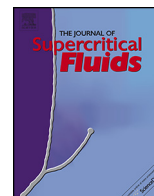




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Extraction of kerogen from oil shale with supercritical carbon dioxide: Molecular dynamics simulations

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ABSTRACT

The extraction process and mechanism of kerogen moieties with supercritical CO₂ are elucidated using molecular dynamics simulations. It is demonstrated that supercritical CO₂ can effectively dissolve the kerogen moieties adsorbed onto the shale surface, and the kerogen moieties dissolved in supercritical CO₂ can be easily extracted from oil shale, because the interaction between the kerogen moieties dissolved in supercritical CO₂ and the shale surface is greatly reduced. The dissolving capacity of supercritical CO₂ is found to effectively increase with increasing pressure before the pressure reaches a critical value (approximately 50 MPa) and then increases slowly. Moreover, the dissolving capacity of supercritical CO₂ increases with increasing temperature at high pressure, which is consistent with experimental results. In addition, the hydroxyl functional groups modified on the shale surface promote the extraction of kerogen moieties with supercritical CO₂, and the polar kerogen moieties were more easily dissolved in supercritical CO₂.

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1. Introduction

The worldwide potential amount of oil shale has been proved to be approximately 80 billion tons [1], which suggests that oil shale is one of the most important sources of liquid fuel after natural petroleum [2]. Using modern petroleum refining technologies, oil shale can be refined into marketable organic products [3]. Shale oil, called “artificial oil”, is produced from organic matter in oil shale, including saturates, aromatics, resins and asphaltenes, by using retorting or pyrolysis [1,2]. The major organic matter in oil shale is kerogen, which is a complex mixture of organic materials tightly adsorbed onto the shale surface and is difficult to be exploited. Therefore, the kerogen extraction from the shale surface is of crucial importance for effective oil extraction from oil shale.

The traditional experimental approaches to extract kerogen from oil shale include differential wettability, sink-float separations, chemical methods and pyrolysis [1,4–8]. Differential

wettability methods are based on the principle of differential wetting of kerogen and minerals. However, the oil shale is required to be of fine particle sizes for a full wetting and successful future separation. Taking advantage of the differential gravity of kerogen and minerals, kerogen and minerals were separated using sink-float separation methods. Although kerogen is not altered chemically by the sink-float method, only low yields of highly enriched organic matters are obtained. Chemical methods, always result in major structural changes in kerogen by chemical agents and are also not reliable for separating kerogen from oil shale for characterization studies. Pyrolysis requires a large amount of energy and results in many harmful toxic compounds. Recently, supercritical fluid extraction (SFE), which uses gases such as carbon dioxide, ethane, propane, toluene and water under supercritical conditions, was reported to be competitive as a new extraction technology. A supercritical fluid has similar density and dissolving ability to a liquid, and has similar diffusivity, viscosity, and surface tension to a gas. Therefore, the great selectivity and rapid mass transfer of supercritical fluid make SFE an efficient, environmentally friendly, and attractive separation technique compared to conventional extraction methods [9,10]. Investigations of kerogen extraction from oil shale with supercritical fluids have been reported [11–14]. However, to our knowledge, the mechanism of SFE of kerogen from the

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shale surface is still unclear, understanding this mechanism is very important to designing effective methods for oil extraction from oil shale.

Supercritical CO₂ has attracted considerable attention in many fields such as solvents, material syntheses, supercritical extraction and enhanced oil recovery [15–25]. The introduction of supercritical CO₂ was found to be a key factor to encourage the dissolution in the water/granite system [26]. Supercritical CO₂ can change the wetting of the surface of silica rock [27], increase oil saturation above the residual saturation, and reduce oil viscosity [21], which can lead to oil flow with better mobility. Moreover, supercritical CO₂ has a stronger interaction with aromatic molecules, which has unique properties as an improved oil recovery fluid compared to other supercritical fluids such as N₂ and CH₄ [28]. Although supercritical CO₂ is a nonpolar solvent, it still has good attraction to polar solutes and many large organic molecules due to its large quadrupole moment [3]; in addition, a wide variety of compounds could be extracted by supercritical CO₂ [3,9,10,29,30]. Therefore, supercritical CO₂ with a low critical point (T_c=304.3 K and P_c=7.38 MPa) [16], a high permeability, a great selectivity and a high dissolving ability has the advantage of being able to extract large organic molecules (such as kerogen).

Even though many investigations of structures and models of kerogen have been reported [31–37], it is still difficult to investigate a complete kerogen. The kerogen moieties identified in kerogen have been used to evaluate the properties of kerogen [33,38]. In addition, these kerogen moieties are also products of oil shale, the extraction mechanism of which may be important for future oil extraction from oil shale. Therefore, in this study, we investigated the extraction of four representative kerogen moieties with supercritical CO₂ using molecular dynamics (MD) simulations. The microscopic behavior of kerogen extraction was revealed using MD simulations, and the supercritical extraction mechanism was proposed. Moreover, the effects of pressure, temperature, spacing between the shale surfaces, functional groups modified on the shale surface and the polarity of kerogen moieties on the extraction of the kerogen moieties with supercritical CO₂ were also investigated.

2. Models and methods

MD simulations are implemented by the DISCOVER code embedded in the Material Studio software developed by Accelrys Inc. The condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) module in the Material Studio software was used to conduct force–field computations to account for the interactions between atoms and molecules [39]. This is the first ab initio force field that is parametrized and validated using condensed-phase properties in addition to various ab initio and empirical data. The force field is expressed as a sum of valence (or bonding), cross-terms, and non-bonding interactions:

$$E_{\text{total}} = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{non-bond}} \quad (1)$$

$$E_{\text{valence}} = \sum [K_2(b - b_0)^2 + K_3(b - b_0)^3 + K_4(b - b_0)^4] + \sum_{\theta} [H_2(\theta - \theta_0)^2 + H_3(\theta - \theta_0)^3 + H_4(\theta - \theta_0)^4] + \sum_{\phi} [V_1 [1 - \cos(\phi - \phi_0^0)] + V_2 [1 - \cos(2\phi - \phi_0^0)] + V_3 [1 - \cos(3\phi - \phi_0^0)]] + \sum_x K_x \chi^2 + E_{\text{UB}} \quad (2)$$

$$E_{\text{cross-term}} = \sum_b \sum_{b'} F_{bb'} (b - b_0) (b' - b'_0) + \sum_{\theta} \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0) (\theta' - \theta'_0) + \sum_b \sum_{\theta} F_{b\theta} (b - b_0) (\theta - \theta_0) + \sum_b \sum_{\phi} F_{b\phi} (b - b_0) \times [V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] + \sum_{b'} \sum_{\phi} F_{b'\phi} (b' - b'_0) (b' - b'_0) \times [F_1 \cos \phi + F_2 \cos 2\phi + F_3 \cos 3\phi] + \sum_{\theta} \sum_{\phi} F_{\theta\phi} (\theta - \theta_0) \times [V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] + \sum_{\phi} \sum_{\theta} \sum_{\theta'} K_{\phi\theta\theta'} \cos \phi (\theta - \theta_0) \times (\theta' - \theta'_0) \quad (3)$$

$$E_{\text{non-bond}} = \sum_{ij} \left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6} \right] + \sum_{ij} \frac{q_i q_j}{\epsilon r_{ij}} + E_{\text{H-bond}} \quad (4)$$

The valence energy, E_{valence} , is generally accounted for by terms of bond stretching, valence angle bending, dihedral angle torsion, and inversion. The cross-term interaction energy, $E_{\text{cross-term}}$, accounts for factors such as bond or angle distortions caused by nearby atoms to accurately reproduce the dynamic properties of molecules. The non-bonding interaction term, $E_{\text{non-bond}}$, accounts for the interactions between non-bonded atoms and results mainly from van der Waals (vdW) interactions. In Eqs. (1)–(4), q is the atomic charge, ϵ is the dielectric constant, and r_{ij} is the i - j atomic separation distance. b and b' are the lengths of two adjacent bonds, θ is the two-bond angle, ϕ is the dihedral torsion angle, and χ is the out of plane angle. b_0 , k_i ($i = 2 - 4$), θ_0 , H_i ($i = 2 - 4$), ϕ_i^0 ($i = 1 - 3$), V_i ($i = 1 - 3$), $F_{bb'}$, b'_0 , $F_{\theta\theta'}$, θ'_0 , $F_{b\theta}$, $F_{b\phi}$, $F_{b'\phi}$, F_i ($i = 1 - 3$), $F_{\theta\phi}$, $K_{\phi\theta\theta'}$, A_{ij} , and B_{ij} are fitted from quantum mechanical calculations and are implemented into the Discover module of the Materials Studio.

2.1. Oil shale surface

The most important inorganic constituents of oil shale are clay, calcite, and silica. Silica is the major mineral constituent in most shale formations. Therefore, the silica surface was investigated as oil shale surface in this work [40–42]. The initial silica lattice was derived from the database of the Material Studio software. The (100) silica surface was cleaved with a thickness of 1.2 nm. To investigate the effect of functional groups modified on the shale surface on the extraction of kerogen moieties with supercritical CO₂, the silica surfaces were modified with –OH (strong polarity) and –H (weak polarity). The structures of the modified silica surface are shown in Fig. S1.

2.2. Supercritical CO₂

Carbon dioxide in the gas phase was built in a 281 × 281 × 281 Å³ box with 600 CO₂ molecules. To obtain supercritical CO₂, we performed a constant-pressure/constant-temperature dynamics (NPT) simulation controlled by the Andersen thermostat method, with a fixed time step of 1 fs. Data were collected every 5 ps, and the full-precision trajectory was then recorded. By changing the simulation pressure and temperature, the supercritical CO₂ in the equilibrium state was finally obtained. Table S1 shows the density of supercritical CO₂ at different temperatures and pressures. The densities of supercritical CO₂ at 333.15 K and 373.15 K calculated in our simulation are quite similar to those in the database reported by Aimoli group [43].

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