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Investigating the Effects of Heating Rate and Granulation on Extracted Oil-Shale using Microwaves and Conventional Heating Methods

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Abstract
The quality and extraction rate of oil shale is a significant challenge in the oil shale processing field. In this article, the effects of heating rate and grain size as fundamental parameters in oil shale production from the QaliKuh reservoir in Iran on the quantity and quality of produced oil shale are explored as other sources. Fisher's developed microwaves at 2450 kHz were used to heat several oil shale samples at power levels of 650, 900, and 1200 watts up to coking temperature (700 °C). It was observed that the amount of oil produced increased from 5.2% to 5.9%, then it reduced to 5% weight of the sample as the microwave heating rate increased; however, the quality of the oil (asphaltene reduced from 25% to 19%, sulfur content reduced from 16% to 7%, and carbon percentage increased from 67% to 78%,) improved. In contrast, conventional oil shale pyrolysis showed that the quality of the oil improved with an increase in the heating rate (asphaltene reduced from 31% to 28 %, sulfur content reduced from 19% to 13%, and carbon percentage near to constant), while the amount of produced oil diminished from 4.7% to 4.3% weight of the sample. The grain size of the shale was divided into three ranges: 7-12 mm, 7-4 mm, and less than 4 mm. In the case of microwave heating, the amount of produced oil increased with the grain size reduction (from 5.9% to 6.8% weight of the sample). Still, the quality fluctuated (asphaltene reduced from 20% to 18 % then increased to 22%, sulfur content reduced from 12% to 10% then increased to 15%, carbon content increased from 75% to 80% then reduced to 69%, Aliphatic component increased from 38% to 40.5% then reduced to 34%, also aromatic index reduced from 0.28% to 0.26% then increased to 0.31%). These results suggest that there is potential for further research to optimize the grain size for oil shale production. With the conventional heating techniques, the quality of the produced oil improved but can also fluctuate with decreases in grain size (from 4.7% to 5.4% then 5.1%). Also, the quality fluctuated (asphaltene reduced from 31% to 30 % then increased to 33%, sulfur content reduced from 19% to 17% then increased to 20%, carbon content increased from 62% to 71% then reduced to 64%, Aliphatic component increased from 28% to 30% then reduced to 25%, also aromatic index reduced from 0.29%, to 0.42% then increased to 0.36%). It was found that microwave pyrolysis yielded more oil produced than the conventional method and improved the quality of the oil. An optimal particle size and heating rate can be established based on the results, sparking interest in further research to explore these possibilities.

Keywords: Oil Shale, Microwave, Pyrolysis, Shale Oil, Upgrading, Qalikuh.

Introduction
In recent years, novel pyrolysis techniques have been suggested for producing oil from oil shale [1]. It was found by Wang et al. that the ideal temperature for extracting the maximum quantity of oil shale from a sample with a water/oil shale ratio of 3 is 365°C. However, this may differ depending on the specific percentages involved. According to Zhao et al. [2] experiments, oil is produced at temperatures above 366-486 °C. Each oil shale sample produces oil or gas at different temperatures depending on its composition [3]. Numerous studies have been conducted to enhance oil quality. Still, the process must be both cost-efficient and profitable regarding economy and energy consumption while preserving high efficiency [4]. Compared to traditional heating methods, microwave heating provides several advantages, including energy and time savings, uniform heating, and selective heating that can affect certain materials more than others [5].

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Using microwaves for oil shale pyrolysis reduces reaction time and improves energy efficiency [6]. In addition, microwave equipment's immediate start and stop feature contributes to its ease of operation and maintenance [7]. Parameters such as temperature, heating rate, and dielectric properties of materials are among the factors that influence the heating process when utilizing microwaves [8]. The use of electromagnetic wave technology in the oil industry has seen significant growth in recent years, with many prominent firms worldwide attempting to use this technology [9]. Microwaves are also used to process oil shale. The alterations in dielectric properties of oil shale caused by microwave radiation are distinct from those caused by conventional heating. This discrepancy may be attributed to varying chemical kinetics in the two processes [10]. It has been suggested that microwaves can improve the grindability of oil shale, likely due to changes in the oil shale matrix or moisture content [11]. This process is related to the absorption of microwaves by oil shale minerals and their coefficient of thermal expansion [12]. Chen et al. [13] researched the effect of microwave radiation on pore water pressure. It was found that microwaves can be used to create light hydrocarbons in oil shale reservoirs by heating pore water and subsequently increasing the pressure. This has been said to be a successful mechanism for rock fragmentation. In addition, the effectiveness of using microwaves to produce shale oil from oil shale may be determined by the dielectric properties [14] and the presence of water in the matrix [15] as well as the temperature of the oil shale [16] and the degree to which microwaves penetrate the oil shale structure [16].

Microwave radiation has been found to cause selective and volumetric heating, resulting in increased shale oil production and decreased levels of sulfur, nitrogen, and oxygen. Furthermore, this type of heating leads to an increase in light hydrocarbons and improves the quality of shale oil [17]. Also, gas can be produced from oil shale [18]. In the conventional heating method, an external heating element with a power of 450 watts was used. The oven had two heating systems and a fan to homogenize the temperature inside the chamber. In microwave radiation, all power levels are 650, 900, and 1200 watts, with a final temperature around 700 °C. To assess the production and enhancement of oil quality in Iranian oil shale samples, this study compared microwaves and conventional heating via the pyrolysis process under identical conditions, focusing on the efficiency based on the quantity and quality of the produced oil shale. Moreover, the main novelty is the effect of the quality of produced oil in production scenarios and the effect of microwave heating on the extent of oil shale quality.

Materials and Methods

The Samples from the Sargelu Formation located in QaliKuh [19,20] were evaluated for their characteristics using Rock eval analysis. Moreover, Rock-Eval pyrolysis is a widely used method to measure source rocks' generation potential and maturity. In Rock-Eval pyrolysis, a sample is progressively heated to 550 °C in a vessel free of oxygen. During this heating process, the hydrocarbons in the sample are volatilized, and the amount of the volatile hydrocarbons is measured and recorded as the S1 peak. The kerogen in the sample is then pyrolyzed. The generated hydrocarbons and hydrocarbon-like compounds are recorded as the S2 peak, the yield of CO_2 formed during pyrolysis as the S3 peak, and the temperature corresponding to the maximum of the S2 envelope (Tmax), mineral carbon content (MinC), and the total organic carbon (TOC) content are also measured (Table 1). Results showed good potential for Sargelo oil shale recovery (83 Lit/Ton) as other sources in word Siberia (113 Lit/Ton) and Green River (151 Lit/Ton) [20].

Each experiment was conducted using 30 grams of samples, the smallest value that can be used to analyze tests related to oil production from oil shale. The samples were then subjected to two types of radiation, conventional heating, and microwaves, to extract oil shale. The Fisher device, which enables both conventional heating and microwaves, was used for this purpose. A schematic of this device is shown in Fig. 1, depicting a quartz reactor containing the oil shale being heated by a microwave oven and the reactor and its path filled with helium via a plastic tube.

Table 1 The specification of the QlaiKuh oil shale samples

Region	Formation	Sample	TOC (%)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	Tmax (°C)	MINC (%)
SomChal	Sargelu	GH-T15-06	16.6	1.95	102.01	0.54	446	9
DareNak	Sargelu	GH-T50-04	21.75	1.47	93.36	3.31	440	6.76
Pirbadoush	Sargelu	GH-T41-09	21.42	2.09	109.55	1.9	443	5.8

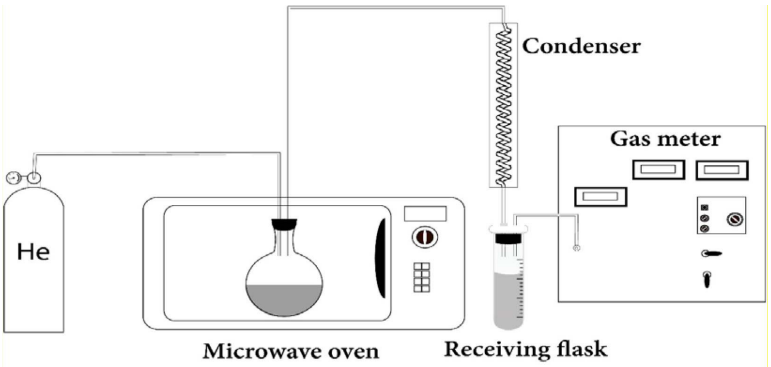

Fig.1 Schematic of Fisher device developed with microwaves

The samples were pulverized by ball milled in a 7-12 mm granulate base and mixed as a homogenous sample; based on the limitation of sample content and the number of parameters for this study, the Taguchi method was used to design experiments. Moreover, the oil produced was rechecked once. In addition, the coking temperature and available microwave power oven with a water base frequency of 2450 kHz were limited parameters. Sample exposed to microwaves with power levels of 650, 900, and 1200 watts. The temperature of the oil shale was measured at different time intervals, each of which was less than 20 seconds. To ensure reproducibility, one experiment was repeated in each section, showing the same trend of results. All efforts were made to achieve the same temperatures under microwave radiation, with a slight variation. The entire setup was filled with helium gas, and the microwave heating process was carried out at a frequency of 2450 KHz. The exhaust gas was then directed to the gas meter, where it was produced by cracking oil shale before entering the collection container and getting cooled by the cooling system. The quantity of SARA compounds in the oil shale was measured using ASTM D-4124 and IP-143 methods. In contrast, the elemental compounds of carbon, sulfur, nitrogen, and oxygen were measured using the Vario Max-CHNS elemental device (ASTM D5453) - (ASTM D4294). Lastly, the compounds and bonds presented in the produced shale oil were determined using the Fourier transform infrared (FTIR) method.

Analysis and Characterization

Heating Rate

The testing conditions and produced oil from samples exposed to microwave radiation are presented in Table 2. The results indicated the highest efficiency in the production of oil shale with microwave radiation at all power levels of 650, 900 and 1200 watts compared to conventional heating.An increase in heating rate at constant power by microwave from 12.6°C/min (sample M1) to 19.9 °C/min (sample M2) caused an increase in the weight percentage of shale oil produced from 5.2% to 5.9%. However, further increasing the heating rate to 27 °C/min (sample M3) resulted in a decrease in yield, with only about 5% of oil shale produced by weight. It was observed that there is an optimal rate for gaining maximum oil-shale yield when exposed to microwave radiation. If the temperature is too low, the oil shale will not vaporize entirely and turn into char during the coking process, leading to a low production yield. On the other hand, secondary cracking of oil shale at high temperatures can lead to its transformation into hydrocarbon gases. The heating rate affects shale oil production and the quality of its conversion parameters. When the heating rate of sample M1 to M2 is increased, the oil shale mass is reduced, increasing shale oil production. Conversely, shale oil production decreases if the heating rate between samples M2 and M3 is increased beyond the recommended limits. This decrease may be accompanied by changes in the composition and physical properties of the shale oil. Although a higher heating rate can lead to increased conversion, it can also reduce the efficiency of shale oil production [22]. As the heating rate increases in oil shale samples undergoing conventional heating, the yield of oil shale production decreases, and the highest yield is observed at the lowest heating rate. This could be because the pyrolysis process is more activated when the heating rate increases, resulting in a substantial conversion of kerogen to gas [23]. More gas is produced than shale oil during the pyrolysis process. Although increasing the temperature during conventional heating causes a higher production of shale oil, the lowest heating rate that permits the maturation process to occur yields the highest amount of shale oil. Moreover, evaluations have found that using microwaves as a heating method is more effective than conventional heating methods. The only processes that can trigger the production and elimination of shale oil from the oil shale block are self-generated intra-particle processes related to the evaporation of shale oil. Increased heating rates in M3, C2, and C3 samples during the oil shale pyrolysis process can result in secondary cracking reactions and coke formation, thus decreasing shale oil production. The coking process, a significant contributor to intra-particle oil decomposition, can be moderated by increasing the heating rate. Additionally, the rise in heating speed boosts shale oil production from samples M1 to M2, likely due to the increased rate of self-generated oil sweep during the pyrolysis process [24]. Nonetheless, shale oil production at higher temperatures induces a gas-phase cracking process, which decreases the quality of the resulting shale oil [25].

Table 2 Heating Rate Experiment

Sample	Type of heatingPower	Time	Final Temperature	Produced oil
	Microwave (650 W)	Min	oC	Wt% of sample
M1		56	707	5.2
M2	Microwave (900 W)	36	719	5.9
M3	Microwave (1200 W)	27	731	5
C1		50	710	4.7
C2	Conventional	35	720	4.5
C3	Conventional	25	730	4.3
	Conventional			

Studies have indicated that raising the heating rate can improve the efficiency of shale oil production [26]. This is because a higher heating rate allows oil shale to be extracted and produced more quickly, although it may not be heated thoroughly. The qualitative analyses of produced oils in Fig. 2 and 3, including SARA compounds and the presence of carbon, sulfur, nitrogen, and oxygen elements, were produced from oil shale using different heating rates of microwaves and conventional heat. When microwaves were used, there was an increase in the concentration of saturated compounds from sample M1 (19% weight) to M2 (28% weight), but this remained practically close to the same in sample M3 (27% weight). With conventional heating, an increase in heating rate showed a decrease in the concentration of saturated compounds in the produced shale oil; for instance, sample C1 had 21% weight of saturated compounds, while samples C2 had 19% and C3 16%.

Upon increasing the heating rate with microwaves, aromatic compounds initially gain roughly 7% in weight. However, in sample M3, they decreased by about 4%. Generally, oil shale samples created under conventional heating rates comprise around 20-23% aromatic compounds. Sample M1 contains the highest amount of resin compounds with a weight percentage of 41%. The resin compound weight percentage drops to 30% as the heating rate increases. Nevertheless, with a further rise in the heating rate, the resin compound weight percentage rises to 36%. Moreover, observations show that the resin compound weight percentage increases with an increase in heating rate. The weight percentage increases from 28% in sample C1 to 31% in sample C2, eventually reaching 36% in sample C3.

Results showed that, when using microwaves, asphaltene compounds decreased by around 5% in the M2 sample as the heating rate increased. In the M3 sample, a reduction in asphaltene compounds was also seen, but the difference was not significant compared to the M2 sample. As the heating rate increased, the weight percentage of these compounds decreased during the heating process. For example, in the C1 shale oil sample, the weight of asphaltene compounds decreased from 31% to 27% in the C2 sample. Conversely, there was only a slight increase of around 1% in weight in the C3 sample compared to the C2 sample. Moreover, increasing the microwave heating rate decreased sulfur content in all shale oil samples. In sample M3, the sulfur content decreased by approximately 56%. Additionally, as a result of conventional heating, the sample of shale oil produced had a decrease in the amount of sulfur of roughly 31%, as displayed in Fig 3.

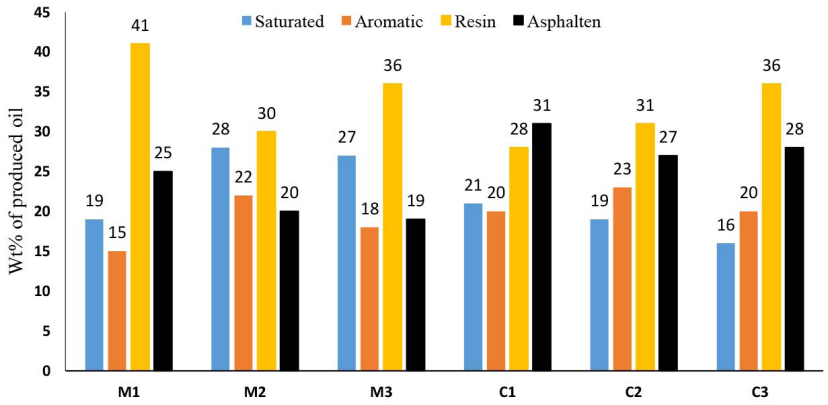

Fig. 2 SARA analysis of produced oil by heating rate.

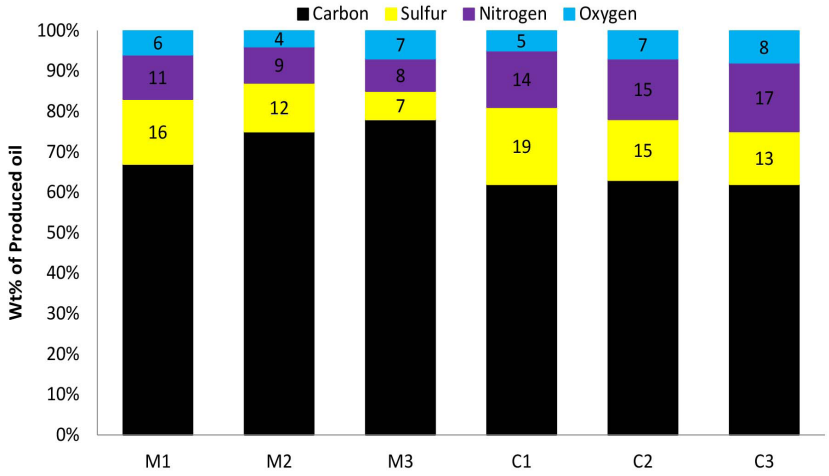

Fig. 3 CSNO reuslts of produced oil by heating rate.

As the microwave heating rate increases, the concentration of nitrogenous compounds in this type of shale oil decreases; this can be observed in samples M1, M2, and M3, wherein the concentration drops from 11% to 9% and subsequently to 8% by weight. Conversely, the shale oil produced through conventional heating exhibits an increase in the nitrogen content, from 14 to 19 percent by weight, in the C1, C2, and C3 samples, respectively.

The oxygen content in the oil-shale sample produced with microwaves decreases initially with an increase in heating rate; however, it then increases. Sample M1 has a weight percentage of oxygen of 6%, M2 is 4%, and M3 is 7%. The amount of oxygen in samples C1, C2, and C3 follows a similar trend to nitrogen, beginning at 5%, then increasing to 7%, and eventually reaching 8%.

It was observed in all samples of shale oil produced through microwave heating and conventional heating that an increase in heating rate may result in higher shale oil density and lower sulfur content [27]. Compounds containing sulfur have a high potential for absorbing microwaves [27, 28, 29], creating hot spots within the material and thus facilitating the removal of sulfur compounds from the sample. As a result, the shale oil produced by pyrolysis with microwaves in all samples contains lower amounts of sulfur than pyrolysis with conventional heating. However, due to the insufficient amount of gas produced in these experiments for analysis, sulfur and nitrogen reduction as Nox or Sox component release to the gas phase [30, 31, 32] could not be accurately determined. As the heating rate increases, the diffusion mechanism becomes more pronounced, causing the products to produce more than the oil shale pores. As they are produced and spread, these reactions lead to secondary adaptations [21]. When pyrolyzing oil shale at higher heating rates, pyrolysis vapors are produced in greater quantities. Still, the porosity of the oil shale may not be developed in enough time, allowing the vapors to escape. This results in a decrease in shale oil yield, as shown in Table 2, but an improvement in its quality, as evidenced in Fig.s 2 and 3. The higher the microwave power is, the higher the heating rate is, which reduces the time particles spend at a certain temperature and shortens the latent period. This accelerates shale oil formation, which is contingent on the pressure and temperature gradient of the gas within the oil shale grains, which is insignificant at lower microwave powers but significant at higher powers [17]. The rate of produced oil is dependent on the petrophysical properties of oil shale, such as grain size, porosity, permeability, and increases in microwave power [33]. Higher microwave power accelerates the destruction of kerogen and the decomposition of the mineral matrix in oil shale during pyrolysis. This can produce polar compounds with high dielectric losses [34], and ionic and conductive compounds can help create uniform heating of oil shale through electric conduction [14], leading to increased cracking of asphaltene compounds in samples M2 and M3. In addition, kerogen products have a high capacity for absorbing microwaves; the residual ash from extracted shale during the pyrolysis process can absorb microwaves, too. This phenomenon increased heating transfer [35], thus enhancing the effectiveness of microwaves in cracking heavier compounds and improving the quality of the produced shale oil (as seen in Figs 2 and 3). Moreover, shale oil produced via microwave radiation has lower levels of asphaltic and polar compounds than conventional heating methods. As microwave power increases, the proportion of polar and aromatic compounds decreases due to the decomposition and destruction of large molecules of kerogen and asphaltene [9, 36]. Sample M3 has more asphaltene compounds, which could be due to the decomposition of other compounds due to increased microwave power. Additionally, the rapid rise in temperature during the heating process can activate cracking reactions in long-chain alkanes, resulting in a decline in their presence in the shale oil. The low presence of saturated compounds in shale oil produced through conventional heating, reduced even further by increasing the heating rate (as observed in samples C2 and C3), confirms this fact.

Fig.s 4 and 5 display the FTIR spectra of shale oil samples extracted via microwave radiation and regular heating.

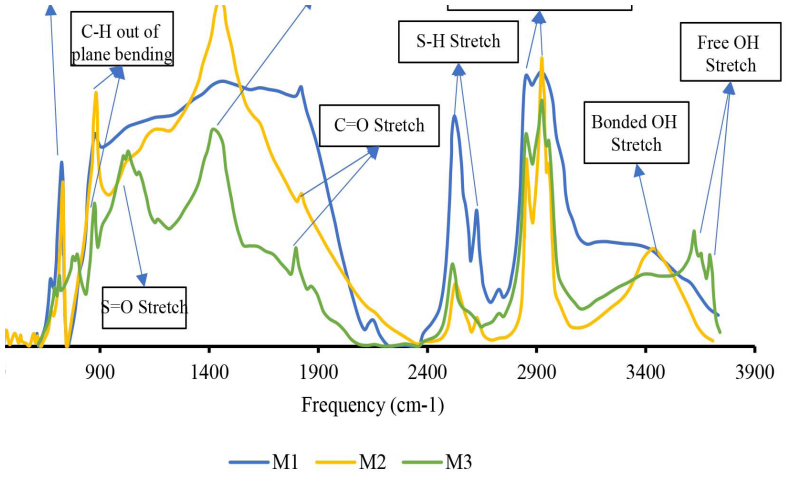

Fig. 4 FTIR of Oil Produced by Microwave Heating.

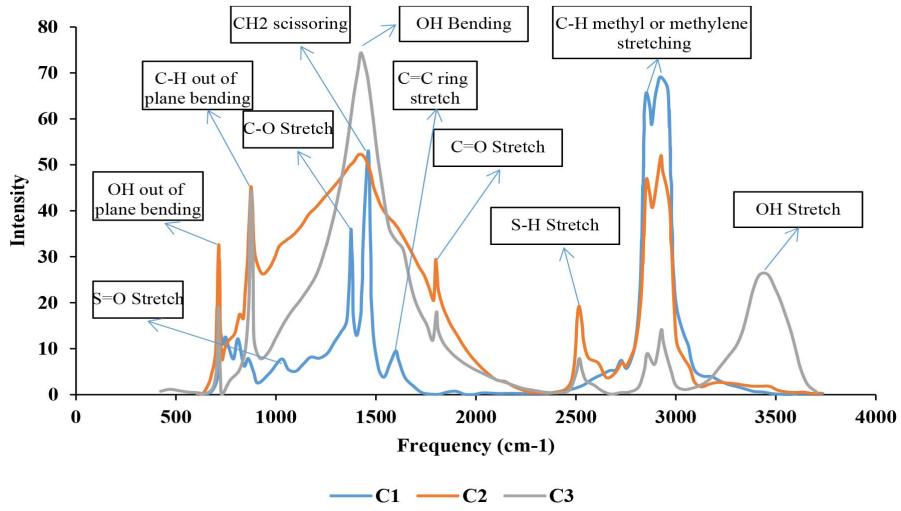

Fig. 5 FTIR of Oil Produced by Conventional heating.

The M3 oil spectrum displays three consecutive peaks in the 3000-3700 cm^{-1} range, at 3694 cm^{-1}, 3649 cm^{-1}, and 3626 cm^{-1}. These peaks signify free hydroxyl functional groups that have not undergone hydrogen bonding with adjacent molecules, and their frequencies have increased. This presence of free hydroxyl is caused by two factors: the low concentration of the hydroxyl functional group in this shale oil sample and other structures in crude oil that act as a barrier, obstructing hydrogen molecules from interacting with each other. There is no peak at the 3000-3700 cm^{-1} range in M1 shale oil, implying that hydroxylated sections of asphaltene and resin are less abundant in this sample. In M2 oil, a broad, medium-intensity peak is present at the frequency of 3425 cm^{-1}, which corresponds to the stretching of the O-H bond in the hydroxyl group. This peak is wider and appears at a lower frequency than the similar peak in M3, likely due to the microwave radiation used to extract the oil, causing a hydroxyl group to form that is not produced by conventional heating methods. Two of the strongest peaks in the spectrum of the oil sample occur in the frequency range of 2700-3000 cm-1. The peak located at 2923 ± 5 cm^{-1} is associated with the C-H asymmetric stretching band, while the peak at 2853 ± 5 cm^{-1} relates to the C-H symmetric stretching band, both of which are from the methylene functional group. The peak at 2953 ± 5 cm^{-1}, which is from the methyl functional group, was only present in two crude oil samples M3 and M2. The lack of this peak in the M1 crude oil spectrum implies a lower aliphatic content and fewer paraffinic compounds than the other two samples. The intensity of peaks related to aliphatic compounds was found to be highest in sample C1 and lowest in sample C3 in the typical heating process.

The frequency range between 2700-3000 cm^{-1} yields some of the strongest peaks in the spectrum of the oil sample, two of them being at 2923 ± 5 cm^{-1} and 2853 ± 5 cm^{-1}, respectively, corresponding to the C-H asymmetric and symmetric stretching bands of the methylene functional group. Additionally, a peak at 2953 ± 5 cm^{-1}, corresponding to the C-H asymmetric stretching band of the methyl functional group, was observed in samples M3 and M2. The absence of this peak in M1 suggests that this sample has a lower aliphatic content and fewer paraffinic compounds than the other two samples. During the standard heating process, the aliphatic compound peaks were most intense in sample C1 and the least intense in sample C3.

The 1000-2000 cm^{-1} range is usually called the 'fingerprint' range. The peaks observed in the three oil samples collected from this region are noticeably different. Sample M3 has a peak occurring at a frequency of 1797 cm^{-1}, associated with C=O stretching from the carboxylic acid functional group rather than the ketone functional group. This can be discerned by analyzing the peak frequency. The presence of a hydroxyl group near a C=O bond reinforces the induction effect on the sigma bond, resulting in a higher frequency of appearance than the pure ketone. The broad and intense peak at the frequency of 1420 cm^{-1} pertains to O-H bending. Its peak is broader than usual since it combines with two adjacent peaks of CH_2 scissoring vibration and C-O stretching.

The M3 crude oil spectrum displayed a peak at 1166 cm^{-1}, corresponding to the C-O stretching vibration. This frequency indicates that the hydroxyl group present in this sample is of the tertiary saturated type. Additionally, two peaks at 1079 cm^{-1} and 1032 cm^{-1} point to a sulfoxide functional group. The peak at 1079 cm^{-1} specifically points to the S=O functional group, in which sulfur is bonded to an aliphatic and aromatic carbon. At 1032 cm^{-1}, a peak is seen, signifying S=O stretching vibration, thus showing that sulfur is connected to two fully saturated carbon atoms. In M1 crude oil, two peaks at 1454 cm^{-1} and 1648 cm^{-1} emerge, signifying C-C ring stretch and demonstrating that the sample is predominantly aromatic. For the M2 oil sample, a wide and strong peak at 1455 cm^{-1} is observed, which relates to O-H bending. The peak is broad as it is merging with near peaks. Additionally, the 1159 cm^{-1} peak corresponds to C-O bond stretching. Within the aromatic region, which lies between 700-1000 cm^{-1}, three moderately intense peaks were seen in the M3 and C3 oil samples. These peaks were attributed to the out-of-plane bending vibration of aromatic C-H bonds, suggesting that the predominant arrangement of aromatic rings was in the form of compounds with three rings. Additionally, the peak at 694 cm^{-1} corresponded to the out-of-plane bending of O-H. Only one peak was observed at a frequency of 880 cm^{-1} in M1, M2, C1, and C2 samples, which, according to past studies, indicates the presence of a four-ring arrangement of aromatic compounds [37]. The summarized results are in Fig. 6.

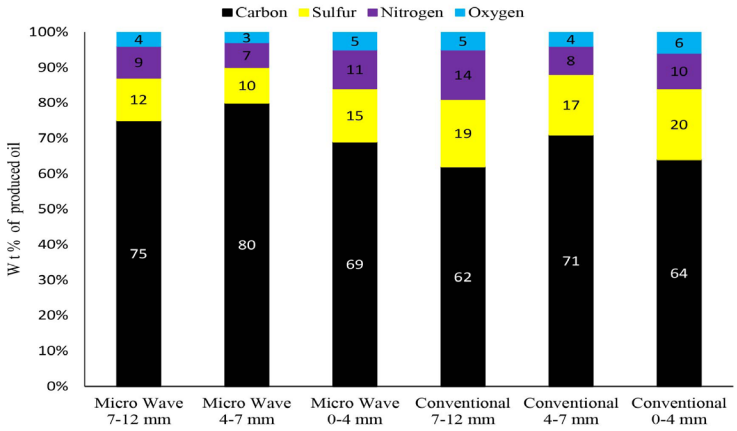

Fig. 6. Result of CSNO analysis on produced oil with varying granularities.

Granulation

The granulation of oil shale samples can be seen as a factor that affects the amount and quality of shale oil produced. This is because the variation in the cross-sectional area of the grains allows for more energy to be taken in. For this research, rock samples of oil shale were heated in three different granulation ranges: 7 to 12 mm, 4 to 7 mm, and below 4 mm. The weight percentages of oil extracted by each process are presented in Table 3.

On average, microwave extraction is observed to yield 25% more oil than conventional heating techniques using the same degree of granularity. Decreased particle size leads to a bigger cross-sectional region, allowing the particles to take in more wave energy. It has been noted that, regardless of the process used to generate oil, the weight percentage of extracted oil increases as the size of the oil shale sample decreases. The greatest amount of oil extracted through microwave mechanisms is lower than 4 mm, while traditional heating yields between 4-7 mm. Moreover, reducing grain size while using microwave heating raised the weight of oil extracted from oil shale by around 1%.

Fig. 6 displays the percentage abundance of carbon, sulfur, nitrogen, and oxygen elements in shale oil produced by two mechanisms: microwave irradiation and conventional heating, with three different granularities. Generally, shale oil produced using the microwave irradiation mechanism has a higher percentage of carbon and lower sulfur than oil produced with conventional heating.

Table 3 Oil Production Versus Granulation (mm)

Granulation (mm)	Produced Oil by Conventional Heating Wt% of sample	Produced Oil by Micro wave Heating Wt% of sample
7-12	4.7	5.9
4-7	5.4	6.6
Less than 4	5.1	6.8

Oil generated with microwaves from shale with a grain size between 4 and 7 mm had the most carbon, the least sulfur, and the least heteroatomic elements, displaying the best quality of all the oils created. On the other hand, the oil generated from microwaves with shale having a grain size less than 4 mm had the lowest carbon abundance (69%), the most sulfur (15%), and the highest concentration of heteroatomic elements out of the three samples of microwave-produced oil.

The amount of sulfur in oils extracted by conventional heating is higher than 15%. of the three samples, oil extracted from shale with a 4-7 mm grain size has the highest amount of carbon (71%) and the lowest amount of heteroatomic elements [37]. Illustrated in Fig. 7 is the relative abundance of the SARA (Saturates, Aromatics, Resins, and Asphaltenes) compounds that were extracted from oil shale of diverse grain sizes.

Results and Discussion

Both microwave and conventional heating mechanisms were employed in the study to extract oil from oil shale of grain sizes ranging from 4 to 7 mm. According to the elemental analysis results, the oil obtained from the 4-7 mm grain size had the lowest asphaltene fraction (the heaviest and most polar fraction of crude oil) and the highest amount of compounds. Generally, the oil obtained by the microwave method had less asphaltene (more than 10%), higher resin, and higher saturation than the same sample obtained by conventional heating. The resin, which has both polar and non-polar properties, did not show any specific behavior when the grain size of the oil shale was changed. In the shale oil produced by microwave radiation, the sample with the lowest asphaltene content also had the highest amount of resin (sample 4-7 mm). The radiation of high-energy microwave waves caused the asphaltene to cut into the resin in this sample [38]. The abundance of resin in the shale oil obtained from the 7-12 mm and smaller than 4 mm samples was the same. However, the amount of resin decreased to 25% in the sample obtained from 4-7 mm using conventional heating. It should be noted that the frequency of aromatic cleavage in the shale oil samples did not significantly change with the change in shale sample size. As seen in Fig. 8, the FTIR spectra of three shale oil samples extracted using microwaves and having varied grain sizes are displayed.

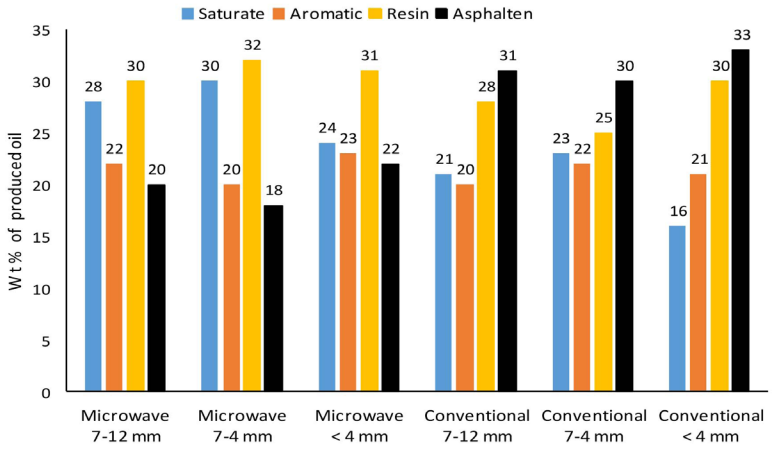

Fig. 7 SARA analysis of produced oil with different granularities.

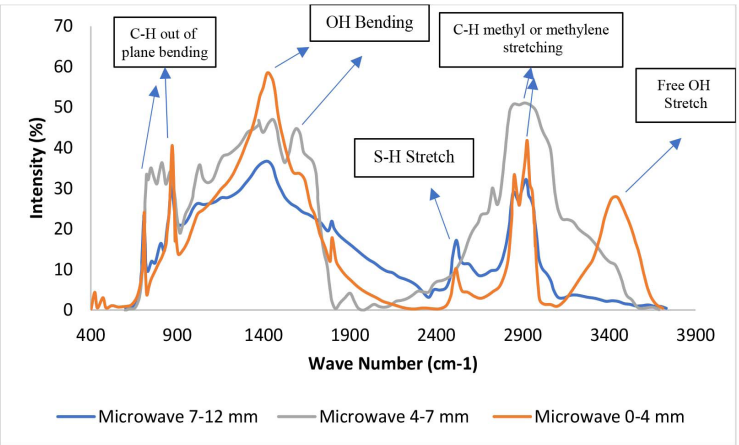

Fig. 8 FTIR of Oil Produced by MW Heating with different granularity.

Due to the exposure to microwave radiation, most of the peaks in the 4-7 mm shale oil sample were detected, though their strength and division were changed. By decreasing the particle size to less than 4 mm, the entanglement, division, and peak intensity can be improved. The out-of-plane C-H and H-C =C-H stretch bonds, which in 4-7 mm shale oil were multi-branched, can be split more distinctly by lessening the size of the particles. This makes their recognition simpler. Additionally, the peak of the aromatic C-C mode stretch bond, which in 4-7 mm shale oil was observed as numerous branches and uneven, manifested conventional and with good intensity when the particle size was reduced from 4-7 mm to less than 4 mm. On the contrary, the peak linked with the hydroxyl functional group was seen in the spectrum when the particle size was decreased. Generally, it can be concluded that the samples exposed to microwave radiation exhibit better quality peaks owing to a decrease in particle size. Two peaks corresponding to C-H out-of-plane bending were prominently present in the 0-4 mm shale oil sample extracted with microwave, with the range of 700-1000. Comparing the spectroscopy and SARA results suggests that these peaks originate from the growth in the aromatic fraction of the shale oil's structure. In the range of 3000-2700, peaks with significant strength were seen in all three samples. Moreover, these peaks were attributed to C-H stretching vibration; the most intense and broadest peak was found in the 4-7 mm shale oil sample extracted with microwave. Furthermore, comparison of the spectroscopy results with SARA results reveals that the substantial rise in intensity and breadth of this peak is due to the remarkable raise of saturated compounds in shale oil. At the frequency of 2500, the peak corresponding to S-H thiol stretching vibration (as the main indicator of the amount of sulfur-containing compounds) [37] was not observed in the spectrum of the oil sample extracted via microwave method from 4-7 mm shale, which is likely due to the lower frequency of sulfur-containing compounds in this sample. Conversely, the strongest peak in this frequency was observed in the sample of oil produced with microwave from less than 4 mm shale. This sample had the highest percentage of sulfur among the three samples, as indicated by the elemental analysis results. Additionally, the peak corresponding to O-H stretching of the carboxylic acid functional group at frequency 3450 was only present in the spectrum of the oil sample produced with microwave from less than 4 mm shale. This sample was also found to have the highest amount of asphaltene and oxygen among the three samples. Therefore, it can be concluded that the appearance or non-appearance of peaks at frequencies 3440 and 2500 is related to the quality of Shale oil.

In Fig. 9, the FTIR spectrum of oil obtained from 7-12 mm oil shale due to conventional heating showed stretching and out-of-plane C-H bonds at 641 cm^{-1} and 874 cm^{-1}, respectively, and stretching =CH bond at 711 cm^{-1} and stretching S-O bond at 812 cm^{-1}. Moreover, when the particle size decreased from 7-12 to 4-7 mm, the separation and intensity of C-H, =C-H, out-of-plane C-H and C-O stretching peaks in the spectrum of the shale oil sample produced from 4-7 mm shale exposed to conventional heating was found to be improved, and aromatic C-C mode stretching peaks appear bifurcated and with greater intensity compared to when exposed to 7-12 mm shale.

By reducing the oil shale particles to less than 4 mm, peaks with better separation and intensity will be observed. This method of reducing sample particles is effective for samples exposed to microwave radiation and conventional heat, leading to higher-quality peaks. However, the OH-stretching vibration peak at frequency 3440 was not seen in the spectrum of shale oil extracted from 4-7 mm shale through conventional heating. The compatibility of spectroscopy and elemental analysis results indicated that the cause of this issue was the decrease of oxygen element in the sample. The frequency of 2700-3000, corresponding to the C-H stretching vibration of methyl and methylene groups in the 4-7 mm shale oil sample obtained from conventional heating, has higher intensity and width of peaks than the other two similar samples. As the oil's hydrocarbon content and, therefore, quality increase, the peaks in this range will also be greater. SARA test results revealed that the 4-7 mm shale oil sample obtained by conventional heating had a higher aromatic content than the other two samples, as seen in the greater intensity of the 800-1000 (aromatic substituted proton bending) and 1602 (C-C aromatic mode) peaks. In addition, despite having higher sulfur content in the 0-4 and 7-12-mm shale oil samples obtained by conventional heating, the intensity of the S-H stretching peak at 2500 was lower than that of the 4-7 mm sample, and the intensity of the S=O sulfoxide stretching peak was much higher in these two samples. Finally, this suggests that desulfurization in this heating method is achieved by removing thiol compounds. Fig.s 10 and 11 display the HNMR and CNMR spectra.

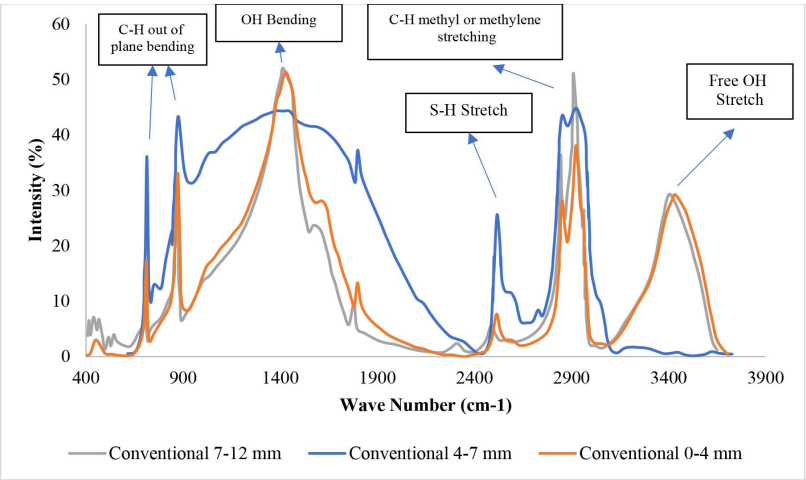

Fig. 9 FTIR of Oil Produced by Conventional Heating with different granularity.

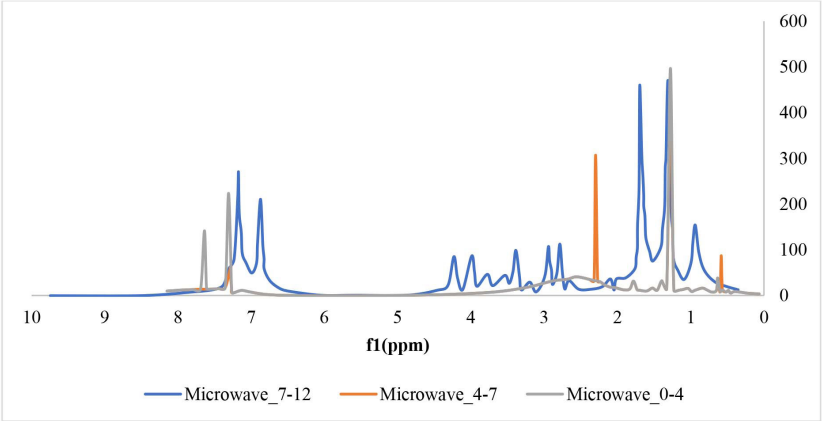

Fig. 10 H-NMR of the oil produced by MW heating with varying granule sizes

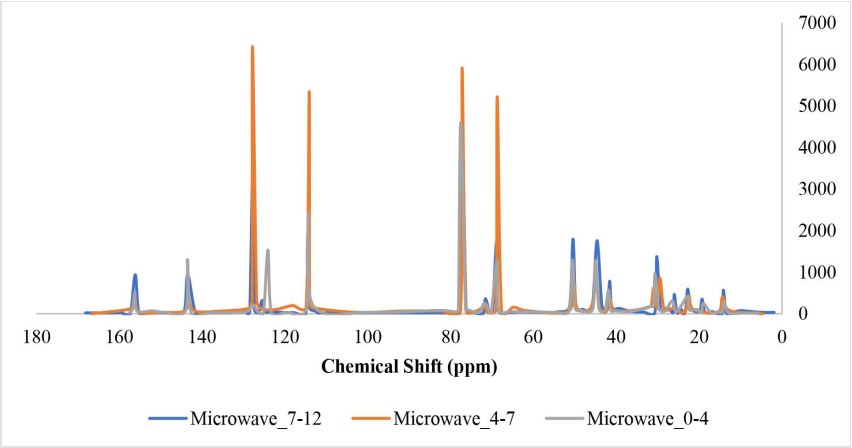

Fig. 11 C-NMR of the oil produced by MW heating with varying granule sizes.

Table 4 presents the average values of molecular indices of shale oil samples extracted by microwave heating from shale of various grain sizes. The shale oil generated with a microwave method from samples with 4-7 and 0-4 mm grain size has the highest and lowest aliphatic content, respectively. The result is that the lower cracking temperature of aliphatic compounds, the smaller the grain size, the more evaporation among the aliphatic samples due to the absorption of higher amounts of energy. Moreover, the mean length of alkyl chain (n) indicators further supports this inference. Furthermore, the oil sample derived from 0-4 mm shale has the least amount of paraffin chain length among the three samples, which is the source of initial cracking and then evaporation of straight chain compounds, thereby causing the aliphatic content of this sample to diminish compared to the aromatic content. In addition, according to the textural entanglement and molecular substitution indices, the oil produced from 0-4 mm shale has the highest amount of aromatic ring entanglement. Meanwhile, these indicators are the lowest value for the sample of 7-12 mm. By examining the results of NMR and FTIR spectra, it is concluded that in 0-4 and 7-12 mm grain size, the absorbed energy is focused on breaking alkane side chains and their evaporation, while for oil produced from shale with 7-7 grain size 4 mm of absorbed energy has been used to break the aromatic molten rings from the binding edge and transform them into lighter or more stable compounds such as dense kata.

Fig. 12, 13, and Table 5 demonstrate the H-NMR and C-NMR spectra and calculated numerical indices for crude oil extracted from oil shale via conventional heating. The sample of crude oil from particles less than 4 mm exhibits the greatest aromaticity of all samples; the sample of oil extracted from 4-7 mm oil shale contains the greatest aliphatic compounds. Generally, the aliphatic compounds in oil samples extracted from microwave heating are higher than those obtained from conventional heating with a similar granulation. Also, changes in properties and indices of shale oil resulting from variations in heating parameters, microwave and conventional heating are seen in Table 6. Moreover, reducing the grain size reduces the average carbon number of free aliphatic chains and those attached to aromatic rings. Numerical indices corresponding to the intermingling of aromatic rings reveal that 4-7 oil has the greatest condensation in aromatic rings despite its lower aromaticity than the other two samples.

Table 4 Properties of shale oil obtained through MW heating methods and various granulation techniques using C-NMR and H-NMR spectra.

Sample	C_{al}	C_{ar}	f_a	n_1	n_2	Θ	ω	$\acute{A}_s$	T
Microwave 7-12 mm	37.98	62.02	0.62	3.86	0.34	0.28	2.19	2.42	0.536
Microwave 4-7 mm	40.51	59.49	0.59	4.4	0.31	0.26	1.78	2.67	0.429
Microwave 0-4 mm	33.94	66.06	0.66	3.63	0.32	0.31	2.89	3.52	0.687

C_{al}: Sum of aliphatic area component
C_{ar}: Sum of Aromatic area component
f_a: Aromatic fraction ($f_{al}+f_{ar}=1$)
n_1: No. of carbon in alkyl (paraffin) group
ϑ : Aromatic Condensation Index
ω: Aromatic condensation degree
As: peripheral aromatic carbon
τ: Substituent rings

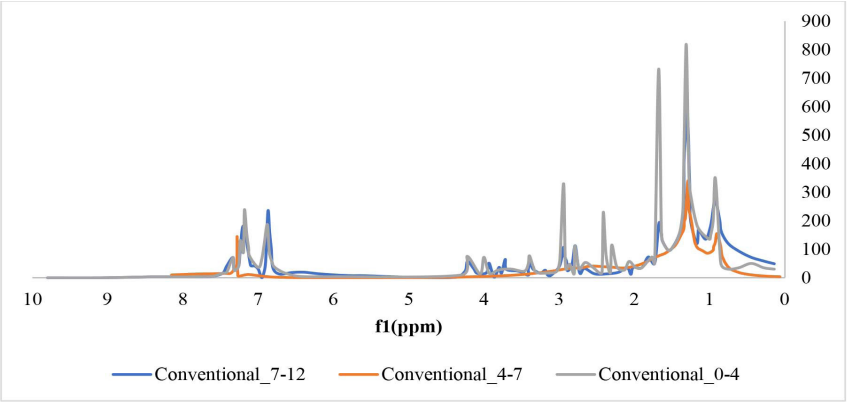

Fig. 12 H-NMR of the oil produced by conventional heating with varying granule sizes.

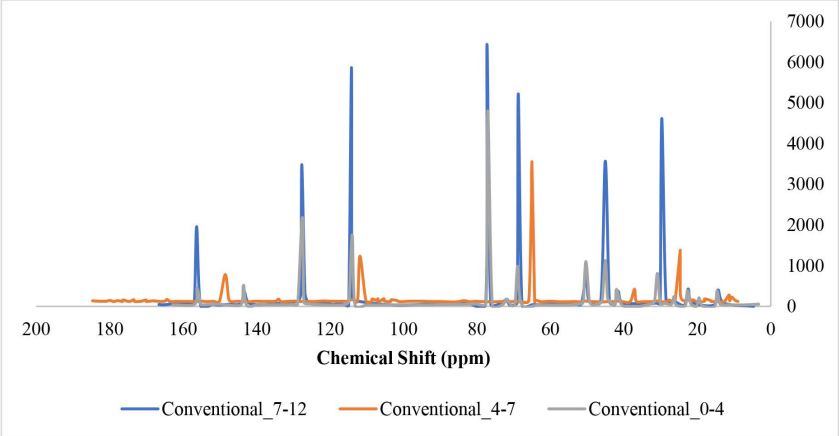

Fig. 13 C-NMR of the oil produced by conventional heating with varying granule sizes

Table 5 Shale oil properties are obtained through conventional heating and various granulation techniques using C-NMR and H-NMR spectra.

Sample	C_{al}	C_{ar}	f_a	n_1	n_2	ϑ	ω	A_s	τ
Conventional 7-12 mm	28.19	71.81	0.71	4.7	0.37	0.29	2.22	2.46	0.41
Conventional 4-7 mm	30.3	69.7	0.69	4.6	0.35	0.42	3.13	3.73	0.42
Conventional 0-4 mm	24.78	75.22	0.75	4.36	0.33	0.36	2.71	3.34	0.39

Table 6 Changes in Properties and Indices of Shale Oil Resulting from Variations in Heating Parameters, Microwave, and Conventional Heating

Produced Oil By Heating Rate	Type of Heating	Time Min.	Produced oil Percent of Sample	Asphalten Percent	Sulfur Percent	Carbon Percent	-OH Group	Sulfur Groups R-S-H R-S=O	Aliphatic Percent Cal	Average Carbon No. n1	Aromatic Condensation Index ϑ
		56		25	16	67	Yes		-		-
		36	5.2	20	12	75	No	R-S-H	-	-	-
	Microwave	27	5.9	19	7	78	Yes	No	-	-	-
			5					Yes			
		50		31	19	62	Yes		-		-
		35	4.7	27	15	63	No		-	-	-
	Conventional	25	4.5	28	13	62	Yes	R-S=O	-	-	-
			4.3					No			
								No			

The intertwined rings of this sample are organized in the peri-condensed form according to the aromatic condensation degree (ω) index. Furthermore, alkyl functional group substitution in the alpha position of the middle polyaromatic nucleus in samples 4-7 is higher than in the two samples. Thus, the higher amount of aliphatic compounds in this sample can be attributed to their substitution with side protons of the Central aromatic nucleus. Table 7 provides a summary of the results.

Table 7: Changes in properties and indices of shale oil resulting from variations in shale sample granulation during microwave and conventional heating.

Produced Oil By granulation	Granulation Range	Type of Heating	Produced oil Percent of Sample	Asphalten Percent	Sulfur Percent	Carbon Percent	-OH Group	Sulfur Groups R-S-H R-S=O	Aliphatic Percent Cal	Average Carbon No. n1	Aromatic Condensation Index ϑ
	0-4	Microwave	6.8	22	15	69	Yes	R-S-H	33.94	3.63	0.31
		Conventional	5.1	33	20	64	Yes	R-S=O	24.78	4.36	0.36
	4-7	Microwave	6.6	18	10	80	No		40.51	4.4	0.26
		Conventional	5.4	30	17	71	No	-	30.3	4.6	0.42
	7-12	Microwave	5.9	20	12	75	No	R-S-H	37.98	3.86	0.28
		Conventional	4.7	31	19	62	Yes	- R-S=O	28.19	4.7	0.29

Conclusions

Using microwaves for oil shale pyrolysis, a more efficient method than conventional heating, can significantly increase the amount of oil shale produced. To further boost production and enhance the quality of oil shale derived from oil shales, it is essential to establish an optimal heating rate for the highest possible yield.

As the heating rate of conventional oil shale pyrolysis increases, the quantity of shale oil produced rises, but unfortunately, the quality of the oil diminishes. Therefore, it is imperative to determine the ideal heating rate for shale oil production based on the quality of the resulting oil.

As the heating rate increases for oil shale produced via microwave heating, the total amount of asphaltene and resin cut decreases. In contrast, the total amount of saturated compounds increases, indicating an improvement in the oil shale's quality. Conversely, asphaltene compounds show no major decrease when utilizing conventional heating with an increasing heating rate, while saturated and resin compounds increase.

As the heating rate in microwaves increases, the amount of sulfur and nitrogen elements in oil shale decreases, and the amount of carbon elements increases. In contrast, the amount of oxygen first decreases and then increases. Conversely, with the increase of heating rate in conventional heating rate, only the sulfur in oil shale decreases, and nitrogen and oxygen elements increase, with carbon staying almost constant. Additionally, oil shale produced with microwaves at all heating rates contains hydroxyl compounds not observed in oil shale produced with conventional heating. Furthermore, the increase in the heating rate in microwaves results in the formation of the methylene functional group in shale oil, which indicates its aliphatic nature and the increase of paraffinic compounds, whereas with conventional heating, the opposite occurs.

By reducing the granulation size of the oil shale sample in the microwave heating process, the shale granulation was divided into three categories: 7-12, 4-7, and less than 4 mm, which improves thermal absorption and increases oil production. However, the decrease in grain size initially reduces sulfur, nitrogen, and asphaltene in the generated oil, and then it increases. Moreover, carbon in the oil also first increases and then decreases.

The optimal grain size of 4-7 mm is confirmed by the percentage of aliphatics, average carbon number, carbon chains, and the index of large molecules with aromatic rings. In conventional heating, the amount of oil produced and the percentage of oil carbon increase and then decrease with the reduction of granulation. The percentage of asphaltene, resin, and elements of sulfur and nitrogen also demonstrate the same trend. However, microwave heating is considered more efficient than conventional heating in all granulation modes. Based on Qali Kouh samples, the oil shale of Iran, like other sources worldwide, has good potential for oil recovery. Several techniques exist for recovering oil shale. This study shows that microwave heating, a new method, has some advantages over conventional heating, both in quantity and quality of produced oil.

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