Catalytic bitumen cracking in sub– and supercritical water

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ABSTRACT

The bitumen cracking reaction under sub– and supercritical water environments in H₂ or N₂ atmosphere using activated carbon (AC) supported nickel catalyst was studied. The sub– or supercritical water provided a unique homogeneous, acidic reaction system for the bitumen cracking reaction, which obviously promoted the bitumen conversion and selectivity of the middle distillates (kerosene and gasoline), and restrained the formation of carbon deposition, if compared with the conventional pyrolysis reaction without water addition. Moreover, the active in–situ H₂ source was provided by the water–gas shift reaction in the sub– and supercritical water environment, thereby enhancing the catalytic activity of bitumen cracking.

Keywords: Bitumen; Cracking; Supercritical Water; Subcritical water; Ni/AC

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1. Introduction

Heavy oil such as oil sand bitumen, vacuum residue, asphalt and coal tar is an important energy resources because of its abundant supply [1,2]. The cracking of heavy oil is an essential process in petroleum industry, but it is difficult due to high impurity content of the heavy oil. In recent years, more attentions have been focused on the production of light hydrocarbons because of their wide application as synthetic middle distillates (kerosene and gasoline) [3–7]. A series of heavy oil cracking technologies have been developed during the past decade [8–9], such as fluid catalytic cracking process and hydrocracking, which can process various heavy oil to reach a high yield of middle distillates. Although these technologies are usually used to treat heavy oil, the consumption of expensive H_2 is high in the cracking process. In order to overcome this disadvantage, the cracking of heavy oil under water environment is probably an alternative method for H_2 supply. The physicochemical properties of supercritical water (critical point: 374 °C, 22.1 MPa), such as viscosity, diffusivity, dielectric constant, acidity and oxidizing property, are different significantly from those of conventional liquid water, which is also an effective solvent in a wide range of promising applications, such as biomass gasification, effluent treatment and heavy oil cracking [10].

Previous studies demonstrated that the utilization of water could promote the conversion of coal or cornstalk [11,12]. The hydrocarbons initially react with water to form CO, subsequently the produced CO undergoes water–gas shift reaction (WGSR, $CO + H_2O \rightarrow CO_2 + H_2$) with supercritical water to generate in–situ H_2 , and finally proceeds to hydrocarbons hydrogenation and hydrocracking. Moreover, in–situ H_2 is more active than the supplied one. Sato et al. reported an increase of asphaltene conversion through in–situ H_2 [13]. The present paper investigated the cracking of Canadian Athabasca oil sand bitumen in sub– and supercritical water with H_2 or N_2

using the activated carbon (AC) supported Ni catalyst. The effects of sub- and supercritical water on bitumen conversion and the selectivity of middle distillates were discussed.

2. Experimental

Canadian Athabasca oil sand bitumen was selected as feedstock. Its component is listed in Table 1. The Ni loaded catalyst (5% Ni/AC) was prepared by the incipient wetness impregnation method on AC with the aqueous solution of nickel nitrate. The AC was pretreated at 120 °C for 4 h in vacuum prior to impregnation. The wet catalyst was first dried at 120 °C in air for 10 h, and then calcined in a ceramic tube furnace with flowing N₂ at 400 °C for 2 h, subsequently reduced with H₂ at 400 °C for 10 h and then followed by passivation with 1%O₂ in N₂. The bitumen cracking reaction was performed in a 20 mL batch autoclave reactor (HASTELLOY Alloy). The schematic diagram of experimental procedure and products analysis are showed in Fig. S1 and S2, respectively.

3. Results and discussion

3.1 Comparison of bitumen cracking under water/without water environment

As shown in Table 2, the selectivity of middle distillates is only 21.8 % and 81.4 % of bitumen conversion is reached for bitumen cracking reaction without water (Run 1). Additionally, the selectivities of naphtha, gaseous products and coke for this conventional pyrolysis reaction are 24.7 %, 23.4 % and 17.3 %, respectively. In contrast, the middle distillates selectivity and bitumen conversion are increased to 44.5 % and 92.0 % for bitumen cracking under supercritical water environment (Run 2), respectively. These results indicate that the bitumen cracking with supercritical water is more favorable to improve bitumen conversion and middle distillates selectivity since the supercritical water affords a unique homogeneous reaction environment. Coke

formation is mainly derived from intermolecular reactions in bitumen [14]. The coke selectivity in Run 2 decreases appreciably due to the slowing down of the coking reaction by the mass-transfer resistance between different emulsion droplets in supercritical water [15].

3.2 Investigation of bitumen cracking under sub- or supercritical water environment in H₂

For the bitumen cracking reaction in subcritical water, the selectivity of the middle distillates is as high as 59.7 %, which is higher than that of supercritical one (Run 2). Furthermore, the naphtha and coke selectivities also decrease due to lower reaction temperature of 350 °C in Run 3. Bitumen conversion is slightly decreased under subcritical water environment at 350 °C compared with Run 2 under supercritical water environment, even if the temperature of the latter is 50 °C higher. The reasons are attributed to the strong oxidizing property of supercritical water, leading to the fact that the active Ni⁰ sites of the Ni/AC catalyst in Run 2 were oxidized and deactivated, as shown in XRD results (Fig. 1). In contrast, the subcritical water afforded a relatively mild environment for the bitumen cracking reaction. Therefore, although the temperature of Run 2 is higher, the bitumen conversion does not increase significantly if compared with that of Run 3.

3.3 Influence of bitumen cracking atmosphere (H₂ or N₂)

As listed in Table 2, the bitumen conversion is higher under N₂ atmosphere than that under H₂. The in-situ H₂ is easily produced by WGS of the produced CO with subcritical water for Run 4 under N₂ atmosphere, whereas its formation is suppressed for Run 3 because of the present high pressure of H₂. The active in-situ H₂ promoted the bitumen cracking, leading to an enhanced bitumen conversion in Run 4. Surprisingly, the selectivity of gaseous products in Run 4 is only 0.1 %, which is significantly lower than that of Run 3. The selectivities of naphtha, kerosene and gasoline are similar between Runs 3 and 4, while Run 4 exhibits a higher VGO selectivity than that

of Run 3, indicating that the coexisting high-pressure H_2 results in a shift toward gaseous products. Therefore, subcritical water environment under N_2 atmosphere is a better reaction condition for bitumen cracking than that under H_2 .

3.4 Effect of sub- or supercritical water for bitumen cracking in N_2 atmosphere

For Run 4, its bitumen conversion as high as 92.8 %, is similar to that under supercritical water condition (Run 5), whereas the naphtha and coke selectivities are lower in Run 4 but the selectivity of the middle distillates are higher. The selectivities of gaseous product, naphtha and kerosene increase when water state is changed by increasing the reaction temperature. Nevertheless, the gasoline selectivity decreases from 46.3 % to 40.6 % with an increasing reaction temperature, along with the decrease of VGO and residue selectivities. In fact, throughout the cracking of heavy oil, a parallel competition exists between decomposition and condensation [16]. The coke derives from the transformation of asphaltenes, while light fractions shift to heavy fractions. Not only coke selectivity increases from 5.8 % to 8.8 %, but also the selectivity of middle distillates decreases from 59.6 % to 57.1 %, since that the decomposition and condensation reactions are accelerated with increasing reaction temperature. Different from supercritical water, subcritical water acts as an organic solvent with high density, excellent solubility, providing milder temperature and pressure of bitumen cracking reaction than those in supercritical water environment. Therefore, under the similar catalytic activity and product distribution, the use of subcritical water remarkably reduces the cost of energy, pressure equipment, especially operational safety when compared with the cost of supercritical one. According to the above findings, the subcritical water environment at 350 °C and initial N_2 atmosphere of 3.0 MPa can be regarded as the most suitable reaction conditions for the bitumen cracking reaction.

3.5 Gaseous products selectivities

As Table 2 shows, the selectivity of total gaseous products obtained by conventional pyrolysis for Run 1 is markedly higher than those in other Runs 2–5 with sub- or supercritical water environment. The selectivity of total gaseous products is as high as 23.4 %, in which H₂S, methane and ethane are main gases in the conventional pyrolysis (Table 3). However, the selectivity of total gaseous products in other reactions (Runs 2–5) is less than 5%. These results indicate that the gaseous products are restrained at higher pressure, which is in good agreement with the report of Bi et al. [17]. It can be observed that H₂S selectivity reaches 60.3 % in the total gaseous products, whereas the total gas selectivity in all cracking products is the lowest for Run 4 under subcritical water and N₂ atmosphere (Table 2). These findings prove that sub- and supercritical water can promote bitumen transformation to obtain middle distillates while suppressing the formation of gaseous products and coking.

3.6 Hydrodesulfurization results

The effect of sub- and supercritical water on the hydrodesulfurization of bitumen is compared with that of the conventional pyrolysis reaction, as shown in Table 4. After the reaction, the sulfur content in Run 1 with each fraction is lower than that of the additional water environment. Runs 2 to 5 show a trace amount of sulfur element in naphtha. The sulfur contents of kerosene, gasoline and VGO in Run 3 are lower than those of the supercritical one (Run 2), indicating that the hydrodesulfurization process was promoted under subcritical water condition. The sulfur contents in kerosene and gasoline under H₂ atmosphere (Run 3) are higher than under N₂ (Run 4). Nevertheless, the sulfur content in VGO is lower than that under N₂. These results imply that the hydrodesulfurization process under N₂ atmosphere was promoted to generate a low sulfur-containing of middle distillates under subcritical water condition. Therefore, subcritical water

environment under N₂ atmosphere is a better reaction condition for bitumen cracking than that under H₂ atmosphere. For Run 5, the sulfur contents in distillates, including kerosene, gasoline and VGO, are higher than those of Run 4, implying that hydrodesulfurization process is promoted under subcritical water condition due to more reactive in-situ H₂ formed through the WGSR.

3.7 XRD analysis

As Fig. 1 displays, the peaks at 37.3° and 43.3° are from the NiO phase, and the diffraction peaks of 44.3° and 51.8° are attributed to the Ni⁰ phase. The other peaks represent Ni₃S₂. The Ni⁰ diffraction peaks are observed from the reduced Ni/AC and spent catalysts in Runs 3 and 4 under subcritical water environment. Alternatively, the diffraction peaks of NiO are observed, which may be ascribed to the oxidation of Ni⁰ to NiO by supercritical water. In addition, Ni₃S₂ is also deactivation and poisoning of catalysts because it is more difficult to remove in hydrodesulfurization process, even under supercritical water environment. All spent catalyst except Run 4, they display the strong Ni₃S₂ crystal peaks, indicating that the partial Ni⁰ particles converted to Ni₃S₂ after reaction.

4. Conclusions

The bitumen conversion and the selectivity of middle distillates under water environment were increased obviously if compared to those in the conventional pyrolysis reaction. Simultaneously, the selectivity of naphtha, gaseous products and coke decreased dramatically for the reaction with supercritical water environment and H₂ at 400 °C. Furthermore, the selectivity of the middle distillates increased, and the coke selectivity decreased for the reaction with subcritical water, compared to the reaction with supercritical water under H₂ atmosphere. On the other hand, sub- and supercritical water with N₂ provided an additional in-situ H₂ source through WGSR, which was

more active than the supplied H₂ in the bitumen cracking reaction. The active in-situ H₂ promoted bitumen cracking, thereby enhancing bitumen conversion, whereas the selectivity of gaseous products was decreased under the sub- or supercritical water environment accompanied by N₂.

Acknowledgements

Financial aid from Japan Petroleum Energy Center (JPEC) is greatly appreciated. International research fund from JST-MOST project of China and Japan supports this research. Key Project for Science and Technology Innovation Team of Zhejiang Province (2011R09028) and Research Program for University Project Plan of Zhejiang Province (Y201120088) also support this research.

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Graphical abstract

Why use the supercritical water as *medium*?

Table 1

Properties of Canadian Athabasca oil sand bitumen.

API gravity	CCR ^a (wt %)	Organic element content (wt%)				Metal content (ppm)		Group composition (wt%)				
		C	H	S	N	Ni	V	Saturate	Aromatics	Resin	Asphaltene	Residue
6.0	14.8	82.9	10.1	4.9	0.5	75	192	10.9	61.5	18.1	9.5	65.2

^a Conradson carbon residue.

Table 2

Bitumen cracking in sub- or supercritical water.

Run No.	Atmo- sphere	T (°C)	H ₂ O (g)	P (MPa)			Conv. (%)	Selectivity (wt%)						
				Before	Reacting	After		Gas	Naphtha	Kerosene	Gasoline	VGO	Residue	Coke
1	H ₂	400		3.0	8.6	3.3	81.4	23.4	24.7	10.4	11.4	0.70	12.1	17.3
2	H ₂	400	11	3.0	30.1	3.0	92.0	3.2	7.7	11.0	33.5	30.9	5.2	8.5
3	H ₂	350	11	3.0	17.3	3.0	86.0	4.6	3.8	13.3	46.4	18.6	9.1	4.2
4	N ₂	350	11	3.0	17.9	3.0	92.8	0.1	3.5	13.3	46.3	26.3	4.7	5.8
5	N ₂	400	11	3.0	30.1	3.1	97.7	1.0	9.0	16.5	40.6	22.6	1.5	8.8

Reaction conditions: bitumen 2 g, 5% Ni/AC, 0.5 g, 1 h; naphtha: IBP-170 °C, kerosene: 170-230 °C, gasoline: 230-343 °C, VGO (vacuum gasoline): 343-525 °C, residue: >525 °C.

Table 3

Selectivity of gaseous products for the bitumen cracking.

Run No.	Selectivity (wt%)									
	H ₂ S	CO	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	iso-C ₄ H ₁₀	C ₄ H ₁₀	C ₄ H ₈
1	14.4	10.0	18.9	33.5	0.2	14.9	0.8	2.4	4.7	0.2
2	15.6	80.6	2.4	0.4		0.5	0.1	0.1	0.2	0.1
3	4.9	66.6	9.5	7.8	0.3	5.9	0.7	1.0	2.9	0.4
4	60.3		14.5	7.5	1.2	8.3	2.9	1.2	3.5	0.6
5	16.3		31.6	17.3	1.8	17.4	4.3	2.6	6.8	1.9

Reaction conditions: bitumen 2 g, 5% Ni/AC 0.5 g, 1 h.

Table 4

Elemental analysis of sulfur in distillates.

Run No.	S content (wt%)			
	Naphtha	Kerosene	Gasoline	VGO
1	0.01	0.19	0.85	1.21
2	Trace	0.42	1.36	1.67
3	Trace	0.31	1.11	1.42
4	Trace	0.25	0.96	1.85
5	Trace	0.29	1.05	2.04

Reaction conditions: bitumen 2 g, 5% Ni/AC, 0.5 g, 1 h; naphtha: IBP-170 °C, kerosene: 170-230 °C, gasoline: 230-343 °C, VGO (vacuum gasoline): 343-525 °C, residue: >525 °C.

Fig. 1. XRD patterns of reduced fresh Ni/AC and spent Ni/AC catalysts under different reaction conditions (●Ni⁰, ★NiO, ▼Ni₃S₂).