



Using Microwave Technology to Extract Organic Matter from Rocks

Ahad D. Sachit, Lamyia J. Basri, Dr. Rana R. Jalil, Ihab S. Hassan

Petroleum R&D center / analytical lab Department

Corresponding Author E-mail: ahadewan@yahoo.com

Abstract:

Rock extraction is one of the most important processes to prepare samples to core analyses but this method consumes large quantity of solvents and time which means high cost; so it is necessary to innovate new high efficiency ways to replace the traditional methods. The use of microwaves in rock processing is an innovative and unobtrusive method in this field. The design of special furnaces to generate microwave and use them in the extraction of crude oil from rocks become a necessity; because of the need to reduce the costs of this treatment and shorten the necessary time to laboratory experiments and decreased conducted solvent for this process.

A number of samples of carbonate reservoir rocks exposed to microwave radiation assisted extraction and many solvents were used to detect more suitable solvent, the results of the experiment show that some solvents were superior to others and the samples did not harm as a result of that processes, note that the type of rocks may be important in determining the ability of microwave waves to perform the required treatment. And it is approved its high efficiency by decreasing time of cleaning up to less than 25% of time, more economical, in term of the least consumption of solvent and safer by comparison with conventional.

Key words: microwave, extraction, rock, plug, solvent.

استخدام تقنية المايكرويف لاستخلاص المواد العضوية من الصخور

الخلاصة:

يعد الاستخلاص من الصخور من أهم عمليات أعداد العينات الصخرية وتجهيتها للتحليلات الأساسية، ولكن هذه الطريقة تستهلك كمية كبيرة من المذيبات والوقت مما يعني تكلفة عالية؛ لذلك من الضروري ابتكار طرق جديدة عالية الكفاءة لتحل محل الأساليب التقليدية.

ان استخدام الموجات الدقيقة في معالجة الصخور هي طريقة مبتكرة وفريدة في هذا المجال. أصبح تصميم الأفران الخاصة بتوليد الموجات الدقيقة واستخدامها في استخراج النفط الخام من الصخور ضرورة؛ بسبب الحاجة إلى تقليل التكاليف والوقت اللازم للتجارب المختبرية بالإضافة إلى تقليل كمية المذيبات المستخدمة لهذه الطريقة.

تم استخدام الكثير من عينات الصخور (نوع كاربونات) والتي تم تعريضها إلى الموجات الدقيقة حيث استخدمت العديد من المذيبات للحصول على النتائج الانسب، وأظهرت نتائج التجربة أن بعض المذيبات كانت متفوقة على غيرها بالإضافة إلى أن العينات لم تتضرر نتيجة لتلك التجارب، لوحظ أن نوع الصخور مهمة في تحديد قدرة الموجات الدقيقة على إجراء المعالجة المطلوبة. اثبتت التجارب كفاءتها العالية من خلال تقليل وقت التنظيف حتى أقل من 25 % من الوقت، والتكلفة، من حيث استهلاك أقل للمذيبات وأكثر أماناً بالمقارنة مع الطرق التقليدية.

1- Introduction:

Microwave heating includes the use of electromagnetic waves ranges from 0.01 to 1m wave length of certain frequency to generate heat in the material. These microwaves lie in the region of the electromagnetic spectrum between IR (infra-red) and radio wave.

The fundamentals of the extraction by the microwave radiation that is named (MAE) process, are different from those of conventional methods (solid-liquid or simply extraction) because the extraction occurs as a result of changes in the cell structure caused by electromagnetic waves. The process acceleration and high-extraction yield may be the result of a synergistic combination of two transport phenomena: heat and mass gradients working in the same direction. However, the mass transfer occurs from inside to the outside in conventional extractions, the heat transfer occurs from the outside to the inside of the substrate. In addition, although in conventional extraction the heat is transferred from the heating medium to the interior of the sample, in MAE the heat is dissipated volumetrically inside the irradiated medium [1].

Microwave dielectric heating uses the ability of polar molecules to transform electromagnetic energy into heat. Therefore, the selected solvent plays an important role in

the analysis divided into two categories of solvents:

- Microwave absorbing solvents are called non-transparent solvents.
- Non-microwave absorbing solvents are called transparent solvents. Polar solvents - Elevated temperature enhances the molecular diffusion through the solid sample to solvent. Non-polar solvents -Water content within the solid sample heats up [2].

The number of samples in the oven has an effect on the heating period until the maximum temperature becomes a constant. When the number of samples increases, the power for each sample decreases because the power would be dispersed on the samples [3].

2- Theory

2-1 Microwave principles and mechanism

The main aim of the heating in microwave oven due to the interaction of charged particle of the reacted material with electromagnetic wavelength of particular frequency. The phenomena of producing heat by electromagnetic irradiation, collision or by conduction, or both. All the wave energy changes its polarity from positive to negative with each cycle of the wave which cause rapid orientation and reorientation of molecule particles and then heating by collision. If the charge particles of material are free to travel through the material (e.g. Electron in a sample of carbon), a current will induce in phase with the field, but if the charge particle are bound within regions of the material, the electric field component would cause them to move until opposing force balancing the electric force [4].

However, the motion of these particles is restricted by resisting forces (inter-particle interaction and electric resistance), which restrict the motion of particles and generate random motion lead to produce heat. Based on their response to microwaves, materials can be classified as follows:

- Materials that are transparent to microwaves, e.g., Sulphur.
- Materials that reflect microwaves, e.g., copper.
- Materials that absorb microwaves, e.g., water.

Only materials that absorb microwave radiation are relevant to microwave chemistry.

In microwave heating, electromagnetic energy is transformed into heat through ionic conduction and dipole rotation Figure (1). Ionic conduction refers to the movement of ions in a solution under an electromagnetic field. The friction between the solution and these ions generates heat. Dipole rotation is the reorientation of dipoles under microwave radiation. A polarized molecule rotates to align itself with the electromagnetic field at a rate of 4.9×10^9 times per second. The larger dipole moment of a molecule is more vigorous oscillation in the microwave field [5].

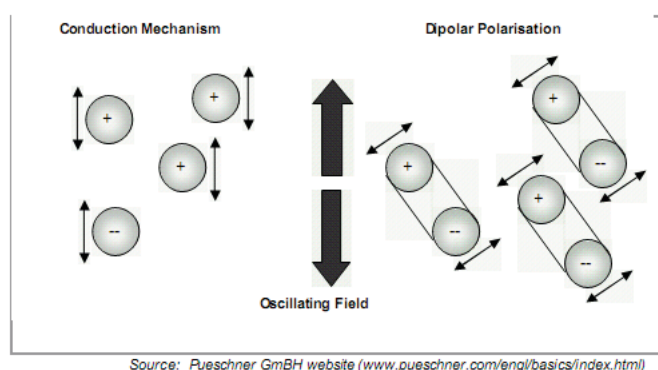


Fig. (1) Methods of Heating by Microwave Radiation

In the system has no temperature control microwave power output and sample weight seem to have minor effects on extraction efficiency, that increment in oven power give higher recovery of hydrocarbons, but for an extraction at a controlled temperature, the oven power output have less influence on recovery [6].

2-2 Effects of solvents:

Every solvent and reagent will absorb microwave energy differently, because they have a different degree of polarity within the molecule, so they will be affected either more or less by the changing microwave field. A solvent is more polar, having a stronger dipole to cause more rotational movement in an effort to align with the changing field. A compound that is less polar, however, will not be as disturbed by the changes of the field and, therefore, will not absorb much microwave energy. Most organic solvents can be broken into three different categories: low, medium, or high absorber, as shown in Table

(1). The low absorbers are generally hydrocarbons while the high absorbers are more polar compounds, such as most alcohols [7, 8].

Table (1) Solvent absorbance

Absorbance level	Solvents
High	DMSO. EtOH. MeOH. Propanols. Nitrobenzene, Formic Acid. Ethylene Glycol
Medium	Water, DMF, NMP, Butanol. Acetonitrile. HMPA. Methy Ethyl Ketone. Acetone. Nitromethane. Dichlorobenzene. 1,2-Dichloroethane. Acetic Acid, trifluoroacetic Acid.
Low	Chloroform. DCM. Carbon tetrachloride. 1,4-Dioxane. EthyAcctate. Pyridine. Triethylamine. Toluene. Benzene. Chlorobenzene. Pentane. Hexane and other hydrocarbons.

3- Experimental:

Microwave oven was used with 2.5 GHz, control temperature with power 600watt as shown in Figure (2).



Fig. (2) Laboratory microwave

A modification on the cell a sample stand was added inside cell as shown in Figure (3) with 1” diameter, 2cm height, and 19 holes, each hole diameter 2mm.the benefit of sample stand is to prevent crude oil that extracted from the core to return into core sample again.

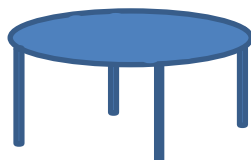


Fig. (3) Sample stand

3-1 Primary test

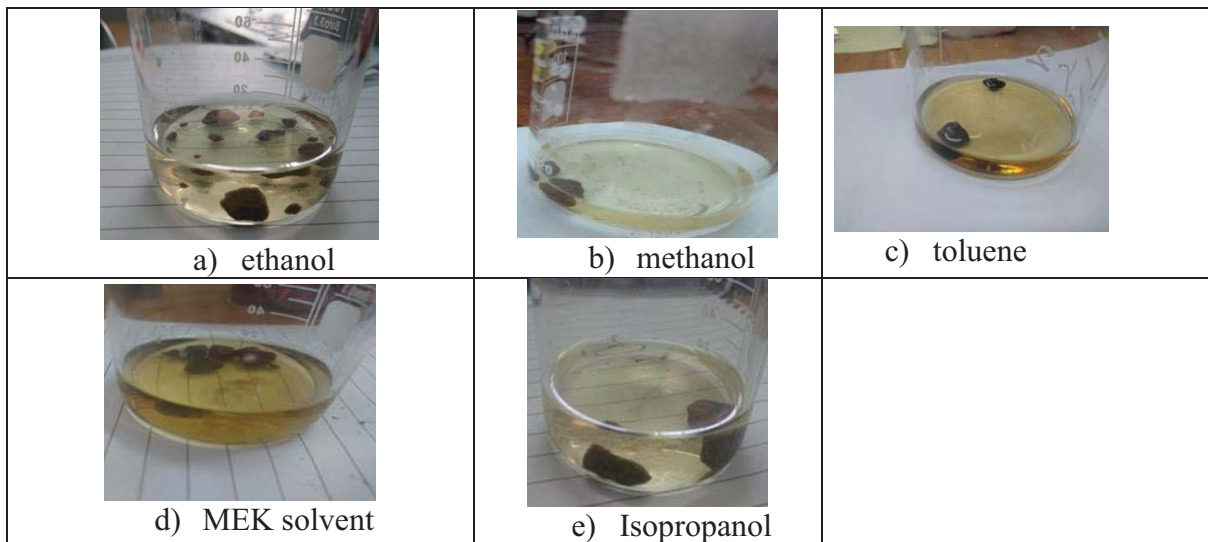
2g of Core sample was crashed and put into the cell of microwave oven and then 10 ml of toluene added, after that heated by microwave to 60°C for 15min. After heating, the samples cooled for 35 min. The cooling is very important, so that the solvent vapors condense. When opening the lids without complete cooling will lead to analytic loss.

3-2 Dielectric test

Different solvent with different dielectric constant used to show the effect of dielectric constant on the ability of these fluids to absorb the microwaves or not as shown in table (2) and figures (4a, b, c, d, and e). The solvents with volume 10ml for each cell and 1.1g limestone sample heated to 60 °C for 20min as hold time and 20min as ramp time. These conditions are based on certain physical properties of fluids, the most important of which is the electrostatic insulation, in addition to the fact that the fluid is polar or not, since polar liquids are more capable of absorbing microwave, but non-polar solvents are very weak and less importance in the term of crude oil extraction from rocks and prevent rocks damage. From experiment, it is concluded that toluene is the best solvent, due to it has medium dielectric constant, and show good ability in extracting oil from the rock by using the microwave.

Table (2) Dielectric constant and vapor pressure for solvents

Solvent	Dielectric constant	Vapor pressure (atm)
Acetone	20	1.13
Ethanol	24.5	0.46
Methanol	33	0.8
Toluene	2.4	0.197
Heptane	1.9	0.272
Hexane	5.8-6.3	0.75

**Fig. (4) Samples cleaned with different solvents****3-3 plug test**

Two Plugs samples taken from carbonate reservoir with properties in Table (3). After cleaning them with conventional method and drying, the samples saturated with crude oil (API 36) with vacuumed desiccator until weight of plug become constant, and then the plugs treated with microwave at 60°C, 600 watt with continuous operation for 3 hr. and 20ml toluene in each cell, and then samples dried and vacuumed then weighted.

Table (3) Plugs propertie

Sample name	depth (m)	permeability	porosity	Diameter * height	Weight (g)	Weight after saturation(g)
C7	4486.15	13.13 md	15.974%	1" * 5cm	29.37	31
C8	4527.1	1.63md	16.784%		32.7	33.3

The above procedure repeated with rising temperature to 100°C, and drying sample after operation at 100°C to remove toluene from the plug and then weighted.

3-4 Trimmed Sample

Two samples were taken from reservoir rock Figure (5) with natural saturation from depth 1837m with weights 9.107g and 9.4390g respectively, cleaned then by microwave with 10ml toluene for each cell. Rock sample dried after operation at 100°C to remove toluene from sample until the weight of rock sample become constant and the toluene completely removed.

**Fig. (5) Trims sample**

4- Result and Discussion:

The analysis of the hydrocarbon content of the cutting detected using FTIR which performed before and after the microwave treatment as shown in the following Figures (6, 7). FTIR absorption peaks for Hydrocarbons between 2800 and 3300 cm^{-1} due to C-H stretching vibrations. The position of substitution on a benzene ring can give characteristic absorptions at about 680-900 cm^{-1} [9].

In Figure (6) FTIR absorption peaks 697, 722 and 779, which refer to benzene ring after treatment with intensity lower than before treatment which characterized 694, 730 and 792 cm^{-1} in Figure (7), furthermore peak with wavelength 886 was disappeared after treatment.

For hydrocarbon absorption peaks before treatment due to C-H bond; 2835, 2925 in other hand, after treatment only 2916 cm^{-1} remained.

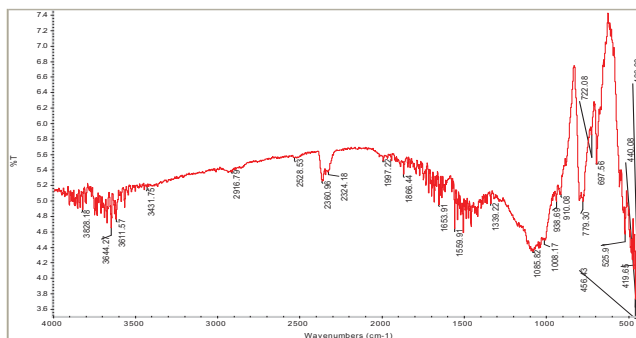


Fig. (6) FTIR Spectrum core sample after treatment

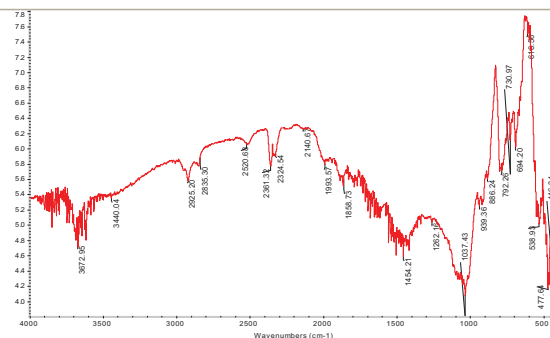


Fig. (7) FTIR spectrum core sample before treatment

4-1 appropriate solvent

The choice of the appropriate solvent is based on the ability of the solvent to absorb the microwave waves and the amount of raised temperature that follows it which effect on vapor pressure of the solvent; so many solvent selected with different dielectric constant and vapor pressure to detect the more suitable solvent.

Table 4 and Figures (8, 9) showed the effect of microwave on oil recovery for different solvent with different vapor pressure and dielectric constant at operation temperature.

Table (4) Solvents properties and oil recovery

solvents	Dielectric constant	Oil recovery %	Vapor pressure mmHg
methanol	33	12	81.06
ethanol	24.5	55	46.6095
acetone	20	81	114.49725
MEK	18.5	70	35.970375
ccl4	17	35	52.689
hexane	6	43	75.99375
toluene	2.4	65	19.961025

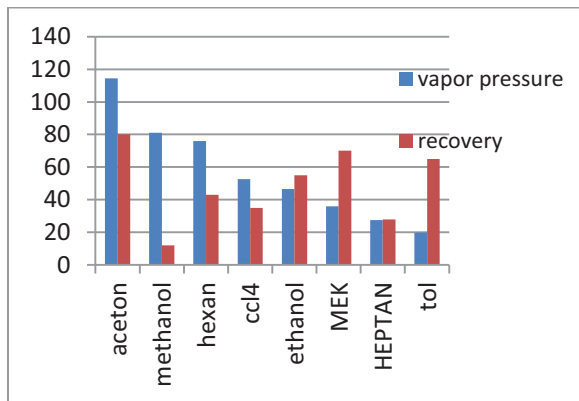


Fig. (8) Comparison between vapor pressure and recovery versus solvent type

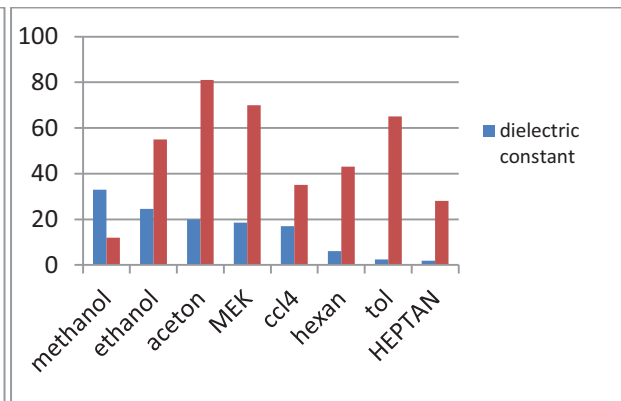


Fig. (9) Comparison between dielectric constant and oil recovery versus solvent type

In view of low dielectric constant for non-polar solvents, it has been used to extract hydrocarbon compounds from the rock by using microwave device which showed good ability in the extraction [10]. Through experiments many solvents used with different dielectric constant it is seen that it is direct proportion with the rate of extraction due to increasing the ability of solvent to transfer and storage microwave energy. Thus, sample temperature rising gradually and homogeneously to maintain the temperature of the sample within the desired range at 100°C [11]. Solubility of organic compounds is purely depends on its polarity. So that to dissolve nonpolar organic compounds it is necessary to use nonpolar or low polarity solvents. So it is better to use the methyl compounds like (toluene, ketones) than using hydroxyl compounds like (methanol, ethanol). Therefore the toluene was preferred due to very low polarity and low vapor pressure lower than Ketones; Furthermore methanol and ethanol have inability to control on its temperature (i.e. rapidly losing temperature), so that it is excluded; furthermore, it is non- environmental friendly

4-2 Temperature effect

Extraction of crude oil by microwave at temperature 60°C, showed that polynomial relation between oil recovery and time as shown in table 5 and Figures (10, 11). Two carbonate plugs with different permeability, it is show with increasing permeability, the time of recovery will decrease.

Table (5) Plugs weight after each run at 60°C

time	Weight (g)	
	C8	C7
0	31	33.3
1	30.96	33.26
2	30.76	33.18
3	30.57	33.14
4	30.54	33.14
5	30.35	33.1
9	29.63	32.83
12	29.55	32.82
15	29.47	32.76
18	29.439	32.751
21	29.4	32.74
24	29.39	32.73
27	29.38	32.7
28	29.37	32.7
30	29.37	32.7

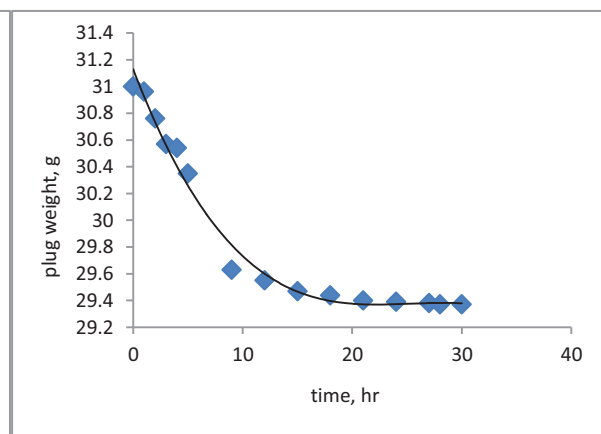
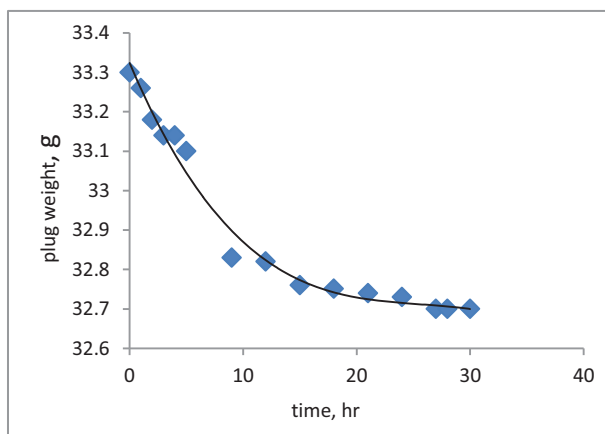


Fig. (10) Oil Recovery versus time at 60°C

Fig. (11) Oil Recovery versus time at 60°C

At high temperature (100°C); solubility increased, because viscosity and surface tension decreased, so that less time for recovery observed and diffusion of crude from high concentration to low concentration become easier.

In Table 6 and Figures (12, 13) at 100°C, the sample weight decreased sharply during the first 5 hours comparing with experiments that processed at temperature 60 °C where samples weight decreased gradually and stabled relatively after 15 hours.

Increasing in temperature of the samples result in evaporating water molecules which rise oil temperature and decrease viscosity so that the the oil simply have transfered from the rock to the solvent.

Table (6) Plugs weight after each run at 100°C

Time hr	weight (g)	
	C8	C7
0	30.88	33.25
3	29.96	32.9
6	29.68	32.81
9	29.53	32.78
15	29.45	32.74
18	29.42	32.72
21	29.39	32.71
24	29.37	32.7

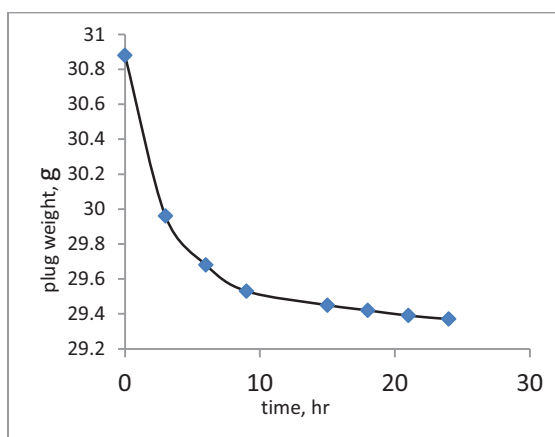


Fig. (12) Oil Recovery versus time at 100°C

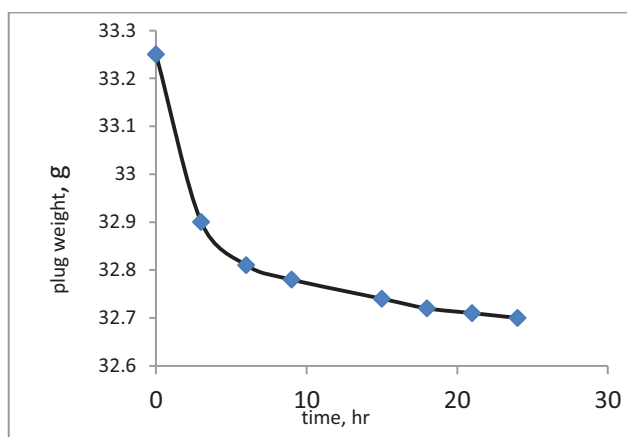


Fig. (13) Oil Recovery versus time at 100°C

Microwave extraction showed higher recovery at 100° C, than traditional method at 110°C, so that extraction by microwave considered appropriate. Water content in the rock is also raised extraction rate by raising the solvent vapor pressure, thus increase absorptivity of

microwaves.

The effect of power on temperature rising during microwave operation for the four samples was cleaned by microwave, where the number of samples in the oven has an effect on the time of heating until the maximum temperature since the global power is kept constant. As the number of samples increases, the power for each sample decreases [3] Table 7 and Figure (14); Therefore, the care should be taken into account for selected a suitable instrument by coinciding the microwave power with the number of samples.

Table (7) Microwave power against sample temperature

Power(watt)	Temp. (K)
600	73
800	91
900	95
1000	99.9
600	73
800	91

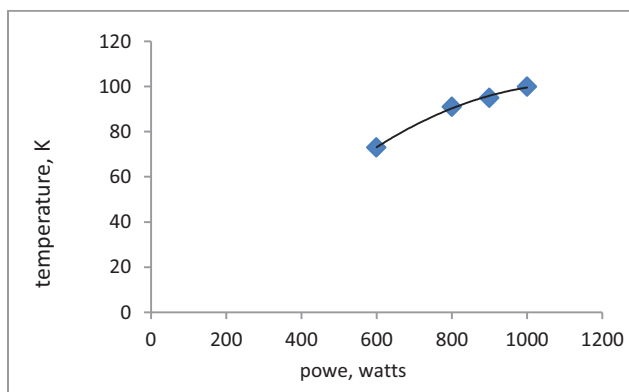


Fig. (14) Power effects on temperature

The natural saturated samples showed the same extraction manner with the artificial saturated samples Table 8 and Figures (15, 16 and 17), but with less time because it is lower saturation than artificial saturated samples as shown in Figures (15, 16).

Table (8) Weight of natural saturated samples after each run

Time hr	w1(g)	w2(g)	w3 (g)	w4(g)
0	9.1079	9.439	3.3852	3.3619
3	8.78	9.17	3.28	3.29
6	8.727	9.106	3.25	3.26
9	8.67	9.042	3.25	3.24
12	8.64	9.03	3.25	3.24
18	8.64	9.03	3.25	3.24

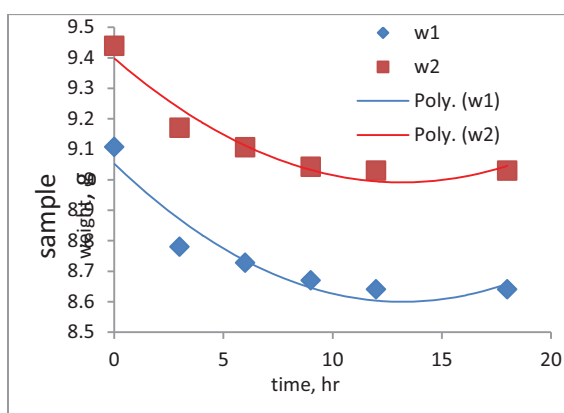


Fig. (15) Oil Recovery against time for natural saturation

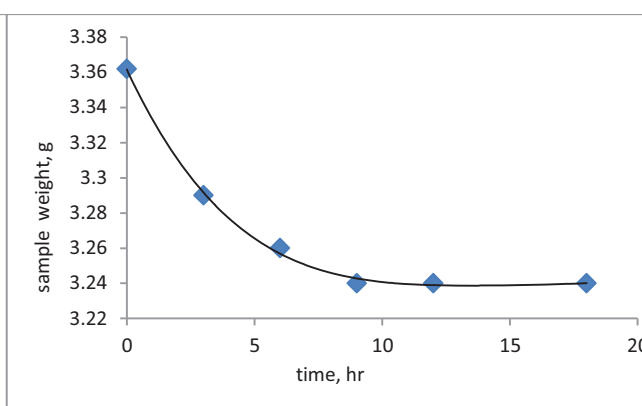


Fig. (16) Oil Recovery against time for natural saturation

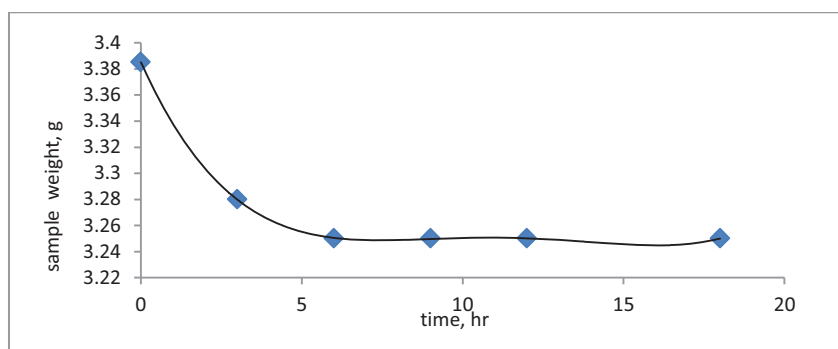


Fig. (16) Oil Recovery against time for natural saturation

4-4 comparison between conventional extraction method and MIE

The main target of all experiments and comparisons between microwaves technique and classic method (Soxhlet extractor) are shown in Table (3); the main advantage of microwave is decreasing cost and time relative to soxhlet extractor, also save the time by

takes a chance for extract many samples in short time with high efficiency. Microwave prevents fumes of solvents to spread in lab environment so keep approximately all amounts of solvents (toluene) and crude oil in core sample. However, the soxhlet extractor method needs more amounts of solvent (toluene) due to the evaporation of toluene in lab, which is considered as non-friendly method.

Table (9) Compression between conventional method and microwave technique

Method target	Conventional method (soxhlet/extraction)	Microwave oven
Extracted time	4.66 as ratio	
Amount solvent used	5 as ratio	
environment hazard	non-friendly environmental	environmental friendly
Sample safer	may cause damage	Safe sample from damage
Extracted oil	useless	useful in deep study for crude oil

A number of parameters (such as time, cost, environment, workers health, lab, and instruments...etc.) have a real role in chose between microwave technique and classic method. Microwave shows keeping all crude oil compounds which may be useful in deep study for crude oil finger-print region. On the other hand, soxhlet extractorshow evaporation in light compounds in crude oil which extracted so cannot take a finger-print region of crude oil.

Economic and technical feasibility:

One of important parameter to improve the advantage of new technique (microwave) is the economically parameter which was very clear as shown below in Table (10), and it is also very important to remember the environmentally role for microwave technique and soxhlet need twice more than microwave of power consumption and need more technical details like chiller and more desktop bench with especial hood to more efficiency exhaust for emissions in microwave just instrument bench may be very sufficient with simply laboratory hood for very small quantities of emissions.

Table (10) Economic and technical feasibility of microwave compared with soxhlet

	microwave	Soxhelt
ID/1lit oil extracted	36000	54000
Power consumption	15 Amp.	40Amp
Environmental hazard	Environmental friendly (no emission)	Non friendly (high emission)
safety	More safety to use	less

5- Conclusion

- 1- Microwave assisted extraction approved its efficiency by decreasing time of cleaning up to less than quarter compared with conventional method;
Furthermore, it is more economical relative to conventional methods because it is the less consumption of solvent and safer by discharge the vapors out of the laboratory through special ventilation technique.
- 2- Another advantage of MIE is saver for sample due to mixing that result from microwaves which distribute the temperature inside the cell.
- 3- The extracted oil properties by microwave can studied compared with Soxhlet extractor oil because get residue with high molecular weight so all light compounds evaporate however residue may be not useful (useless).
- 4- The overall work was to find an innovative and economical way to apply real samples. The choice of microwaves was the most suitable solution for treating rock samples containing crude oil by using microwave that give the crude oil the thermal energy necessary to reduce its viscosity.
- 5- The energy of microwave is high enough to penetrate the non-polar solvent (toluene) and raise the pressure inside the rock by raising the heat of the water molecules within the rock and thus help push the crude oil through the pores out of the rock.
- 6- Toluene is the best solvent, due to it has medium dielectric constant and show good ability in extracting oil from the rock by using the microwave.

References:

1. **Chemat , F, Abert-vian, M and Zill-e-Huma, Y-J.** Microwave assisted separations: green. 2009, pp. 33-62.
2. *source identification of volatile organic compounds.* **Zhao, W, Hopke, P and Karl, T.** 1338, s.l. : Environ. Sci. Technol, 2004, Vol. 38. 47.
3. **Lopez-Avila, V, Young , R and Beckert, W.** Micro- wave-Assisted Extraction of Organic Compounds from Standard Reference Soils and Sediments. 1994, Vol. 66.
4. **Dzieraba, D and Combs,, P.** *Microwave assisted chemistry as a tool for drug discovery.* s.l. : Annual reports in medicinal chemistry, academic press,, 2002.
5. **WELLS, M.** Principles of extraction and the extraction of semivolatile organics from liquids. [book auth.] Somenath Mitra. *Sample Preparation Techniques in Analytical Chemistry.* s.l. : John Wiley & Sons, Inc, 2003.
6. **Piñero-Iglesias, M, et al., et al.** Microwave assisted extraction of polycyclic aromatic hydrocarbons from atmospheric particulate samples. 2000, Vol. 367, 1.
7. **Thostenson, ET and Chou, TW.** Microwave processing: fundamentals and applications. *Composites Part A: Applied Science and Manufacturing.* 9, 1999, Vol. 30, pp. 1055-1071.
8. **Raval,, C.** Studies on some Heterocyclic Compounds of Pharmaceutical Importance. 2012.
9. **Schrawts, M.** Interpretation Of Infrared Spectra. <http://ocw.umb.edu/chemistry/organic-chemistry-i-lecture/lecture-links/notes92208.pdf>. [Online] 2008.