

## STUDY ON ULTRASONIC EXTRACTION OF KEROGEN FROM HUADIAN OIL SHALE BY SOLVENTS

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**Abstract.** *Ultrasonic extraction of kerogen derived by acid treatment of Huadian oil shale is performed using an organic solvent. The most effective solvent is the 60:40 (wt%) mixture of chloroform and carbon disulfide, and the suitable mass ratio of the demineralized oil shale to solvent is 1:20. The oil yield by ultrasonic extraction can reach 15.6% based on the demineralized oil shale, compared with a Fischer Assay oil content of 18.9%. The optimum operating parameters as determined by the orthogonal test are: 60 kHz ultrasonic frequency, 200 W ultrasonic power, 30 min extraction time, and 313 K extraction temperature. Through the gas chromatographic-mass spectrometric analysis, the most plentiful compounds in the extracts are low molecular weight alicyclic hydrocarbons, accounting for about 68.3% of total species. The physicochemical properties of the extracts indicated that these can act as an important complementary resource for the production of diesel after appropriate processing.*

**Keywords:** *oil shale, ultrasonic extraction, organic solvent.*

### 1. Introduction

Energy plays an important role in the economic growth and development around the world. Though conventional oil resources like petroleum and natural gas are still the main sources of energy [1], the depletion of oil reserves and the continuing soaring oil price indicate that countries should turn to unconventional oil resources as reliable and secure energy sources [2, 3]. Oil shale, an important complementary and alternative fossil fuel resource, is a fine-grained sedimentary rock which contains a solid hydrocarbonaceous material (kerogen) that can be converted to crude shale oil.

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Worldwide deposits of recoverable oil in oil shale are estimated at 2.8 trillion barrels [4]. The oil equivalent of oil shale around the world is estimated to be around 30 times the reserve of crude oil [5]. Oil shale resources of China are estimated at 720 billion tons [6]. Huadian oil shale, located in Huadian county, Jilin province, has an oil reserve of 3.06 billion tons. Huadian oil shale originates from algal flora, and is classified as being of sapropelic nature [7]. The Fischer assay oil content of Huadian oil shale ranges from approximately 5 to 20 wt% [8, 9]. There are various possibilities worldwide for oil shale utilization, including currently practiced retorting to produce shale oil [10], direct combustion for electricity generation [11], and solvent extraction for potential shale oil production [12–15]. However, the methods based on the thermal behavior of oil shale (such as retorting, combustion, gasification) require high energy consumption and provide relatively low carbon conversion, in addition to resultant environmental pollution. Thus, the solvent extraction of oil shale is a promising method which requires more attention. Recently, supercritical fluid extraction has been tested as a new separation method to recover oil from oil shale [10, 16–18]. Though the carbon conversion and oil yield by supercritical fluid extraction are found to be higher than those by conventional methods such as burning and retorting [10], the operating conditions are harsh and restricted. Therefore, developing a mild and highly efficient technology to utilize oil shale has become the research focus.

Ultrasonic energy waves can cause cavitation, heating and intense agitation, which is conducive to activate chemical processes and enhance heat and mass transfer processes [19]. Ultrasonic vibrations penetrate into different regions of a multi-phase system. The separation of aggregates of solid particles occurs under the effect of shock waves. The chemical reagent or solvent can penetrate into the pores under the action of capillary forces enhanced by the ultrasonic capillary effect. In addition, it is reported that ultrasound is able to reduce the viscosity of heavy oils [19, 20].

In the present work, the primary objective is to investigate the extraction process of Huadian oil shale under the effect of ultrasonic energy in the presence of a range of solvents. Huadian oil shale was first preprocessed by acid treatment and demineralization, followed by ultrasonic extraction using organic solvents. A series of experiments were carried out to identify a suitable organic solvent for the extraction process, the optimum operation parameters were determined by studying the effect of ultrasonic power, frequency, time, temperature and the dosage of solvent on oil yield. In addition, the physicochemical properties of the extracts were also investigated.

## 2. Experimental

### 2.1. Materials

The oil shale used in the experiment was obtained from Huadian oil shale deposits, Jilin province, China. The data about proximate, ultimate and

Fischer assay analyses of the oil shale sample are presented in Table 1. The collected oil shale samples were crushed using a jaw crusher, and sieved to the size fraction of 80–100 mesh. Purchased from Kelong Reagent Factory (Chengdu, China), the hydrochloric acid (HCl), hydrofluoric acid (HF), n-hexane ( $C_6H_{14}$ ), methanol ( $CH_3OH$ ), chloroform ( $CHCl_3$ ), carbon disulfide ( $CS_2$ ) and toluene ( $C_7H_8$ ) used in this study were of analytical grade. Distilled water was also used for solutions preparations and washing.

**Table 1. Proximate, ultimate and Fischer assay analyses of Huadian oil shale**

Proximate analysis, wt%		Ultimate analysis, wt%		Fischer assay analysis, wt%	
Ash	54.67	C	33.84	Shale oil	18.9
Volatile matter	36.72	H	4.11	Gas	5.83
Fixed carbon	4.65	N	0.83	Water	8.17
Moisture	3.96	S	1.12	Residue	67.1

## 2.2. Experimental setup

A schematic diagram of the experimental setup for the continuous-loop ultrasonic extraction of kerogen derived from oil shale by organic solvent is presented in Figure 1. The set-up mainly consists of systems of three processes: preprocessing by acid treatment and demineralization, ultrasonic extraction by organic solvent, and organic solvent recycling.

The most common and, usually, most suitable method for removing inorganic minerals from oil shale is successive chemical treatment. HCl and

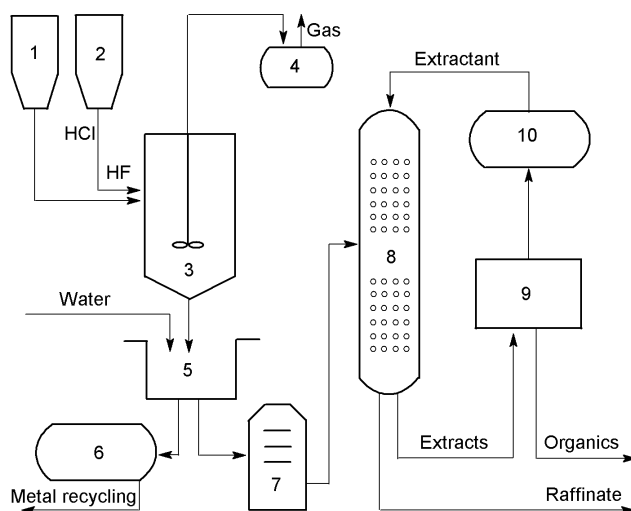


Fig. 1. Schematic diagram for the continuous-loop ultrasonic extraction of oil shale by organic solvent, 1 – oil shale hopper; 2 – acid container; 3 – acid treatment tank; 4 – gas washing bottle; 5 – rinsing bath (demineralization); 6 – solution tank; 7 – drying apparatus; 8 – ultrasonic extraction column; 9 – vacuum distillation plant; 10 – solvent tank.

HF treatments to remove respectively carbonates, and silica and silicates from oil shale samples are sufficient to give a more or less mineral-free kerogen [5, 21]. Aboulks and Ei Harfi reported that HCl and HF solutions did not alter the composition of organic matter [22]. Besides, after HCl treatment, the decomposition of metal salts led to an increase in the amount of extractable fatty acids in oil shales, and the increase of the solubility of oil shale resulted in an increased accessibility of solvent molecules to soluble material [23, 24]. The principal problem encountered in HF treatment is the formation of insoluble fluorides such as  $\text{CaF}_2$ . Dilute HF solutions and the presence of excess HCl tend to prevent the formation of such fluorides. The ultrasonic extraction column includes the ultrasonic generation instrument and extraction reactor. The ultrasonic instrument (TEM-200) was purchased from Tianzhengtong Industry & Trade Co., Ltd., Beijing, China, and its maximum power was 200 W. The extraction column is characterized by low acoustic energy loss and evenly distributed sound field. From the economic and environmental point of view, the organic solvents will need to be recycled. A clean solvent for recycling can be produced from the vacuum distillation of extracts.

### 2.3. Experimental procedure

A 10 g finely ground oil shale sample (80–100 mesh) was mixed with 3 mol/L HCl at a solid–liquid mass ratio of 1:4. The sample was then stirred for 2 h under a nitrogen atmosphere at 333 K in the acid treatment tank. The HCl attack was repeated twice to eliminate carbonates. Then, the decarbonated oil shale was mixed with the twofold-volume mixed acid, which was prepared by the addition of 6 mol/L HCl and 5 wt% HF (volume ratio 1:1), and treated as before. The decarbonated and silicate-free oil shale obtained in the above steps was then washed with distilled water to remove soluble inorganic salts and acid residues, followed by centrifugalization. Subsequently, the demineralized oil shale (kerogen) was dried overnight at 333 K in vacuum oven to remove moisture. The kerogen was subjected to ultrasonic extraction by organic solvents under the following operating conditions: 60 kHz ultrasonic frequency, 200 W power, 313 K extraction temperature, and 30 min extraction time. The extract and raffinate phases were separated by filtration, and the vacuum distillation of extracts was performed to recover the solvent. Finally, the distilled solvent was reused after cooling, and the physicochemical properties of the extracts were analysed.

### 2.4. Optimization of operating conditions

It is well known that the ultrasonic frequency, ultrasonic power, extraction temperature, extraction time, extractant type and dosage have a significant effect on oil yield during the ultrasonic extraction of oil shale by organic solvent [25]. Therefore, in order to optimize the experimental operating

parameters, the orthogonal test was carried out. The oil yield was calculated by Equation 1:

$$Y = \frac{M_O}{M_{OS}} \times 100\% , \quad (1)$$

where  $Y$  is the oil yield, %;  $M_O$  is the mass of organics obtained from the vacuum distillation of extracts, g;  $M_{OS}$  is the mass of demineralized oil shale, g.

### 3. Results and discussion

#### 3.1. Influence of extractant on oil yield

Toluene, n-hexane, methanol, chloroform and carbon disulfide were selected as solvents for extracting hydrocarbons from the decarbonated and silicate-free oil shale. The solid-liquid mass ratio (oil shale kerogen sample/extractant) was 1:20, and ultrasonic extraction conditions were as follows: 60 kHz ultrasonic frequency, 200 W ultrasonic power, 30 min extraction time, and 313 K extraction temperature. The oil yield was computed and the results are given in Table 2.

As shown in Table 2, the order of extraction capacity for Huadian oil shale was chloroform > carbon disulfide > methanol > toluene > n-hexane. It should be noted that the difference in oil yield between chloroform and carbon disulfide extractions was slight. The recovery of organics from the demineralized oil shale kerogen was subject to stages of liberation and extraction. The ultrasonic excitation produced four additive effects: interface, perturbation, turbulence and cumulative energy effects [16]. These effects weakened the adhesion force between organics and shale, and accelerated the separation of organics, thus facilitating the liberation process. In addition, organic solvents caused the accumulation (reorganization) of polar and non-polar components into a continuous single phase. The organic components of demineralized oil shale were carried into the homogeneous phase, finalizing the solvent extraction of kerogen (demineralized oil shale).

For a further study on the extraction potential of various mixtures of chloroform and carbon disulfide, a series of experiments were carried out, including the effects of these blends at different compositions and solid-liquid mass ratio, on the oil yield. The results are shown in Figure 2. It is defined that  $X_b = M_b/(M_a+M_b)$ , wherein  $M_a$  is the mass of carbon disulfide, g;  $M_b$  is the mass of chloroform, g.

**Table 2. Oil yield from ultrasonic extraction by solvent**

Extractant	C <sub>7</sub> H <sub>8</sub>	C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> OH	CHCl <sub>3</sub>	CS <sub>2</sub>
Oil yield	2.92	1.71	2.25	10.73	10.64

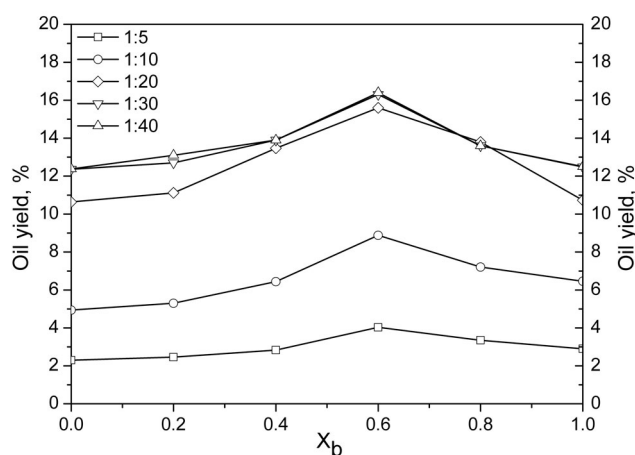


Fig. 2. Effect of  $\text{CHCl}_3\text{-CS}_2$  blends and dosage on oil yield.

As shown in Figure 2, with increasing chloroform content, the oil yield first increased, then achieved a maximum of 15.6% at an approximately 60 wt%  $\text{CHCl}_3$  dosage, and finally decreased. Carbon disulfide as a good solvent could destroy the charge transfer force and association between oil shale components, resulting in an increased ease of penetration and diffusion of solvent mixtures. Due to chlorine atoms with lone pairs of electrons, chloroform was an excellent hydrogen bond acceptor, and it could produce strong hydrogen bonds with hydroxyl and carboxyl, as well as the  $\pi$ -electrons of cyclohexane. Thus, the original hydrogen bonds in the kerogen would have been destroyed, allowing  $\text{CHCl}_3\text{-CS}_2$  to preferentially extract the organic molecules from within the structure of the kerogen of oil shale. In addition, the total dosage of extractant had a significant influence on the oil yield. With increasing extractant dosage, the oil yield increased, but the rate of increase dropped progressively due to the extraction process becoming gradually saturated [26]. Therefore, from the viewpoint of economy and efficiency, the suitable mass ratio of demineralized oil shale to  $\text{CHCl}_3\text{-CS}_2$  was 1:20, with the  $\text{CHCl}_3$  content of 60 wt%.

### 3.2. Optimization of experimental operating parameters

The ultrasonic frequency, ultrasonic power, extraction time, and extraction temperature had a substantial effect on the oil yield by the ultrasonic extraction. The orthogonal test  $L_9(3^4)$  was carried out to determine the optimum operating parameters, and the results are presented in Table 3.

It can be seen from Table 3 that the order of influence of ultrasonic parameters on the oil shale extraction by  $\text{CHCl}_3\text{-CS}_2$  was the following: extraction temperature > extraction time > ultrasonic power > ultrasonic frequency. The elevated temperature would be good for improving the mass transfer rate, and also for reducing the surface tension and viscosity coef-

**Table 3. Results of the orthogonal test  $L_9(3^4)$** 

Entry	Frequency, kHz	Power, W	Time, min	Temperature, K	Oil yield, %
1	20	100	20	303	11.62
2	20	150	30	308	13.64
3	20	200	40	313	14.40
4	40	100	40	308	11.86
5	40	150	20	313	15.21
6	40	200	30	303	13.74
7	60	100	30	313	15.09
8	60	150	40	303	12.59
9	60	200	20	308	13.38
K1	39.66	38.57	40.21	37.95	
K2	40.81	41.44	42.47	38.88	
K3	41.06	41.52	38.85	44.7	
k1	13.22	12.86	13.4	12.65	
k2	13.60	13.81	14.16	12.96	
k3	13.69	13.84	12.95	14.9	
R	0.373	1.864	2.244	8.922	

ficients of solvents. Then the increased temperature led to the increase of vapor pressure and decrease of the ultrasonic cavitation threshold, which was conducive to generate a large number of cavitation bubbles. In addition, the sound intensity increased with rising ultrasonic power. Therefore, the optimum operating parameters were determined to be the following: 60 kHz ultrasonic frequency, 200 W ultrasonic power, 30 min extraction time, and 313 K extraction temperature.

### 3.3. Physicochemical properties of the extracts

The gas chromatography-mass spectrometry (GC-MS) analysis of extracts was carried out with an HP 6890/5973 GC-MS instrument using an HP190915-433 column (30 m  $\times$  250  $\mu$ m  $\times$  0.25  $\mu$ m). Helium was used as the carrier gas at a constant column flow rate of 1 mL/min, the split ratio was 20:1. The inlet temperature was controlled at 573 K. The mass spectrometry detector was operated in a scan mode with a 70 eV of ionization energy from 30 to 500 every second at 503 K (EI). The results are shown in Figure 3.

Through the GC-MS detection and computer retrieval, there were typically 41 species, which were the most prevalent compounds in the extracts. Among the species, there were 28 kinds of low molecular alicyclic hydrocarbons, accounting for about 68.3% of total species. In addition, aromatic compounds (9.8%) and heteroatom compounds (21.9%) containing an N or S atom were detected. It should be noted that the major components of alicyclic hydrocarbons were n-alkanes of C<sub>9</sub>–C<sub>34</sub>, isoparaffin, cycloalkanes and light olefins. According to the component analysis of aliphatic hydrocarbons, the aliphatic compounds are similar to those of commercial diesel. The physical properties of extracts are presented in Table 4. As indicated, the extracts can basically meet quality requirements for fuel and, after appropriate processing, can act as an important complementary resource of diesel.

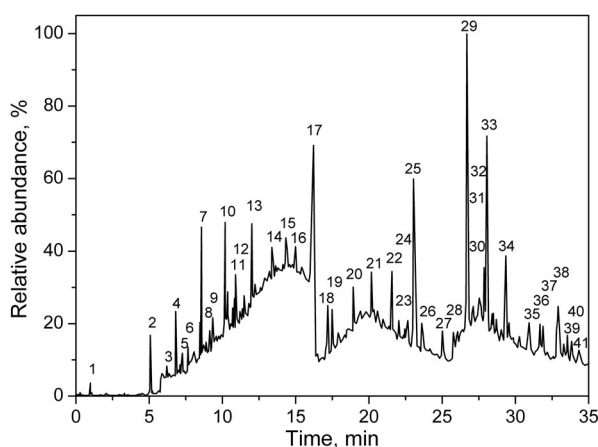


Fig. 3. Total ionic chromatogram of GC-MS of oil shale extracts.

**Table 4. Physical properties of extracts**

Entry	Experimental value	Quality index
Density (20 °C), g/cm <sup>3</sup>	0.8408	0.790–0.845
Closed-cup flash point, °C	134	≥ 55
Cold filter plugging point, °C	12	≤ 12
Solidification point, °C	18	≤ 10
Ash content, %	0.0108	≤ 0.01
Carbon residue, %	0.44	≤ 0.3
Sulfur content, %	0.48	≤ 0.2
Kinematic viscosity (20 °C), mm <sup>2</sup> /s	9.95	3.0–8.0
50% distillate temperature, °C	285	≤ 300
90% distillate temperature, °C	347	≤ 355
95% distillate temperature, °C	423	≤ 365

#### 4. Conclusions

A novel utilization system of oil shale involving acid treatment and demineralization, ultrasonic extraction by organic solvent, and solvent recycling is adopted for Huadian oil shale. The most effective solvent for the ultrasonic extraction of oil shale is the 60:40 mixture (wt%) of CHCl<sub>3</sub> and CS<sub>2</sub>, and the suitable mass ratio of demineralized oil shale to CHCl<sub>3</sub>-CS<sub>2</sub> is 1:20. The optimum operating parameters are determined by the orthogonal test and are the following: 60 kHz ultrasonic frequency, 200 W ultrasonic power, 30 min extraction time, and 313 K extraction temperature. The oil yield by the ultrasonic extraction of Huadian oil shale can reach 15.6% based on the demineralized oil shale. Through the GC-MC analysis, the most probable high-abundance compounds in the extracts are low molecular alicyclic hydrocarbons, accounting for about 68.3% of total species. The physicochemical properties of the extracts indicated that they can act as an important complementary resource of diesel after appropriate processing.



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