[Review Paper]

Upgrading of Heavy Oil by Hydrogenation through Partial Oxidation and Water-gas Shift Reaction in Supercritical Water

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Partial oxidation of hydrocarbons including heavy oil in supercritical water forms CO and CO₂, which undergoes the water-gas shift reaction to form active hydrogen and then hydrogenation of heavy oil proceeds. In the case of partial oxidation of hydrocarbons and bitumen in supercritical water, the selectivity for partial oxidative products such as CO increased with increasing water density. In the case of hydrogenation of heavy oil in supercritical water through the water-gas shift reaction, reverse water-gas shift reaction and decomposition of formic acid that is a reaction intermediate of the water-gas shift reaction, coke formation was suppressed compared to that in only supercritical water. The main factors for suppressing coke formation were as follows: high water density improving the reactivity of hydrogen source in the oil-rich phase that enhanced hydrogenation of asphaltene core, direct injection of hydrogen source into the oil-rich phase increasing the concentration of active hydrogen in that phase, and coexisting gases with supercritical water facilitating the extraction of coke precursor from the oil-rich phase. The upgrading of heavy oil through a series of partial oxidation and hydrogenation reactions in supercritical water proceeded in the presence of catalyst and possible optimum conditions were proposed.

Keywords

Heavy oil upgrading, Supercritical water, Partial oxidation, Hydrogenation, Water-gas shift reaction, Bitumen

1. Introduction

Upgrading of heavy oil with water is likely to be an economical process because inexpensive water can be used as the solvent. Supercritical water (SCW; $T_c = 647$ K and $P_c = 22.1$ MPa) easily dissolves light hydrocarbons¹⁾ and disperses heavy fractions such as coke precursor^{2),3)}. Conversion of heavy oil in SCW occurs mainly by physical effects of water such as the dispersion of heavy fractions rather than reactions such as hydrogen transfer from water to the oil³⁾. The utilization of the hydrogen atoms of water as a hydrogen source, such as catalytic steam reforming of heavy oil⁴⁾, is one of the most effective methods for upgrading of heavy oil.

Hydrogenation through the water-gas shift reaction (WGSR: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is another method to utilize water as a hydrogen source for upgrading of heavy oil in SCW, because the active hydrogen molecule forms during the WGSR. Partial oxidation of heavy oil is important to supply CO for hydrogenation through the WGSR. **Figure 1** shows the concept of upgrading of heavy oil through partial oxidation and the WGSR in SCW^{5),6)}. First, partial oxidation of heavy oil occurs to form CO. Next, CO reacts with water in

the reaction field to produce active hydrogen through the WGSR. The reactive intermediates derived from heavy oil decomposition are hydrogenated by the active hydrogen, which makes the heavy oil lighter. Active hydrogen formation can also occur through the reverse WGSR ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) or decomposition of HCOOH as well as through the WGSR. Hydrogenation through the WGSR assumes a real process whereas hydrogenation through the reverse WGSR and decomposition of HCOOH are considered to require theoretical study. The WGSR, reverse WGSR, and decomposition of HCOOH are supposed to be essentially equivalent in the process of active hydrogen formation. The conditions of partial oxidation and

Fig. 1 Concept of Upgrading of Heavy Oil through Partial Oxidation and the Water-gas Shift Reaction in SCW

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hydrogenation are not necessarily the same.

In this study, the effect of water on partial oxidation of hydrocarbons including heavy oil in SCW was evaluated. Next, the hydrogenation of heavy oil through the WGSR, reverse WGSR, and decomposition of HCOOH were examined to reveal the essential factors for suppression of coke formation. The current status of a series of processes including both partial oxidation and hydrogenation is summarized and possible optimum conditions are proposed.

2. Partial Oxidation of Hydrocarbons and Heavy Oil in Supercritical Water

2.1. Partial Oxidation of Hydrocarbons

Various studies of the partial oxidation of hydrocarbons in SCW have tried to confirm the effect of water on the selectivity of partial oxidative products such as CO in SCW. Partial oxidation of *n*-hexadecane in SCW was investigated using a tube bomb reactor⁷⁾. The selectivity for CO and H₂ which was probably derived from CO through the WGSR in gas products, increased with increasing water density at 673 K and initial oxygen/carbon molar ratio of 0.3. Furthermore, the relative yield of aldehyde and ketone to alkane and alkene increased with increasing water density. The proposed reaction pathway of CO formation was as follows. First, partial oxidation of hydrocarbons formed aldehyde and ketone, which then decomposed to form CO. In the case of partial oxidation of hexylbenzene at 673 K, the selectivity of CO also tended to increase with increasing water density^{5),6)}, similar to the partial oxidation of *n*-hexadecane. The partial oxidation of methane in SCW using a temperature-controlled flow type reactor was examined using O₂/CH₄ molar ratio of 0.03 at 673 K under 20 to 30 MPa that corresponded to water density of 0.1 to 0.47 g/cm³⁸⁾. The major products were CO, formaldehyde, methanol, CO₂ and H₂.

Figure 2 shows the selectivity for the main carbon-containing products *versus* methane conversion at each pressure. The oxidation level decreased in the order of CO₂, CO, formaldehyde and methanol. The selectivity for formaldehyde was greater at high pressure than at low pressure whereas the selectivity for CO was slightly lower at high pressure than at low pressure, and the selectivity for methanol and CO₂ was relatively independent of pressure. Water enhanced the partial oxidation route. These results indicate that water in the high water density region enhanced the partial oxidation of hydrocarbons in SCW regardless of feedstock and reactor type.

The key elementary reactions governing the positive water density effect on partial oxidation of methane were predicted using the radical elementary reaction model⁸⁾. However, the simple radical reaction model cannot predict the water density effect. The change in

△: 20 MPa, ○: 25 MPa, ▼: 30 MPa, ■: 35 MPa.

Fig. 2 Selectivity for Main Carbon-containing Products *vs.* Methane Conversion at Each Pressure in Partial Oxidation of Methane in SCW at 673 K and O₂/CH₄ Molar Ratio of 0.03 (Reprinted from ref. 8), Copyright 2004, with permission from Elsevier.

fugacity of radical species in SCW or the contribution of ionic reactions may account for the enhancement of partial oxidation in SCW in the high water density region.

2.2. Partial Oxidation of Heavy Oil

We investigated partial oxidation of bitumen in SCW using 10 cm³ batch type reactors containing 1.0 g of bitumen⁹⁾. In this system, 2.1 MPa of air corresponds to 4.7 wt% of initial bitumen. The effect of water/oil ratio was elucidated at 673 K and air pressure of 2.1 MPa for 30 min. Both asphaltene yield and coke yield were almost constant against water/oil ratio. **Figure 3** shows the amount of gases except nitrogen with water/oil ratio. The oxygen conversion was more than 74 % and the main gas products were CO, CO₂ and methane. The amount of produced gas tended to decrease with increasing water/oil ratio, which is probably due to Le Chatelier's principle that suppresses gas formation in the high pressure region, that is, the high water/oil ratio region. The amount of CO once decreased and then increased with increasing water/oil ratio whereas the amount of CO₂ first increased and then decreased. The ratio of CO/(CO + CO₂), that is, the partial oxidation selectivity, increased by about two times with the increase in water/oil ratio from 0.5 to 3. High water/oil ratio was effective for selective partial oxidation of bitumen in SCW.

Figure 4 shows the main reaction route for CO and CO₂ formation during the partial oxidation of bitumen in SCW. The partial oxidation of bitumen produced CO, the oxidation of CO formed CO₂¹⁰⁾, and the WGSR

of CO formed $\text{CO}_2 + \text{H}_2^{11}$. The latter two reactions result in CO consumption. The effect of the WGSR was very small under these conditions. Both partial oxidation of bitumen by SCW and oxidation of CO^{10} in SCW should be enhanced in the high water density region, that is, with high water/oil ratio. The experimental results indicate that the enhancement of partial oxidation of bitumen by SCW was dominant compared to that of CO oxidation in SCW.

Fig. 3 Amount of Gases with Water/Oil Ratio at 673 K and Air Pressure of 2.1 MPa for 30 min in Partial Oxidation of Bitumen in SCW

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Fig. 4 Main Reaction Route for CO and CO_2 Formation in Partial Oxidation of Bitumen in SCW

The effects of temperature and air pressure are summarized in **Table 1**. The first four columns show the effect of temperature. The asphaltene yield decreased and coke yield increased with increasing temperature. The amount of gas increased and the ratio of $\text{CO}/(\text{CO} + \text{CO}_2)$ tended to decrease with increasing temperature. The effect of air pressure was also evaluated at 673 K. The asphaltene yield decreased and coke yield increased with increasing air pressure. The oxygen in SCW was enhanced to produce heavier products as in the previous study¹². The amount of gas products including CO and CO_2 significantly increased with increasing air pressure whereas the $\text{CO}/(\text{CO} + \text{CO}_2)$ ratio decreased. The low temperature and air pressure region was advantageous to promote selective partial oxidation with suppression of coke formation. The maximal amount of CO in this study was 1.2 wt% of introduced bitumen. More effective partial oxidation in SCW should be developed in the future.

3. Hydrogenation of Heavy Oil through Water-gas Shift Reaction in Supercritical Water

3.1. Catalytic Reaction

The catalytic hydrogenation of heavy oil model compounds through the WGSR in SCW has been examined. The hydrogenation of dibenzothiophene⁵), carbazole⁶) and naphthalene⁶) proceeded with $\text{NiMo}/\text{Al}_2\text{O}_3$ in SCW at 673 K in the presence of CO (SCW + CO), H_2 (SCW + H_2), $\text{H}_2 + \text{CO}_2$ (SCW + $\text{H}_2 + \text{CO}_2$) and HCOOH (SCW + HCOOH) as an intermediate of the WGSR. The reactivity of hydrogenation was in the order of $\text{SCW} + \text{CO}$, $\text{SCW} + \text{H}_2 + \text{CO}_2$, $\text{SCW} + \text{HCOOH} > \text{SCW} + \text{H}_2$. Active hydrogen obtained through WGSR was effective for hydrogenation than that of molecular hydrogen. Furthermore, catalytic hydrogenation through the WGSR proceeds in emulsion^{13,14}. Hydrodesulfurization of benzothiophene and dibenzothiophene proceeds in emulsions with dispersed Mo in subcritical and supercritical water. The hydrogenation of real oil through the WGSR in SCW has also been examined. Guao residual oil is hydrocracked through the WGSR with catalysts in SCW^{15,16}). Furthermore, the hydrogen atom of water is incorporated into the

Table 1 Effect of Temperature and Air Pressure in Partial Oxidation of Bitumen in SCW^{a)}

Temp. [K]	Initial air pressure [MPa]	Yield [wt%]		Total gas [$\times 10^{-4}$ mol]	O_2 conv. [%]	$\text{CO}/(\text{CO} + \text{CO}_2)$
		Asphaltene	Coke			
653	2.1	18.4	0.4	8.7	76	0.33
673	2.1	14.8	3.1	12.7	83	0.22
703	2.1	14.8	3.4	21.1	95	0.23
723	2.1	11.2	5.1	43.0	96	0.18
673	0	17.1	0.3	3.2	-	0.30
673	5.1	10.3	7.7	30.1	79	0.20

a) water/oil ratio = 1, reaction time = 30 min.

Fig. 5 Semi-batch Apparatus for Upgrading of Bitumen in SCW + CO, SCW + H₂ and SCW + H₂ + CO₂

products¹⁷⁾. Similar incorporation of the hydrogen atom of water would occur in upgrading of heavy oil without catalyst.

3. 2. Non-catalytic Reaction

Extraction of oil sand bitumen with SCW + CO in the absence of catalyst showed that the coke yield in SCW + CO was significantly lower than that in SCW¹⁸⁾. We conducted upgrading of bitumen with apparatus including the semi-batch type reactor as shown in Fig. 5¹⁹⁾. Bitumen (1.0 g) was extracted with SCW, SCW + CO, and SCW + H₂ at 673 K, 30 MPa, and 1 cm³/min of water and 1.1×10^{-3} mol/min of gas for 60 min. The detailed experimental and analysis method was almost the same as in ref. 19). **Figure 6** shows the apparent boiling-point distribution of raw bitumen and oil recovered under each condition. In all experiments, the total yield was lower than 84 wt%. The mass balance probably corresponded to the volatiles below 423 K released during evaporation of the recovered solvent from the recovered oils. The yield of coke in SCW + CO was lower than those in SCW and SCW + H₂. Furthermore, total yield was the lowest in SCW + CO. These results suggest that SCW + CO was the most effective system for upgrading of bitumen and prevention of coke formation.

The internal functions of the reactor for hydrogenation of heavy oil through the WGSR in SCW are shown in Fig. 7. Upgrading of bitumen in SCW probably involves two phases in the reactor according to previous studies^{9),20)}, the upper water-rich phase and the bottom oil-rich phase. The asphaltene, that is, the coke precursor, was mainly in the oil-rich phase. Therefore,

Fig. 6 Apparent Boiling-point Distribution of Raw Bitumen and Oil Recovered in SCW, SCW + CO and SCW + H₂ at 673 K, 30 MPa and 1 cm³/min of Solvent at STP for 60 min

Fig. 7 Diagram of the Semi-batch Type Reactor for Hydrogenation of Heavy Oil through the WGSR in SCW

hydrogenation of asphaltene in the oil-rich phase was effective to suppress coke formation. In this case, CO and water were injected directly into the oil-rich phase. Then the WGSR proceeded in that phase and active hydrogen was formed to cause the hydrogenation of asphaltene. Such hydrogenation of asphaltene suppressed repolymerization of asphaltene, which reduced coke formation. During the reaction, extraction of some oils in the oil-rich phase to the water-rich phase with solvent occurred. The detailed phenomena in the reactor as shown in Fig. 7 are discussed later.

3. 2. 1. Effect of Water on Hydrogenation

Here, we focus on the hydrogenation of asphaltene in the oil-rich phase. Water probably affects the hydrogenation kinetics in the oil-rich phase. We examined the upgrading of bitumen in SCW with HCOOH²¹⁾.

(a): asphaltene yield, (b): coke yield. ○: SCW, △: SCW + HCOOH.

Fig. 8 Asphaltene Yield and Coke Yield with Water/Oil Ratio at 723 K for 30 min

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The reaction was conducted with a 10-cm³ batch type reactor containing 1.0 g of bitumen and formic acid. The effects of water and HCOOH on product distribution were elucidated.

Figure 8 shows the asphaltene yield and coke yield with various water/oil ratios at 723 K for 30 min. In the absence of HCOOH, the asphaltene yield decreased with increasing water/oil ratio whereas coke yield increased. Water enhanced the decomposition of oil to produce reactive intermediates that change to both lighter fractions and heavier fractions through polymerization. In the case of SCW + HCOOH in the presence of water, the asphaltene yield was always lower than in SCW and decreased with increasing water/oil ratio, whereas the coke yield was lower than in SCW and was almost constant against water/oil ratio. HCOOH promoted the decomposition of asphaltene to lower molecular weight products in SCW.

On the other hand, the asphaltene yield was relatively low and coke yield was significantly higher in the presence of HCOOH without water, that is, with water/oil ratio = 0 in SCW + HCOOH. This result indicates that

Fig. 9 Proposed Reaction Model for the Decomposition of Bitumen in SCW and SCW + HCOOH

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the species derived from the WGSR acted as an initiator for promoting the decomposition of heavy oil to reactive intermediates. Some intermediates polymerized to form coke. In the presence of water, water dispersed oil including these intermediates to suppress the polymerization of such intermediates. Furthermore, the increase in the amount of water probably promoted not only dispersion of oil in the oil-rich phase and but also hydrogenation of reactive intermediates by the WGSR. In the case of the WGSR in the high water density region, protons would be preferentially formed over hydrogen radicals because the increase in water density would form ionic reaction conditions. Protons may have higher activity for hydrogenation than hydrogen radicals.

We proposed a reaction model for the decomposition of bitumen in SCW and SCW + HCOOH applicable to the upgrading of heavy oil through the WGSR in SCW²¹⁾ by considering previous studies^{22),23)}. A similar mechanism was proposed²⁰⁾ after our research to support the validity of this model. **Figure 9** shows the proposed reaction model. In this model, there are two phases in the reaction field. The fractions are reactant asphaltene (A^+), reactant maltene (H^+), product maltene (H^*), asphaltene core that can accept hydrogen

(A^{*A}), asphaltene core that cannot accept hydrogen (A^{*NA}), and cracked distillate products (V). Asphaltene core is a relatively heavy component of heavy oil. The subscript W indicates a SCW (water) rich phase and the subscript O indicates a heavy oil (oil) rich phase, and E_A , E_H and E_V are the partition coefficients of the asphaltene, maltene, and distillate products.

The initial reactions are as follows:

where b , c , d are stoichiometric coefficients.

The solubility limit (S_L) defines how much reacted asphaltene in the oil-rich phase ($A_{O,W}^{*A}$, $A_{O,W}^{*NA}$) can dissolve in the oil-rich phase.

$$A_{\max,O}^* = S_L (H_{O,W}^+ + H_{O,W}^* + V_{O,W}) \quad (3)$$

The asphaltene core in excess of the solubility limit ($A_{\max,O}^*$) in the oil-rich phase becomes coke because the asphaltene would be relatively more soluble in the oil-rich phase than in the water-rich phase.

The asphaltene core in excess can be expressed as follows:

$$A_{\text{ex}}^* = A_{O,W}^{*NA} + A_{O,W}^{*A} - A_{\max,O}^* \quad (4)$$

$$= A_{O,W}^{*NA} + A_{O,W}^{*A} - S_L (H_{O,W}^+ + H_{O,W}^* + V_{O,W}) \quad (5)$$

$$= (A_W^{*A} + A_W^{*NA})/E_A - S_L (H_W^+/E_H + H_W^*/E_H + V_W/E_V) \quad (6)$$

The coke formation is assumed to occur from the asphaltene core in excess and can be expressed as follows:

The hydrogenation of maltene and asphaltene core that can accept hydrogen can be stated as follows:

To control coke formation, a decrease in A_{ex}^* is the key factor to suppress coke formation, that is, a decrease in $A_{O,W}^{*NA} + A_{O,W}^{*A}$ and an increase in $A_{\max,O}^*$.

Here, the effect of water on coke formation is discussed in the absence of HCOOH. Water would extract oils from the oil-rich phase to the water-rich phase, so that the partition coefficients (E_A , E_H , E_V) should increase with higher water/oil ratio. In the experiment, coke yield increased with increasing water/oil ratio in the absence of HCOOH. The decrease in the magnitude of the first term of Eq. (6) when the effect of ($A_W^{*A} + A_W^{*NA}$) is smaller than $1/E_A$, and the increase in the magnitude of the second term of Eq. (6) when the effect of partition coefficients is smaller than H_W^+/E_H and V_W/E_V should suppress coke formation. If the formation of

asphaltene core in the water-rich phase was suppressed or the extraction of maltene and cracked distillate products from the oil-rich phase to the water-rich phase was small, coke formation in the high water/oil ratio region should be suppressed.

In SCW + HCOOH, hydrogenation was promoted as in Eqs. (8) and (9). The decrease in $A_{O,W}^{*A}$ to produce $H_{O,W}^*$ and $V_{O,W}$ occurs, which is followed by a decrease in A_{ex}^* according to Eq. (5) to suppress coke formation. In the experiments, higher water/oil ratio enhanced asphaltene decomposition with the suppression of coke formation. This result can be explained by considering the enhancement of hydrogenation in the high water density region caused by the high reactivity of ionic species such as protons for hydrogenation, resulting in the effective suppression of coke formation in the region of high water/oil ratio.

3. 2. 2. Effect of Hydrogenation on Asphaltene

We examined upgrading of bitumen through the reverse WGSR in SCW using a semi-batch type apparatus as shown in Fig. 5. $H_2 + CO_2$ was supplied by complete decomposition of HCOOH in 10 wt% HCOOH aq. in the preheater. Bitumen (1.0 g) was extracted with SCW, SCW + $H_2 + CO_2$ and SCW + H_2 from 623 to 693 K, at 30 MPa. The discussion in sections 3. 2. 2. and 3. 2. 3. is based on experiments using this apparatus.

Figure 10 shows the changes in asphaltene yield and coke yield with temperature. The asphaltene yield decreased and the coke yield increased with increasing temperature regardless of the presence of $H_2 + CO_2$.

○: asphaltene yield in SCW, ●: asphaltene yield in SCW + $H_2 + CO_2$, △: coke yield in SCW, ▲: coke yield in SCW + $H_2 + CO_2$.

Fig. 10 Asphaltene and Coke Yields with Temperature at 30 MPa and 1 cm³/min of Solvent at STP for 60 min
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Table 2 H/C Atomic Ratio of Asphaltene^{a)}

Condition		H/C
Raw asphaltene		1.21
SCW	653 K	1.06
	673 K	1.26
	693 K	1.33
SCW + H ₂ + CO ₂	653 K	1.24
	673 K	1.32
	693 K	1.39

a) 1 cm³/min at STP, 60 min, 30 MPa.

In the presence of H₂ + CO₂, the asphaltene yield was larger than in the absence of H₂ + CO₂ at each temperature, whereas the coke yield was significantly lower. H₂ + CO₂ in SCW suppressed the decomposition of asphaltene to both light fraction and coke.

The H/C atomic ratio of asphaltene is summarized in **Table 2**. After the reaction, the H/C atomic ratio of asphaltene in SCW was always lower than in SCW + H₂ + CO₂ at each temperature. In particular, the H/C atomic ratio was in the order of SCW + H₂ + CO₂ > SCW > raw asphaltene at temperatures over 673 K. The asphaltene was hydrogenated more in SCW + H₂ + CO₂ than in SCW.

The average molecular structure of asphaltene was estimated according to the published methods^{(24),(25)} using average molecular weight, elemental analysis, and hydrogen-type distribution. **Figure 11** shows the average molecular structures of raw asphaltene, asphaltene obtained in SCW at 673 K, and asphaltene obtained in SCW + H₂ + CO₂ at 673 K. The structure consisted of monomers and dimers. The raw asphaltene contained the monomer fused ring unit, which consisted of 10 carbon rings including 2 naphthalene rings. The ratio of monomer to dimer was 2 : 8. In SCW, the monomer ring units consisted of 10 carbon rings including 7 naphthalene rings. The ratio of monomer to dimer was 1 : 9. In SCW + H₂ + CO₂, the monomer ring units consisted of 8 carbon rings including 3 naphthalene rings. The ratio of monomer to dimer was 5 : 5. In SCW and in SCW + H₂ + CO₂, hydrogenation of the aromatic ring proceeded. The ratio of monomer to dimer in SCW + H₂ + CO₂ was significantly lower than that of raw asphaltene and in SCW, and hydrogenation of the aromatic ring proceeded to some extent. The active hydrogen formed through the reverse WGSR probably capped the active sites of reaction intermediates derived from the decomposition of asphaltene, which suppressed the polymerization of reaction intermediates to form coke.

3. 2. 3. Effect of Extraction

Extraction of oil by water and coexisting gases affected the kinetics of the upgrading reactions. **Figure 12** shows the apparent boiling point distributions of raw bitumen, oil in SCW at 0.5 cm³/min (SCW-

Raw asphaltene; 1(a) : 1(b) = 2 : 8, in SCW; 2(a) : 2(b) = 1 : 9, in SCW + H₂ + CO₂; 3(a) : 3(b) = 5 : 5.

Fig. 11 Average Molecular Structure of Asphaltene at 673 K, 30 MPa and 1 cm³/min of Solvent at STP for 60 min
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0.5) and at 0.8 cm³/min (SCW-0.8), oil in SCW + H₂ at 0.45 cm³/min of water, and oil in SCW + H₂ + CO₂ at 0.5 cm³/min of 10 wt% HCOOH aqueous solution. In these experiments, the products inside the reactor (raffinate oil) and outside the reactor (extract oil) were recovered separately. Coke was produced inside the reactor only and coke formation was suppressed more in SCW + H₂ and SCW + H₂ + CO₂ than in SCW. The amount of the fraction with boiling point of 823 K + decreased by about a half after the reaction in all conditions. SCW + H₂ + CO₂ provided the most effective upgrading conditions in terms of coke formation and upgrading of high boiling point fraction.

Moreover, the amounts of raffinate oil and extract oil were significantly different under different conditions. Most of the oil recovered was raffinate oil in SCW, about a half of the oil was obtained as both raffinate and extract oils in SCW + H₂, and most of the oil was recov-

R: raffinate oil, E: extract oil.

Fig. 12 Apparent Boiling Point Distribution of Raw Bitumen and Oil Recovered for 30 min at 673 K, 30 MPa and 0.5 or 0.8 cm³/min of Water at STP in SCW (SCW-0.5 and SCW-0.8), 0.45 cm³/min of Water at STP and 1.25×10^{-3} mol/min of Hydrogen in SCW + H₂, 0.5 cm³/min of 10 wt% Formic Acid Aqueous Solution at STP in SCW + H₂ + CO₂ (Reprinted with permission from ref. 19), Copyright 2013 American Chemical Society.

ered as extract oil in SCW + H₂ + CO₂. In addition to the differences in the amounts of oils, the ratio of the higher boiling point fraction of raffinate oil was higher than that of the extract oil under all conditions. The ratio of raffinate oil to extract oil in SCW-0.5 was similar to that in SCW-0.8, and was significantly higher than that in SCW + H₂ whereas the actual flow rate in SCW + H₂ under the reaction condition was almost the same as that in SCW-0.8. The ratio of extract to raffinate in SCW + H₂ + CO₂ was significantly higher than under other conditions. These results indicate that coexisting gases greatly supported the extraction of oil.

Assuming two phases in the reactor as shown in Fig. 7, the extract oil should be present in the water-rich phase. The differences in the amounts of extract oil to raffinate oil would depend on the solubility of oil in each system. The Hansen solubility parameter²⁶⁾ of each system suggests that the presence of H₂ and CO₂ in SCW enhanced the dissolution of bitumen in the water-rich phase and the solubility of bitumen in the water-rich phase was in the order of SCW < SCW + H₂ < SCW + H₂ + CO₂. The coexisting gases in SCW enhanced the extraction of oil to the water-rich phase.

3.3. Main Factors for Suppressing Coke Formation

Control of the reaction pathway in the oil-rich phase is essential to suppress coke formation which will occur in that phase. The main factors for suppression of

coke formation are summarized in Fig. 7. The direct injection of hydrogen sources such as CO + H₂O, H₂ + CO₂ and HCOOH into the oil-rich phase would concentrate active hydrogen in that phase. The hydrogenation of asphaltene core with active hydrogen occurred in the oil-rich phase, which improved the formation of lighter oil that dissolves asphaltene core in the oil-rich phase to prevent transformation to coke. The reactivity of active hydrogen would be enhanced in the high water density region as discussed in section 3. 2. 1. Furthermore, coexisting gases such as CO, CO₂ and H₂ in SCW promoted the extraction of oils including coke precursor from the oil-rich phase to the water-rich phase, which suppressed coke formation. On the other hand, extraction of light oil enhanced coke formation because of the reduced solubility of coke precursor in the oil-rich phase. From the experimental results, hydrogenation by direct injection of hydrogen source into the oil-rich phase and with active hydrogen through WGS-related reactions was typically strong enough to cancel the factors promoting coke formation.

4. Series of Partial Oxidation and Hydrogenation for Upgrading of Heavy Oil in Supercritical Water

Hydrogenation through partial oxidation and the WGS in SCW by introducing oxygen has been mainly examined using catalytic reactions. Catalytic hydrodesulfurization of dibenzothiophene was examined through partial oxidation of hexylbenzene with NiMo/Al₂O₃ at 673 K in SCW⁵⁾. The residual yield of dibenzothiophene was around 50 % and that of biphenyl and cyclohexylbenzene as hydrodesulfurized products were 27 % and 3 % after 60 min, respectively. Benzothiophene was desulfurized with CoMo/Al₂O₃ in the presence of *n*-heptane, water and oxygen²⁷⁾, and quinoline was denitrogenated with NiMo/Al₂O₃ in the presence of *n*-heptane, water and oxygen²⁸⁾. Judging from these results, partial oxidation of hydrocarbons occurred to produce CO, followed by desulfurization and denitrogenation through the WGS in SCW. Real heavy oil can be desulfurized. The sulfur in VR was desulfurized with CoMo/Al₂O₃ in the presence of oxygen in SCW²⁷⁾. On the other hand, non-catalytic desulfurization of asphalt in SCW from 613 to 673 K with oxygen revealed that reactive sulfur-containing radicals were polymerized followed by sulfur transfer to coke¹²⁾. Non-catalytic hydrogenation by introducing oxygen is difficult around 673 K in SCW.

Here, we propose a possible process for upgrading of heavy oil through partial oxidation and the WGS in SCW based on the previous partial oxidation and hydrogenation studies as shown in Fig. 13, although few studies have examined the series of reactions of partial oxidation and hydrogenation. The partial oxidation of

Fig. 13 Possible Process for Upgrading of Heavy Oil with Partial Oxidation and Hydrogenation through the WGSR in SCW

heavy oil as a first step should be operated below about 673 K with the amount of oxygen at under several % of the oil. The high water density region is recommended for high selectivity of CO. The oxygen is completely consumed with suppression of CO₂ and coke formation, leading to formation of high ratios of CO and residual oil. The next step of hydrogenation of residual oil through the WGSR should be operated under different conditions from partial oxidation. In some cases, additional CO from other systems may be necessary due to the insufficiency of CO derived from partial oxidation of heavy oil. The reaction temperature should be above 673 K to promote the decomposition of heavy oil. The high water density region and direct injection of hydrogen source into the oil-rich phase would be effective to enhance the reactivity of active hydrogen with asphaltene core. By using a flow or semi-batch type reactor, the extraction of oil by coexisting gases and SCW and removing coke precursor from the oil-rich phase would improve the suppression of coke formation. Introducing a suitable catalyst would be effective for desulfurization and denitrogenation of heavy oil.

5. Conclusion

Partial oxidation of hydrocarbons including heavy oil in SCW was reviewed. In all cases, water enhanced partial oxidation to produce partial oxidation products such as CO although the mechanism was not clear. High water density, low temperature, and low oxygen pressure regions were suitable for the partial oxidation of hydrocarbons in SCW. In the case of hydrogenation of heavy oil through the WGSR and its related reactions, the presence of CO, H₂ + CO₂, HCOOH in SCW caused the suppression of coke formation. The reactor contained water-rich and oil-rich phases and coke formation mainly occurred in the oil-rich phase by polymerization of asphaltene core. The factors for the suppression of coke formation were as follows: Higher water density promoting the hydrogenation of asphaltene core by improvement of the reactivity of active hydrogen in the oil-rich phase, direct injection of hydrogen source into the oil-rich phase increasing the

concentration of active hydrogen in that phase, and coexisting gases in SCW facilitating the extraction of coke precursor from the oil-rich phase. Evaluation of the effect of water density on hydrogenation in flow and semi-batch type reactors is required. The upgrading of heavy oil through partial oxidation and the WGSR in SCW proceeded in the presence of catalyst, but very few studies have investigated the series of reactions of partial oxidation and hydrogenation. The possible process was proposed by considering previous studies.

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要 旨

超臨界水中での部分酸化と水性ガスシフト反応による水素化反応を利用した重質油改質

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超臨界水中にて重質油等の炭化水素と酸素を共存させると、炭化水素の部分酸化が生じて CO が生成する。この CO が反応場に存在する水と水性ガスシフト反応 ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) を生じる際に生成する活性水素により、重質油の水素化が進行する。超臨界水中での炭化水素およびピッチューメンの部分酸化については、いずれの場合でも、水密度の増大に伴い CO 選択性が増大して部分酸化が促進されていた。超臨界水中での重質油水素化については、水性ガスシフト反応、逆水性ガスシフト

反応、水性ガスシフト反応中間体のギ酸分解のいずれの場合も、超臨界水のための分解と比較してコーク生成が抑制されていた。高水密度域における油リッチ相での活性水素の活性増大、油リッチ相への水素源の直接注入による活性水素濃度の増大、超臨界水と共存ガスの混合流体によるコーク前駆体抽出の促進が、コーク抑制因子であった。部分酸化と水素化を組み合わせた一連のプロセスに関する報告例は少ないが、これまでの結果をもとに最適条件を提案した。

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