The Effect of Supercritical Water on the Hydroconversion of Tahe Residue

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The effect of supercritical water (SCW) on the hydroconversion of Tahe residue has been investigated at different temperatures and hydrogen pressures. It was demonstrated that introduction of water into the reaction could reduce the amount of coke formed and increased the yield of liquid product. The isotopic tracer method was used to determine quantitatively the extent of hydrogen exchange between water and the liquid product. The results indicated that the degree of hydrogen exchange of the liquid product with water decreased slightly with increasing hydrogen pressure. About 40% of the water molecules involved in hydrogen exchange with the oil residue as the concentration of water in the reaction mixture was 10 wt %. © 2010 American Institute of Chemical Engineers *AIChE J*, 56: 3236–3242, 2010

Keywords: heavy oil, hydroconversion, supercritical water, isotopic tracer method

Introduction

Hydroprocessing of heavy oils to produce light valuable distillates is of great commercial importance and some efficient processes have been developed, such as EniTechnologie's Eni Slurry Technology (EST) Process, Alberta Energy's $(HC)_3$ Process, Hydrocarbon Research Corp.'s H-Oil Process, and IFP's Hyvahl process. However, the compound precipitation caused by too high conversion of heavy oils was unfavorable to long term operation. During heavy oil hydroprocessing, both too deep hydrogenation and too deep cracking of the heavy oils lead to the instability of the colloids consisting of resin and asphaltene in the heavy oils. When the compatibility between the bulk of the heavy oil and the resin and asphaltene is poor, the resin and asphaltene molecules are inclined to aggregate and precipitate. Addition of supercritical water (SCW) may alleviate the precipitation of the molecules because of its special solvation power and weak acidity.

The use of water as additive in processing extra-heavy crude oil has been studied by different researchers,[1,2] which showed its beneficial properties in terms of reducing coke formation during visbreaking processes. Clark and Kirk[3] investigated the upgrading of bitumen with water at elevated temperatures up to 688 K, and found that SCW reduced the amount of insoluble products and also decreased the sulfur content of the liquid products. The mechanism of the effect of SCW on heavy oil upgrading has also been investigated.[4–7] Adschiri et al.[6,7] have systemically investigated the hydro-thermal cracking of dibenzothiophene(DBT)in SCW systems with more than 80 wt % water up to 30 MPa and 703 K. By comparing the experiments under different conditions with H_2-SCW'CO-SCW, CO_2-H_2-SCW, HCOOH-SCW, and O_2-SCW, respectively, they found that the CO-SCW, CO_2-H_2-SCW, and HCOOH-SCW systems were more favorable to DBT hydrogenation than that of H_2-SCW system. Further analysis on the gas and liquid products indicated that CO could react with water to produce active hydrogen on line in the presence of $NiMo/Al_2O_3$

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Table 1. The Detailed Properties of the Tahe Residue Used in this Study

Properties	Value	Properties	Value
Density (20°C), g/cm^3	0.9914	Elemental analysis, wt %	
Viscosity, mm^2/s		C	85.38
80°C	304.5	H	10.77
100°C	102.1	S	2.11
CCR, wt %	16.6	N	0.50
Ash, wt %	0.052	Metal content, μg/g	
Acidity, mg KOH/g	0.3	Ni	35.9
Saturation, wt %	30.8	V	201
Aromatics, wt %	36.2	Na	5.5
Residue, wt %	22.1	Fe	15.0
Asphaltene, wt %	10.9		

catalyst. The results also showed that the hydrogen atom of water enters the products by gas–water shift reaction at low temperature.

Dutta et al.[8] studied the hydrogen exchange from steam to thermally cracked bitumen molecules under coking condition in the temperature range of 623 K–803 K. They measured the degrees of the hydrogen transferring for the three kinds of H in bitumen and found that the H located on the carbon atoms adjacent to aromatic rings are tended to be exchanged with the H of water. By using an internal standard sample consisted of CH_2Cl_2 and CD_2Cl_2, they obtained the relative values of the degrees of H-D exchange of the liquid products. It is known that the actual amount of the H and D and the percentage of the water involved in the reaction cannot be obtained directly by the commonly method.

In this work, we studied the effect of SCW on the hydroconversion of Tahe residue at different conditions. Furthermore, a method to determine the actual moles of H and D directly in the liquid product is proposed. The influence of the hydrogen pressure on the degree of hydrogen exchange between water and the residue and the ratio of water participating the hydroconversion has been obtained. We believe that the results of this work are also useful for the hydroprocessing of some other oil residues because the properties of oil residue used are similar to those of some other oil residues, such as Arab heavy oil.

Experimental Section

Materials

The properties of the Tahe residue used in this study are listed in Table 1. It was characterized by high contents of sulfur, nitrogen, asphaltene, Conradson carbon residue (CCR) and high content of metals, such as nickel, vanadium, and iron. The catalyst used in this study was an ultrafine bulk multimetallic oxides catalysts prepared by sol-gel method,[9,10] which comprised molybdenum oxide and iron oxide with particle diameters of less than 20 nm. It could be well dispersed in the feedstock and sulfided on-line to catalyze heavy oil hydroconversion efficiently.

Apparatus and procedures for hydroconversion

The apparatus used for the hydroconversion was a 500 ml autoclave with stirrer manufactured by Yantai Automaton Company in Shandong Province, China. It could be used up to 26 MPa and 773 K and its structure is shown in Figure 1. In a typical experiment, desired amount of the Tahe residue feedstock and catalyst were charged into the autoclave. The catalyst concentration ranged from 100 μg to 1000 μg per gram of the feedstock. The sublimed sulfur was used as a sulfiding agent with a dosage of 0.8 times of the catalyst. After the oil residue, catalyst, sulfiding agent, and water were loaded, the autoclave was sealed and purged with hydrogen three times to replace the air in the autoclave. Then hydrogen was charged to the desired pressure. Before the autoclave was heated to the desired hydroconversion temperature, it was maintained at 593 K for 30 min to ensure complete sulfiding of the catalyst. The time was recorded when the thermocouple inserted in the autoclave reached the desired reaction temperature. After suitable reaction time, the autoclave was cooled to room temperature quickly in water to terminate the reaction. The gas, liquid, and solid products were collected and analyzed. Figure 2 shows a flowchart for the analysis of gas, liquid, and solid products.

In this work, five parameters were used to evaluate the hydroconversion performance, namely coke yield (CY), gas product yield (GPY), liquid product yield (LPY), middle distillate yield (MDY), and total conversion (TC). The meanings of the parameters are defined as follows: MDY = mass of the liquid phase product with boiling point less than 797 K/mass of the feedstock × 100%; TC = total mass of the gas and liquid product with boiling point less than 797 K/mass of the feedstock × 100%; CY = mass of the toluene insoluble solid/mass of the feedstock × 100%; GPY = (mass of the feedstock − total mass of liquid and solid products)/mass of the feedstock × 100%; LPY = mass of the liquid phase product/mass of the feedstock × 100%.

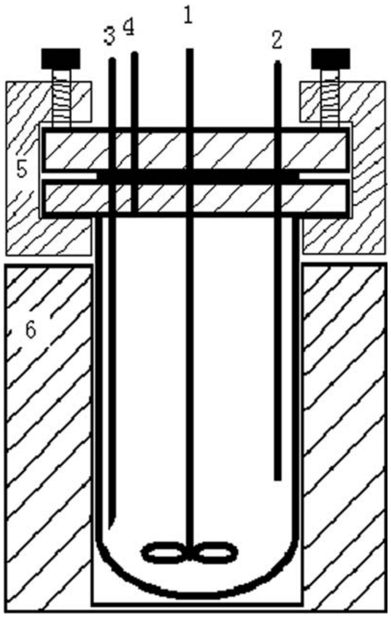

Figure 1. View of the high pressure stirred autoclave. 1-stirrer; 2-thermocouple cannula; 3-gas inlet; 4-gas outlet; 5-sealed cap; 6-oven.

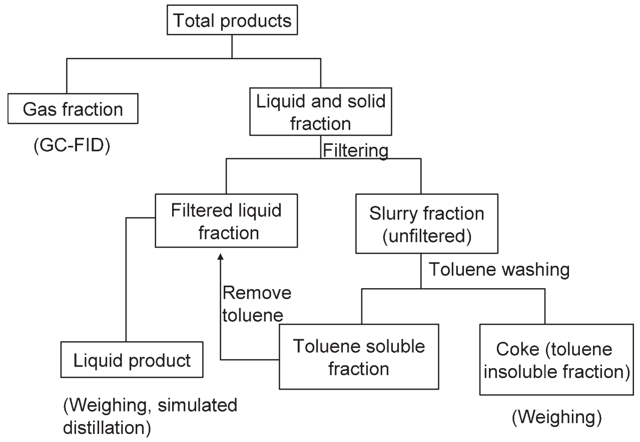

Figure 2. Flowchart for analysis of the gas, liquid, solid products.

Determination of hydrogen exchange by the isotopic tracer method

The isotopic tracer method was employed to determine the extent of hydrogen exchange between the SCW and the liquid products of the Tahe residue in the hydroconversion process. In the experiment, part or all of the water was substituted with deuterium oxide in the hydroconversion. After removing water by heating the liquid product at 373 K for 2 h, the liquid product was characterized by ^{2}H NMR and ^{1}H NMR to determine the extent of hydrogen exchange, both qualitatively and quantitatively.

To obtain the quantity of deuterium transferred to the liquid products, a combination of the internal standard method and the external standard method was designed based on previous work.[8,11] A mixture of H_2O and D_2O was sealed in a quartz capillary and used as the internal standard, which was inserted into the quartz tube used for NMR measurements. The amounts of H and D in the internal standard were determined by the external standard method. The external standard was a solution of 90.39 wt % o-dichlorobenzene and 9.61 wt % fully deuterated o-dichlorobenzene-d_4. 0.4445 g of the external standard, containing 1.090×10^{-2} mole of H and 1.159×10^{-3} mole of D, was injected into the quartz tube containing the capillary of the internal standard. ^{1}H NMR and ^{2}H NMR measurement gave the number of moles of H and D in the internal standard as 1.993×10^{-2} and 0.749×10^{-3} moles, respectively. The internal standard capillary was used throughout the measurement to ensure consistency.

Results and Discussion

Hydroconversion without water

Many factors influence the hydroconversion of heavy oils, such as the properties of the catalyst, reaction time, temperature, and pressure of hydrogen. The main criteria employed to determine the optimized factors were coke yield (CY), liquid phase product yield (LPY), and middle distillate yield (MDY).

Table 2. The Repeatability of the Experiments

	GPY (wt %)	LPY (wt %)	CY (wt %)	MDY (wt %)	TC (wt %)
1	8.4	86.3	7.0	73.7	82.1
2	8.9	84.4	6.3	73.3	82.2
3	8.5	85.4	6.0	73.9	82.6

Reaction conditions: 688.2 K ± 2.0 K, hydrogen pressure of 5.00 ± 0.1 MPa, reaction time of 50 min, and feedstock of 100.0 g ± 0.1 g.

Table 3. Effect of Catalyst Dosages on Heavy Oil Hydroconversion

Dosage/μg/g	GPY (wt %)	LPY (wt %)	CY (wt %)	MDY (wt %)	TC (wt %)
200	11.0	78.5	10.5	64.8	75.8
400	8.9	84.4	6.3	73.3	82.2
600	8.7	85.4	6.0	73.9	82.6
800	8.5	84.0	7.1	73.1	81.6
1000	7.1	84.4	8.4	74.3	81.4

Reaction conditions: 100.00 ± 1.00g heavy oil feedstock, 693.2 ± 2.0 K, initial hydrogen pressure is 5.00 ± 0.10 MPa, reaction time 50 min

To check the reproducibility of the experiments, we conducted the hydroconversion of the Tahe residue at 688.2 K ± 2.0 K, hydrogen pressure of 5.00 ± 0.1 MPa, reaction time of 50 min, and feedstock of 100.0 g ± 0.1 g three times. The results are presented in Table 2. The data indicate that the reproducibility of the experiments were satisfactory.

The results of the residue hydroconversion with different catalyst dosages are presented in Table 3. The reaction was conducted at 693.2 K with an initial hydrogen pressure of 5.00 MPa and a reaction time of 50 min. The results indicated that 0.04–0.06 wt % catalyst in the residue was sufficient for hydroconversion at the experimental condition.

The reaction results with different reaction times are given in Table 4. It can be seen from the data in the table that the optimum reaction time was 50 min. Longer reaction time led to deeper cracking of the residue, which was disadvantageous because more coke and less liquid product were produced.

The hydroconversion was also performed at different reaction temperatures and the results are listed in Table 5. It can be known from the data that the reaction temperature had a significant effect on the hydroconversion of the residue. Although the CY was 6.3 wt % at 688.2 K, which was higher than that at 663.2 K and at 678.2 K, the MDY and TC were higher than that at lower or higher temperatures.

The results of hydroconversion at 688.2 K and various initial hydrogen pressures are given in Table 6. The results demonstrated that, as expected, increasing hydrogen pressure promoted the hydroconversion of the residue.

It can be known from the results above that the optimum operating conditions of the hydroconversion were: reaction temperature of 688.2 K, and hydrogen pressure of 5.00 MPa, reaction time of 50 min, and 0.04 wt % catalyst in the oil.

Table 4. Yields of Various Products After Different Reaction Times

Reaction Time (min)	GPY (wt %)	LPY (wt %)	CY (wt %)	MDY (wt %)	TC (wt %)
15	2.5	97.3	0.2	63.5	66.0
30	7.0	89.7	3.3	69.5	76.5
50	8.9	84.8	6.3	73.3	82.2
60	8.7	85.8	6.5	74.5	83.2
80	12.3	80.3	7.5	72.1	84.4

Reaction conditions: 100.00 ± 1.00 g heavy oil feedstock, 688.2 ± 2.0 K, initial hydrogen pressure 5.00 ± 0.10 MPa, catalyst amount 500 μg/g feedstock,

Table 5. Effect of Reaction Temperature on the Hydroconversion

Temperature/K	GPY (wt %)	LPY (wt %)	CY (wt %)	MDY (wt %)	TC (wt %)
663.2 ± 2.0	4.2	95.8	<0.05	65.1	69.3
678.2 ± 2.0	4.4	94.5	1.1	66.6	71.1
688.2 ± 2.0	8.9	84.8	6.3	73.3	82.2
703.2 ± 2.0	11.0	78.5	10.5	69.2	80.2

Reaction conditions: 100.00 ± 1.00 g heavy oil feedstock, initial hydrogen pressure 5.00 ± 0.10 MPa, catalyst amount 500 μg/g feedstock, reaction time 50 min.

Effect of water amount on the hydroconversion

Based on the optimization of the reaction conditions above, the effect of water amount added on the hydroconversion was studied at 678.2 K and 688.2 K, and the results are presented in Table 7. The pressure of the reaction system increased with increasing amount of water added into the reaction system. At 678.2 K, the water added did not significantly affect the LPY and CY. At 688.2 K, the LPY increased from 84.1 wt % to 90.3 wt % and the CY was reduced from 6.3 wt % to 1.9 wt % as the amount of water added changed from 0 to 15.03 wt %. This demonstrates that introduction of SCW enhanced considerably the hydroconversion of the residue both by reducing coke formation and increasing the amount of liquid product formed.

It should be mentioned that the phase behavior of the reaction system may be very complex, and it varies with reaction going on. At the beginning of the reaction, there may be three phases, vapor phase, liquid phase, and the solid catalyst phase. There should be no water-rich phase because the experimental temperature was much higher than the critical temperature of water, and so it cannot be liquefied. It is known that supercritical water is miscible with hydrogen. Therefore, water exists mainly in the vapor phase and the liquid phase. However, with the hydroconversion going on, a coke phase may appear. The phase behavior of the reaction system may affect the reaction considerably, and this needs to be studied further.

Effect of initial hydrogen pressure on hydroconversion

The effect of initial hydrogen pressure on heavy oil hydroconversion with and without water was studied at 688.2 K with a reaction time of 50 min. The results are illustrated in Figure 3. In the low pressure region, an increase in hydrogen pressure enhanced the LPY. In the higher hydrogen pressure region, however, the effect of the pressure on the amounts of liquid product was not considerable. The CY decreased monotonously with increasing hydrogen pressure without water. In the presence of water, the CY declined first and then became nearly unchanged as hydrogen pressure was raised. However, the CY with water was lower considerably than that without water in the whole pressure region studied.

Table 6. Effect of Initial Hydrogen Pressure on the Hydroconversion

Initial H_2 pressure (MPa)	GPY (wt %)	LPY (wt %)	CY (wt %)	MDY (wt %)	TC (wt %)
1.0	7.8	78.6	10.5	62.1	69.9
2.6	7.9	82.9	9.3	67.1	74.9
3.8	8.2	84.7	8.5	69.4	77.6
5.0	8.9	84.8	6.3	73.3	82.2
5.5	7.1	88.7	4.2	75.4	82.5

Reaction conditions: 100.00 ± 1.00 g heavy oil feedstock, 688.2 ± 2.0 K, catalyst amount 500 μg/g feedstock, reaction time 50 min.

Table 7. Results of Hydroconversion with Different Amounts of Water Added

Water Content (wt %)	Reaction Pressure /MPa	GPY (wt %)	LPY (wt %)	CY (wt %)	MDY (wt %)	TC (wt %)
678.0 ± 2.0 K						
0.00	8.50	4.4	94.5	1.1	66.6	71.1
5.10	11.21	3.6	95.2	1.2	64.7	68.3
10.2	13.36	4.6	94.5	1.7	70.4	75.0
15.15	16.84	4.7	93.2	2.1	68.9	73.6
20.04	19.14	4.0	94.2	1.8	68.8	72.8
688.0 ± 2.0 K						
0.00	10.05	8.9	84.8	6.3	73.3	82.2
10.03	15.78	8.7	88.4	2.9	70.5	79.2
15.03	18.92	7.8	90.3	1.9	70.4	78.2

Reaction conditions: 100.00 ± 1.00 g heavy oil feedstock, initial hydrogen pressure 5.00 ± 0.10 MPa, catalyst amount 500 μg/g feedstock, reaction time 50 min.

Comparison of gaseous components with and without water

Table 8 lists the distributions of the gaseous products with and without water. It can be known that water affected the amounts of the main gaseous products slightly. Addition of 10 wt % water could increase amounts of ethylene and propylene in the gaseous sample obviously, suggesting that water reduced the hydrogenation of the olefins.

Hydrogen transfer between water and the liquid products

As discussed above, introduction of water into the hydroconversion system led to a change in the distribution of liquid and solid products, and also influenced the composition of the gaseous product, and the water was "inert" during the reaction. The mechanisms of some relevant reactions, such

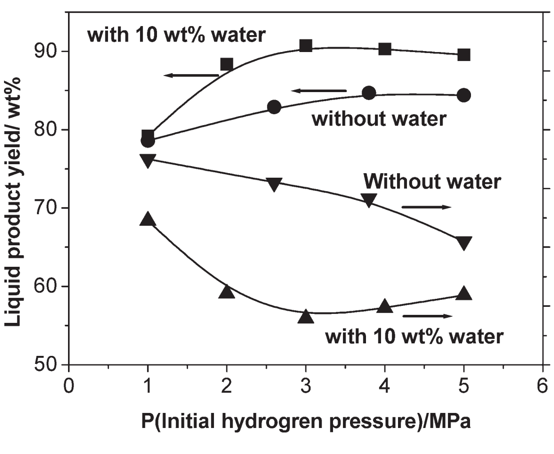

Figure 3. The effect of hydrogen pressure on the yields of liquid product and coke with and without water.

Table 8. Distribution of Gaseous Components With and Without Water

Component	Values	
	Without Water (mol %)	With 10 wt % Water (mol %)
H_2	71.3	65.3
CO	0.448	0.937
CO_2	0.269	0.724
H_2S	0.341	1.02
CH_4	17.0	18.5
C_2H_4	0.143	0.255
C_2H_6	6.04	6.98
C_3H_8	3.01	3.85
C_3H_6	0.305	0.575
>C4	1.13	1.83
Total	100	100

Reaction conditions: 100.00 ± 1.00 g heavy oil feedstock, 688.2 ± 2.0 K, initial hydrogen pressure 5.00 ± 0.10 MPa, catalyst amount 500 μg/g feedstock, reaction time 50 min.

as hydro-conversion of coals, polymers, and modulated compounds, have been studied previously.[12] Tennoh et al.[13] and Suzuki et al.[14] investigated the hydrolysis of polymers in SCW by ^{13}C NMR spectroscopy, HPLC and GC/MS, and the results showed that water molecules donated hydrogen atoms during the thermal hydrolysis. Cheng et al.[15] carried out the hydrocracking of Gudao residual oil with synthesis gas (consisting of hydrogen and carbon monoxide). They suggested that water initially reacted with CO to produce active hydrogen atom in situ for the subsequent hydrogenation of the residual cracking distillates. Ding et al.[16] studied the hydrolysis of some model compounds in SCW conditions and pointed out that water took part in radical reactions. Our previous work indicated that hydrogen exchange between water and naphthalene occurred during the hydrogenation of the aromatic compound in the presence of water.[17] However, quantitative study of hydrogen exchange between water and organic compounds remains scarce.

In this work, we determined the extent of hydrogen exchange between the Tahe residue and water qualitatively and quantitatively. The isotopic tracer method, which is an efficient method to investigate hydrogen transfer, was used. Figure 4 shows the proton-decoupled ^{2}H NMR spectrum of one of the liquid samples without an internal standard. The peaks with NMR chemical shift of 0.5–4.0 ppm represent the C-D of alkyl groups, and those with chemical shift 6.0-10.0 ppm correspond to the C-D of aromatic rings. The data show qualitatively that there was hydrogen exchange between the water and the liquid product.

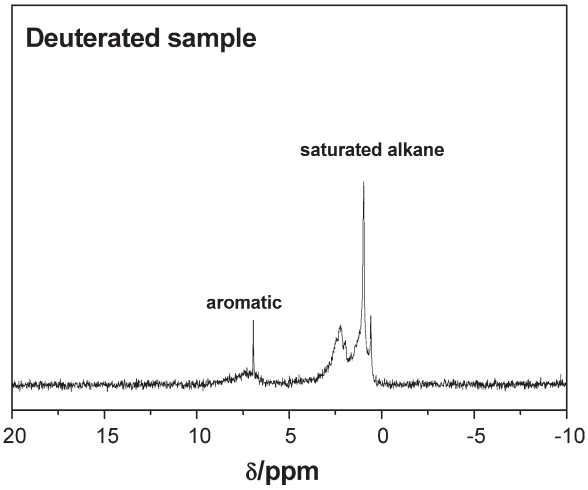

Figure 4. Proton-decoupled ^{2}H NMR spectrum of the liquid product sample.

To obtain quantitative results, ^{1}H NMR and proton-decoupled ^{2}H NMR measurements were also carried out with an internal standard to obtain the total amounts of H and D in the liquid products. A mixture of H_2O and D_2O was used as the internal standard because their NMR chemical shifts (4.9 ppm) do not overlap with the peaks of the samples.

Five liquid product samples from hydroconversion at different initial hydrogen pressures were studied. The experiments were carried out at 688.2 K with a catalyst loading of 0.05 wt %, and a reaction time of 50 min. The initial pressures of hydrogen were 1.0, 2.0, 3.0, 4.0 and 5.0 MPa. The samples were accurately weighed in a quartz tube containing the capillary of internal standard and the ^{1}H NMR and ^{2}H NMR spectra were recorded. Table 9 lists the moles of H and D in the alkyl bonds and the aromatic bonds. The mass of the samples was obtained precisely to calculate the H concentration per gram. Based on the data in Table 9, the percentage of hydrogen transferred from water to the liquid products and the moles of H in per gram of the sample can be calculated by the following equations:

$$X_{\mathrm{D/H}} = \frac{A_{D1} + A_{D2} - (A_{H1} + A_{H2}) \times C_D}{(A_{H1} + A_{H2}) \times (1 - C_D) + A_{D1} + A_{D2}} \times \frac{1}{1 - X_{\mathrm{H}}} \times 100\% \quad (1)$$

$$C_{\mathrm{H}} = \frac{(A_{\mathrm{H1}} + A_{\mathrm{H2}}) \times (1 - C_{\mathrm{D}}) + A_{\mathrm{D1}} + A_{\mathrm{D2}}}{\mathrm{M}} \quad (2)$$

Table 9. Number of Moles of H and D in the Samples Obtained at Different Initial H_2 Pressures

Init. P_{H2} /MPa	Alkyl C—H δ: 0.5–4.0/mol	Aromatic C—H δ: 6.0–10.0/mol	Alkyl C-D δ: 0.5–4.0 /mol	Aromatic C-D δ: 6.0–0.0 /mol	Mass of Sample /g
1.0	2.85×10^{-2}	0.261×10^{-2}	0.677×10^{-3}	0.719×10^{-4}	0.2340
2.0	2.64×10^{-2}	0.227×10^{-2}	0.614×10^{-3}	0.704×10^{-4}	0.2356
3.0	3.47×10^{-2}	0.373×10^{-2}	0.764×10^{-3}	0.354×10^{-4}	0.3210
4.0	2.62×10^{-2}	0.176×10^{-2}	0.520×10^{-3}	0.599×10^{-4}	0.2447
5.0	3.13×10^{-2}	0.237×10^{-2}	0.656×10^{-3}	0.674×10^{-4}	0.3070

Reaction conditions: 100.00 ± 1.00 g heavy oil feedstock, 688.2 ± 2.0 K, catalyst amount 500 μg/g feedstock, water content is 10.0 wt % of the feedstock; reaction time 50 min.

where $X_{D/H}$ is the ratio of deuterium transferred in the liquid product, i.e., degree of H exchange; A_{D1} and A_{D2} are the moles of D in alkyl bonds and aromatic bonds, respectively; A_{H1} and A_{H2} represent the moles of H in alkyl bonds and aromatic bonds, respectively; X_H denotes the molar ratio of the water in the H_2O/D_2O mixture, which was added in the reaction system; C_D is the natural abundance of deuterium; C_H refers to the moles of H in per gram of the sample; M is the mass of the sample. The calculated results are listed in Table 10.

The average value of the H content determined was 0.12 mol/g residue. Figure 5 demonstrates the degree of H exchange as a function of hydrogen pressure. The figure indicates that the degree of H transfer decreased slightly with the increase of hydrogen pressures. The main reason for the inhibition of hydrogen exchange between water and the residue by hydrogen gas may be that hydrogenation and hydrogen exchange are partly competitive reactions.

The percentage of water involved in the hydrogen exchange can be easily calculated from the degree of H exchange, the amounts of water and residue, and the yield of the liquid product. The proportion of water molecules that exchanged hydrogen with the residue was about 40% when the water content in the reaction mixture was 10 wt %.

Mechanism for the effect of SCW on the hydroconversion

In heavy oil hydroprocessing, water participates the reaction by general free radical mechanism, which is similar to that for gas-water oxidation reactions in the same temperature range. In this work, the catalyst consisted of MoS_2 and $Fe_{(1-x)}S$. The free radicals, such as $R^\bullet$, $MS^\bullet$ and $S^\bullet$ are produced by the cleavage of C—C bonds and M—S bonds at high temperature. Then the radicals react with other organic compounds and H_2, H_2S, and H_2O during the free radical transfer steps to produce $R^\bullet$, $HS^\bullet$, $H^\bullet$, and $OH^\bullet$.[16,18] In the free radical termination steps, the free radicals are quenched by reacting with other radicals, some of which are as follows:

$$R^\bullet + H^\bullet \rightarrow RH \quad (3)$$

$$R^\bullet + R' \rightarrow R - R' \quad (4)$$

$$H^\bullet + H^\bullet \rightarrow H_2 \quad (5)$$

$$H^\bullet + OH^\bullet \rightarrow H_2O \quad (6)$$

$$R^\bullet + OH^\bullet \rightarrow ROH \quad (7)$$

Table 10. Data for the Degree of H Exchange and Total H Content as Measured by NMR

P_{H2}/MPa	Degree of H exchange /%	H content /mol g^{-1}
1.0	4.66	0.136
2.0	4.62	0.125
3.0	4.15	0.122
4.0	4.01	0.117
5.0	4.10	0.112

Reaction conditions: 100.00 ± 1.00 g heavy oil feedstock, 688.2 ± 2.0 K, catalyst amount 500 μg/g feedstock, water content is 10.0 wt% of the feedstock; reaction time 50 min.

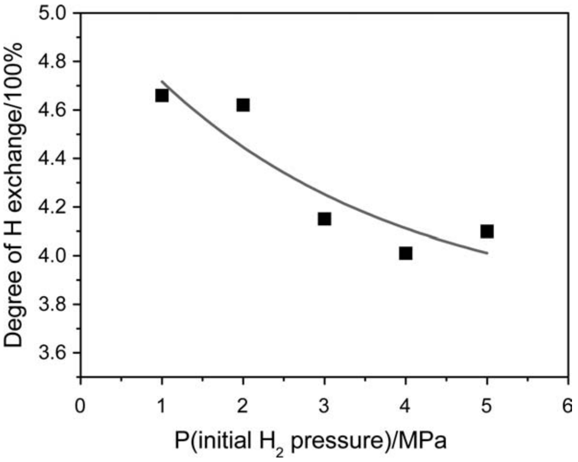

Figure 5. Degrees of H exchange at different initial hydrogen pressures.

The ROH including phenolic compounds or alcohols produced by the reactions between $R^\bullet$ and $OH^\bullet$ are unstable at high temperature. Therefore, the —O—H was undetectable in the H NMR spectrum.

Based on the free radical reaction mechanism, there exists competition between water and hydrogen molecules during the chain transfer step. The elevated partial pressure of hydrogen should increase the solubility of H_2 in residue fuel.[19,20] Therefore, when the water content in the hydroconversion system of this work was fixed, the participation of water in the reaction was repressed by increasing hydrogen pressure, which is consistent with the experimental results in Figure 5.

As discussed above, the percentage of ethylene and propylene in the gas phase products with 10 wt % water was higher than that obtained at water-free condition. The main reason may be that some of the $H^\bullet$ free radicals were quenched by the water molecules, which is unfavorable to the hydrogenation of the ethylene and propylene.

Water may affect the reaction in different ways. For example, its existence may be unfavorable to free radicals transferring and may quench the free radicals. Thus restrains the hydrogenation reactions and represses the deep cracking and condensation of the high molecular weight compounds, which enhances the yields of liquid products and reduces the coke formation. The dissolution of water in the liquid phase can decrease the viscosity of the liquid phase, and water molecules may have a considerable effect on the structure and adsorption properties of the catalysts. Study on the detailed mechanism is a very interesting and challenging topic.

Conclusions

Introduction of SCW is beneficial to the hydroconversion of the Tahe residue in that it reduces coke formation and increases liquid product yield. At 688 K, adding 15 wt % water can decrease the coke yield from 6.3 wt % to 1.9 wt %, while the liquid product yield increases from 84.1 wt % to 90.3 wt %. The percentage of ethylene and propylene in the gas phase products with water is higher than that obtained at water-free condition. The isotopic tracer method has been used to explore quantitatively the hydrogen exchange between SCW and the residue by using D_2O to replace water in the reaction. The percentage of hydrogen exchange between water and the liquid product decreases from 4.6 to 4.0% with the increase of initial hydrogen pressure from 1.0 to 5.0 MPa because the hydrogenation reaction and hydrogen exchange are competitive. The proportion of water molecules involved in the hydrogen exchange is about 40% when the water content in the reaction mixture is 10 wt %.

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