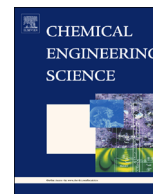




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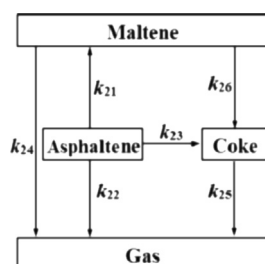
Kinetic and reaction pathway of upgrading asphaltene in supercritical water

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HIGHLIGHTS

- Asphaltene was converted to gas, maltene and coke in SCW (supercritical water).
- Asphaltene transformation in SCW obeyed the first-order kinetic.
- A new reaction pathway model was proposed for upgrading asphaltene in SCW.
- The possibility of secondary reaction of coke to gas was illustrated.

GRAPHICAL ABSTRACT



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ABSTRACT

Experiments of upgrading asphaltene in Supercritical Water (SCW) were conducted in autoclaves with sealed gold tube reactors to elucidate the reaction pathway and reaction kinetics. The experiments were performed at temperature of 400–450 °C, pressure of 30 MPa and residence time ranging from 0 to 120 min. The products obtained from the upgrading asphaltene in SCW included gas, maltene and coke. Kinetic analysis showed that upgrading asphaltene in SCW obeyed a first-order kinetic with apparent activation energy of 51.11 kJ/mol. Three possible 4-lump kinetic models were proposed to discuss the detailed reaction pathway of upgrading asphaltene in SCW. The first-order kinetic equations were used to evaluate the reliability of each model from the aspect of correlation coefficient (R^2). The results showed that Model 2, considering the parallel reaction of asphaltenes transformation to gas, maltene and coke, the consecutive reaction from maltene to gas and coke, the secondary reaction of coke to gas, was illustrated as the optimal reaction pathway model for upgrading asphaltene in SCW.

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1. Introduction

Asphaltene, insoluble in light *n*-alkanes and soluble in aromatic solvents, is known as the most complex and heaviest fractions of crude oil, bitumen, heavy oil, or vacuum residue (Savage and Klein, 1988; Sun et al., 2010; Yasar et al., 2001). It usually consists of highly

condensed polyaromatic macromolecules bearing long aliphatic chains and alicyclic substituents (Mandal et al., 2012a, b). In the refining processes, asphaltene is prone to form coke and deactivate catalyst (Akmaz et al., 2012; Ayala et al., 2012; Zhao and Yu, 2011). Moreover, high concentrations of heteroatoms (N, S) and metal elements (Ni, V) in asphaltene will seriously interfere with the refining processes (Zhang et al., 2011; Zhao et al., 2011). These situations will become worse with the depletion of the conventional light crude oil reserve and the use of more heavy oils with significant portion of asphaltene as substitute (AlHumaidean et al., 2013). To

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maximize the useful value of heavy oil, it is necessary to optimize the utilization of asphaltene.

Nowadays, numerous technologies based on carbon rejection and hydrogen addition route have been applied to address the problematic asphaltene. Among the technologies of carbon rejection, the technique of deasphalting is often used because of its effective removal of heteroatoms in the extraction processes (Ali and Abbas, 2006). However, the extraction processes usually need to consume large amounts of organic solvent and the mass loss of heavy oil after the asphaltene precipitation reaches highly 30% (Bronson and Yu, 1995). The other techniques of carbon rejection, especially delayed coking, are also preferred by the refineries due to their lower investment (Rana et al., 2007). But with the decreasing demand for fuel oil, these processes will fall into dilemma as little liquid products but much coke were formed from these thermal processes (Siskin et al., 2006; Xu et al., 2007). Although the hydrogen addition processes can retard the formation of coke and convert heavy components into valuable light fraction, the cost of hydrogen is considerable (Furimsky, 2013; Zhao and Wei, 2008). Additionally, the deposition of coke and metals can easily deactivate the expensive catalysts for upgrading heavy oil (Xu et al., 2009). Therefore, novel processes, using alternative hydrogen sources to replace expensive molecular hydrogen and retard the coke formation, need to be developed.

SCW is defined as the thermodynamic state above the critical temperature and pressure (374.3 °C and 22.1 MPa). In recent years, the ubiquitous solvent properties and potential abilities to donate hydrogen of SCW have aroused great interest in the scientific community (Yan et al., 2009). Some researchers believe that SCW could not only serve as the solvent but also provide the active-hydrogen for capping of reactive fragments to form more light components and less coke in upgrading heavy oil (Cheng et al., 2009; Kozhevnikov et al., 2010; Morimoto et al., 2010; Sato et al., 2003; Watanabe et al., 2010; Zhao et al., 2006). It is also reported that C–O bonds in ethers and esters, C–S bonds in aliphatic chain and metal elements incorporated in asphaltene are easily broken in SCW (Mandal et al., 2011, 2012b; Savage, 1999). Unfortunately, upgrading asphaltene in SCW has not garnered attention until recently. Kozhevnikov et al. (2010) reported that the formation of gas and maltene was mainly through the dealkylation of aromatic substituents and aromatization for the cracking of asphaltene in SCW. Morimoto et al. (2012) discussed the influence of temperature and pressure on the extraction of asphaltene with SCW.

For upgrading asphaltene in SCW, kinetic study is an effective way to predict the product distribution and to optimize the reaction conditions (AlHumaidan et al., 2013; Galarraga et al., 2012). However, most of the kinetic studies were focused on asphaltene pyrolysis system while kinetic of upgrading asphaltene in SCW system was seldom investigated. Although temperature has a decisive effect on kinetic for upgrading asphaltene in both systems, effect of reaction environment on kinetic cannot be neglected. It is reported that the miscibility of SCW with most organic compounds and gases may provide a mass transfer environment that is completely different from the pyrolysis system. Considering the huge differences in mass transfer environments and the solvent effect of SCW, kinetic study of upgrading asphaltene in SCW is essential. The transformation of asphaltene, involving polymerization, condensation, carbonization and lots of intrinsic reactions among the products, is a complicated process (Zhao et al., 2011). Therefore, a simplified modeling approach, namely the discrete lumping, is adopted to study the kinetic of upgrading asphaltene in SCW. In this modeling approach, the products for upgrading asphaltene in SCW are lumped into gas, maltene and coke.

To avoid the catalytic effect of the reactor walls, experiments of upgrading asphaltene in SCW were conducted in an autoclave

with gold tubes. In this study, effects of temperature and reaction time on upgrading asphaltene in SCW were studied. Meanwhile, the reaction pathway and kinetics for upgrading asphaltene in SCW were analyzed in detail based on experimental data.

2. Experimental section

2.1. Chemicals and materials

Asphaltene was separated from Tahe heavy crude oil following a method similar to the ASTM D 6560. The asphaltene samples were precipitated from crude oil by ultrasonic dispersion in 40:1 (v/v) excess of *n*-hexane overnight. The precipitate separated by centrifugation at 6000 r/min for 10 min was dissolved in toluene with a ratio of 20:1. Subsequently, after separation by centrifugation and concentration, the asphaltene was subjected to Soxhlet extraction with *n*-hexane until the reflux remained colorless. Finally, the extracted asphaltene was dried at 150 °C in the nitrogen gas atmosphere and was finely pulverized. The asphaltene elemental compositions and metal contents determined by a Vario EL-III Elemental analyzer and an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700X, USA), respectively, are shown in

Table 1
Properties of the asphaltene.

Properties	Units	Values
Carbon	wt%	84.63
Hydrogen	wt%	6.97
Oxygen	wt%	2.75
Nitrogen	wt%	1.07
Sulfur	wt%	4.29
Nickel	mg/kg	90.4
Vanadium	mg/kg	720.1
Atomic ratio of H/C	–	0.98

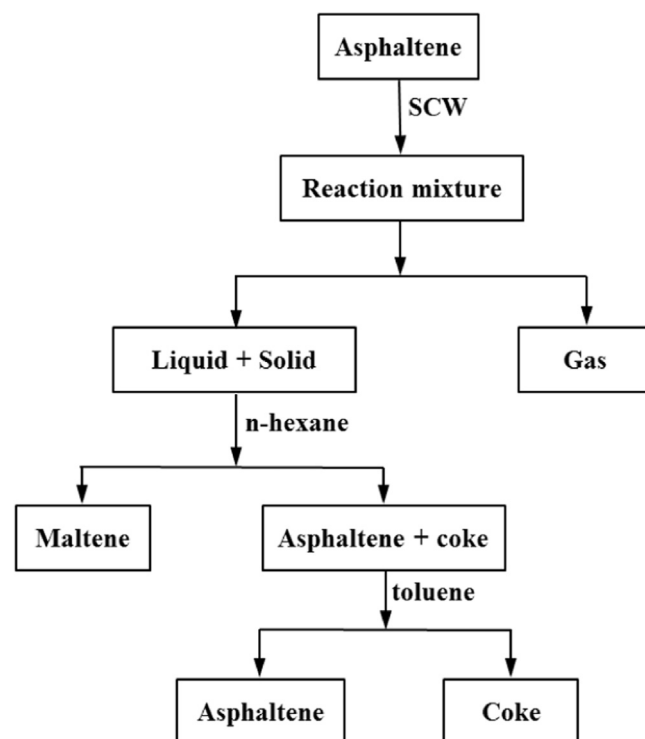


Fig. 1. Product separation flowchart.

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