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CO_2 supercritical fluid extraction of Jordanian oil shale utilizing different co-solvents

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ABSTRACT

In this study, extracting shale oil from Jordanian oil shale using supercritical fluid extraction has been investigated. Experimental data indicates that by using supercritical extraction with carbon dioxide, using co-solvents can be viable. A relatively high yield can be obtained at relatively moderate pressure. At the highest temperature and pressure of 450 °C and 3200 psi, respectively, and with hexane as a co-solvent, the highest yield obtained was 100 kg/ton of oil shale, which was at the highest temperature and pressure of 450 °C and 3200 psi, respectively, and with hexane as a co-solvent. Increasing both the operating pressure and temperature increases the oil yield. In the supercritical state, carbon dioxide along with other co-solvents, such as hexane and acetone, interact with the kerogen leading to the dissolution of fragments due to an increase in solubility and mass transfer.

Increasing the particle size of oil shale for extraction decreases the oil yield. Most of the extracted oil obtained is saturated hydrocarbons, olefinic and a portion of aromatic hydrocarbons. As the extraction temperature increases, the production of low-molecular weight compounds increases.

1. Introduction

The term oil shale generally refers to any sedimentary rock that contains solid bituminous materials called kerogen, that are released as petroleum-like liquids when the rock is heated through the chemical process of pyrolysis. Oil shale generally contains enough oil that it will burn without any additional processing, and it is known as "the rock that burns". Although resources of oil shale occur in many countries, only 33 countries possess known deposits of possible economic value. Well-explored deposits, potentially classifiable as reserves, include the Green River deposits in the western United States, the tertiary deposits in Queensland, Australia, deposits in Sweden and Estonia, the El-Lajjun deposit in Jordan, and deposits in France, Germany, Brazil, China, southern Mongolia and Russia. These deposits have given rise to expectations of yielding at least 40 l of shale oil per ton of shale, using the Fischer Assay [1]. Jordan possesses a very large energy resource in its vast reserves of oil shale. It is estimated to be over 50 billion tons of geological reserves [1]. Current methods of recovering hydrocarbons from shale oil mainly depend on retorting or pyrolysis through either excavation of oil shale or through in-situ processes. These methods depend on heating the oil shale to temperatures in excess of 500 °C, and have been employed for many years and are well studied. The high-energy requirements and the low conversion of hydrocarbons, as well as the limitations on the waste treatment of spent shale made decision makers reluctant to pursue this technology for the utilization of oil shale.

Unlike normal bitumen, kerogen contained in oil shale is normally insoluble in common solvents under conventional conditions. The extraction of oil shale using the supercritical fluid extraction (SFE) method has been applied for a variety of reasons. The primary reasons include the production of liquid fuels from oil shale. Another being that supercritical extraction shows promise for increasing yields and improving oil quality in addition to the selective nature of extraction. This method could also be utilized for other valuable products from oil shale.

CO_2 supercritical fluid extraction offers several advantages over conventional supercritical gas extraction and solvent extraction. CO_2 supercritical fluid extraction has a higher diffusivity and lower viscosity compared to liquid solvents, which should result in improved mass transfer properties during extraction. The solvent strength of CO_2 supercritical fluid extraction is dependent on its temperature and pressure, which can easily be manipulated to extract certain classes of compounds.

Supercritical fluid has been used for several industrial applications, from cleaning to pharmaceutical manufacturing, with the most important one being petrochemical applications as useful alternate techniques, which employ conventional liquid solvents. Some research has been conducted on extraction of oil shale by supercritical fluid.

Bondar et al. [2] studied the supercritical fluid extraction (SFE) of oil shale with carbon dioxide, utilizing the ability of supercritical fluids to extract rapidly specific solute classes from complex matrices. Yields

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of the extracts obtained were comparable with those of the hydrocarbon fractions of Soxhlet chloroform extracts of oil shale, but depended greatly on the inorganic matrix. The lowest SFE extract yield obtained was from Krasava oil shale with a primarily ceolite mineral matrix, and the highest from kukersite with a predominantly carbonate mineral matrix. Erol et al. [3] investigated supercritical fluid extraction (SFE) of two Turkish lignites and oil shale with toluene mixtures (methanol and toluene; toulene and *n*-hexane mixtures).

Extracts recovered from SFE were fractionated into oils, asphaltenes and preasphaltenes by solvent extraction. The conversion of lignites decreased with increasing n-pentane content in the mixture. The extraction yield and the products (oils, gas) increased with increasing n-pentane content in its range below 15%.

El Harfi et al. [4] subjected Timahdit oil shale to supercritical water extraction. The results reveal significant differences in oil yields and composition when compared with those obtained from conventional pyrolysis. The results revealed that the yield and the fraction of paraffin and aromatics increases, while the percentage of asphaltenes decreases as the temperature is increased from 380 to 400 °C. The residence time was found to affect the yield and the fraction of asphaltenes and polar compounds. Olukcu et al. [5] subjected Beypazari oil shale to supercritical fluid extraction with water and toluene separately. Considerable differences were observed in the yields, and compositions of the oils obtained from oil shale by supercritical water (SCW) gave a higher conversion degree of kerogen in oil shale than supercritical toluene (SCT).

Koel et al. [6] presented results on the application of supercritical carbon dioxide extraction (SFE) at different temperatures, and compared them with classical Soxhlet chloroform extracts. Pure carbon dioxide extracts primarily n-alkanes, whereas modifying of the fluid with methanol intensified the extraction of more polar compounds and increased, as a result, total yield of extract. An increase in SFE temperature had the same influence on the yield of extract, however, already at 200 °C partial heterolytic cracking of the kerogen of kukersite started. Tucker et al. [7] compared the use of nitrogen retorting, carbon dioxide retorting, CO_2 supercritical fluid extraction and supercritical H_2O for oil yield, quality, types and amounts of compounds extracted from Jordanian El-Lajjun oil shale. Results show that supercritical H_2O (SC-H_2O) produces 50% higher yields than nitrogen retorting (R-N_2) while releasing higher molecular weight materials through solvation and pyrolysis. However, the required operating pressure when using SC-H_2O is relatively high (approximately two times the required pressure for CO_2 supercritical fluid extraction). This, along with the extended residence time utilized in this study to extract small quantities of oil shale (2) can hinder the economic benefits of employing this method. Although the oil yield obtained when using SC-CO_2 was lower, the oil quality obtained was better than that obtained when using SC-H_2O.

Rudolf et al. [8] described the extraction of aliphatic and aromatic hydrocarbons from New Albany Shale by supercritical carbon dioxide at different extraction temperatures. The main goal of this work was to determine the effect of the temperature on the extraction process (i.e. relative extraction rate and efficiency). The data suggest that temperature changes of 20 and 40° for the relatively moderate extraction temperatures tested (55, 75, and 95 °C), can have significant effects on both relative extraction rates and yields, particularly for the aromatic hydrocarbons. Kesavan et al. [9] described the recovery of oil from Stuart oil shale using a supercritical extraction technique employing carbon dioxide as solvent. This supercritical technique provides yields superior to comparable retorting techniques. Zhongmin et al. [10] experimented with the extraction of organic matter by supercritical fluids ($CO_2 + 1\%$ isopropanol) from petroleum source rocks of different thermo-maturities and different buried depths in the same stratigraphic unit in the Dongying Basin. The results showed that supercritical fluid extraction (SFE) is more effective than Soxhlet extraction (SE).

Haddadin et al. [11] studied the extraction of hydrocarbon compounds from El-Lajjun oil shale using biosurfactant produced from two strains of Rhodococcus erythropolis and Rhodococcus rubber. The results have shown that optimal biosurfactant production was found using naphthalene and diesel as a carbon source for R. erythropolis and R. rubber, respectively. Hu et al. [12] experimented with the water extraction of Huadian oil shale from the Jilin Province of China. The effects of temperature and pressure were investigated in terms of degree of conversion, extract as well as gas yield and formation rate, and the compositions of extract and gas. The results indicated that the extract was obtained mainly in the temperature range between 300 °C and 500 °C and gas formation was only observed at temperatures higher than 350 °C. A maximum formation rate exists for extract and gas at about 390 °C.

Kramer et al. [13] studied the supercritical extraction of oil shale which was carried out on a number of solvents and solvent mixtures at 400 °C. Shale from Mishor Rotem in Israel and from Kentucky and Green River in the USA were studied and compared. Extraction was carried out, both batch-wise in autoclaves, and in a continuous flow system. The best solvents seem to be isopropanol/water and water/CO mixtures. After extraction, an additional kerogen fraction can be recovered by heating the shale to 600 °C in an inert atmosphere.

Funazukuri et al. [14] discussed the supercritical fluid extraction of Chinese Maoming oil shale with water and toluene, separately. The oil shale was also subjected to pyrolysis in argon atmosphere and the Soxhlet extraction with tetrahydrofuran. It was found that polar components were more easily decomposed with water than with toluene. The solvents, water and toluene did not affect the yield of non-polar components. Brandt [15] studied the Shell in-situ conversion process (ICP), which is a novel method of retorting oil shale in place. The energy inputs and outputs from the ICP, as applied to oil shale of the Green River formation, were modeled. Using these energy inputs, the greenhouse gas (GHG) emissions from the ICP are calculated and are compared to emissions from conventional petroleum. Energy outputs (as refined liquid fuel) are 1.2–1.6 times greater than the total primary energy inputs to the process. In the absence of capturing CO_2 generated from electricity produced to fuel the process, well-to-pump GHG emissions are in the range of 30.6–37.1

This study aims to extrapolate the method of using the CO_2 supercritical fluid extraction in the extraction of Jordanian oil shale by the use of co-solvents. In addition, the method CO_2 supercritical fluid extraction will be optimized in terms of the operating conditions such as time, temperature, pressure, co- solvent type, and mean particles diameter.

2. Experimental

2.1. Materials

2.1.1. Oil shale

The oil shale chosen for this study originated from the El-Lajjun deposits, which is one of the most important deposits in Jordan. The El-Lajjun oil shale deposit is located in the western part of central Jordan. It is located approximately 110 km south of Amman and mid-way along the highway between Karak and Qatrana. The deposit is 10 km long and 2 to 2.5 km wide. The oil shale deposit consists of limestone, marl, cherts, shales and phosphates of Campanian–Maestrichtian. The average thickness of oil shale is 30 m. The average stripping ratio is approximately 1. The proven reserve amounts to 1.2 billion tons of oil shale containing oil content of approximately 115 million tons. In Jordan, the oil content of the El-Lajjun oil shale deposit is relatively high and the shale oil contains predominantly aliphatic compounds. The specific gravity of the oil shale is high, mainly because of the high sulfur content (10%). The approximate