Heavy Oil Upgrading in Supercritical Water: Basic Study

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Abstract: Heavy oil upgrading in supercritical water (at 723 K) was performed by small batch reactors. Yields of asphaltene, maltene, and coke were evaluated. At 200 kg/m^3 of water density, the rate of coke formation promoted compared to neat pyrolysis, but the yield of coke, about 10 wt % based on the starting heavy oil, was not enhanced by water. In order to know the mechanism of coke formation, asphaltene reaction was also conducted. In the absence of supercritical water, the yield of coke was still 20 wt%. On the other hand, by adding supercritical water (200 kg/m^3 of water density), the coke formation was suppressed (below 10 wt%). Based on the results, the reaction mechanism of heavy oil was considered: lighter oil was dissolved in supercritical water and the concentration of light hydrocarbon in heavier oil phase was lower. Still heavier oil was formed oil-rich phase and heavier oil was concentrated. Thus, the lighter oil decomposed further in supercritical water phase and the heavier oil combined together to form coke due to higher concentration. Now we are studying of effect of physical phenomena (such as mass trasfer, the oil/water ratio, and so on) on the reaction.

Keywords: bitumen, asphaltene, upgrading, supercritical water, coke formation, phase behavior

1. Introduction

In these days, while crude oil has became heavier and the amount of impurities such as sulphur, nitrogen, and heavy metals, have been higher than ever, demand of lighter liquid oils has been increasing. Due to the dwindling amount of petroleum, heavier bitumens, tar sand, and oil shale will have to be used in the near future. Steam stimulation is often used to recover the highly viscous oil from reservoirs. As a result, heavy oil emulsions are formed at wellheads. For such reasons, water is common solvent for bitumen process such as extraction and recovery of bitumen from soil. Further utilization of water for upgrading of bitumen such as dilution solvent, hydrogen donor, and so on, would be required for improving the quality of bitumen and cut cost of bitumen process.

Supercritical state of water is attractive for new upgrading technique of bitumen and many researchers have investigated to look for an optimum condition and an additive. For the case of the catalytic cracking processes, coke deposition, which deactivates the catalysts, is a serious problem. One idea to solve these problems is to use supercritical fluids for the reaction media, since both hydrogen and oils are miscible with supercritical water. To reduce viscosity of bitumen without forming coke by no use of hydrogen and expensive catalyst is one of ideal procedures. In order to idealization of the new upgrading process, mechanism of coke formation and effect of supercritical water on it must be revealed.

In this study, we carried out several batch experiment of bitumen and asphaltene reaction in the present and absent of supercritical water. Based on the results, the effect of supercritical water on coke formation was discussed, mainly by focusing on phase behaviour between asphaltene aggregates and supercritical water.

2 Experimental

Bitumen that is used in this study consists of 90 % maltene and 10 % of hexane asphaltene. In the case of asphaltene reaction, an amount of asphaltene was extracted by hexane and toluene from raw bitumen, followed by filtration and evaporation of toluene.

Experiments were conducted with stainless steel (SS 316) tube bomb reactors (6 cm^3), of which schematic diagram was shown in Figure 1. A 0.6 g of bitumen was loaded in a reactor. The loaded amounts of water ranged from 0 g to 1.2 g (water densities: 0 kg/m^3 to 200 kg/m^3). Air in the reactor was purged with Ar gas.

The loaded reactor was submerged in a malten salt bath whose temperature was controls to be 723 K ± 1 K. Heat-up time required was around 90s. After a reaction time up to 30 min, the reactor was taken out of the bath and rapidly cooled in a cold water bath.

The liquid products were collected by rinsing reactor with hexane and toluene. Gas and hexane soluble compounds were defined as maltene in this study. Toluene soluble was asphalene. The insoluble in toluene was divided by filtration with membrane filter and was weighted as coke after drying for a day. Molecular weight distribution of asphaltene was evaluated by MALDI-TOF-MS.

Asphaltene and coke yields were evaluated based on the weight of the recovered asphaltene and coke, as follows:

$$\text{Asphaltene (Coke) yields [wt\%]} = \frac{\text{Amount of Asphaltene (Coke) [g]}}{\text{Amount of loaded sample [g]}} \times 100 \qquad 1)$$

Maltene yield was evaluated as follow:

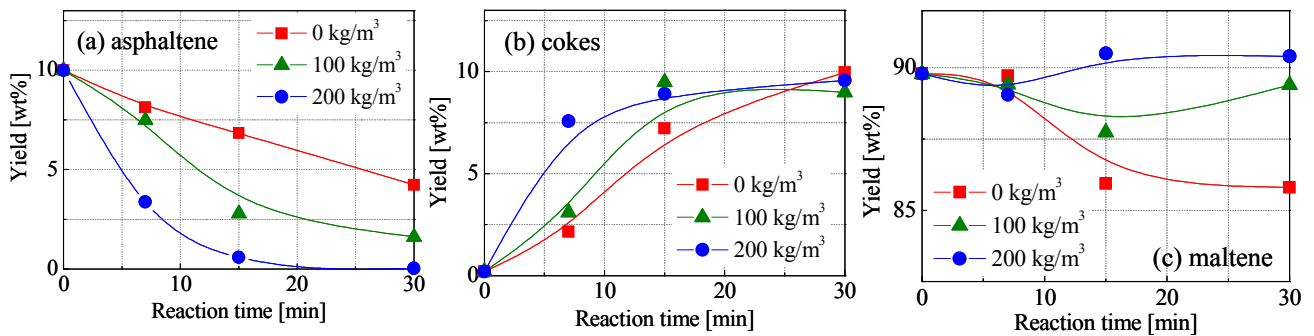$$\text{Maltene yields [wt\%]} = 100 - \text{Aphaltene yield} - \text{Coke yield} \qquad 2)$$

Fig. 1 Batch reactor used in this study

3 Results and Discussion

Fig. 2 Variation of yields with reaction time and water density at 723 K for (a) asphaltene, (b) cokes, (c) maltene
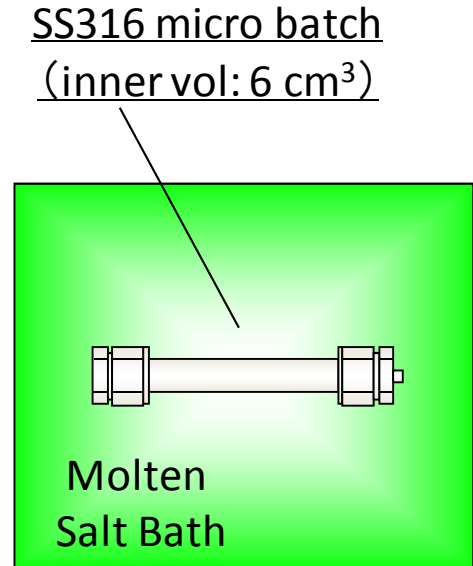
Figure 2 shows the time profile of the yields of the products, that is, (a): asphaltene, (b):coke, and (c) maltene. Fig.2 (a) shows that the decrease of asphaltene with time promoted with increasing water density. In response to changing the asphaltene yields, the coke formation enhanced with increasing water density, as shown in Fig. 2 (b). The maltene was no significant change in high density of supercritical water. From Fig. 2 (a)-(c), coke formed by reaction between asphaltene and maltene and thus the coke yield would increase at a longer reaction time because of still existence of asphaltene. On the other hand, at 200 kg/m^3, asphaltene completely consumed by the reaction and maltene seemed to have no relation of coke formation.

Fig. 3 shows the molecular weight distribution of asphaltenes obtained by pyrolysis (0 kg/m^3) and decomposition in supercritical water (200 kg/m^3) for 15 min and 30 min.
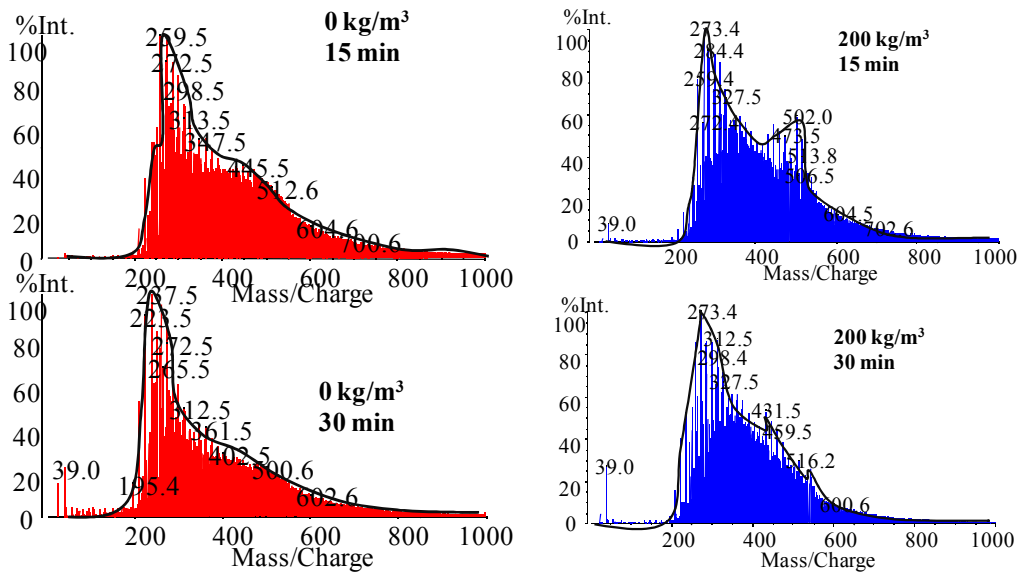

Fig. 3 Molecular weight distribution of asphaltene after pyrolysis and decomposition in supercritical water

By adding supercritical water, asphaltene became heavier, as shown in Fig. 3. According to the literature (Wieche, 1992), the molecular weight of asphaltene decreased with the coke formation increase. While coke yield in supercritical water was higher than that in the absence of water, the molecular weight was heavier in supercritical water, that is, opposite trend to the literature.

We also conducted the experiments with asphaltene. As a results, the coke yield in pyrolysis without water was 60 % at 723 K for 15 min. In the presence of supercritical water (200 kg/m^3), the coke yield was 30 %.

Towfighi et al. (2002) reviewed the literatures concerning coke formation in heavy oil upgrading and suggested that there were 3 routes of coke formation: (1) from an active site on the catalyst and reactor wall, (2): from the reaction in an asphaltene aggregate, and (3): from the reaction between asphaltene precursor and low molecular radicals.

Figure 4 shows the assumption of reaction in this study. In the absence of water, heavier oil liquid dissolved a small hydrocarbons. With heating up, radicals produced in the heavier oil phase and radicals and heavier hydrocarbons (such as asphaltene aggregate) easily reacted with each other and coke formed (Fig. 3 (i)). On the other hand, supercritical water dissolved a small hydrocarbon and the small hydrocarbons mainly decomposed into small fragment in supercritical water phase. However, Brunner (1990) reported that phase diagram of hydrocarbon and water system was type III and thus higher molecular weight hydrocarbon is immiscible even in supercritical water. Stevenson et al. (1994) measured water-squalane (C30 hydrocarbon) system and reported that liquid-liquid phase separation appeared at high water composition and higher pressure. Thus, even in supercritical water, heavier hydrocarbons formed liquid phase in the bottom of the reactor and the concentration of the heavy hydrocarbons was higher in the presence of supercritical water because small

hydrocarbons by supercritical water were extracted by supercritical water. The concentrated asphaltene aggregates easily combined with each other and the reaction rate of asphaltene disappearance and coke formation were promoted by supercritical water.
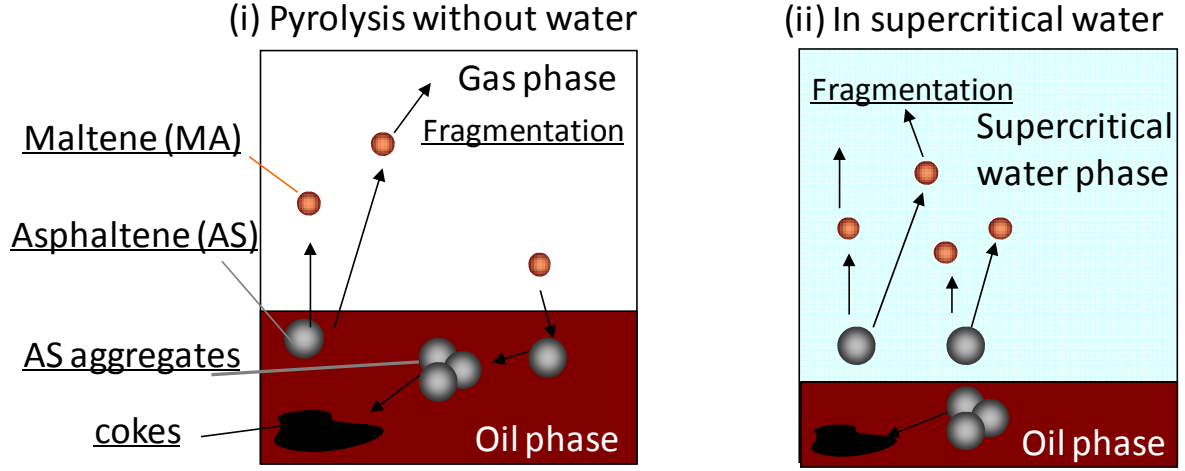
(i) Pyrolysis without water   (ii) In supercritical water

Fig. 4 Assumption of phase in the reaction: (i) pyrolysis without water, (ii): in supercritical water

In order to confirm the mechanism, we performed the simple kinetic analysis by phase separation kinetic model proposed by Weiche (1993). We also developed a simple model based on the phase separation kinetic model. The model is briefly explained as follows: reactive asphaltene (A^+) and non volatile maltene (M^+) produce asphaltene core (A^*), as shown in Eqs. 3) and 4), where k is rate constant and c is stoichiometric constant.

$$M^+ \xrightarrow{k_B} A^* \qquad \qquad 3)$$
$$A^+ \xrightarrow{k_A} cA^* + (1-c)M^+ \qquad \qquad 4)$$

Non volatile maltene (M^+) can dissolve some amount of asphaltene core, but the excess amount of asphaltene core (A_{ex}^*) precipitated when the amount of asphaltene core exceeded the solubility limit, as shown in Eq. 5),

$$A_{ex}^* = A^* - A_{max}^* = A^* - S_L(M^+) \qquad \qquad 5)$$

where A_{max}^* was the maximum amount of soluble asphaltene core in non volatile maltene and S_L was the solubility limit coefficient. After the precipitation, the precipated asphaltene core (A_{ex}^*) was changed into coke as written in Eq. 6).

$$A_{ex}^* \xrightarrow{k_C} C \qquad \qquad 5)$$
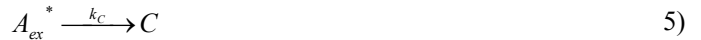
The value of c (stoichiometric constant) was set 0.543 (Rahmani et al. (2002)). We simulated the experimental data (Fig. 1) by fitting the kinetic parameter and the solubility coefficient (S_L) of the model. Every reaction was first-order to reactant concentration. Strictly, the concentrations of asphaltene and maltene in the reactor were not same at the different reaction condition and the kinetic parameter must be constant because all of the experiments were performed at the same temperature. However, the concentration of the reactants was not known. In order to estimate the relative phase behaviour, we fitted the experimental data by changing the kinetic parameters. Table 1 shows the kinetic parameters, which were normalized by the kinetic parameter at pyrolysis (without water). Figure 5 shows the comparison of asphaltene and coke yields between the experimental data and the simulation. As shown in Fig. 5, the simulation well described the experimental data.

Table 1 Normalized kinetic parameter

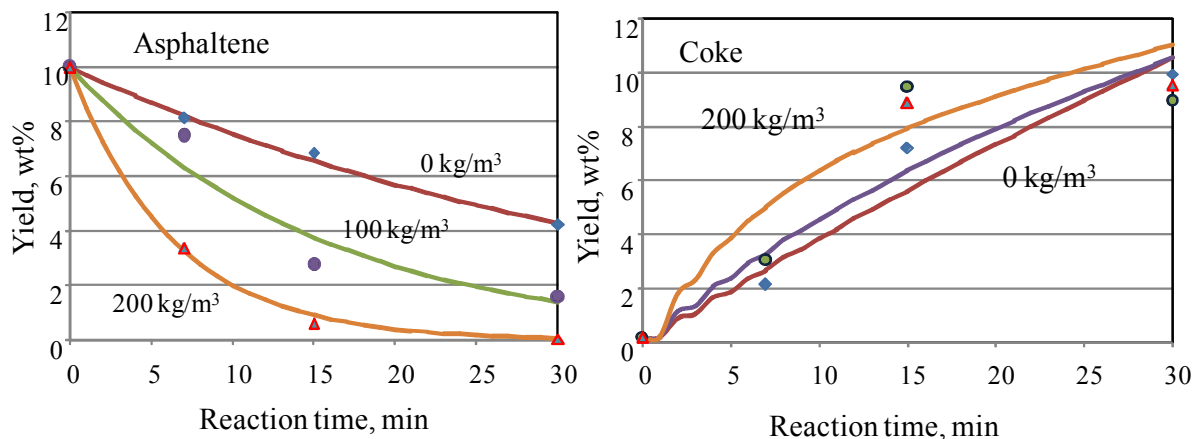|	0 kg/cm^3	100 kg/cm	200 kg/cm^3
k_{A_n}	1.00	2.32	5.68
k_{B_n}	1.00	0.75	0.67
k_{C_n}	1.00	0.97	0.88

Fig. 5 Comparison of asphaltene and coke yields between experimental and simulation

As shown in Table 1, the rate constant of asphaltene core formation (k_A) increased with increase of water density, while that of maltene decomposition into asphaltene core (k_B) decreased. The asphaltene core formation was first-order to the asphaltene concentration and the maltene concentration. When some amount of maltene (relatively low molecular weight) was dissolved into supercritical water, the concentration of asphaltene in the liquid maltene phase was condensed. On the other hand, in supercritical phase, the concentration of maltene was diluted and the maltene conversion into ashaltene core was prohibited. The rate constant of coke formation (k_C) slightly decreased with water density increase and the coke formation was affected by water to some extent.

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