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Upgrading of residual oil in sub- and supercritical water: An experimental study

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ABSTRACT

To increase the understanding of the reaction behavior of heavy hydrocarbons in the presence of sub- and supercritical water, upgrading of residual oil was applied in a batch reactor at temperatures of 653 to 713 K and water densities of 0.05 to 0.20 g/cm^3. It is confirmed that upgrading of residual oil in sub- and supercritical water is still dominated by the free radical mechanism based thermal cracking. The ion mechanism based hydrolysis only has an extremely limited influence on the upgrading performance. With the increase in water density, the upgrading system may evolve from a partially miscible two-phase structure to a pseudo single-phase structure in which asphaltenes are highly dispersed in the continuous water phase. Prompt diffusion of aromatic radicals from asphaltenes into the water phase both depresses the coke formation and improves the liquid product distribution.

1. Introduction

In the near-critical region, the properties of water change dramatically between gas- to liquid-like extremes as a result of the partially destructed hydrogen bonding network. Organic reactions applied in sub-critical or supercritical water (sub-CW or SCW) can occur in a single dense phase with favorable transport properties and high diffusivities, thus improving the reaction kinetics [1–5]. Among these, upgrading of heavy hydrocarbons such as vacuum residue and coal tar in SCW has been attracting increasing attention in the literature due to the worldwide shortage of non-renewable fossil fuels [6–14].

One of the important motivations for upgrading hydrocarbons in SCW is that the saturation of hydrocarbon radicals through the direct H-abstraction from water once was considered to be viable, which means SCW may serve as a cheap and an environmentally benign H donor. However, in the degradation of polyethylene in SCW using D_2O and $H_2^{18}O$ as tracers, it was reported that H atoms from water participated in the reaction network by the hydration of α-alkene rather than by the H-abstraction from H_2O [15,16]. In other words, SCW would appear to be an inert reaction medium for the free radical mechanism based thermal cracking.

Although SCW does not seem to participate in the thermal cracking of hydrocarbons, many experimental studies did have observed intricate reaction behavior under varied SCW environments. Cheng et al. suggested that asphaltenes can be partially dissolved and dispersed in SCW to form an emulsion [17,18]. The presence of SCW not only improves the yield and quality of light product, but also slows down the coking process because of the mass-transfer resistance between emulsion droplets. Such a positive role was confirmed by Bi et al. in the upgrading of coal tar in SCW [19,20]. However, Takanohashi et al. reported that the middle distillate of the upgrading of oil sand bitumen in SCW actually has no significant

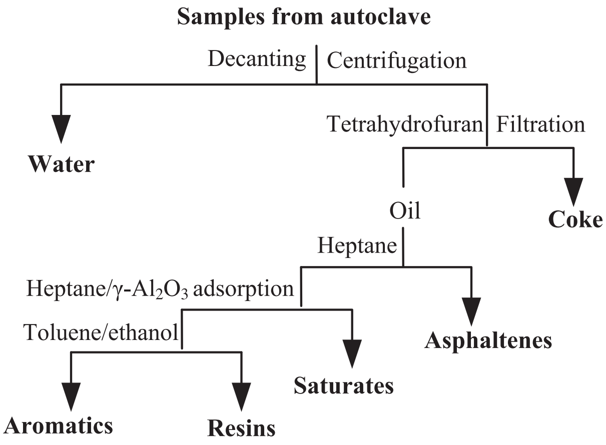

Fig. 1. SARA separation procedure for raw residual oil and upgrading products.

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Table 1
Properties of the raw residual oil.

ρ (g/cm^3)	H/C	SARA fraction (wt.%)				H distribution (%)			
		Saturates	Aromatics	Resins	Asphaltenes	H_{Ar}	H_α	H_β	H_γ
0.98	1.1	15.2	20.0	27.5	37.3	5.7	18.3	57.3	18.7

difference from that applied under N_2 atmosphere [21]. Watanabe et al. also proposed that the mixture of sub-CW and heavy oil can be in a two-phase structure at high water densities [22]. The concentration of heavier fraction in the oil phase is increased by extracting light oil into the dense water phase, which promotes the coke formation in the condensed oil phase. So far, the interpretation of the essential functions of SCW is still ambiguous.

Due to the presence of heteroatom-containing functional groups, the composition of heavy hydrocarbons is more complicated than that of pure hydrocarbons, e.g. *n*-hexadecane and polyolefins. The hydrolysis resulted from the acid/base nature of water in the vicinity of the critical point is likely to occur, superimposing an additional influence on the thermal cracking. On the basis of the available information, the authors proposed that both the reaction mechanism and the phase structure should be vital to the upgrading of heavy hydrocarbons in sub-CW or SCW.

Hereby, upgrading of residual oil under severe hydrothermal environments was experimentally studied in this work. By comprehensive characterizations on upgrading products, the possible reaction mechanisms at different upgrading stages were surveyed. Special focuses were emphasized on the evolution of the phase structure of the upgrading system, followed by a further discussion on the resulted influences on the upgrading performance as well as the coking behavior.

2. Experimental

2.1. Apparatus and reaction run

Upgrading of residual oil with the asphaltene fraction of 37.3 wt.% was performed in a Parr 4598 HPHT autoclave with a capacity of 0.1 L. The reaction temperature and density of water were varied from 653 to 713 K and 0.05 to 0.20 g/cm^3, respectively. In each run the reactor was pre-heated to a desired reaction temperature. Then, 20.0 g residual oil and a given amount of deionized water were charged into the autoclave with metering pumps in 2 min. At a fixed stirring rate of 1000 rpm, the reaction might last 15 to 60 min in terms of the scheduled arrangement. After that, the reactor was subjected to forced air cooling to rapidly terminate the reaction.

2.2. Characterization and analytical procedures

The upgrading products were separated sequentially according to a procedure as shown in Fig. 1. By decanting and centrifugation, most water was removed from the cracking product. Then, the product was dissolved in tetrahydrofuran, followed by filtration to separate coke. After that, tetrahydrofuran was removed from the product by rotary evaporation. Subsequent separation of the obtained liquid product was based on the Industrial Standard of Chinese Petrochemical NB/SH/T 0509-2010. Basically, *n*-heptane insoluble asphaltenes were first separated from the liquid product. The remaining maltenes were further divided into saturates, aromatics, and resin by washing with different solvents in an activated γ-Al_2O_3 chromatographic column.

Table 2
True boiling points of the raw residual oil.

Volume (%)	0	5	10	30	50	70	90	95	100
Temperature (K)	635	679	693	733	773	818	879	904	943

The yield of liquid fractions and coke (*Yield*) were evaluated by

$$Yield = m_i / m_{raw\_oil} \times 100\% \tag{1}$$

where m_i denotes the weight of the collected liquid fractions or coke. m_{raw_oil} is the weight of the loaded raw residual oil.

The mass balance (*MB*) in each run was evaluated by

$$MB = \left(\sum m_i\right) / m_{raw\_oil} \times 100\% \tag{2}$$

Usually, a mass balance between 92% and 98% could be observed mainly because of the neglected gas production and loss during product separation.

Elemental analysis of raw residual oil and upgrading products was applied on a vario EL III element analyzer. The XRD pattern of coke was recorded on a Bruker D8 advance X-ray diffractometer using Ni-filtered Cu K_α radiation, the morphology of coke being observed on a NanoScope IIIa MultiMode AFM microscope. ^{1}H NMR spectra of the raw residual oil and upgrading products were analyzed on a Bruker AVANCE 500 MHz NMR Spectrometer. Protons in oil were classified as H_{Ar}, H_α, H_β, and H_γ with the specific chemical shift in ^{1}H NMR spectra [23–25].

The properties of raw residual oil were measured based on the established methods, with the results listed in Table 1.

2.3. Phase structure calculation

The phase structure of residual oil in the presence of sub-CW and SCW was calculated using Aspen Engineering Suite 2006. The calculation applied a flash operation of the mixture of residual oil and water under a preset hydrothermal condition, during which the SRK equation of state was implemented. Assay data about the true boiling points (TBP) of residual oil are listed in Table 2.

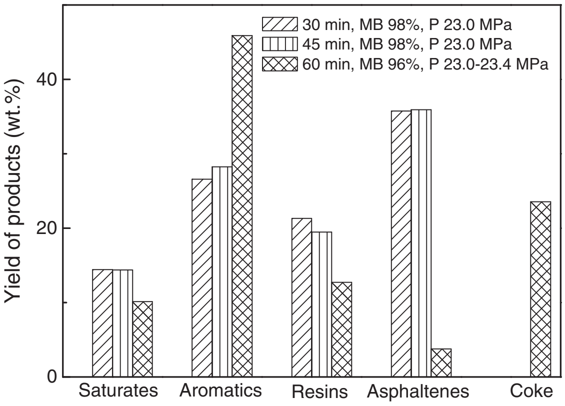

Fig. 2. Yield of upgrading products vs. reaction time; T = 653 K, ρ_{water} = 0.20 g/cm^3.