

Effect of water, toluene, and water-toluene mixture in their supercritical condition on bitumen pyrolysis

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We observed phase behavior of Canada oil sand bitumen in some solvents (water, toluene, and water-toluene mixture) over their critical temperatures and pressures. Gas and liquid phase separation was seen in all the cases. In addition, liquid-liquid-gas phase separation was observed in the presence of water. In these solvents, bitumen pyrolysis was performed at 430 °C. In toluene and water-toluene mixtures, the yield of cokes was suppressed compared with in the absence of solvent. By adding water to toluene (it means water-toluene mixture), the formation of coke was higher than that in toluene. This is probably because inhibition of vaporization of some part of maltene due to higher pressure in the presence of water. A mathematical kinetic model was applied to analyze the effect of the solvents on the bitumen pyrolysis. The effect of the solvents on the pyrolysis was evaluated by the comparison of the rate constant in the model. In the analysis, it was considered that the change of the rate constant was reflected in change of the concentration of the reactants. As a result, the concentration of maltene was diluted by extraction to the gas phase, on the other hand, that of asphaltene was concentrated in the presence of solvent.

INTRODUCTION

In these days, while crude oil has become 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.

Previously, we studied the effect of supercritical water (400 °C ~ 450 °C, 100 ~ 200 kg/m³ of water density) on bitumen pyrolysis without catalyst [1]. As a result, water behaved extraction solvent of lighter fraction from bitumen and thus heavier fraction in bitumen changed into coke rapidly. Advantage of water usage in bitumen pyrolysis was to reduce coke because some of lighter fractions, which combined with heavier one to coke without

water, escaped to supercritical water phase. We expected that water dissolved in liquid phase of heavier oil to dilute the concentration of heavy asphaltene. To dissolve a solute in liquid asphaltene, the solute might have polarity and aromatic ring to interact with hetero atom in bitumen and with aromatic rings via π - π interaction, respectively. Water has a polarity but does not have aromatic ring and thus was not effective for reducing coke formation.

Toluene is well known to be good solvent for asphaltene because of π - π interaction by its aromatic ring. In this study, we carried out several batch experiment of bitumen reaction in the present and absent of supercritical water, toluene, and mixture of water and toluene. To know phase behaviour during bitumen pyrolysis, we also conducted observation of phase behavior by optical view cell. Based on the results, a phase separation kinetic model was developed and the effect of solvent on bitumen reaction was discussed by the kinetic model.

EXPERIMENTAL

We observed the phase behaviour of bitumen in the presence of water, toluene, and water-toluene mixture by the optical view cell. Figure 1 shows the schematic diagram of total configuration of the view cell. Here (a) in Fig. 1 is a back light, (b) is the view cell (the detail was shown in Figures 2), (c) is acryl resin board, (d) is a video camera, (e) is temperature control unit, (f) is a VHS/DVD recorder, and (g) is a display.

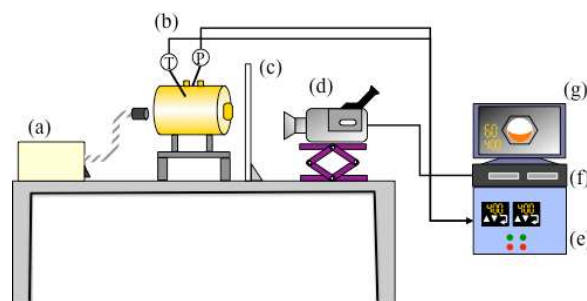


Figure 1 Total configuration of optical view cell

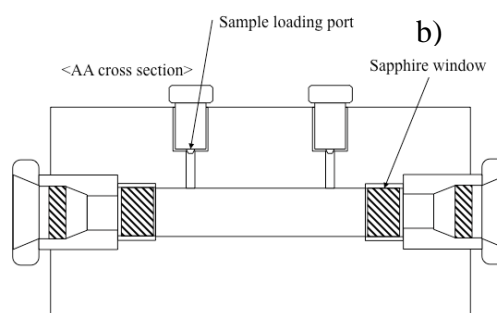
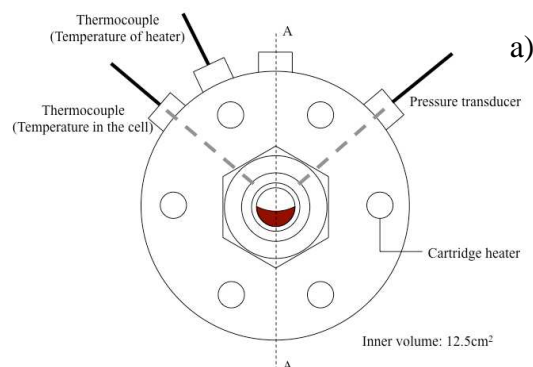


Figure 2 Detail of optical view cell : a) front view, b) AA cross section of a)

Figures 2-a and 2-b shows front view and cross section of the view cell, respectively, made by Taiatsu Glass Co. LTD. Inner volume of the cell was 12.5 cm³.

Table 1 Experimental conditions of phase observation.

Run Number	Bitumen amount [g]	Toluene amount [g]	Water amount [g]	Final Temp. [°C]	Final Pressure [MPa]
1	1	-	2.5	380	20.1
2	1	2.5	-	400	5.7
3	1.25	1.25	1.25	400	20.1

Table 1 listed experimental conditions of the phase observation (the amount of bitumen and the solvents, observation temperature, and pressure). Here pressure was the final value when the temperature inside the cell achieved at the set point. Briefly the procedure of the observation was follows: an amount of bitumen and solvent (water, toluene, or the mixture) were loaded from the sample loading port. The sample in the cell was heated up to 380 °C or 400 °C.

Bitumen that is used in this study consists of 84.6 % maltene and 15.6 % of pentane asphaltene.

Pyrolysis experiments were conducted with stainless steel (SS 316) tube bomb reactors (6 cm³), of which schematic diagram was shown in Figure 3. A 0.6 g of bitumen was loaded in a reactor. The loaded amounts of solvnet ranged from 0 g to 1.2 g. The detail experimental conditions are listed in Table 2. Air in the reactor was purged with Ar gas.

The reactor was submerged in a molten salt bath whose temperature was controls to be 430 °C ± 1 °C. Heat-up time required was around 90 s. 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 pentane and toluene. Gas and pentane soluble compounds were defined as maltene in this study. Toluene soluble was asphaltene. The insoluble in toluene was divided by filtration with membrane filter and was weighted as coke after drying for a day.

SS316 micro batch
(inner vol: 6 cm³)

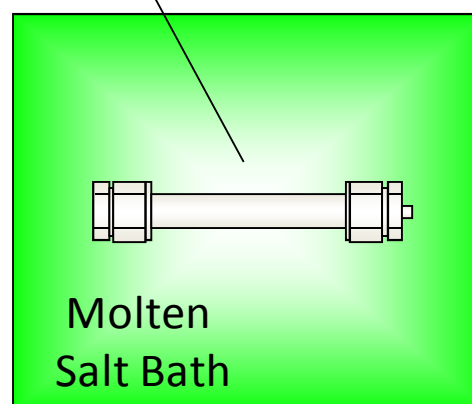


Figure 3 Batch reactor used in this study

Table 2 Experimental conditions of bitumen pyrolysis.

Run Number	Temperature [°C]	Toluene [g]	Water [g]	Bitumen [g]
4		0		
5		0.15	0	
6		0.3		
7	430	0.6		0.6
8		0.15		
9		0.3	0.6	
10		0.6		

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

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

Maltene yield was evaluated as follow:

$$\text{Maltene yields [wt\%]} = 100 - \text{Asphaltene yield} - \text{Coke yield} \quad (2)$$

RESULTS AND DISCUSSION

(1) Phase observation

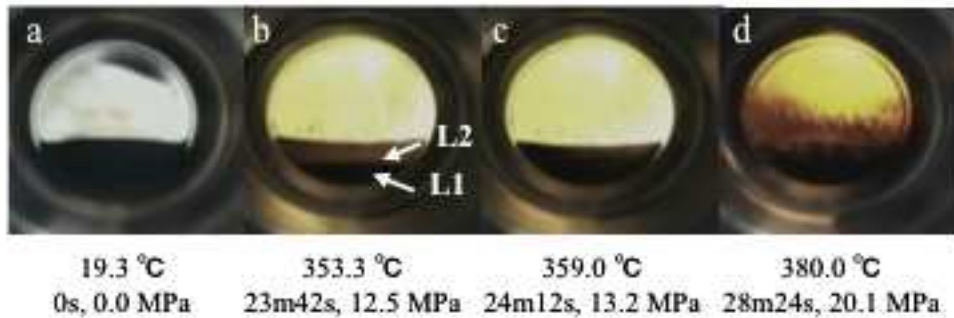


Figure 4 Phase observation of water/bitumen=2.5/1(w/w) up to 380 °C (Run1).
a; heating start, b; VLL, c; VL, d; final temperature

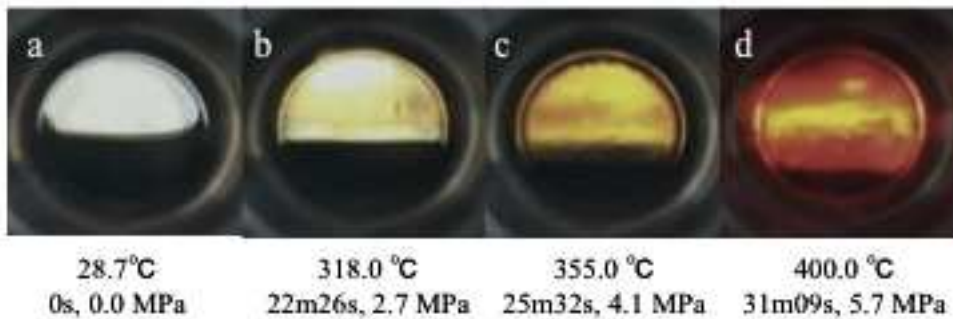


Figure 5 Phase observation of toluene/bitumen=2.5/1(w/w) up to 400 °C (Run2).
a; heating start, b; VL, c; VL, d; final temperature

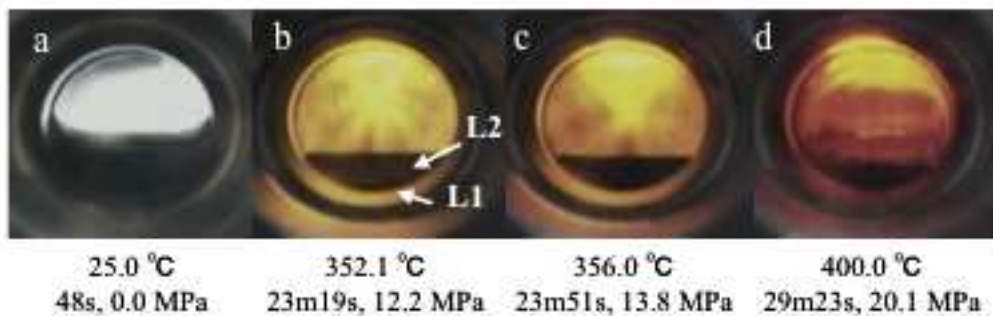


Figure 6 Phase observation of water/toluene/bitumen=1/1/1(w/w) up to 400 °C (Run3).
a; heating start, b; VLL, c; VL, d; final temperature

Figures 4, 5, and 6 shows the phase behavior of bitumen in water (water/bitumen = 2.5/1 w/w), that in toluene (toluene/bitumen = 2.5/1 w/w), and that in water-toluene mixture (water/toluene/bitumen = 1/1/1 w/w/w), respectively. One can see that two phase (gas and liquid phase) was observed in all the systems. Note that liquid-liquid separation was also observed at around in the presence of water (Fig. 4-b and Fig. 6-b) . As reported by Brunner, phase behavior of long chain hydrocarbon and water system is Type III and 3 phase region (vapor-liquid-liquid) can be seen along with vapor pressure curve of water [2]. In the bitumen, aromatic hydrocarbon has to be main component and the phase behavior of whole bitumen is not same as a long chain hydrocarbons, however, some of middle fraction in

bitumen probably has a similar feature to long chain hydrocarbon and forms Type III phase behavior.

(2) Bitumen Pyrolysis

To know the effect of the solvent on bitumen pyrolysis easily, we compared the asphaltene and coke yields at 30 min of reaction time in toluene and water-toluene mixture. Figure 7 shows the yields of asphaltene and coke produced by bitumen pyrolysis. In the absence of solvent, 9 wt% of asphaltene was remained and 5 wt% of coke was formed. In the addition of toluene, both yield of asphaltene and coke were reduced. In the water-toluene mixture, asphaltene decomposition was also promoted but the yield of coke was accelerated compared with neat pyrolysis (in the absence of solvent).

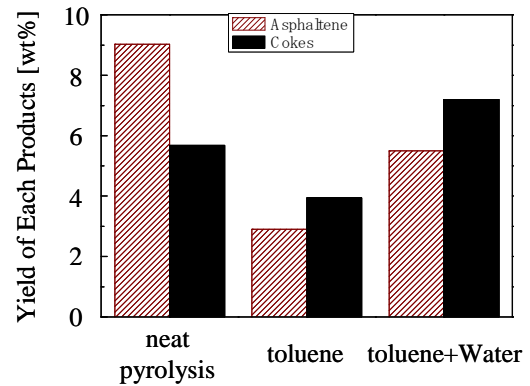


Figure 7 Effect of solvents on bitumen pyrolysis (430 °C and 30 min)

Figure 8 shows the time profile of the yields of maltene, asphaltene, and coke in bitumen pyrolysis without solvent. As shown in this figure, coke formed continuously and the yield of coke might further increase if the reaction continue over 60 min.

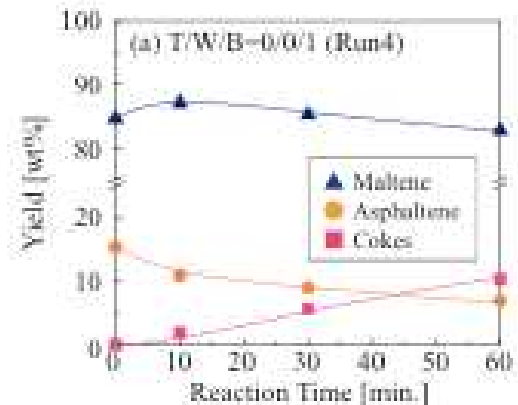


Figure 8 Time profile of the products yields of bitumen pyrolysis without solvent

Figures 9 and 10 show the time dependence of the products distribution in water and that in water-toluene mixtures.

In toluene (Fig. 9), the coke yield depended on the amount of toluene. With increasing the amount of toluene, the yield of coke was remarkably reduced and the rate of coke formation was also decreased. One can expect that the formation of coke almost stopped after 30 min when

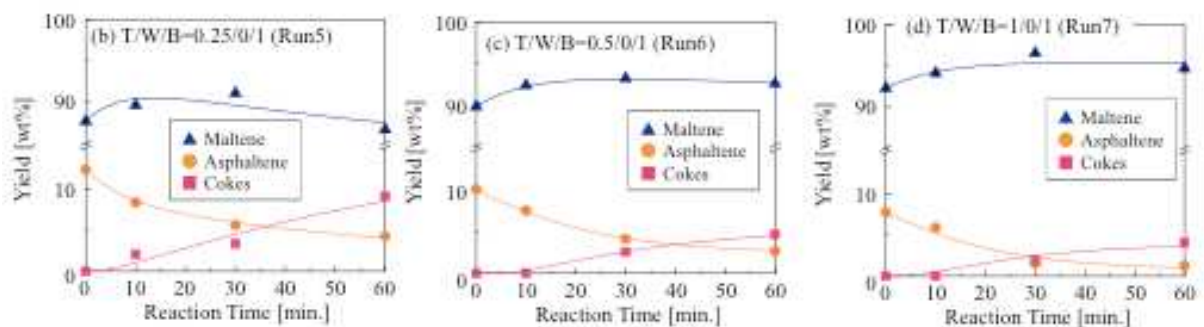


Figure 9 Time dependence of products distribution of bitumen pyrolysis in toluene

toluene/bitumen was 1/1.

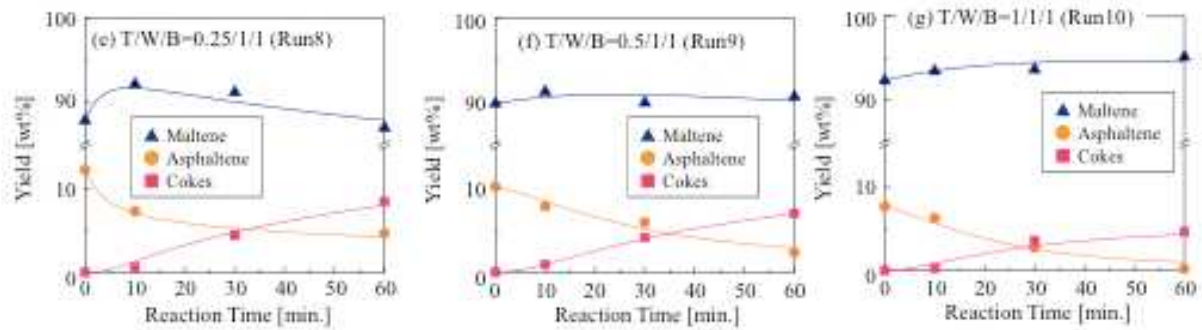


Figure 10 Time dependence of products distribution of bitumen pyrolysis in toluene-water mixtures

In water-toluene mixture (Fig. 10), coke formation was enhanced compared with the results in sole toluene addition experiments (Fig. 9) when the same amount of toluene was added. When toluene/water/bitumen was 1/1/1 (Run 10, Fig. 10-g), it can be seen that the coke formation was almost terminated at 60 min of reaction time as well as the experiments in toluene addition system (Run 7, Fig. 9-d). But the coke yield in water-toluene mixture was higher than that in toluene.

(3) Kinetic model

To know the effect of solvent on the bitumen pyrolysis in more detail, a phase separation kinetic model was applied because the phase observation told us that liquid phase existed in all the experiments and so coke formation has to progress in the dense liquid phase. Wiehe originally proposed a phase separation kinetic model for open system [3] and Rahmani et al. modified the phase separation kinetic model for a closed system [4].

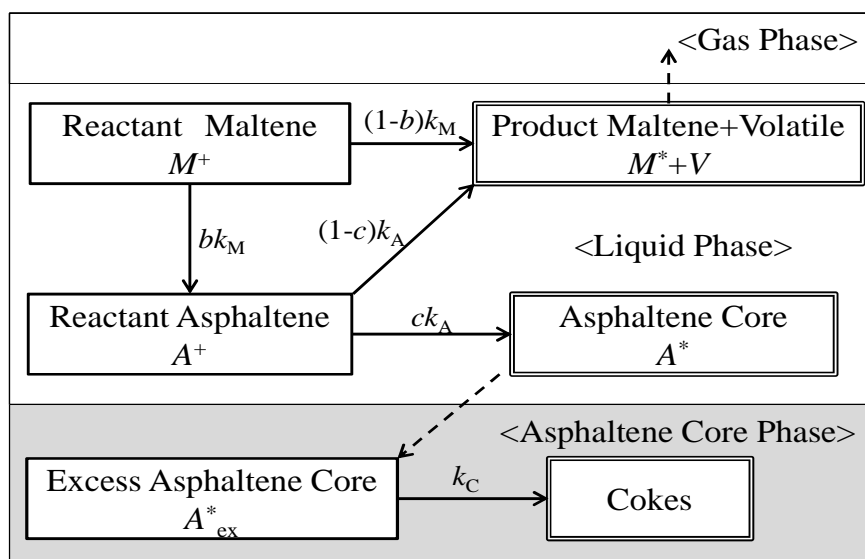


Figure 11 Reaction scheme of Phase Separation Kinetics Model [4]

In this study, the phase separation kinetic model modified by Rahmani et al. was employed and shown in Figure 11.

Initially, there are reactive asphaltene (A^+) and reactive maltene (M^+) in bitumen. The M^+ converts into A^+ and volatile (V) with stoichiometric constant b ($b=0.33$ [4]). The A^+ decomposes into asphaltene core (coke precursor, denoted as A^*) and non-reactive maltene (M^*) with the production of V . Here c is stoichiometric constant ($c=0.543$ [4]).



Here k_M and k_A are rate constants of maltene conversion and asphaltene decomposition, respectively.

The A^* (asphaltene core) dissolves in liquid phase maltene and asphaltene. With progressing pyrolysis reaction, the liquid maltene and asphaltene changes into V and A^* . Overcoming the solubility of A^* in liquid maltene and asphaltene (S_L), excess A^* (A^*_{ex}) is precipitated.

$$A^*_{max} = S_L (M^* + M^+ + V) \quad (5)$$

$$A^*_{ex} = A^* - A^*_{max} \quad (6)$$

The A^*_{ex} polymerizes with each other to form cokes, as shown in Eq. 7.



Here k_c is rate constant of coke formation.

It was found that toluene and water reacted with reactive compound in bitumen or heavy oil [5], [6], however the reaction of the reactive compound with the solvent (toluene and water) was not major and thus disregarded in this study.

The rate constants in Eqs. 3, 4, and 7 and the solubility limit (S_L) were fitting parameter and were determined to be minimum value of SSR (Eq. 8). Here YE_i was the experimental yield of species i and YCi was the calculated yield of i . The yield of each component was defined by Eq. 9.

$$SSR = \sum_{i=1}^n (YE_i - YC_i)^2 \quad (8)$$

$$Yield[wt\%] = \frac{\text{Each product [g]}}{\text{Bitumen [g]} + \text{Toluene [g]}} \quad (9)$$

To solve the model, we have to decide the rate constant and the concentration of each component i . The intrinsic rate constant of each reaction of component i (i =asphaltene: A , maltene: M , and cokes: C) was dependent on only temperature even in any solvent. While

the concentration of i can not be evaluated because phase behavior was not known. Therefore, the ratio of the rate constant at different condition was closely related to partition coefficient of component i between liquid and gas phase. In this case, the ratio of the rate constant in neat pyrolysis ($k_{i,NP}$) to that in a solvent ($k_{i,Sol}$) was seen to be proportionally related to the partial coefficient of i component between gas and liquid.

$$\frac{k_{j,Sol}}{k_{j,NP}} = \frac{k_{j,true} \cdot \alpha_{j,Sol}}{k_{j,true} \cdot \alpha_{j,NP}} = \alpha_j \quad (\alpha_{j,NP} = 1) \quad (10)$$

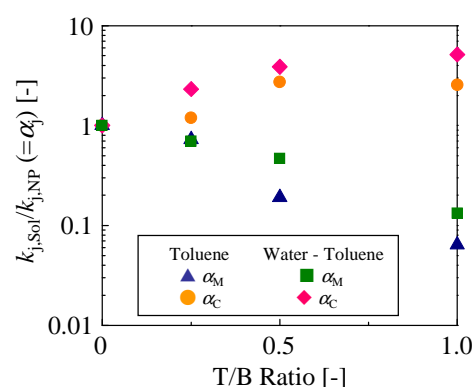
The reaction order for each component was considered to be 1st order. We fitted the experimental data with the model. As shown in Figs. 8~10, the fitting results well expressed

Table 3 Reaction rate constants and SSR for each condition.
(T: Toluene, W: Water, B: Bitumen)

Run Number	Temperature [°C]	T/W/B Ratio [-]	k_C [min ⁻¹]	k_M [min ⁻¹]	$k_{C,NP}/k_{C,Sol}$ [-]	$k_{M,NP}/k_{M,Sol}$ [-]	SSR [-]
4	430	0/0/1	0.027	0.014	1.00	1.00	1.48
5		0.25/0/1	0.070	0.001	2.55	0.06	3.71
6		0.5/0/1	0.066	0.003	2.41	0.20	0.22
7		1/0/1	0.035	0.010	1.27	0.69	6.27
8		0.25/1/1	0.141	0.002	5.15	0.13	2.88
9		0.5/1/1	0.106	0.007	3.86	0.47	2.86
10		1/1/1	0.063	0.010	2.32	0.70	4.00

the experimental value. Table 3 listed $k_{i,NP}$, $k_{i,Sol}$, and α_i at each run.

Figure 12 shows the Toluene/Bitumen (T/B) ratio dependence of α_i . Regardless of the absence and presence of water, the rate of maltene reaction was suppressed with increasing toluene amount. This was probably due to the dilution of the maltene with toluene. On the other hand, coke formation promoted with toluene addition. The partition of asphaltene core in liquid phase increased with increasing the amount of solvent because the solvent extracted liquid phase maltene into gas phase and the asphaltene core might be concentrated.



The differences of α_i between with and without water were not large but both α_i were

Figure 12 T/B ratio dependence of α_i

higher with water than without water. For α_M , the partition of maltene in gas phase was suppressed and liquid maltene in the presence of water might be higher than that in absence of water probably due to high vapor pressure of water. The partition of maltene to gas phase caused by its vapor pressure and solubility in the

solvent. From the observation by the view cell, the system pressure in the presence of water was higher (around 20 MPa) compared with that in the absence of water (around 6 MPa). Higher system pressure prohibits vaporization of a component that has relative high vapor pressure.

This consideration, indeed, contradicts high value of α_C in the presence of water. By increasing liquid maltene by high system pressure, the concentration of asphaltene core might be diluted and thus α_i must be smaller in the presence of water than in the absence of water. But the results were opposite. To consider this phenomena further, several factors must be considered, for example, the effect of solvent on mass transfer between gas and liquid and/or that between liquid and solid, and so on.

CONCLUSION

We evaluated that the effect of toluene and the mixture of water and toluene on bitumen pyrolysis at 430 °C.

At first, the phase observation was conducted. For comparison, the effect of water on the phase behavior was also observed. As a result, at every solvent system, gas and liquid phase was observed at the target temperature. Around 350 °C, liquid-liquid-gas 3 phases was observed in the presence of water. The system pressure was higher in the presence of water (around 20 MPa) compared with the system of only toluene addition (6 MPa).

The batch type reactor was employed to measure the reaction rate of bitumen pyrolysis. The formation of asphaltene, maltene, and coke were evaluated. In the presence of solvent, the coke formation almost stopped at 60 min of reaction time. The yield of coke in toluene was lower than that in water-toluene mixture.

To analyze the kinetics of bitumen pyrolysis, the phase separation kinetic model was applied. The solvent basically extracted the liquid phase maltene into gas phase and thus the cross reaction between asphaltene and liquid maltene was possibly eliminated. The addition of water inhibited maltene conversion probably due to high vapor pressure of water. The reason why the coke formation was promoted by water addition was not clarified in this study. Further investigation including mass transfer has to be done in future.

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