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INTENSIFICATION OF SHALE OIL EXTRACTION FROM OIL SHALE – AN ALTERNATIVE SOLUTION FOR SUSTAINABLE ENERGY IN JORDAN

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Abstract

The present study proposes a prototype comprising a set of unit operations for the intensification of shale oil extraction from Jordanian oil shale. The extraction process involves the utilization of microwave irradiation, ultrasound irradiation and solvent extraction as tools for process intensification. Full factorial design methodology of type 2^4 was applied to study the main and interaction effects of process variables. The extent of extraction of shale oil was found to be strongly affected by the power of microwave and time of microwave irradiation with an appreciable interaction effect. At optimized conditions, the extent of extraction of shale oil was 38.8%. A first-degree polynomial model was employed to correlate the extent of extraction to the process input variables and their interactions.

Keywords: Factorial design, Microwave, Oil shale, Shale oil, Ultrasound.

1. Introduction

Jordan is one of the top leading countries in terms of oil shale resources. About 50 billion tons of oil shale deposits are available in Jordan [1]. It is expected that Jordan will utilize the oil shale for energy production to reduce its dependency on fossil fuel [2].

There are two ways for the beneficiation of oil shale for energy production. It has been proposed that oil shale might be utilized via direct combustion to generate the required energy to run power plants [3-5]. Alternatively, shale oil can be extracted or retorted from oil shale then upgraded to various fuel fractions. The average oil content of oil shale is generally in the range of 5.7-10.5% based on Information from boreholes drilled in the area of different deposits of oil shale in Jordan [6]. The reported oil content is based on the Fischer assay analysis.

The organic matters in oil shale are basically organic solvents soluble bitumen and insoluble kerogen. Kerogen can be retorted by heating to produce combustible gases, crude shale oil, and a solid residue. Hrayshat [7] explained that Jordanian oil shale is characterized by the presence of many foraminifers' shells instead of the usual calcite. These shells are filled with bitumen or kerogen. Therefore, kerogen can be extracted from the oil shale only after its thermal or chemical decomposition [8].

Many attempts have been made for the extraction of shale oil from oil shale using conventional and advanced extraction techniques. For example, solvent extraction [8-12], froth flotation [13], supercritical extraction [14], ultrasound-assisted extraction [15], microwave-assisted extraction [16] and microwave heating for extracting oil from oil sands [17].

The combination of two or more conventional unit operations within one prototype may lead to a synergistic effect on process performance. Looking for a synergistic effect among all the conventional unit operations involved is considered an important aspect for process development and intensification [18]. Based on studies by Stankiewicz, and Moulijn [19], microwave and ultrasound irradiation has been viewed as process intensification methods.

Process intensification by ultrasound irradiation can promote mass transfer increase among liquid-solid systems by 20-25 fold [18]. This mass transfer enhancement by ultrasound irradiation will eventually enhance the extractability of oil shale via liquid-solid operation such as solvent extraction. The effect of ultrasound irradiation might be attributed to the acoustic cavitations generated by the interaction of the sound waves with the compounds resulting in intense mixing in the system. Thostenson and Chou [20] explained that microwave irradiation delivers directly the energy to the system via conversions of electromagnetic energy into thermal energy.

The combined synergism of microwave and ultrasound effects has not been explored for shale oil extraction from oil shale. In this work, a framework of unit operations is proposed to recover the organic matter from the oil shale. Several unit operations are combined sequentially or simultaneously for shale oil extraction from oil shale. A full factorial design methodology is employed to study the main effects of process variables and possible interaction effects among the process variables on the percentage of extraction of shale oil. Finally, a regression model is proposed to correlate the extent of extraction to the operating conditions.

2. Experimental

Oil shale was obtained from El-lajjun region in southern Jordan. The oil shale was crushed then sieved to different size fractions. In this study, a particle size fraction of 1-1.4 mm was used. Prior to experimentation, the oil shale particles were dried in an oven overnight at 105 ^{o}C to remove the moisture. Figure 1 shows a flow diagram for the procedure followed for the extraction of shale oil.

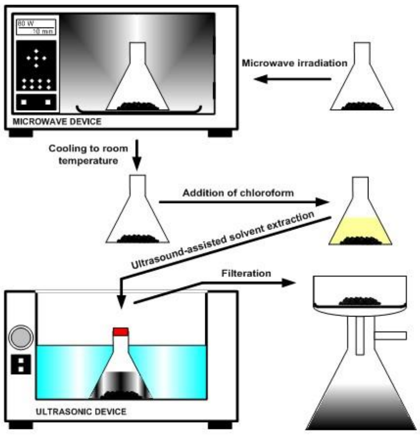

Fig. 1. Experimental procedure for shale oil extraction.

The typical procedure involved weighing 20 g of dried oil shale in 250 ml Erlenmeyer flask and subjecting the flask to microwave irradiation either at 20, 50 or 80 % of the maximum irradiation capacity for a prescribed time. Microwave irradiation was provided by using a kitchen microwave oven (maximum irradiation capacity 800 W). After microwave irradiation, the sample was left for 15 min to cool down to room temperature. Less than 3 wt % loss of sample weight was noticed after microwave irradiation. The temperature of samples after the microwave irradiation could not be immediately measured. However, based on the weight loss measurements and TGA measurement reported in the literature [16] for similar samples, it is believed that the temperature were in the range of 150-200 ^{o}C. During this temperature rise, the loss in sample weight corresponds mainly to the loss of all type of water (structural, associated and free water). Typical values for the total water in similar samples are ~ 2 wt% [7, 16]. The remaining loss in sample weight is attributed to the release of trapped gases. Therefore, microwave irradiation under the studied operating conditions is unlikely causing a loss in the amount of shale oil.

After the microwave irradiation, a prescribed amount of chloroform solvent then was added to the sample. Chloroform has been reported in the literature as a suitable solvent for oil shale salvation [12]. The solvent extraction process was conducted under ultrasound irradiation for a prescribed time. Ultrasound irradiation was provided by using an ultrasonic cleaner device (38 kHz). No mechanical mixing was used in this study. It is recommended that for large scale operation to carry out simultaneously both mechanical mixing and ultrasound irradiation. After extraction, the spent oil shale was filtered by using low ash-content filter paper. During filtration, methanol was added successively to wash the particles for complete removal of solvent and oil. The filtered oil shale was dried in an oven overnight at 105 °C, and then weighted. The Extent of Extraction (EE) was estimated as follows:

$$EE = \frac{w_o - w_f}{2.4} \times 100 \qquad (1)$$

where the w_o is the weight of the sample after microwave irradiation, w_f is the final weight of oil shale and 2.4 is the amount of shale oil that can be obtained from 20 g oil shale based on Fischer assay analysis (12 wt% oil content).

3. Experimental Design and Statistical Analysis

Full factorial design methodology was applied to study the effect of four factors (process input variables), namely: power of microwave irradiation (X_1), Microwave irradiation time (X_2), ultrasound-assisted solvent extraction time (X_3) and mass of oil shale to solvent volume ratio (X_4) on extent of extraction (*EE*) being the response. The levels of selected factors are summarised in Table 1.

Factorial design of type 2^4 with three centre points was used to study the effect of the process input variables on the response. According to Montgomery [21], experiments were run in random order to minimize the effect of unexpected variability in the observed responses. The data were subjected to Analysis of Variance (ANOVA) to examine the effect of input process variables and their potential interaction effects on the extent of extraction.

A first-order polynomial model with interaction terms was used to fit the data. Statistical software (MINITAB 17) was used to analyse the results of the experimental design, namely: the effects, the statistical parameters, and the statistical plots (main effects, interaction plots, Pareto plot, and normal probability plot of the standardized effects).

Table 1. Test model specifications and test conditions.

Factor	Low level (-1)	Center point (0)	High level (+1)
X_1	20 %	50 %	80 %
X_2	5 min	7.5 min	10 min
X_3	5 min	7.5 min	10 min
X_4	(20/100) g/ml	(20/150) g/ml	(20/200) g/ml

4. Results and Discussion

Table 2 shows the extent of extraction of shale oil for all runs based on the full factorial design of type 2^4 with three centre points. The results shown in Table 2 indicate that the extent of extraction for samples under the same experimental conditions exhibited high reproducibility. This can be reflected by the low value of standard deviation as the data points are close to the mean. However, few data points exhibited high values of standard deviation, namely: data points of experimental conditions 2, 10, 12 and 14. These data are common in the experimental condition of using (20 g of oil shale /200 ml solvent). The use of a large volume of the solvent caused high variability in the extent of extraction. The large volume of solvent might cause variability in the effect of ultrasound irradiation. More elaboration will be given later in this paper upon discussion possible interaction effects between these parameters.

Table 2. Experimental design matrix with experimental values for extent of extraction of shale oil from oil shale.

	Experimental conditions				Extent of extraction (%)				
No.	X_1	X_2	X_3	X_4	**Run 1**	**Run 2**	**Run 3**	**Average**	**Standard deviation**
1	-1	-1	-1	-1	13.75	13.75	12.92	13.47	0.48
2	-1	-1	-1	+1	16.67	8.75	22.92	16.11	7.10
3	-1	-1	+1	-1	2.92	2.92	3.33	3.06	0.24
4	-1	-1	+1	+1	35.83	31.67	31.25	32.92	2.53
5	-1	+1	-1	-1	20.83	18.33	23.33	20.83	2.50
6	-1	+1	-1	+1	32.08	32.08	30.42	31.53	0.96
7	-1	+1	+1	-1	22.92	20.83	23.33	22.36	1.34
8	-1	+1	+1	+1	15.83	14.58	15.00	15.14	0.64
9	+1	-1	-1	-1	22.92	32.50	31.67	29.03	5.31
10	+1	-1	-1	+1	4.17	8.33	5.00	5.83	2.20
11	+1	-1	+1	-1	27.92	21.67	19.58	23.06	4.34
12	+1	-1	+1	+1	7.92	9.58	3.75	7.08	3.00
13	+1	+1	-1	-1	19.58	22.08	20.00	20.56	1.34
14	+1	+1	-1	+1	4.17	12.50	7.92	8.19	4.17
15	+1	+1	+1	-1	15.42	22.50	23.33	20.42	4.35
16	+1	+1	+1	+1	27.08	23.75	24.17	25.00	1.82
17	0	0	0	0	37.50	39.17	39.17	38.61	0.96

Table 3 shows the analysis of variance of data and gives the estimated effects of variables and their associated coefficients.

The significance of each coefficient was determined using p-value ($p < 0.05$) and the smallest p-value indicates the high significance of the corresponding coefficient. The results revealed that both the power of microwave irradiation (X_1) and microwave irradiation time (X_2) have a significant effect on the extent of extraction within 95% confidence level. In addition, a significant interaction effect exists among variables. The results indicate that significant two-, three-, and four-factor interaction exists between variables within 95% confidence interval.

The absolute effect of microwave irradiation time (4.184) was almost double the absolute effect of the power of microwave irradiation (-2.031) on the extent of extraction. The results show that increasing the power of microwave irradiation from 20 to 80 % decreased the extent of extraction from 20 to 17 %. In contrast, increasing the exposure time of microwave irradiation from 5 to 10 minutes, increased the extent of extraction from 16 to 21%.

Scanning electron microscopy of oil shale samples obtained from the same deposit as this study indicated that shale oil are encapsulated within mineral shells [12, 22, 23]. Al-Harahsheh et al. [24] proposed that these minerals upon subjection to high power microwave heating, exhibit high dielectric loss factor values, thereby, causing thermal runaway in the oil shale. This sharp heating in the oil shale caused carbonization of the organic matters encapsulated within the mineral shells.

Table 3. Estimated effects and coefficients for the extent of extraction of shale oil from oil shale.

Term	Effect	Coefficient	SE Coef	T-value	P-value
Constant		18.411	0.456	40.37	0.000
X_4	1.372	-0.686	0.456	-1.5	0.142
X_3	0.434	0.217	0.456	0.48	0.637
X_2	4.184	2.092	0.456	4.59	0.000
X_1	-2.031	-1.016	0.456	2.23	0.033
X_4*X_3	4.184	2.092	0.456	4.59	0.000
X_4*X_2	0.295	0.148	0.456	0.32	0.748
X_4*X_1	-10.37	-5.182	0.456	-11.36	0.000
X_3*X_2	0.017	0.009	0.456	0.02	0.985
X_3*X_1	2.552	1.276	0.456	2.8	0.008
X_2*X_1	-1.892	-0.946	0.456	-2.07	0.046
$X_4*X_3*X_2$	-4.427	-2.214	0.456	-4.85	0.000
$X_4*X_3*X_1$	1.858	0.929	0.456	2.04	0.050
$X_4*X_2*X_1$	7.552	3.776	0.456	8.28	0.000
$X_3*X_2*X_1$	5.33	2.665	0.456	5.84	0.000
$X_4*X_3*X_2*X_1$	6.858	3.429	0.456	7.52	0.000
Ct Pt		20.2	1.88	10.74	0.000

It is worth mentioning that there is an appreciable interaction effect between the power of microwave interaction and the time of microwave irradiation. This effect can be visualized by constructing the interaction plot shown in Fig. 2.

The interaction plot shows the effect of one parameter at two levels of another parameter. If the effect of parameter is different for both levels of the other parameter, then an interaction effect exists between the two parameters. The interaction between power of microwave irradiation and the time of microwave irradiation has a negative value (-1.892). The negative value of interaction indicates that the effect of power of microwave irradiation does not effectively change the extent of extraction at lower time of irradiation (5 min).

However, the power of microwave irradiation is strongly and reversibly affecting the extent of reaction at higher time of irradiation (10 minutes). Oil shale subjected to long exposure to high power microwave irradiation will deliver more thermal energy to the system, which might cause shale oil degradation or carbonization.

The interaction plots are shown in Fig. 2 also indicate the presence of antagonistic interaction between X_1 and X_4 and another one between X_3 and X_4. Samples of oil shale treated with low power microwave irradiation exhibited an increase of extent of extraction with increasing the solvent volume. This might be explained by the fact that the use of larger solvent volume will induce more solvation for the shale oil.

In addition, the effect of ultrasound irradiation in promoting shale oil extraction was more pronounced at 20 g sample/200 ml than at 20 g sample/100 ml. This might be attributed to sonication effect through a promotion in the mass transfer between the liquid-solid systems.

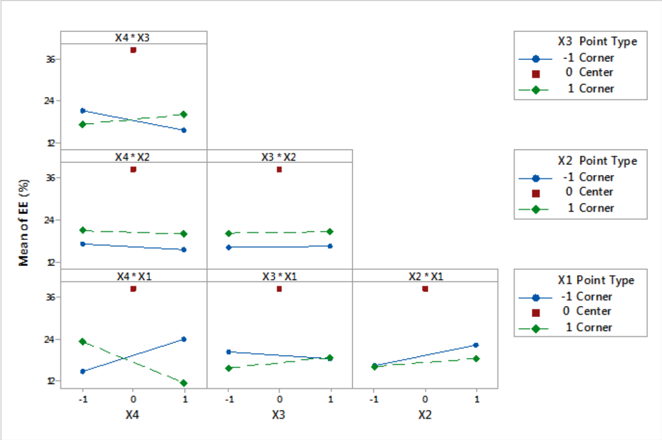

Fig. 2. Interaction plots for process variables.

Figure 3 shows the normal probability plot.

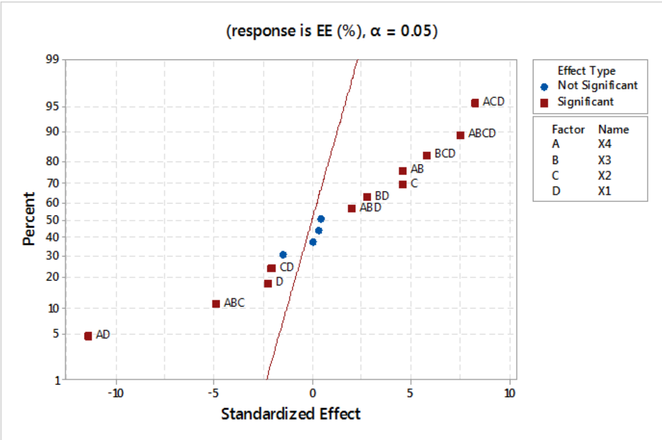

Fig. 3. Normal probability plot of standardized effects.

The normal probability plot identifies whether the results are real or chance. It also identifies the unimportant effects. The factors X_1 and X_2 and their interactions were far away from the straight line representative of the normal distribution and are therefore, considered to be “real”. Because X_1, X_4X_1, $X_4X_3X_2$, and X_2X_1 lie to the left of the line, their contribution had a negative effect on the extent of extraction. On the other hand, X_2, $X_4X_2X_1$, $X_4X_3X_2X_1$, $X_3X_2X_1$, X_4X_3, X_3X_1 and $X_4X_3X_1$ lie on the right of the line, indicating that contribution had a positive effect on the extent of extraction. Among parameter main effects, the time of microwave irradiation had the largest effect because its point lies farthest from the line. These results from the normal probability plot are in agreement with those shown in Table 2.

The relative importance of the main effects and their interactions can be also be visualized by the Pareto chart (Fig. 4).

To make a statistical comparison of the importance of factors, a limit value based on t-test was estimated to be 2.03 for 95% confidence level than compared to the absolute value of effects. Any effect that has an absolute value larger than 2.03 can be considered statistically important. Figure 4 indicates that X_1, X_2 and ten other interactions effects are statistically important effects. However, X_3, X_4, and three other interaction effects are statistically unimportant effects.

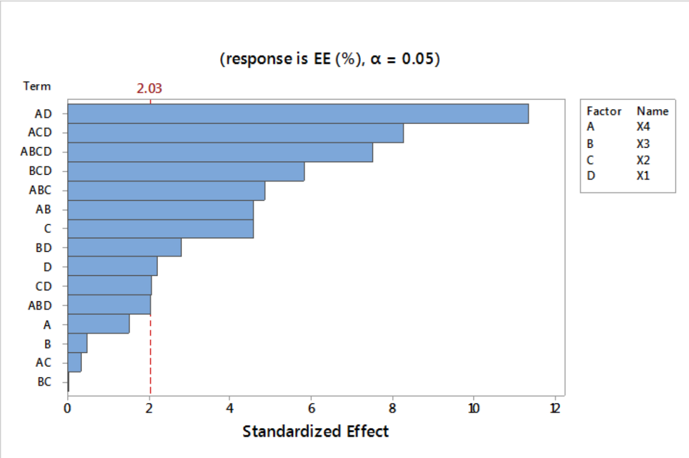

Fig. 4. Pareto chart of the standardized effects.

Three-dimensional response surface for the extent of extraction as a function of the power of microwave irradiation and time of microwave irradiation is given in Fig. 5.

The strong interaction among process variables shows a significant curvature in the extent of extraction. The three-dimensional response surface for the extent of extraction as a function of the power of microwave irradiation and time of microwave irradiation (Fig. 5) enables identifying the optimum conditions for maximum shale oil extraction. Maximum extent of extraction was obtained when the operating conditions are at their central levels.

Processing 20 g of oil shale with medium power of microwave radiation for 7.5 min, then extracting the shale oil with 150 ml solvent under ultrasound irradiation for 7.5 min enabled extracting 38.8% of the shale oil. This extent of extraction is higher than those reported under ultrasound-assisted solvent extraction alone or microwave-assisted solvent extraction alone. Information from literature indicated that ultrasound-assisted solvent extraction could extract 90% of the bituminous fraction of shale oil [15], and microwave-assisted solvent extraction exhibited the maximum extractive capacity of about 23% of shale oil [16].

The amount of shale oil obtained in this study is more than the amount of bitumen in the oil shale, indicating that the extracted shale oil is from both bitumen and kerogen.

A first-order polynomial model was developed to correlate the dependency of the extent of extraction on the process input variables. All process input variables and their possible interaction were included in the empirical model. The analysis of variance and regression of data gave the following best-fit equation in terms of coded values of the variables:

$$
\begin{aligned}
EE = 18.411 - 0.686X_4 + 0.217X_3 + 2.092X_2 - 1.016X_1 \\
+2.092X_4X_3 + 0.148X_4X_2 - 5.182X_4X_1 \\
+0.009X_3X_2 + 1.276X_3X_1 - 0.946X_2X_1 \\
-2.214X_4X_3X_2 + 0.929X_4X_3X_1 + 3.776X_4X_2X_1 \\
+2.665X_3X_2X_1 + 3.429X_4X_3X_2X_1 + 20.2C_tP_t
\end{aligned} \qquad (2)
$$

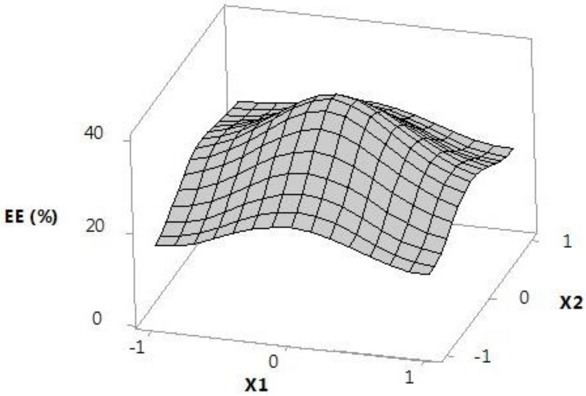

Fig. 5. Three-dimensional response surface for extent of extraction as a function of power of microwave irradiation and time of microwave irradiation.

Figure 6 shows a comparison between the experimental values with model predicted values.

The fit of the model was evaluated by considering the value of the coefficient of determination (R^2), which was found to be 0.935. This value indicates that 93.5% of the variability in the extent of extraction could be explained by the empirical model. The value also indicates that 6.5% of the total variation was not explained by the model. The higher value of the correlation coefficient (R = 0.967), indicates a strong strength and linearity between the independent variables and the dependent variable. The value of the adjusted coefficient of determination (Adj = 0.905) is fairly adequate to indicate the suitability of the model.

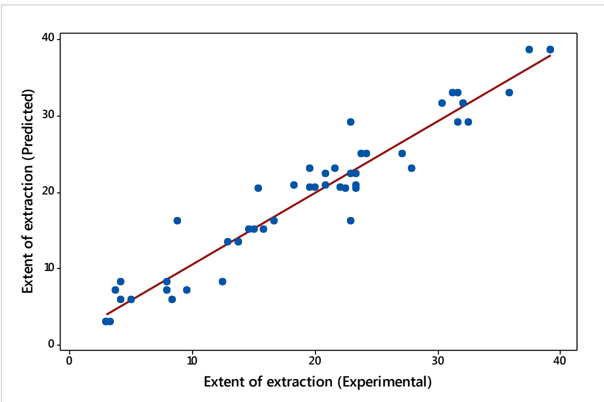

Fig. 6. Predicted values versus experimental values.

4. Conclusions

A framework of sequential and simultaneous unit operations was successfully implemented to extract shale oil from Jordanian oil shale. The effect of operating conditions was examined by applying a full factorial design methodology. The design-of-experiment approach was able to reveal the existence of interaction effects between process variables.

- At 95% confidence level, the main influential parameters on the extent of extraction were the power and time of microwave irradiation.
- Low (20%) and medium (50%) power of microwave irradiation enabled the high extent of extraction of shale oil.
- High (80%) power of microwave irradiation was not appropriate for the recovery of shale oil from oil shale.
- Ultrasound irradiation effectively promoted the solvent extraction of shale oil when high solvent volume to oil shale mass ratio was employed.
- A regression of the first order polynomial model was successfully developed to correlate the dependency between process input variables and the extent of extraction.

Nomenclatures

EE	Extent of extraction, %
w_f	Final weight of oil shale, g
w_o	Weight of sample after microwave irradiation, g
X_1	Power of microwave irradiation, %
X_2	Microwave irradiation time, min
X_3	Ultrasound-assisted solvent extraction time, min
X_4	Mass of oil shale to solvent volume ratio, g/ml

Greek Symbols

α	Significance level

Abbreviations

ANOVA	Analysis of variance

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