



Upgrading of crude oil in supercritical water: A five-lumped kinetic model[☆]



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ABSTRACT

Experiments on upgrading crude oil in supercritical water (SCW) were conducted in an autoclave to investigate the influence of reaction conditions on pyrolysis and a five-lumped kinetic model was established. It can be illustrated that coke is mainly generated by asphaltenes and changing phase structure of the reaction system and enlarging the specific surface area of asphaltenes droplets via increasing water density or water–oil ratio can enhance the output of light components and suppress the formation of coke. The five-lumped kinetic model consists of saturates, aromatics, resins, asphaltenes, coke and coincides well with the experimental data.

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1. Introduction

It is essential and urgent to increase the yield of exploitation of crude oil nowadays, but more and more pore throats in oil reservoirs are plugged by precipitation of organic compounds, such as resins, asphaltenes, and other heavy components of crude oil. To optimize the production of oil wells, it is necessary and urgent to remove the precipitated heavy-compounds in the flow channels near down-hole zones.

Recently, high energy gas fracturing (HEGF), an effective oil recovery technique to stimulate wellbores via producing cracks around the holes with the combustion of energetic materials such as solid rocket propellants, has been utilized to exploit the petroleum resources. It does not only release high pressure gas to fracture the rock layers of oil reservoirs but also substantial thermal energy to transform the aqueous phase into supercritical state in down-hole zone during the combustion process [1].

SCW is a thermodynamic state of water, of which the temperature and pressure reach critical values ($T_c = 647.5$ K, $P_c = 22.05$ MPa,

$\rho_c = 0.31$ g/cm³) [2–4]. With its solvent properties and potential ability to donate hydrogen [5,6], SCW could take part in reaction as a solvent as well as a reactant or even catalyst [7–10] to transform the large molecules. Since SCW has a lower viscosity coefficient which significantly accelerates mass transfer rate and a higher dissociation constant which improves its ability to catalyze chemical reactions [11,12], it was believed that those unique properties of SCW can have a positive influence on the upgrading of heavy components in oil reservoirs. With the cracking of long-carbon chains of heavy compounds in SCW condition and decomposition of macromolecules into relatively smaller molecules [7,13,14], SCW could play an important role in decomposing the organic precipitates, treating the paraffin and upgrading heavy compounds in the near perforation area so that the flow channels could be reopened for the increase in the yield of petroleum exploitation. Hence, a need for the study of oil upgrading reactions in SCW. Studies in this research area regarding the influence of reaction factors and kinetics of upgrading of crude oil in SCW were reported in a few papers [15,16].

Yong Ding et al. [17] reported that reaction temperature should not be too high so that the formation of coke could be controlled when upgrading vacuum residuum in SCW without oxidation. The optimum reaction conditions are as follows: the reaction temperature is 420 °C with reaction time of 1 h, while water density is 0.15 g/cm³ and water/oil ratio is 2 g/g. In addition, the cleav-

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Table 1
Properties of the feedstock.

$\rho(\text{g}/\text{cm}^3)$	SARA fraction(wt%)			
	Saturates	Aromatics	Resins	Asphaltenes
0.86	70.51	18.00	7.75	3.74

age reaction can be improved significantly with the simultaneous increase of water density and water-oil ratio. Takafumi Sato et al. [18] have studied the upgrading of asphalt at 613–673 K temperature range, and 0–0.50 g/cm³ water density in SCW. It was found that asphaltenes conversion increased with increasing in water density. Moreover, water apparently participated in the reaction and its hydrogen was advantageous to the free radical path, which resulted in an increased yield of maltene. Ying Liu et al. [19] confirmed that upgrading of residual oil in sub- and super-critical water is based on the free radical mechanism. And then, with the increase in water density, the upgrading system became a pseudo single-phase structure in which asphaltenes are highly dispersed in the continuous aqueous phase rather than a miscible two-phase structure. In other words, the aromatic radicals generated by asphaltenes diffusing into aqueous phase were prompted, which can both depress the formation of coke and promote the distribution of the liquid products.

It is known that kinetic study is an effective way to predict the products distribution and choose the best reaction condition, however, most of the kinetic studies focus on thermal cracking system of crude oil without water while researches on kinetics of upgrading oil in SCW system are few [20,21]. Moreover, most of these studies divided the lumps by boiling points of oil components [22,23]. Xuecai Tan et al. [16] reported that the reaction system was lumped into gas, maltene, asphaltenes and coke according to components' structures. However, no one is yet to lump maltene into saturate, aromatic and resin in lumped models, which is essential in this work since the viscosity of resin is significantly higher than that of saturates and aromatics while viscosity is closely related with the flowability of oil reservoirs near perforation area.

In this work, crude oil pyrolysis was conducted in SCW to study the upgrading results under different reaction conditions. In addition, a kinetic model, which lumped as saturates, aromatics, resins, asphaltenes and coke, by contrast from previous lumps, was developed and evaluated by experimental data.

2. Experimental section

2.1. Pyrolysis experiments

The experiments were carried out in an autoclave (Hartz alloy material, 50 ml, 773 K, and 40 MPa) in which the pressure and temperature could be measured precisely. The feedstock was supplied from Yan Chang oil field, Shaanxi Province, whose basic components are listed in Table 1. According to the preliminary thermo-gravimetric analysis, the lowest temperature in which crude oil could be cracked is around 623 K [16].

For the pyrolysis experiments, 10 g crude oil and 10 g water were loaded into the autoclave. Then the reactor was sealed and placed into an electric heating jacket. When the reaction temperature approaches the set-value, heating strategy will be changed to stabilize the temperature of reactor and start timing. At the end of reaction, the reactor was cooled by water-bath to aid the stoppage of the reaction within two minutes. The products were collected by washing the internal surface of the reactor with *n*-heptane for component analysis. All of the pyrolysis reactions were carried out in the temperature range of 653–693 K and pressure range of 23–38 MPa,

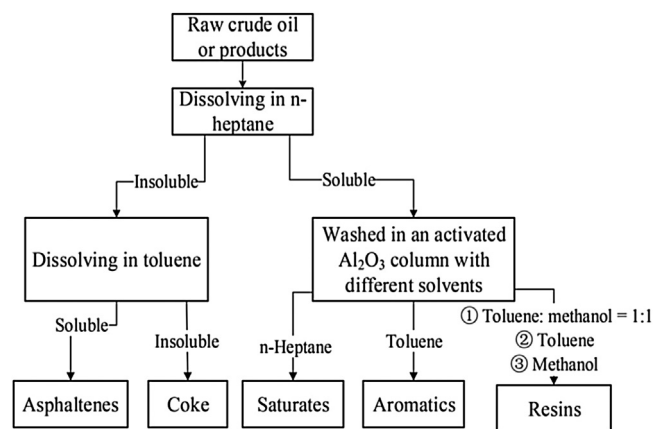


Fig. 1. SARA separation procedure for raw crude oil and upgrading products.

which was believed to be under SCW condition. The reaction time ranges from 30 to 180 min.

2.2. Product separation and analytical procedures

Following the Industrial Standard of Chinese Petrochemical NB/SH/T 0509-2010 shown in Fig. 1, the obtained products were separated sequentially into saturates, aromatics, resins, asphaltenes (SARA groups) and coke. Then the reactor was washed with *n*-heptane to collect liquid and solid products. The organic phase and inorganic phase were separated by decantation and centrifugation.

Firstly, the organic products were dissolved in *n*-heptane so that asphaltenes and coke which cannot be dissolved by *n*-heptane could be separated from the products and purified by toluene extraction. The dissolved products were classified into three groups: saturates, aromatics and resins; they are separated by an activated Al₂O₃ (0.075–0.150 mm) chromatographic column with different solvents as shown in Fig. 1. After separated, the three components were purified by rotary evaporation and vacuum drying to remove the solvents, which causes the mass loss of some small molecules in feed stock or pyrolysis products, especially gas molecules in products. Moreover, a few of products could stay in the chromatographic column that can be observed through the change of color in chromatographic column. These factors make the total mass recovery rate ranges from 93% to 98%. The solvents (*n*-heptane, toluene and methanol) used in chromatographic column are analytical reagents and purchased from Beijing Chemical Works. Al₂O₃ powder for the chromatographic column was purchased from Sinopharm Chemical Reagent Co. Ltd. Each experimental run was repeated three times, while the maximum errors of the product distribution fell within a reasonable range of 5%. Only the average values were reported and were adopted in the calculation on reaction kinetics.

The mass balance in each experiment was calculated by Eq. (1), which was formed by loss of gas and residue in alumina chromatography column:

$$MB = \sum m_i / m_{\text{raw-oil}} \times 100\% \quad (1)$$

In the formula, m_i represents the weight of each collected component in the product, and $m_{\text{raw-oil}}$ denotes the weight of feed stock. Only when the value of MB is more than 92% can the data be considered credible.

The yield of each collected component was indicated by eq. (2):

$$Y_i = \frac{m_i}{m_{\text{raw-oil}}} \times 100\% \quad (2)$$

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