van der Waals interactions and leads to noticeable changes in wettability [14].

In their 2018 study, Hui Shang et al. examined the effects of microwave irradiation on crude oil

viscosity and concluded that the degree of viscosity change depends on the composition and types of compounds present in the oil [15].

Of these, microwave heating offers distinct advantages, including minimal energy loss and independence from the surrounding formation's thermal conductivity. In this approach, a microwave-emitting antenna is installed in a wellbore drilled adjacent to the main production well [16-18]. As reservoir fluids migrate toward the production zone, they are directly exposed to microwave radiation, leading to efficient and uniform heating in the vicinity of the well. This localized thermal enhancement helps counteract pressure depletion and significantly lowers the viscosity of heavy and extra-heavy crude oils—ultimately improving reservoir performance and oil recovery rates [19].

The use of ATR-FTIR analysis provided crucial insights into the interactions at the rock-fluid interface during acidizing at a molecular level. The results indicated that microwave irradiation significantly boosts the desorption of organic compounds from rock surfaces, such as aromatic hydrocarbons, long-chain alkanes, and polar functional groups including hydroxyl (O–H), amine (N–H), and carbonyl (C=O) groups. This enhanced desorption suggests that microwave energy aids in breaking down complex hydrocarbon structures, which helps in the efficient removal of asphaltene sludge typically formed during acid treatments. Given that asphaltenes are large, high-molecular-weight substances that can block pore spaces and impede fluid flow, microwave-assisted desorption presents a promising technique to improve the performance and effectiveness of acidizing processes[20].

In 2023, Le et al. proposed a novel approach for synthesizing zeolite 4A using microwave-assisted techniques, which significantly improved porosity and reduced crystallization time compared to traditional hydrothermal methods. The resulting zeolite 4A displayed high crystallinity, a uniform cubic structure, and an enlarged surface area, as verified by XRD and SEM characterizations. Notably, the process utilized a standard household microwave oven, demonstrating considerable energy savings and suggesting strong potential for industrial application. This method presents a more sustainable and efficient alternative for producing zeolite 4A with enhanced adsorption capabilities [21].

Recent investigations have explored various techniques to enhance oil recovery from carbonate reservoirs, including matrix acidizing, surfactant flooding, and electromagnetic (microwave) stimulation. For instance, several studies reported that microwave heating accelerates oil desorption by disrupting polar and asphaltenic bonds, while others emphasized the role of acid type and brine composition in modifying rock wettability[15,19,20,30].

Despite numerous studies on matrix acidizing and electromagnetic-assisted recovery, the independent (single-variable) influence of microwave power and acid composition on carbonate-rock wettability and hydrocarbon desorption has not been clearly established. Most previous investigations combined chemical and thermal effects, making it difficult to isolate their individual roles. In this study, we systematically decouple these effects by (i) applying 2.45-GHz microwave irradiation at powers of 780 W and 1300 W for 1–11 min, and (ii) performing acid treatments using 15 wt% HCl prepared in deionized water (ADW), synthetic seawater (ASW), and formation water (AFW) for 2–22 min. Wettability was quantified by sessile-drop contact angle, and interfacial chemistry was examined using ATR-FTIR spectral indices (Aromatic/Aliphatic, Polar/Aliphatic, C=O/Aliphatic). The results demonstrate that microwave treatment alone drives a pronounced water-wet shift through the thermal desorption of surface-bound hydrocarbons, whereas acid efficiency is strongly affected by the ionic composition of the base water. These controlled single-factor experiments provide clear mechanistic insight and practical guidance for optimizing wettability alteration in carbonate reservoirs.

2. Materials and method

2.1 Materials

2.1.1 Rock sample

To examine the impact of microwave-assisted acid treatment on the wettability of rock surfaces, a carbonate rock sample was studied. Based on the results from X-ray fluorescence (XRF) analysis shown in Table 1, calcium carbonate ($CaCO_3$) makes up about 94.50% of the rock's composition. Additional X-ray diffraction (XRD) analysis confirms that the primary mineral in the rock is $CaCO_3$. The XRD pattern also indicates the presence of smaller

quantities of gypsum, microcline, and muscovite. It is important to note that the rock samples analyzed in this research share similar geological characteristics with those studied by Tanhaei et al. (2023). [20]. Figure 1 illustrates the XRD spectrum of the powdered carbonate rock sample.

Table 1. The XRF analysis of the rock sample [20]

Mineral	Apparent percentage	LOI	Actual percentage
Na_2O	0.035	41.09	0.059413
MgO	0.565	41.09	0.95909
Al_2O_3	0.178	41.09	0.302156
SiO_2	0.697	41.09	1.183161
P_2O_5	0.081	41.09	0.137498
SO_3	0.735	41.09	1.247666
Cl	0.009	41.09	0.015278
K_2O	0.037	41.09	0.062808
CaO	55.675	41.09	94.50857
TiO_2	0.067	41.09	0.113733
Fe_2O_3	0.146	41.09	0.247836
Sr	0.684	41.09	1.161093

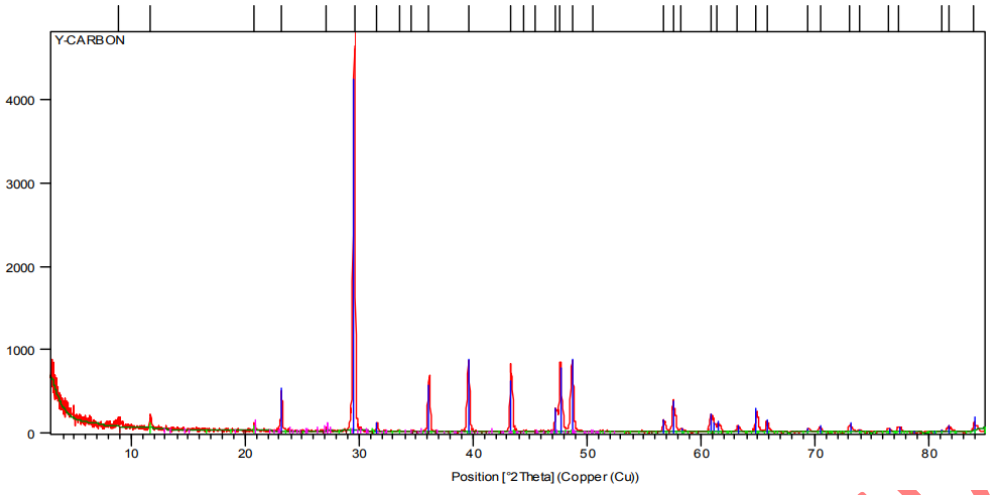

Fig 1. The XRD spectrum of the pulverized carbonate rock section. (Also used by Tanhaei et al. 2023 [20])

2.1.2 Oil sample

The crude oil sample used in this study was obtained from an oil field located in southern Iran. Table 2 presents key properties of the oil, including its API gravity, viscosity, acid number, and asphaltene content. Furthermore, the detailed compositional analysis of the oil sample utilized in the experiments is provided in Table 3[22,23].

Table 2. API gravity, viscosity, acid number, and asphaltene content of this oil sample[22,23]

Physical properties	API	Viscosity (cP) (@ temperature26° C)	Acid number	Asphaltene content (%)
Crude oil	20.65 ˚	37	0.6	16

Table 3. The composition of oil sample used for aging the rock sections [20]

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

2.1.3 Acid solution

To simulate the early stage of rock-acid interaction during injection, acid solutions with a 15% concentration were prepared. Three types of base waters—distilled water, seawater, and formation water—were used in preparing these acid solutions. The composition of the seawater, detailed in Table 4, is based on the characteristics of water from the Persian Gulf. Furthermore, the formation water was designed to replicate the chemical properties of the produced water from the reservoir where the crude oil sample was sourced[20,22,23].

Table 4. The composition of brine water compositions (formation water and sea water) [20,22,23]

Composition	Concentration(ppm)		
	Distilled water	Seawater	Formation water
NaCl	0	28323	177465
Na_2SO_4	0	4936	0
$CaCl_2$	0	1630	28036
$MgCl_2.6H_2O$	0	10510	6561
KCl	0	1032	3440
TDS	0	46431	215502

2.2 Methods

A standard household microwave oven operating at 2.45 GHz with adjustable output power (260–1300 W) was used for irradiation. The temperature of the rock samples was monitored using an infrared thermometer with ±1 °C accuracy.

2.2.1 Microwave treatment

A typical household microwave oven was used to carry out the microwave treatments. The oven operates at a frequency of 2.45 GHz, with an adjustable power output ranging from 260 W to 1300 W. The dimensions of the microwave's internal chamber are 10 × 17 × 20 cm. Like standard microwave devices with a magnetron, this unit emits radiation at a fixed frequency. After immersing the aged rock samples in the prepared acid solutions, they were exposed to microwave radiation at power settings of 780 W and 1300 W for periods between 1 and 3 minutes. A control group of similar rock samples was also treated with acid but without microwave exposure, to assess the impact of microwave radiation alone [20,22,23].

2.2.2 Temperature changes

The temperature of the rock sections was measured using a digital laser thermometer (GM-320, Benetech) with an accuracy of ±1℃. Since this type of thermometer determines temperature based on infrared radiation reflected from the surface, continuous monitoring during microwave exposure was not feasible. To obtain temperature readings during the microwave treatment, the radiation process was paused at 30-second intervals to allow for measurement. The rock sections were cut to be in a rectangular cube form with the dimensions of 15 cm×10 cm×5 cm[20.22].

2.2.3 Contact Angle Analysis

Wettability plays a crucial role in fluid movement within porous media. To assess the change in wettability of carbonate rock samples before and after treatment, contact angle measurements were conducted. The rock samples, sourced from the previously described carbonate material, underwent thorough cleaning to remove petroleum and salt-based

contaminants. This cleaning process was carried out using a Soxhlet extractor with methanol for two days and toluene for ten days. After cleaning, the rock samples were saturated with formation water and subjected to aging at 90°C for two days. Following this, crude oil was injected into the water-saturated rock samples, which were then aged in crude oil at 90°C for 35 days to simulate reservoir conditions and restore the original wettability [20]. The rationale for selecting 90 °C and 35 days for the aging procedure is based on reservoir representativeness, mechanistic considerations, and consistency with prior studies. The crude oil and carbonate samples used in this work originate from a southern Iranian oilfield with an average reservoir temperature of approximately 90 °C. Aging the samples at this temperature ensures that oil rock brine interactions occur under conditions closely mimicking the natural subsurface environment, allowing for more realistic adsorption of heavy oil fractions particularly asphaltenes and resins—onto the carbonate surface. Extended aging for 35 days is essential to re-establish the native oil-wet state of carbonate rocks. Previous studies (Tanhaei et al., 2023) have shown that shorter durations (<20 days) are insufficient for complete adsorption of surface-active components, often leading to mixed-wet conditions that do not accurately represent the reservoir. By contrast, 30–40 days of exposure at elevated temperature allows heavy polar compounds to strongly adsorb and organize into multilayer films, producing a stable oil-wet surface with a baseline contact angle of ~132°. Mechanistically, higher temperatures enhance the molecular diffusion and mobility of asphaltenes and resins, accelerating their migration toward and binding with calcite sites on the rock surface. This thermodynamically favored process is promoted by reduced oil viscosity and stronger surface energy interactions. The prolonged duration ensures that equilibrium surface coverage is reached, minimizing variability in wettability across replicate samples. These aging conditions are also consistent with widely reported protocols in carbonate wettability research, where temperatures of 80–100 °C and durations of 30–40 days

are typically adopted. Thus, the selected conditions provide both scientific validity and comparability with prior works. In summary, aging at 90 °C for 35 days replicates in-situ reservoir conditions, enables complete adsorption of polar components, and ensures a stable and reproducible oil-wet baseline for subsequent wettability alteration experiments, so that the observed changes in contact angle and FTIR indices result solely from the applied treatments rather than incomplete wettability restoration[20].

The aged rock sections were then exposed to acid solutions at 70℃ for 2-22 min. After acid treatment, microwave radiation was applied for 1- 11 minutes at power levels of 780 and 1300 W. The wettability of the treated rock sections was evaluated using the pendant drop method. Each contact angle measurement was repeated three times, and the median value was reported. The measurements had a precision of ±0.6° based on the obtained data.

2.2.4 ATR-FTIR spectrums

Although the sessile-drop contact-angle technique provides valuable information on wettability changes, it does not offer details on the chemical composition of the desorbed hydrocarbons. To address this, Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy was conducted on the treated rock samples using a refractometer (PerkinElmer, USA). The spectra were recorded within the range of 600–4000 cm^{-1}, with a resolution of 1 cm^{-1}. Quantitative data was extracted from the ATR-FTIR spectra by calculating the integrated areas of the hydrocarbon-related peaks. These values were then used to derive characteristic indexes based on the method proposed by Karami et al. (2022)[20]. Using these indexes, the content of polar, carbonyl, aliphatic, and aromatic functional groups in the rock samples was determined [20].

3. Results and Discussions

3.1 Temperature Changes

According to figure 2 ,the temperature evolution of carbonate rock samples under microwave irradiation is illustrated in Fig. 2. After 3 minutes of exposure, the surface temperature of the rock sections rose to approximately 94°C and 120°C under radiation powers of 780 W and 1300 W, respectively. This increase in temperature can be attributed to fundamental electromagnetic heating mechanisms associated with microwave energy. Microwave radiation induces heating primarily through the interaction with polar molecules and materials possessing high dielectric constants. When polar molecules are subjected to an oscillating electromagnetic field, such as that generated by a microwave at 2.45 GHz, the continuous reorientation of their electric dipoles leads to internal friction and, consequently, heat generation. This phenomenon, known as dielectric heating, is especially pronounced in substances with high dielectric loss factors, which quantifies a material's ability to convert electromagnetic energy into thermal energy. Materials with higher dielectric constants and dielectric losses absorb microwave energy more efficiently, resulting in more significant thermal responses. In this study, the observed temperature increase in rock sections can be rationalized by their relatively high dielectric constant. For instance, calcium carbonate ($CaCO_3$), which comprises the majority of the rock sample (approximately 94.5%), has a dielectric constant of approximately 9.2 . In contrast, crude oil components typically exhibit much lower dielectric constants, ranging from about 1.0 to 4.5 depending on their molecular structure and polarity . Consequently, the rock matrix is more susceptible to microwave-induced heating than the oil phase.

The temperature increase during microwave exposure is critical, as it can induce both physical and chemical transformations in the adsorbed organic matter. Elevated temperatures may cause thermal cracking of heavy polar hydrocarbon fractions, such as asphaltenes, leading to their desorption from the rock surface. In addition, the breakdown of polar functional groups can modify the surface energy of the rock, promoting a shift in wettability. These effects are particularly relevant in carbonate reservoirs, where wettability alteration can significantly enhance oil recovery efficiency.

It should be noted that although the temperature rise observed under microwave exposure may appear modest compared with conventional thermal methods (e.g., hot-water or steam flooding), the underlying mechanism and spatial heating pattern are fundamentally different. Microwave heating is

characterized by volumetric and selective energy absorption, where electromagnetic energy is directly absorbed by the material rather than being transferred via conduction or convection from an external source. This leads to localized and highly efficient energy deposition in components with strong microwave affinity [20].

Moreover, the apparently limited temperature increase recorded in this study should be interpreted with caution. The surface temperature values were measured using a non-contact digital infrared thermometer, which provides macroscopic surface readings rather than real-time volumetric internal temperatures. Therefore, the internal temperature of the rock matrix may be considerably higher than the measured surface temperature, particularly in zones with concentrated microwave absorption.

In summary, the enhanced temperature rise observed in the carbonate rock sections, as compared to the crude oil, aligns with theoretical expectations based on the dielectric properties of the materials. This localized heating effect plays a pivotal role in altering the physicochemical state of the adsorbed hydrocarbons, thereby contributing to wettability modification and potentially improving hydrocarbon displacement efficiency in carbonate formations.

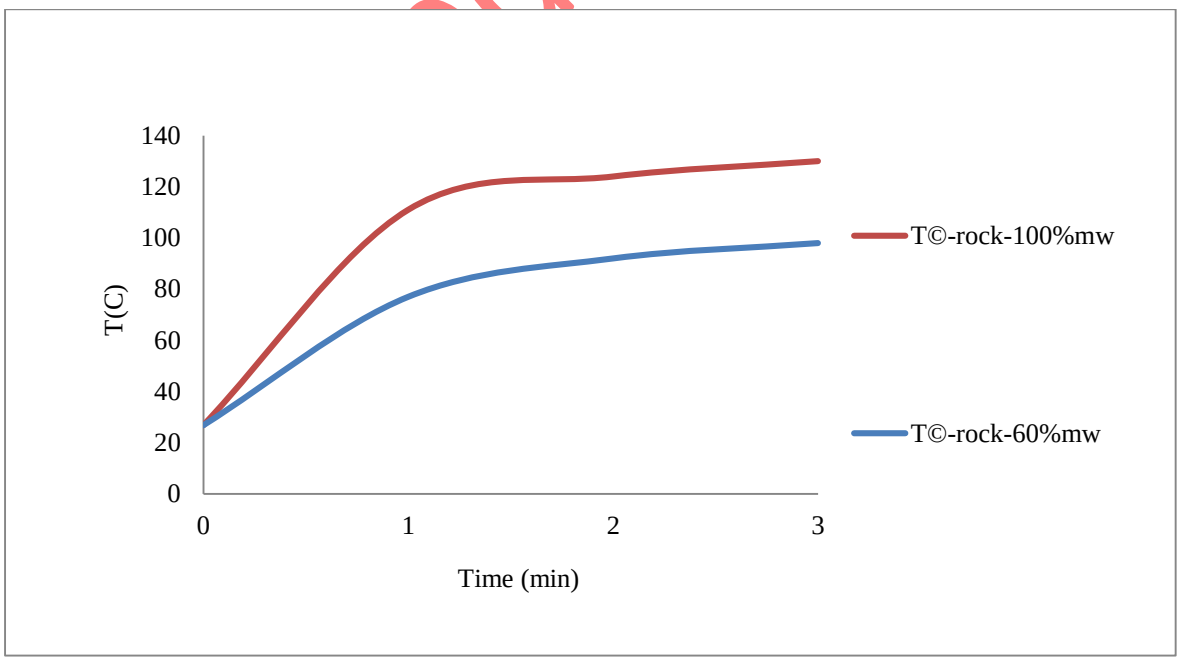

Fig 2. Temperature changes of aged rock sections treated by microwave and [20]

3.2 Contact Angle

3.2.1 Contact Angle With Acidic Solution

According to the figure 3 , the dataset presents a time-resolved measurement of contact angle evolution for three treated carbonate samples AFW, ASW, and ADW monitored over a 22-minutes period. Initially, all samples exhibit a contact angle of 132.535°, characteristic of a strongly oil-wet surface. As time progresses, the contact angles decrease at varying rates depending on the treatment type, indicating a wettability alteration process influenced by the nature of the aqueous phase.

The ADW-treated sample exhibits the most pronounced reduction in contact angle, dropping sharply from 132.5° to 57.1° within the first few minutes of exposure. This substantial decrease reflects a rapid transition from oil-wet to water-wet conditions, likely resulting from the high reactivity of the acid in deionized water, which contains no competing ions to hinder surface reactions. Between 12 and 22 min, the ADW curve plateaus at approximately 58.0°, suggesting that the surface has reached a quasi-equilibrium state in terms of wettability alteration.

For the ASW-treated sample, a moderate reduction is observed: the contact angle decreases to 90.1° after 12 min, followed by a slight increase to 91.3° at 22 min. This behavior indicates partial wettability alteration, where seawater-derived divalent ions such as calcium and magnesium may buffer the acid reactivity and stabilize some adsorbed hydrocarbon species. The minor increase at later times likely reflects surface reorganization or re-adsorption of hydrophobic components.

The AFW-treated sample shows the least effective alteration, with the contact angle decreasing only to 108.2° after 12 min and then gradually increasing to 123.5° by 22 min. This trend suggests that the formation water either suppresses acid–rock interactions or promotes re-adsorption of hydrocarbons onto the mineral surface, leading to a reversal toward more oil-wet conditions. This behavior can be attributed to the specific ionic composition of formation water, which may contain reservoir-specific ions that reinforce the original surface characteristics.

Comparatively, the data clearly demonstrate that ADW treatment is the most effective in promoting water-wet conditions, followed by ASW, while AFW appears to hinder wettability alteration. The

observed trends underscore the critical influence of brine chemistry on acid-induced surface modifications. These findings have significant implications for enhanced oil recovery operations, where efficient wettability alteration can substantially improve oil displacement efficiency in carbonate reservoirs.

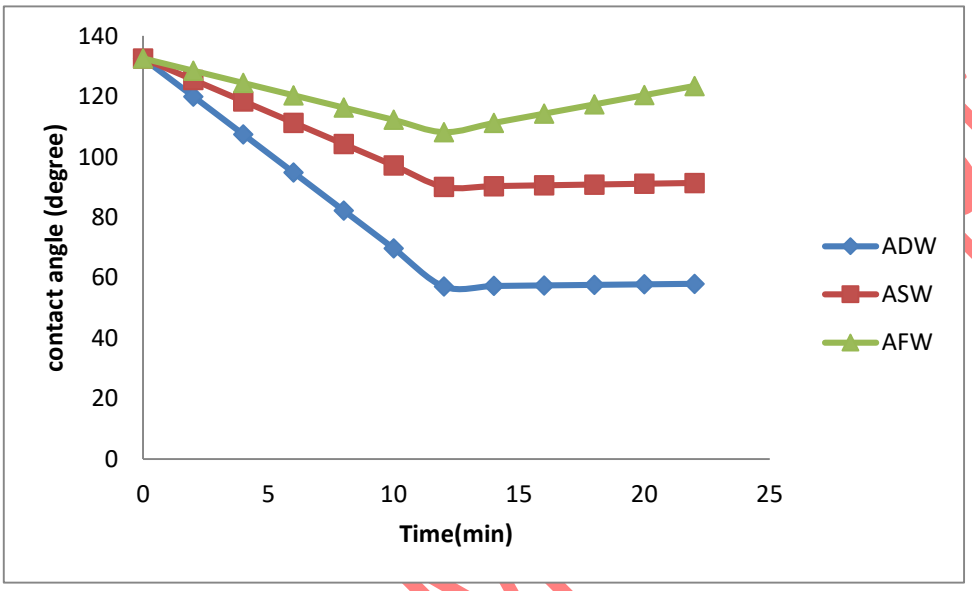

Fig 3. The contact angle between aged rock sections and crude oil being treated with acidic solutions

Among the three, the ADW-treated sample exhibits the most significant and rapid reduction in contact angle, dropping sharply to around 57° within the first hour. This indicates a highly efficient transition from oil-wet to water-wet behavior. The pronounced decline can be attributed to the purity of deionized water, which lacks interfering ions, thus enabling the hydrochloric acid to react unhindered with the carbonate surface. This promotes the dissolution of surface-bound hydrocarbons and exposes more hydrophilic mineral sites. After the first hour, the contact angle curve levels off, suggesting that a chemical equilibrium has been reached and further acid-rock reaction is minimal.

In contrast, the ASW-treated sample shows a more moderate reduction in contact angle, stabilizing at approximately 90°. This partial wettability alteration is likely due to the presence of divalent cations such as Ca^{2+} and Mg^{2+} in synthetic seawater, which can compete with hydrogen ions during acidization. These ions may form precipitates or passivate the rock surface, limiting further reaction

and hindering complete transition to water-wet conditions. The constant contact angle after the first hour reflects a relatively stable interfacial state, where acid accessibility is chemically buffered.

The AFW-treated sample shows the least reduction in contact angle, with values remaining relatively high and even increasing slightly after one hour. This trend is particularly noteworthy as it suggests a reversal or suppression of wettability alteration. Formation water typically contains reservoir-specific ions, high salinity, and sometimes organic compounds that can strongly adsorb onto the rock surface. These constituents may block active sites, reduce acid effectiveness, or enhance the re-adsorption of oil components, thereby maintaining or even reinforcing the oil-wet state. The mild increase observed in the contact angle beyond the one-hour mark may be due to reorganization of surface-bound species or a secondary adsorption process, possibly involving organic material from the formation water itself.

In the ADW system, the acid is diluted in deionized water, which lacks dissolved ions. As a result, the 15wt% HCl remains highly reactive and unbuffered, enabling aggressive interaction with the carbonate surface. This leads to rapid dissolution of the rock matrix, enhanced removal of surface-bound hydrocarbons, and a strong shift toward water-wet conditions. Consequently, the contact angle drops sharply from approximately 132° to 57° within the first hour, and then stabilizes indicating that the rock-fluid interface has reached chemical and wetting equilibrium.

In contrast, the ASW solution contains a mixture of salts representative of synthetic seawater, including divalent cations such as Mg^{2+} and Ca^{2+}, as well as monovalent ions like Na^{+} and K^{+}. These ions influence the acid-rock interaction by buffering the reactivity of HCl and participating in surface adsorption and complexation processes. The presence of magnesium and calcium ions in particular can form precipitates or occupy active sites on the rock surface, reducing the extent of acid-driven wettability alteration. As a result, the contact angle decreases more moderately, stabilizing at approximately 90°, indicating a partial transition from oil-wet to mixed-wet or weakly water-wet conditions.

The AFW treatment, involving formation water, introduces a highly complex ionic environment with potentially high salinity and the presence of reservoir-specific ions and organic matter. These constituents can inhibit the action of hydrochloric acid by saturating reactive sites or enhancing the re-adsorption of oil components through ionic bridging or surface passivation. The contact angle in the AFW system shows only a slight decrease, followed by a gradual increase after one hour, ultimately stabilizing above 120°, suggesting that the surface remains dominantly oil-wet throughout the experiment.

Overall, the trend observed in the graph highlights the critical role of brine composition in acid-induced wettability alteration. The absence of interfering ions in ADW maximizes acid efficiency, while the complex ionic environments in ASW and especially AFW reduce acid performance. Understanding the interactions between acid, ions, and rock surfaces is essential for optimizing stimulation fluids in carbonate reservoirs, where wettability alteration significantly influences oil recovery efficiency.

In the ADW system, the acid is diluted with deionized water, containing no dissolved salts. This ion-free medium allows the 15% HCl to remain in its most reactive and unbuffered form. As a result, HCl reacts aggressively with the carbonate minerals, promoting rapid dissolution of calcite and effective desorption of surface-bound oil films. This leads to a sharp decrease in contact angle from 132° to approximately 57° within the first hour, reflecting a strong transition from oil-wet to water-wet conditions. The absence of salts ensures that there is no competition at the mineral surface, allowing complete exposure of hydrophilic sites.

In the ASW solution, the HCl is mixed with synthetic seawater containing, Sodium chloride (NaCl) A monovalent salt that generally increases ionic strength but does not significantly compete with H^+ ions. However, it can affect the electrical double layer at the rock-fluid interface. Magnesium chloride ($MgCl_2$), A divalent salt with strong surface activity. Mg^{2+} can adsorb onto the carbonate surface or form insoluble salts with carbonate ions, reducing acid access to reactive sites and buffering acid reactivity. Sodium sulfate (Na_2SO_4), Sulfate ions (SO_4^{2-}) can compete with carbonate or interact with

calcium to form gypsum or other precipitates, altering surface charge and potentially stabilizing oil films. Calcium chloride ($CaCl_2$): A divalent salt that also reduces surface reactivity by occupying active sites or forming precipitates with sulfate or carbonate ions. It plays a critical role in moderating wettability alteration. Potassium chloride (KCl), A monovalent salt with lower surface activity than divalent ions but contributes to overall ionic strength and potential clay swelling control if applicable.

These salts collectively buffer the HCl, reduce its reactivity with the rock, and compete for surface adsorption, leading to only partial wettability alteration. Consequently, the contact angle for ASW-treated samples stabilizes at around 90°, indicating an intermediate or mixed-wet state.

In the AFW system, which contains reservoir-derived formation water, the ionic composition is typically complex and may include high concentrations of:

١- NaCl and $CaCl_2$ in large amounts, which buffer acid action and stabilize oil-wet conditions.

٢- $MgCl_2$, which can form precipitates or enhance surface charge shielding.

٣- Organic matter and hydrocarbons, which may be present in trace quantities and promote the re-adsorption of oil components onto the rock.

The interaction of these species with 15% HCl is more restrictive. The acid's reactivity is heavily moderated, and the surface becomes resistant to full wettability alteration. The result is a relatively high and stable contact angle above 120°, with a mild increase observed after 1 hour, likely due to re-adsorption of hydrophobic species or secondary ionic interactions that reinforce oil-wet behavior.

In conclusion, the presence of specific salts in the acid solution has a profound effect on the efficiency of wettability alteration. While ADW achieves the most significant wettability shift due to the absence of interfering ions, the presence of NaCl, $MgCl_2$, Na_2SO_4, $CaCl_2$, and KCl in ASW and AFW diminishes acid effectiveness by buffering, surface site competition, precipitation reactions, and possible organic interactions. Understanding the distinct chemical roles of each salt is essential for tailoring acidizing fluids in carbonate reservoirs to maximize wettability modification and improve oil recovery.

3.2.2 Contact Angle by Microwave

According to the figure 4 , the table presents a time-dependent comparison of contact angle measurements for surfaces exposed to microwave radiation at two different power levels, 780 watts and 1300 watts. Measurements were recorded over a 11-minute period at 1-minute intervals, capturing the evolution of surface wettability under varying energy inputs. All contact angles begin at high values (above 100°), indicating initially oil-wet surfaces, and progressively decrease over time, suggesting a shift toward more water-wet conditions as exposure continues.

At 1 minutes, the contact angle is 111.354° for 780 W and 101.255° for 1300 W, reflecting the early stage of wettability alteration. By 30 minutes, the difference between the two treatments becomes more pronounced: the 1300 W condition results in a sharper decrease to 90.516°, compared to 102.309° for 780 W. This pattern continues consistently throughout the duration of the experiment.

As time progresses, the 1300 W treatment consistently produces lower contact angle values than the 780 W treatment at every time point. For example, at 6 minutes, the contact angle is 74.988° for 1300 W, whereas it remains at 85.003° for 780 W. By the end of the experiment at 11 minutes, the contact angle reaches 68.673° for 1300 W and 72.176° for 780 W.

This consistent difference illustrates a key phenomenon, higher microwave power results in a more rapid and more effective wettability alteration. The greater energy input likely enhances molecular agitation, accelerates surface reactions, and increases desorption of hydrophobic components, thereby facilitating a quicker transition from oil-wet to water-wet surface conditions.

Moreover, the rate of decrease is steeper during the first half of the experiment for both power levels, particularly between 1 and 11minutes. This suggests that the majority of the microwave-induced surface reconfiguration occurs early in the exposure process. After about 6 minutes, the curves begin to flatten, indicating a gradual approach toward equilibrium where additional exposure contributes to only minor changes in contact angle.

In conclusion, the data clearly show that microwave-assisted wettability alteration is power-dependent. The 1300 W treatment leads to faster and deeper reductions in contact angle, making it more effective for altering surface conditions in a shorter timeframe. This insight is especially valuable for applications such as enhanced oil recovery or surface treatment processes, where rapid and efficient wettability modification is desired.

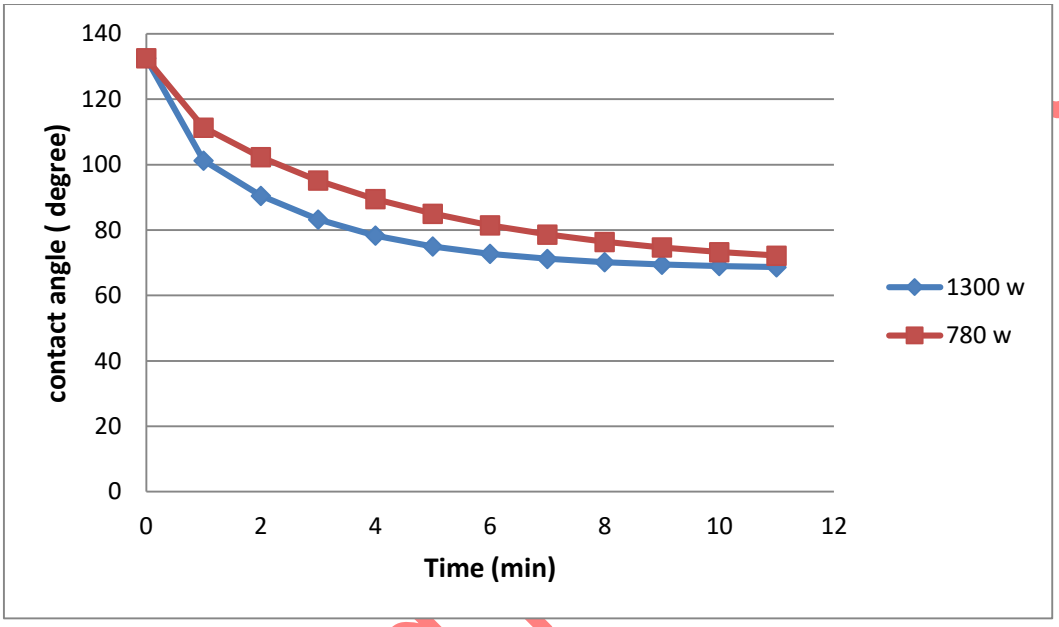

Fig 4. The contact angle between rock sections and crude oil after being exposed to microwave.

This study investigates the impact of microwave irradiation on wettability alteration of oil-wet rock surfaces under two different power settings , 780 W and 1300 W. The results demonstrate that higher microwave power significantly enhances the rate and extent of wettability transition, as evidenced by a faster and greater reduction in contact angle. At 1300 W, the contact angle drops more rapidly than at 780 W, indicating a more effective shift from oil-wet to water-wet conditions. This improved performance is attributed to intensified dielectric heating, which promotes molecular agitation, thermal desorption of surface-bound hydrocarbons, and surface energy reorganization. Most of the contact angle reduction occurs within the first 6 minutes of exposure, suggesting that key surface transformations take place early in the treatment. Beyond this point, the system tends toward equilibrium, with only marginal changes observed. Overall, these findings underscore the importance of microwave power intensity in controlling wettability dynamics and support the application of

microwave-assisted methods in enhanced oil recovery and surface conditioning, where efficient fluid–rock interaction is critical to improving hydrocarbon recovery.

3.3 ATR-FTIR spectroscopy

The contact angles, measured using the sessile drop technique, were employed to assess the wettability of the treated rock sections. However, no information was provided regarding the desorption of hydrocarbons from the rock surface. To investigate the chemical changes on the surface of the rock and the behavior of adsorbed hydrocarbons, the ATR-FTIR spectra of the acid-treated rock sections are presented in Fig. 5. Additionally, Fig. 6 shows the ATR-FTIR spectra of rock sections treated with both acid solution and microwave radiation at 780 W and 1300 W, respectively.

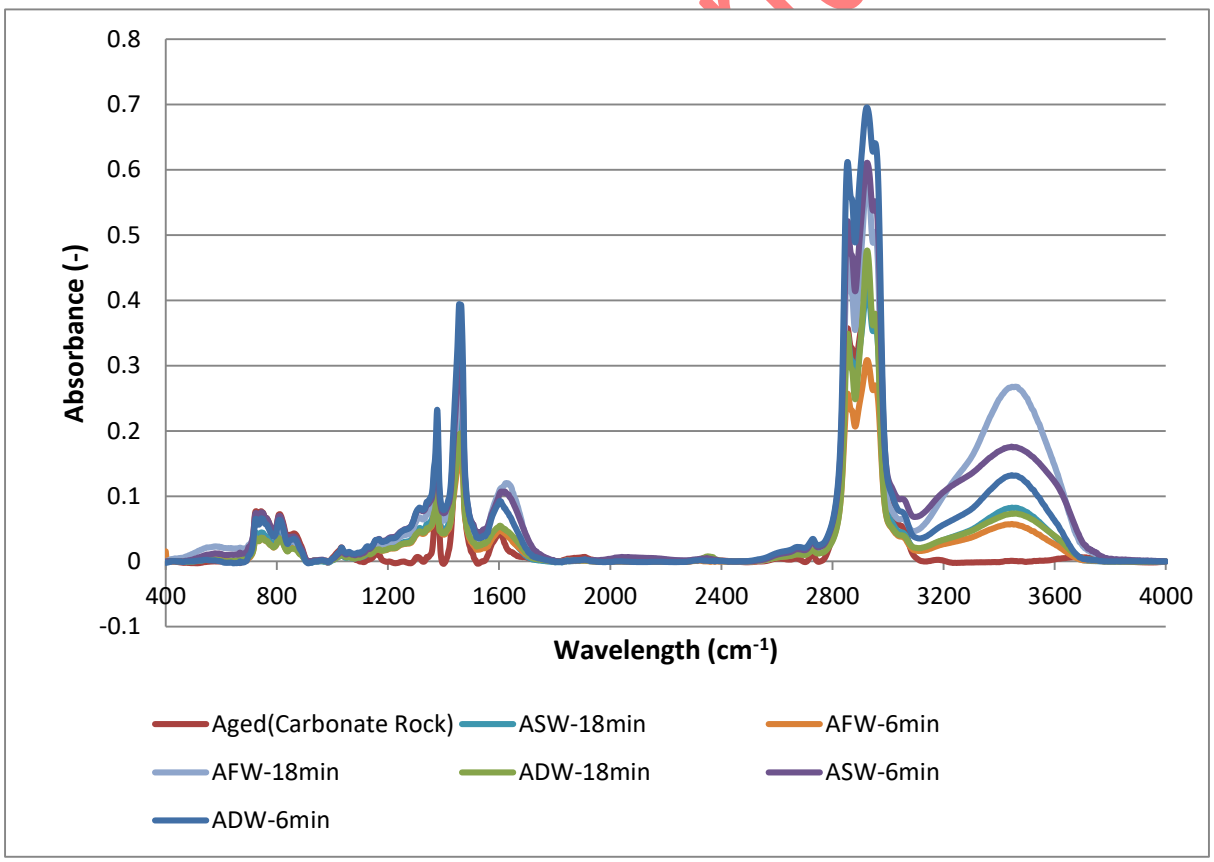

Fig 5. The normalized ATR-FTIR spectrums for acidized rock sections

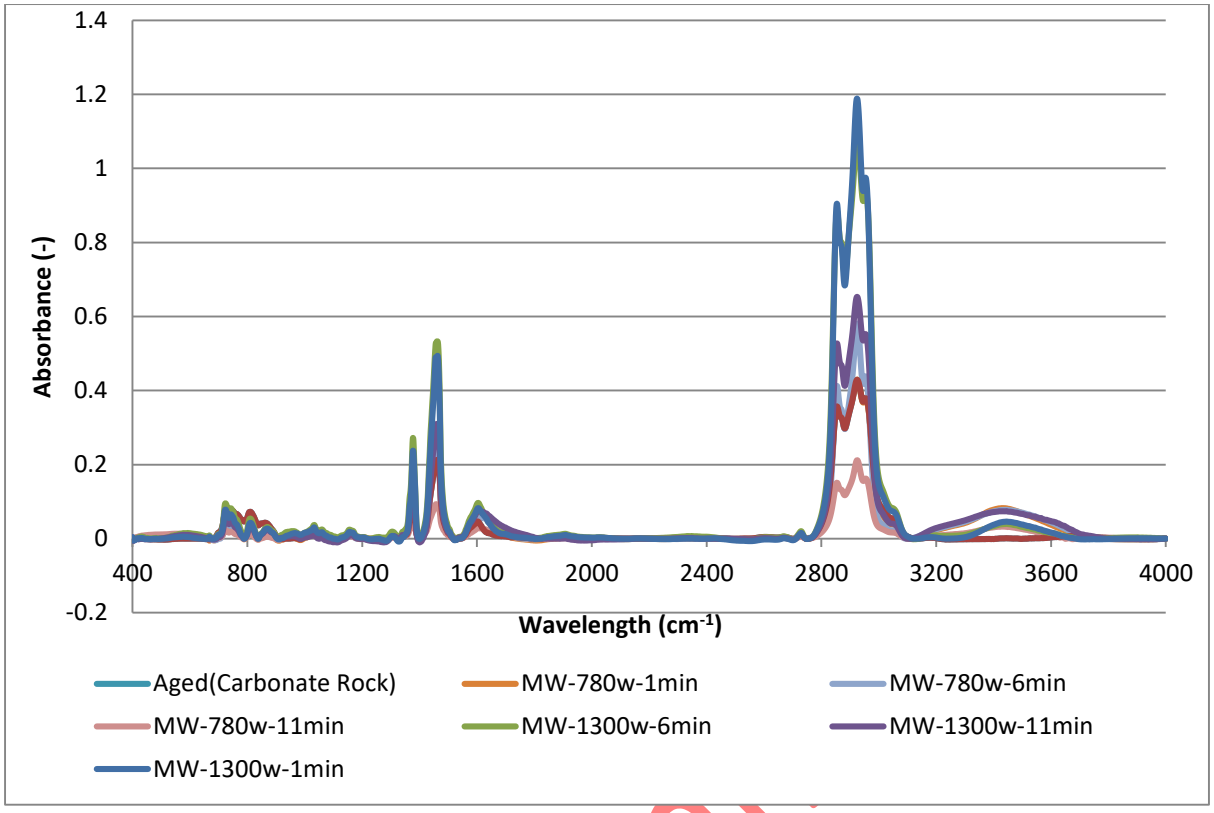

Fig 6. The normalized ATR- FTIR spectrums for crude section and sections treated by the microwave radiation power

The peaks observed in the ATR-FTIR spectra represent both the hydrocarbons adsorbed on the rock surface and the minerals within the rock. These peaks can be categorized into three groups: rock-related, hydrocarbon-related, and common peaks. Since the primary focus of the ATR-FTIR spectra was on the hydrocarbon chemistry, only those peaks specifically associated with hydrocarbons were considered in the analysis. As shown in Table 5, the aliphatic C-H bonds are characterized by peaks within the range of 2755-3000 cm-1. Additionally, the ranges of 3000-3100 cm-1 and 1566-1668 cm-1 correspond to the C-H and C=C bonds in aromatic rings, respectively. Ketone-based functional groups, including carboxylic acid groups, exhibit vibrations in the 1668-1800 cm-1 range. The amine and alcohol functional groups appear in the 3100-3500 cm-1 range. More detailed information on hydrocarbon chemistry can be found in Table 5. As previously mentioned, the characteristic indexes provided by Tanhaei et al. (2023) were used to extract numerical data from the ATR-FTIR spectra. [20,27,28].The Aromatic/Aliphatic, Aliphatic Length, C=O/Aliphatic, C=O/Aromatic,

٤٨٩ Polar/Aliphatic, and Polar/Aromatic indices were determined based on the integral areas of the
٤٩٠ corresponding peaks. The characteristic indices (Acidic Solution) derived from the ATR-FTIR spectra
٤٩١ are presented in Table 6.

٤٩٢ Table 5. The assignments of the peaks in the ATR-FTIR spectrums [24,25,28].

Wavelength	Assignment
3100-3500	N-H, O-H
3000-3100	C–H stretch in aromatic
2946-3000	CH_3 asymmetric stretch
2881-2946	CH_2 asymmetric stretch
2755-2881	CH_2 symmetric Stretch
1668-1800	C=O stretch in ketones, aldehydes, and carboxylic acids
1566-1668	Aromatic C=C stretch

٤٩٣ To investigate the chemistry of the hydrocarbons, which have a greater tendency for desorption from
٤٩٤ the rock surface, the ATR-FTIR spectrums were analyzed from an analytical point of view. In this
٤٩٥ regard, the integral area of each hydrocarbon-assigned peak was employed to be used in the
٤٩٦ characteristic equations given by Tanhaei et al .2023 [20,28]. Equations 1-6 show the ratios used to

characterize the chemistry of hydrocarbons adsorbed on the rock surface. In Equations 1-6, the 'Ai' stands with the integral area below the peak in the range of 'i'.

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

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

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

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

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

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

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

Acidic solution	Time(min)	C=O/Aliphatic	C=O/Aromatic	Aromatic/Aliphatic	Aliphatic length	Polar/Aliphatic	Polar/Aromatic
ADW	6	0.197755	0.326208	0.611396	0.35966	3.038896	5.290352
ADW	18	0.215396	0.312785	0.690783	0.34662	2.521153	3.806541
ASW	6	0.136844	0.304551	0.437237	0.378158	4.095579	10.02738
ASW	18	0.102712	0.27272	0.368589	0.380843	4.476024	12.57007
AFW	6	0.204071	0.33433	0.613652	0.346575	3.019946	5.25516
AFW	18	0.227082	0.32781	0.694957	0.322414	2.486096	3.741435

The presented table 6, offers a detailed quantitative analysis of ATR-FTIR-derived chemical indices that reflect molecular-level changes on carbonate rock surfaces treated with 15% hydrochloric acid (HCl) in different aqueous solutions ADW (acid in deionized water), ASW (acid in synthetic seawater), and AFW (acid in formation water)—at three time intervals, 20 and 60 minutes. These solutions contain varying combinations of key inorganic salts such as sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and sodium sulfate (Na_2SO_4), which significantly influence acid–rock interaction and surface chemistry during treatment.

For the ADW system, which contains no dissolved salts, the acid remains highly active and unbuffered. This enables free interaction with carbonate minerals, promoting strong decarbonation and dissolution processes. Over time, the increase in C=O/Aliphatic and C=O/Aromatic ratios (from 0.197 to 0.221 and 0.326 to 0.307 respectively) indicates the gradual breakdown of polar oxygen-containing groups and aliphatic chains, with partial oxidation of surface-bound hydrocarbons. The Aromatic/Aliphatic ratio increases notably from 0.61 to 0.72, suggesting selective degradation of aliphatic components, leaving more stable aromatic structures. Simultaneously, Polar/Aliphatic and Polar/Aromatic ratios decrease steadily, reflecting the overall reduction in polarity as the surface becomes cleaner and less hydrocarbon-saturated.

In the ASW system, where HCl is mixed with synthetic seawater containing NaCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, and KCl, distinct chemical behavior is observed. These salts, particularly the divalent cations (Ca^{2+}, Mg^{2+}), can buffer HCl activity, precipitate on mineral surfaces, and compete for adsorption sites. The C=O/Aliphatic ratio shows a strong decrease from 0.137 to 0.090 over time, reflecting limited acid accessibility and partial surface deactivation. The Aromatic/Aliphatic ratio drops from 0.437 to 0.344, indicating slower degradation of surface hydrocarbons, possibly due to salt shielding or inhibition of polar group removal. Interestingly, the Polar/Aromatic and Polar/Aliphatic indices increase with time, reaching 13.48 and 4.61 at 11 minutes. This suggests a higher retention or

exposure of polar functionalities, potentially due to sulfate complexation and limited desorption in the presence of seawater ions.

For the AFW system, composed of formation water and 15% HCl, the complex ionic composition (high salinity with NaCl, $CaCl_2$, $MgCl_2$, and possibly organic residues) alters the interaction further. The C=O/Aliphatic and C=O/Aromatic ratios increase slightly over time, indicating slower oxidation and a less aggressive acid attack, likely due to ion competition or saturation of reactive sites. The Aromatic/Aliphatic ratio increases from 0.61 to 0.72, which is consistent with partial removal of aliphatic chains. However, compared to ADW, the reduction in Polar/Aliphatic and Polar/Aromatic indices is less pronounced, and their final values (2.29 and 3.20) remain higher, suggesting that surface cleaning is less complete. This may be attributed to persistent ion interference or re-adsorption of organics facilitated by divalent ions and high ionic strength.

In summary, the data clearly show that ionic composition of the solution plays a crucial role in acid–rock chemical interactions. The ADW system, free of salts, exhibits the most effective hydrocarbon removal and wettability alteration. In contrast, the ASW and AFW systems, containing salts such as NaCl, KCl, $CaCl_2$, $MgCl_2$, and Na_2SO_4, demonstrate suppressed acid reactivity, limited surface cleaning, and altered surface functionality due to competitive adsorption, buffering effects, and possible precipitation. These findings are critical for optimizing acidizing fluid design in carbonate reservoirs, where controlling surface chemistry directly impacts wettability, permeability, and overall recovery efficiency.

The dataset presents of table 7, the detailed chemical analysis of surface changes induced by microwave irradiation on carbonate rock samples treated at two different power levels 780 watts and 1300 watts over exposure durations of 1, 6, and 11 minutes. The table includes a set of molecular indices derived from ATR-FTIR spectroscopy, which provide insight into the evolution of surface functionality, polarity, and hydrocarbon composition. These results have significant implications in the context of petroleum engineering and chemical surface modification, particularly for enhanced oil recovery (EOR) processes.

For the 780 W treatment, the contact surface shows a gradual and consistent increase in aromatic character and polarity with exposure time. The C=O/Aliphatic ratio decreases from 0.1711 to 0.1555, suggesting partial breakdown of oxygenated aliphatic compounds or desorption of less stable polar species. Simultaneously, the C=O/Aromatic ratio slightly increases, implying that aromatic structures retain or accumulate polar functionalities more effectively under lower-energy microwave exposure. The Aromatic/Aliphatic ratio rises from 0.5447 to 0.6161, indicating preferential degradation of aliphatic hydrocarbons and relative enrichment of aromatic groups. Additionally, the Polar/Aliphatic and Polar/Aromatic ratios also increase with time, reflecting an overall enhancement in surface polarity. These trends suggest that 780 W microwave energy facilitates gradual desorption and molecular rearrangement on the rock surface, but does not completely eliminate polar and hydrocarbon content.

In contrast, the 1300 W treatment results in more aggressive and efficient molecular transformations. The C=O/Aliphatic ratio drops significantly from 0.1623 to 0.1228, indicating a more extensive removal of oxygen-containing aliphatic species. Likewise, the Aromatic/Aliphatic ratio decreases from 0.4885 to 0.4096, suggesting deeper structural degradation of hydrocarbons, affecting both aliphatic and aromatic components. Importantly, the Polar/Aliphatic and Polar/Aromatic indices decline markedly from 3.1981 and 6.4107 to 1.9946 and 4.7383, respectively. This reflects a significant reduction in surface polarity, likely due to efficient desorption of polar organic matter and transformation of the surface to a more mineral-dominated, less hydrocarbon-saturated state.

From a microwave physics perspective**,** higher power (1300 W) delivers greater electromagnetic energy, which translates into stronger dielectric heating. This enhances molecular vibration, promotes bond cleavage, and facilitates thermal desorption and decomposition of organic films adhered to the rock surface. The selective and volumetric heating characteristics of microwaves at this power level enable more uniform and deeper interaction with the porous structure of carbonates, leading to more complete surface cleaning and wettability alteration.

In the context of petroleum engineering, these findings are highly significant. The observed reduction in polar indices and aliphatic content indicates that higher microwave power increases the exposure of hydrophilic mineral surfaces, thereby promoting water-wet conditions a desirable outcome for enhancing oil displacement efficiency in carbonate reservoirs. Moreover, the results suggest that microwave-assisted treatments can be effectively optimized by adjusting the irradiation power and exposure time to achieve the desired surface chemistry under specific reservoir conditions.

Table 7. The characteristic indexes calculated from the ATR-FTIR spectrums of the treated rock section, which by microwave

Time(min)	Power(w)	C=O/Aliphatic	C=O/Aromatic	Aromatic/Aliphatic	Aliphatic length	Polar/Aliphatic	Polar/Aromatic
1	780W	0.171148	0.344926	0.54471	0.395107	4.004907	7.325382
6	780W	0.162057	0.349471	0.5862	0.426341	4.559309	7.774894
11	780W	0.155496	0.352752	0.616148	0.448887	4.959493	8.099366
1	1300W	0.162257	0.346277	0.488514	0.374775	3.198058	6.410718
6	1300W	0.139356	0.35292	0.442712	0.374425	2.499141	5.439437
11	1300W	0.122825	0.357715	0.409651	0.374173	1.994642	4.738336

In conclusion, the analysis clearly shows that microwave power intensity plays a pivotal role in governing the chemical and physical evolution of carbonate rock surfaces. While 780 W results in moderate, progressive surface modification, 1300 W achieves a more substantial and efficient transformation, making it more effective for applications aimed at wettability alteration, hydrocarbon desorption, and formation stimulation. These findings support the integration of high-power microwave technologies in advanced EOR strategies and surface treatment systems.

4. Conclusion

In this research, comprehensively investigated the independent effects of microwave irradiation and acidic fluids on wettability alteration and hydrocarbon desorption in carbonate reservoir rocks. Through a series of contact angle measurements and ATR-FTIR spectroscopic analyses, it was

demonstrated that both treatments significantly impact the rock-fluid interface, albeit through different mechanisms.

- Microwave irradiation particularly at 1300 W for up to 11 minutes proved highly effective in reducing the contact angle from 132.5° to 68.7°, indicating a substantial transition toward water-wet conditions. This effect is attributed to dielectric heating, which facilitates the thermal desorption of polar and aromatic hydrocarbon compounds, as evidenced by the observed decreases in the Polar/Aliphatic and Aromatic/Aliphatic indices in the FTIR spectra.
- Acid treatment with 15 wt% HCl, particularly when prepared in deionized water (ADW), exhibited the greatest wettability alteration, reducing the contact angle to 57.1°. In contrast, the presence of ions in synthetic seawater (ASW) and formation water (AFW) decreased the acid's effectiveness due to buffering effects, surface passivation, and precipitation reactions. These trends were further supported by ATR-FTIR spectroscopy, which revealed more extensive desorption of hydrocarbon compounds in the ADW-treated samples. Specifically, the ADW system showed a pronounced decrease in the Polar/Aliphatic and Polar/Aromatic indices over time, indicating efficient removal of polar functional groups and surface-bound hydrocarbons. Conversely, the ASW and AFW treatments displayed higher polarity indices and smaller variations in aliphatic and aromatic signatures, suggesting incomplete surface cleaning and persistent hydrocarbon retention.

Importantly, the results revealed that while both microwave energy and acid solutions independently enhance wettability alteration, their combination yields superior performance particularly in complex reservoir environments where salinity and organic deposition limit conventional acidizing efficiency. These findings offer valuable insights for designing advanced enhanced oil recovery (EOR) techniques and support the integration of microwave-assisted stimulation as a complementary strategy to traditional acidizing methods in carbonate reservoirs.

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