Research article

Catalytic bitumen cracking in sub- and supercritical water

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ABSTRACT

The bitumen cracking reaction under sub- and supercritical water environments in H_2 or N_2 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 H_2 source was provided by the water–gas shift reaction in the sub- and supercritical water environment, thereby enhancing the catalytic activity of bitumen cracking.

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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 oils 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 hydrocarbon 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 N_2 at 400 °C for 2 h, subsequently reduced with H_2 at 400 °C for 10 h and then followed by passivation with 1% O_2 in N_2. The bitumen cracking reaction was performed in a 20 mL batch autoclave reactor (HASTELLOY alloy). The schematic diagram of experimental procedure and product analysis is showed in Figs. S1 and S2, respectively.

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.	Atmosphere	T (°C)	H_2O (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.

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 distillate 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 distillate 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 H_2

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 Ni^0 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 (H_2 or N_2)

As listed in Table 2, the bitumen conversion is higher under N_2 atmosphere than that under H_2. The in-situ H_2 is easily produced by WGSR of the produced CO with subcritical water for Run 4 under N_2 atmosphere, whereas its formation is suppressed for Run 3 because of the present

high pressure of H_2. The active in-situ H_2 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
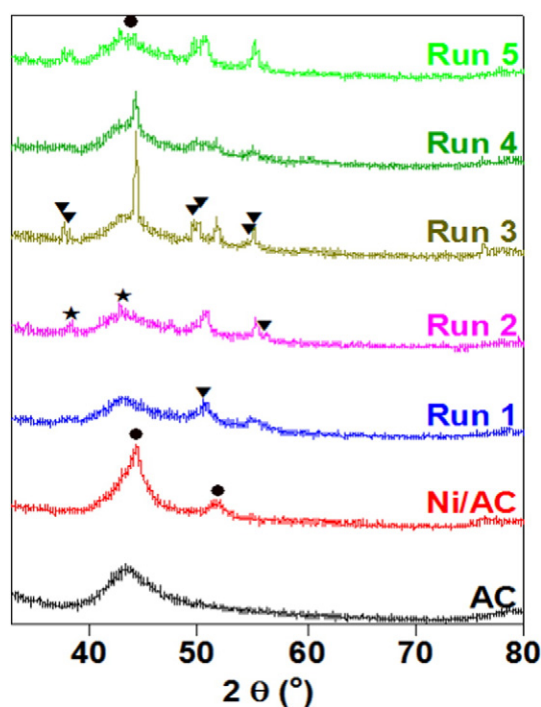

Fig. 1. XRD patterns of reduced fresh Ni/AC and spent Ni/AC catalysts under different reaction conditions ($\bullet$Ni^0, $\star$NiO, $\blacktriangledown$Ni$_3$S$_2$).