

GREEN PROCESS FOR SIMULTANEOUS EXTRACTION OF OIL SHALE AND ENRICHMENT OF ETHANOL

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Pure ethanol and its mixtures with water were used as extraction solvents for two Israeli's oil shales. Using bioethanol-like mixtures to produce organic matter from oil shales made the extraction process environmentally friendlier, while simultaneously enriched the ethanol to a level that it can be used as a fuel. It was found that oil shale characteristics, such as organic and water content and particle size, as well as extraction parameters such as shale loading and mixing speed, were found to highly affect the extraction yield. Under optimum conditions up to 8 wt% of organic matter was extracted by ethanol.

Introduction

Oil shales are an important future substitute to crude oil [1–3]. Although these organic-rich sedimentary rocks can be used directly as solid fuels and burned to generate electricity, they have gained strong interest as possible source for the extraction of hydrocarbon mixtures. The organic part of the oil shale is generally divided into kerogen, an insoluble macromolecular mixture that has to be broken down in order to be liquefied, and a soluble portion, which is usually between 10–20 wt% of the organic matter, also known as bitumen. Kerogen is a complex solid mixture of large organic molecules and its composition can greatly vary from sample to sample. Bitumen is made of the same kind of molecules as crude oil, but in different proportion. It contains paraffins, cycloalkanes, aromatics and hetero-aromatics with nitrogen, sulphur and oxygen atoms.

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The most common method to produce synthetic crude oil from oil shale is high-temperature pyrolysis (i.e. retorting) [1, 4, 5], a method extensively studied [6–10]. Since pyrolysis requires relatively high energy input, it is economically feasible only for oil shales containing a high organic fraction. Hence, there is high interest in finding alternative methods that operate near ambient temperature to convert kerogen into soluble products.

Recently, attention has been focused on solvent extraction as a general method, which may provide a commercially feasible process for the treatment of oil shales [1, 11, 12]. Considerable effort has been directed towards selection of an appropriate solvent or mixture of solvents for this purpose, including aromatic and aliphatic hydrocarbons, alcohols, amines, ethers, esters, and chlorinated hydrocarbons [11, 12]. Although kerogen in oil shale is relatively insoluble in most organic solvents at their normal boiling point, it can be extracted when oil shale is heated to temperature above 600 K, whereas bitumen can be extracted by various organic solvents also at low temperatures (near ambient temperature). Supercritical extraction of oil shales with several organic solvents as well as water has also been studied [13–15]. Integration of chemical or physical processes like hydrolysis [16] or microwave [17, 18] and ultrasonic [12, 19] power during the extraction process was found to increase the permeability of the extraction solvent and also the overall extraction yield. Extraction of organic matter from oil shales requires a high amount of hazardous organic solvent that has to be evaporated afterwards, using a high amount of energy. Therefore it is important to search for an environmentally friendlier extraction solvent and ways to utilize the extracted organic matter more efficiently.

Bioethanol is an important alternative fuel to the gasoline [20–22]. It is a renewable fuel generated by fermentation of starch or sugar from a wide variety of crops. It was used at the beginning of the car industry but due to lower price of gasoline it was pushed aside. The increase in oil prices and global concern about the negative effects of emission of greenhouse gases has led to think about producing biofuels from plant forms that extract carbon dioxide from the atmosphere. Since the energy per unit volume of ethanol is 34% lower than for gasoline, ethanol is usually enriched before being used as fuel and different mixtures of ethanol and gasoline are commonly used for compensation [22].

It seems that using bioethanol as the extracting solvent to produce organic matter from oil shales combines the advantages of making the extraction process greener while simultaneously enriching the bioethanol to a level that it can be used as a fuel. Thus, in this paper we have studied the extraction of hydrocarbons from two different types of Israeli's oil shales by ethanol and mixtures of water and ethanol, which resemble to the composition of water in bioethanol, to increase their caloric value as potential biofuels. The effects of different types of oil shales, their organic and water content as well as extraction parameters on the overall extraction yield were examined.

Experimental

Characterization of oil shales

The oil shales originate from the Rotem plain in the southern side of Israel and were provided by PAMA (Energy Resources Development) Ltd, Israel.

Organic content of oil shale

The percentage of total organic compounds in the oil shale was determined using the PAMA standard method based on oxidation of the oil shale with K_2CrO_7 followed by reduction of the excess of the oxidant with Fe^{+2} . 0.1 g of oil shale and 20 mL of 0.2 N solution of K_2CrO_7 were added to a 150 mL glass and heated at 100 °C for 2 h on a heating plate until all the water was evaporated. Then, 10 mL of 98% H_2SO_4 was added to the glass. The mixture was mixed, heated up to 175 °C and then cooled down to a room temperature by adding 100 mL of distilled water. Then, the mixture was titrated with a 0.1 N Fe^{+2} solution to determine the residual K_2CrO_7 and the amount of the organic matter.

Thermal analysis

Thermal analysis of the oil shale and enriched ethanol after extraction of organic matter from the oil shale were performed using a Parr Automatic Isoperibol Calorimeter-Model 6300, calibrated with benzoic acid. Experiments were carried out according to the Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (ASTM-D240). The oil shale samples used in all experiments had a particle size of 70 Mesh and the experiments were repeated three times to confirm their reproducibility.

Wetness analysis

The water content in the oil shale was determined as follows: 15 g of oil shale rock was added to a ceramic crucible and calcined in an oven at 105 °C for 10 h at a heating rate of 5 °C/min. The water content was calculated as the difference in the weight of the oil shale before and after calcination.

Summary

Characteristics of the two Israeli's oil shales used in this work (OS-A and OS-B) are listed in Table 1. The results indicate that OS-A contains much higher amount of organic material compared to OS-B and is almost dry. As a result, the caloric value of OS-A is also much higher and does not change after drying.

Table 1. Characterization of Israeli's oil shales

	OS-A	OS-B
Water content, %	0.87	17.80
Organic content before drying, %	23.32	13.00
Organic content after drying, %	23.34	15.80
Caloric value before drying, cal/g	2058	864
Caloric value after drying, cal/g	2058	881

Extraction of oil shale

Small scale extraction experiments

In a typical experiment 2 g of ground oil shale was added to the glass vial together with 20 mL of solvent. The vial was sealed and the mixture was mixed with a magnetic stirrer for 24 h at room temperature. It was then allowed to reach phase separation for another 24 h after which the oil shale was filtrated. Finally, the solvent extract was poured into a 50 mL evaporation flask and evaporated under reduced pressure in a Büchi 461 batch rotavapor until all the solvent was removed. The extraction yield was calculated by dividing the amount of the organic liquid that was left in the evaporation flask at the end of the evaporation stage by the total amount of organics in the parent oil shale.

Large scale extraction experiments

Large scale extraction experiments were done in a 1 L glass Büchi reactor. 10 to 50 g of oil shale was mixed with 300 mL of ethanol and added to the vessel. The vessel was sealed and the mixture was mixed for 3 h at room temperature at a selected speed (200–1000 rpm). Finally the mixture was allowed to reach phase separation for 24 h after which the oil shale was filtrated. Then, the solvent extract was poured into 500 mL evaporation flask and evaporated under reduced pressure in a Büchi 461 batch rotavapor until all the solvent was removed. The extraction yield was calculated by dividing the amount of the organic liquid that was left in the evaporation flask at the end of the evaporation stage by the total amount of organics in the parent oil shale.

Results and discussion

As previously reported, the type of extraction solvent affects the extraction yield [6, 7]. Hence, the extraction of hydrocarbons from two samples were first tested with four representative organic solvents: hexane, methanol, ethanol, and chloroform (Table 2, entries 1–4). The experiments were performed with dried and crushed oil shales as both, the particle size of oil shale and wetness, were expected to affect the extraction yield. The results in Table 2 illustrate that in general the extraction yields of OS-A are higher than those of OS-B with all tested solvents. Probable reason for this is the

higher organic content of OS-A (Table 1). In addition, as extraction of the oil shale by simple mixing at low temperature is not expected to degrade the kerogen, it seems that smaller soluble hydrocarbons were the ones mainly extracted. As the difference between the two types of oil shale might be also in the composition of their organic matter, it might be that the content of smaller soluble hydrocarbons in OS-A is higher than in OS-B, leading to higher extraction yields.

Table 2. Extraction yields from Israeli's oil shales using different organic solvents^a

Entry	Solvent	Dielectric constant	log Pow ^b	Yield, wt% OS-A	Yield, wt% OS-B
1	Hexane	1.89	3.9	0.3	0.1
2	Methanol	32.6	-0.82	1.5	0.6
3	Ethanol	24.6	-0.3	1.9	0.8
4	Chloroform	4.81	1.9	3.2	1.1
5 ^c	Ethanol	24.6	-0.3	1.7	0.3
6 ^c	Chloroform	4.81	1.9	2.8	0.4

^a Extraction conditions: 2 g of dried oil shales with particle size 70 Mesh, 20 mL of solvent, 24 h mixing at room temperature, 24 h phase separation.

^b Octanol/water partition coefficient.

^c 2 g of non-dried oil shales.

Another issue presented in Table 2 is the difference in the extraction yields with different solvents. It can be seen that the extraction yield from both oil shales with different solvents decreases in the following order: chloroform>ethanol>methanol>hexane. This result may be attributed to the physical and chemical properties of the solvents, which affect their ability to dissolve or break bonds based on electron donor-acceptor interactions and hydrogen bonding [6, 7]. Moreover, the polarity of the solvent undoubtedly affects its dissolving ability, hence the structure and the functional groups of the solvent should also be considered. In addition, it should be taken into account that the solubility of the oil from the oil shale is also dependent on the nature of organic composition in the oil shale as well as on the structure of the oil shale. Oils having polar compounds, for example, will dissolve better in more polar solvents, but the effects of functional groups on hydrogen bonds formation as well as the size of the solvent molecules and the porosity of the oil shale are also important. As shown in Table 2, the polarity of the four extraction solvents, illustrated by their dielectric constant or partition coefficient between octanol and water (log Pow), is different. Methanol and ethanol, which are protic polar solvents, have high dielectric constant and low log Pow, while less polar solvents, like hexane and chloroform, have low dielectric constant and high log Pow. It seems that hydrophobic solvents like hexane poorly dissolve organic matter in the oil shales, while employing more polar solvents, such as chloroform and alcohols,

increased the extraction yields. On the other hand, employing highly polar solvents may decrease the solubility of very hydrophobic hydrocarbons. It seems that chloroform, which is a medium polarity non-protic solvent, has the right balance between polarity and hydrophobicity to dissolve the highest amount of organic material. Finally, in order to check that the difference between the extraction yields of the different solvents is not due to evaporation of extracted volatile organic compounds during the elimination of the extraction solvent under reduced pressure, a mass balance for the whole system was carried out. The results indicate that the amounts reduced from the oil shales are comparable to the amounts of the residual extract after evaporation of the extraction solvent. This finding, as well as the analysis of the organic extract after evaporation of the extracting solvent that yielded negligible traces of all the solvents, reveals that the difference in extraction yield is not due to incorporation of the extracting solvent into the extract.

Extraction of both oil shales without previous drying resulted in lower extraction yields with ethanol and chloroform as extraction solvents, and especially in the oil shales of type OS-B, which have higher water content (Table 1). Again, as the total amount of organic compounds per gram of oil shale decreases with the increase of water content of the oil shale.

The effects of extraction duration and oil shale particle size on extraction yield were studied with both oil shales using chloroform and ethanol as extraction solvents. The results are illustrated in Fig. 1 and 2, respectively.

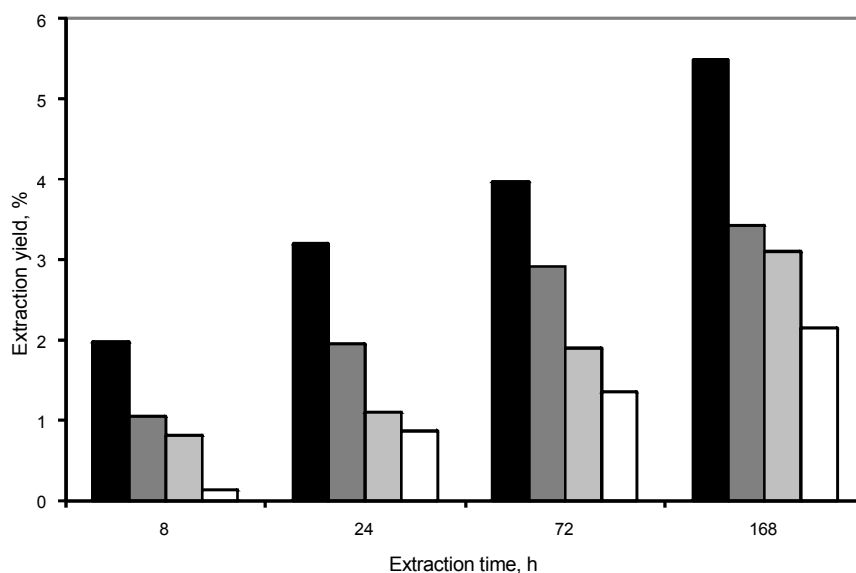


Fig. 1. Effect of the extraction time on extraction yields: OS-A in chloroform (black); OS-A in ethanol (dark-gray); OS-B in chloroform (light-gray); OS-B in ethanol (white). Extraction conditions: 2 g of dried oil shale with particle size 70 Mesh, 20 mL of solvent, mixing time 24 h at room temperature, 24 h phase separation.

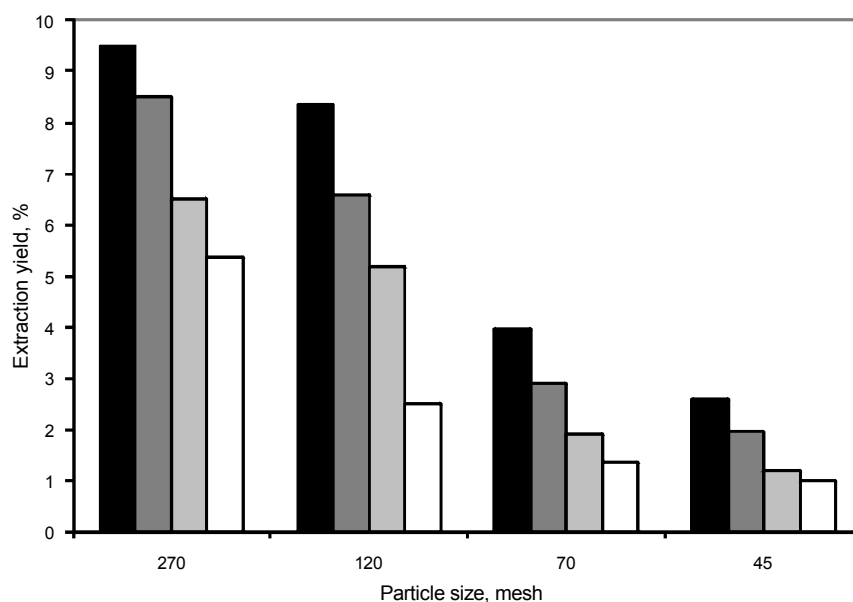


Fig. 2. Effect of particle size on extraction yields: OS-A in chloroform (black); OS-A in ethanol (dark-gray); OS-B in chloroform (light-gray); OS-B in ethanol (white). Extraction conditions: 2 g of dried oil shale, 20 mL of solvent, mixing 24 h at room temperature, 24 h phase separation.

As shown in Fig. 1, chloroform was again more efficient extraction solvent and the extraction of OS-A, which contains a higher amount of organic material, resulted in higher extraction yields. In addition, increasing the mixing time linearly increased the extraction yields for both type of oil shales in two selected solvents. This result proves that the extraction yield did not reach the saturation even after 7 days. However, when ethanol was employed as extracting solvent the slope of the line changed after 72 h, implying that the extraction with ethanol moved towards saturation. These results also confirm that chloroform has a higher solvation capacity for organic matter. As expected, decreasing the oil shale particle size increased the extraction yield (Fig. 2) as the external surface area per gram of oil shale increased.

Since the aim of the study was to enrich ethanol fuel by hydrocarbons from oil shales, and as bioethanol produced by fermentation also contains a high amount of water and requires distillation step before using it in an engine, we also examined the effect of water content in ethanol on the extraction yield, using dried OS-A (Table 3, entries 1–4). Results show that increasing water content in ethanol linearly increased the total amount of the extract. When the fraction of water in ethanol was higher than 20%, the extract became turbid and evaporation of the solvent mixture resulted in a mixture of brownish organic liquid and white powder. It appears that water

can assist in dissolution of polar organic compounds from the oil shale but it also extracts inorganic compounds, which are hardly soluble in ethanol. In addition, although the oil shales were dried before extraction of an organic compound, combined water that is chemically or physically bonded to the inorganic matrix may have leached out during extraction with water and might have increased the extraction yield.

Table 3. Extraction yields from Israeli's oil shales using ethanol^a

Entry	Solvent	Yield, wt% OS-A
1	100% Ethanol	1.9
2	95% Ethanol	2.0
3	90% Ethanol	2.8
4	80% Ethanol	5.9
5 ^b	100% Ethanol	2.8
6 ^c	100% Ethanol	4.1
7 ^d	100% Ethanol	2.7
8 ^e	100% Ethanol	1.8
9 ^f	100% Ethanol	0.9

^a Extraction conditions: 2 g of dried oil shales with particle size 70 Mesh, 20 mL of solvent, 24 h mixing at room temperature, 24 h phase separation.

^b 1 g of dried oil shales with particle size 70 Mesh.

^c 0.5 g of dried oil shales with particle size 70 Mesh.

^d 40 mL of solvent.

^e Second extraction step of the oil shale from entry 1 by fresh ethanol.

^f Third extraction step of the oil shale from entry 1 by fresh ethanol.

The effect of ethanol on the extraction yield was also studied using small particles of dried OS-A by changing either the quantity of oil shale or the total amount of the solvent (Table 3, entries 1 and 5–7). As illustrated in Table 3, decreasing the ratio of oil shale to ethanol from 0.1 g/L to 0.05 g/L and 0.025 g/L by decreasing the quantity of the oil shales while retaining the volume of ethanol (entries 1, 5 and 6), increased the overall extraction yield from 1.9 to 2.8 and 4.1 wt%, correspondingly. Alternatively, decreasing the ratio of oil shale to ethanol from 0.1 g/L to 0.05 g/L (entries 1 and 7) by doubling the volume of ethanol also increased the extraction yield from 1.9 to 2.7 wt%. As previously illustrated in Fig. 1 the extraction yield increased with the increase of mixing time and did not reach saturation. This refers that the extraction experiments presented in Table 3 (performed during 24 h) were not limited by saturation.

In another test, the samples of oil shale that were filtrated from ethanol after extraction of organic matter were added to fresh ethanol for the second and third extraction steps (Table 3, entries 8 and 9) and extracted again under similar conditions. As shown in Table 3 the extraction yield of the second extraction step (entry 8) was similar to the first one (entry 1) while the yield of the third extraction step (entry 9) was cut by half. This result

implies that the oil shale contains higher amount of soluble organic compounds, which can be further extracted by increasing the extraction time (Fig. 1) or the total volume of the extraction solvent.

Extraction of dried oil shale of type OS-A with particle size of 70 Mesh was also tested in larger scale extraction experiments. The experiments of extraction were performed by ethanol for 3 h at room temperature. First, the influence of quantity of the oil shale on the extraction yield was tested as illustrated in Fig. 3. As seen previously in Table 3 (entries 5–7), increasing the quantity of the oil shale in the reactor linearly decreased the extraction yield. The extraction yield in the reactor was much higher with respect of time compared to the extraction yield in a vial (extraction yield was 3 wt% in 3 h extraction time and 1.9 wt% in 24 h extraction time, respectively; oil shale ratio to ethanol was 0.1 g/L). This might be due to more homogeneous and efficient mixing.

The effect of mixing speed on extraction yield was also examined and a maximum extraction yield of 5.3 wt% was detected at 500 rpm (Fig. 4). Increasing the mixing velocity from 200–500 rpm linearly increased the dispersion of the oil shale particles in the extraction solvent and therefore the rate of mass transfer of the organic compounds from the oil shale surface resulting in increase of the extraction yield. Increasing the mixing velocity from 500 to 1000 rpm crushed the floating particles and therefore they were not mixed so well in the extraction solvent.

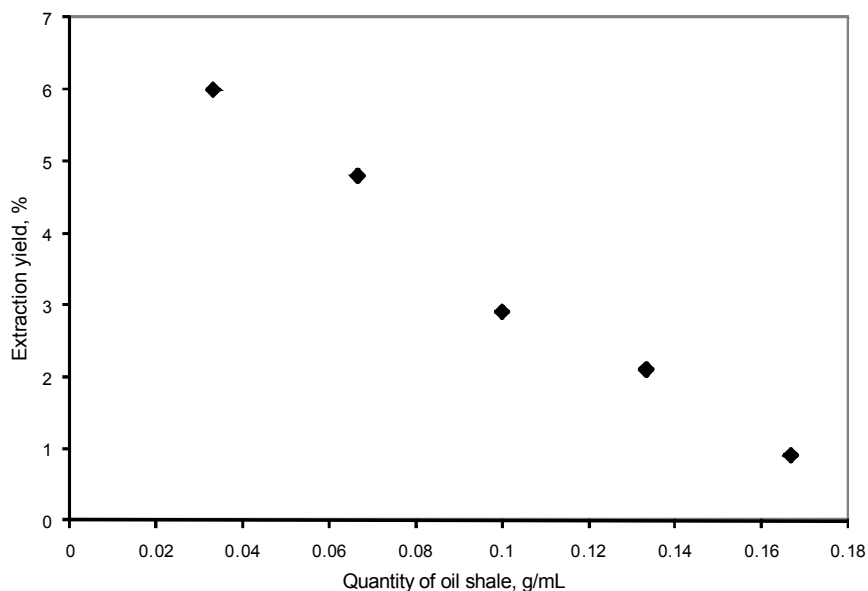


Fig. 3. Effect of quantity of oil shale on extraction yields in Büchi reactor. Extraction conditions: 30 g of dried OS-A with particle size 70 Mesh, 300 mL of ethanol, mixing 3 h at room temperature, 24 h phase separation.

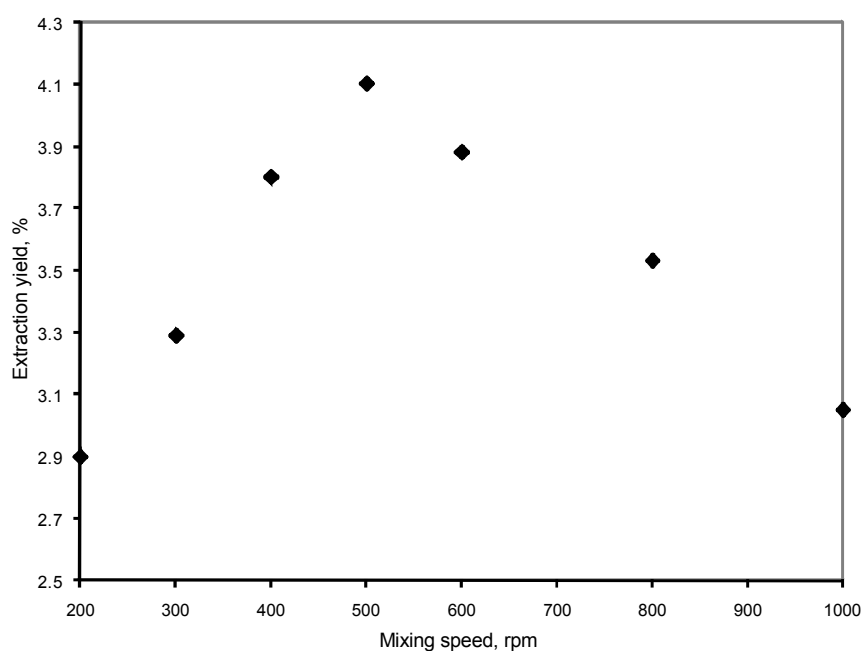


Fig. 4. Effect of mixing speed on extraction yields in Büchi reactor. Extraction conditions: 30 g of dried OS-A with particle size 70 Mesh, 300 mL of ethanol, 3 h mixing at room temperature, 24 h phase separation.

Finally, the difference in caloric value of ethanol before and after extraction of oil shale was tested. 2 g of dried oil shale of type OS-B with particle size of 70 Mesh was added to 20 mL of ethanol and mixed for 168 h at room temperature. Then the mixture was allowed to reach phase separation for 24 h. The extraction yield was 2.3 wt%, corresponding to $3.6 \cdot 10^{-4}$ g of organic matter in mL of ethanol and 0.046 wt% of organic matter in ethanol. It increased the caloric value by 7% from 6205 cal/g of pure ethanol to 6646 cal/g of enriched ethanol.

Conclusions

Ethanol was successfully enriched with hydrocarbons by employing it as extraction solvent of two Israeli's oil shales. The type of oil shale as well as its organic and water content affected the extraction yield. In addition, decreasing the oil shale particle size or increasing the mixing time increased the extraction yield. Moreover, changing the mixing speed of the extraction from 200 to 1000 rpm resulted in maximum extraction yield of 4.1 wt% at 500 rpm. At higher speeds the particles were crushed and floating on the surface of the liquid.

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