Aquathermolysis of conventional heavy oil with superheated steam

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Abstract: This paper presents a new aquathermolysis study of conventional heavy oil in superheated steam. A new high temperature autoclave was designed, where volume and pressure could be adjusted. Aquathermolysis was studied on two different conventional heavy oil samples under different reaction times and temperatures. Experimental results show that aquathermolysis does take place for conventional heavy oil. As reaction time increases, the oil viscosity reduces. However, the reaction will reach equilibrium after a certain period of time and won't be sensitive to any further reaction time any more. Analysis shows that, while resin and asphaltenes decrease, saturated hydrocarbons and the H/C ratio increase after reaction. The main mechanism of aquathermolysis includes hydrogenization, desulfuration reaction of resin and asphaltenes, etc.

Key words: Conventional heavy oil, superheated steam, aquathermolysis, viscosity reduction

1 Introduction

Clark et al (1983) studied the high-temperature hydrolysis and thermolysis of tetrahydrothiophene and found that the hydrolysis of tetrahydrothiophene produced hydrogen sulphide, carbon dioxide and hydrocarbon gas, together with a complex array of liquid products. A few years later, by means of analyzing compositions and gases of heavy oils from Canada (Clark et al, 1984a; 1984b; 1984c; 1987a; 1987b; 1990a; 1990b), researchers found that, under high-temperature and high-pressure conditions, desulfuration, denitrification, hydrogenization and water-gas-shift reactions could occur between heavy oil and steam. They referred to this process as aquathermolysis.

The effect on Cold Lake crude oil during steam stimulation was studied (Gould, 1983). After steam stimulation, H/C ratio decreased and aromatic carbon increased. The study concluded that some changes had occurred during aquathermolysis of heavy oil, which included side-chain dealkylation, aromatization of hydroaromatic rings and alteration of some heteroatomic functional groups, etc.

In recent years, more and more attention has been given to aquathermolysis of heavy oil. Fan and Liu found that the viscosity of heavy oil from the Liaohe Oilfield, Northeast China, decreased significantly after aquathermolysis. The contents of heteroatoms, such as S, O, and N, reduced

(Fan et al, 2001a; 2001b; 2002; Zhao et al, 2002). Further experimental study indicated that the reaction could be promoted by adding catalysts (Liu et al, 2004; Fan et al, 2004; 2007). This technology has been successfully applied in the field with good results. For super-heavy oil from the Shengli Oilfield, China, the viscosity could reduce by more than 70% after catalytic aquathermolysis in the presence of a hydrogen donor (Fan et al, 2006).

Most studies tend to focus on the composition analyses of gas and liquid products when analyzing mechanisms of aquathermolysis. Heavy oils used by Clark et al (1987b) contained high percentage of sulfur, and samples from Liaohe Oilfields (Fan et al, 2001b) were ultra heavy oils. They paid more attention to improving the catalysts. However, the importance of system pressure on the reaction has not been investigated. Furthermore, the previous studies of aquathermolysis were only focused on super-heavy oil. The reaction of conventional heavy oil has not been studied.

To study the two issues mentioned above, we designed a new high-temperature autoclave, where pressure could be controlled. Based on the autoclave design principle published (Du et al, 2001; 2002), we made a volume-variable autoclave. In this autoclave, aquathermolysis of conventional heavy oil with superheated steam was studied.

2 Experimental

2.1 Experimental materials

Distilled water and two crude oil samples, whose properties are listed in Table 1, were used in the experiments.

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Table 1 Ultimate analysis and properties of crude oil samples

Oil sample	Oilfield	Relative density	Viscosity, mPa·s / temperature, °C	C, %	H, %	O, %	N, %	S, %	H/C
1	Kenneyak Oilfield	0.91	82.97 / 40	86.41	12.33	0.21	0.15	0.900	1.71
2	Bozhong 25-1 oil field	0.87	3760 / 50	81.45	11.3	-	-	0.326	1.66

2.2 Experimental apparatus

Aquathermolysis of conventional heavy oil was conducted in a high-temperature autoclave we made. Fig. 1 shows the schematic section of the autoclave. The body and the lid of the autoclave were made of stainless steel for better corrosion resistance. The internal pressure was controlled by manually adjusting the autoclave volume, ensuring that water in the autoclave was superheated. The maximum operating temperature and pressure were 350 °C and 40 MPa, respectively. The volume of this autoclave ranged from 50 to 300 ml.

The viscosity of oil samples was measured with a NDJ-1 rotary viscosimeter (provided by Shanghai Ande Instrument Equipment Co., Ltd.). A water thermostat system was used to keep the samples at a specified temperature when their viscosity was measured.

Fig. 1 Schematic section of the high-temperature autoclave

The composition of oil samples were analyzed by China State Key Laboratory of Heavy Oil Processing, China University of Petroleum. The hydrocarbon distribution was analyzed by gas chromatography with the ASTM D5307 standard procedure (Agilent 6890). Elemental composition of the samples was determined with a Carlo Erba EA1108 model elemental analyzer using 3-4 mg samples.

Saturates, aromatics, resins, and asphaltenes (SARA) analysis of oil samples were determined by high performance liquid chromatographic analysis of the deasphalted oil (SH/T0509-92). The asphaltene was removed by precipitation with addition of 40-volume excess of dry hexane to the solution of the heavy oil sample in dichloromethane.

2.3 Experimental procedure

Based on previous studies, the influence of other factors was neglected and the mass ratio of water to oil was kept at 0.3 during the entire experiment, and the influence of reaction time and temperature on aquathermolysis of conventional heavy oil was investigated. First, keep the autoclave at the minimum volume and fill it with 50 g crude oil and 15 g distilled water. Maintain the reaction temperature at 240, 300, and 350 °C, respectively. Set reaction time as 24, 36, 48 and 72 h. When heated to the set-point, the pressure of system will increase. This can be controlled by manually adjusting the autoclave volume, ensuring that water in the autoclave is superheated. After reaction, put the oil into the water thermostat system. Finally measure the oil viscosity using the viscosimeter.

3 Results and discussion

Table 2 shows the experimental pressures at different experimental temperatures. This indicates that all the reactions has occurred in the superheated steam system at high temperatures.

Table 2 Comparison of experimental pressures and steam saturation pressures

Crude oil sample	Experimental pressure MPa	Experimental temperature °C	Degree of superheat °C
1	0.50	240	88
	1.60	300	99
	4.10	350	98
2	1.00	240	60
	1.52	300	101

3.1 Hydrocarbon distribution

Fig. 2 show the distribution of hydrocarbons in oil samples before and after aquathermolysis. The corresponding reaction temperatures were 300 and 350 °C, respectively. The components of crude oil changed noticeably, and the content of high carbon number hydrocarbons became lower and the

content of light hydrocarbons higher.

Analysis results proved that conventional heavy oil could react with superheated steam at high temperatures and the crude oil was upgraded. The decrease in high carbon number hydrocarbons indicates that the main reason is the cracking of long-chain hydrocarbons.

Fig. 2 Hydrocarbon distribution of 1[#] oil sample before and after aquathermolysis

Table 3 SARA components and elementary composition of crude oil samples before and after aquathermolysis

Crude oil sample	Reaction temperature, °C	Reaction time, h	SARA, wt%				H/C	S
			Saturates	Aromatics	Resins	Asphaltenes		
1	Before reaction		63.37	25.00	10.98	0.65	1.71	0.90
	300	72	63.61	25.10	10.64	0.65	1.72	0.89
	350	72	66.18	24.98	8.39	0.45	1.72	0.86
2	Before reaction		45.81	26.81	24.81	2.57	1.59	0.326
	300	36	52.88	22.62	22.62	1.88	1.65	0.315

3.3 Effects of reaction time

Aquathermolysis of heavy oil samples was conducted at 240 °C for different periods of reaction time (24, 36, 48 and 72 h). Figs. 3 and 4 show the effect of reaction time on viscosity of oil samples. After reaction, the viscosity of oil samples reduced significantly. The viscosity of oil samples decreased with reaction time before 48 h, and after the reaction time exceeded 48 h, the oil viscosity reduction became very slight. The result indicated that the reaction would reach its equilibrium after 48 h.

Fig. 3 Effect of reaction time on the viscosity of 1[#] oil sample

3.2 SARA analysis and element analysis

SARA analysis and element analysis of oil samples were carried out before and after reaction and experimental results are shown in Table 3.

A significant increase in the content of saturates was observed for 1[#] oil sample after aquathermolysis at 350 °C for 72 h and for 2[#] oil sample after aquathermolysis at 300 °C for 36 h. However, a decrease in the contents of resin and asphaltenes were also observed due to the thermolysis of condensed nucleus and heterocyclic compounds. An increase in H/C ratio after reaction indicated that hydrogenization took place in the thermolysis process.

For 1[#] oil sample, the aromatics content increased first and then decreased as reaction temperature increased. For 2[#] oil sample, the aromatics content decreased noticeably. The phenomena can be explained by hydrogenization and side-chain dealkylation of hydroaromatic rings.

In crude oil, sulfur exists as thioalcohols, sulfur ethers, and thiophenes. The sulfur content reduced after reaction, which illustrated that the carbon-sulfur bond might be broken and gaseous sulfides might escape.

Fig. 4 Effect of reaction time on the viscosity of 2[#] oil sample

3.4 Effects of reaction temperature

In order to study the effect of reaction temperature on the aquathermolysis of heavy oil sample, experiments were conducted on 1[#] oil sample at different temperatures (240, 300, and 350 °C). The reaction time was kept constant at 72 h to eliminate its influence.

Fig. 5 shows the viscosity of oil samples after reaction. Even as the reaction temperature was raised from 240 to 300

°C, the viscosity changed very slightly. However, when the reaction temperature was raised to 350 °C, the viscosity of oil sample declined sharply. Previous research has demonstrated that the optimum temperature range of aquathermolysis of heavy oil is 220-280 °C (Liu et al, 2004). Based on the previous research and experimental results obtained in this study, the viscosity of 1[#] oil sample is not very sensitive to reaction temperature during a 72 hr reaction time, but it reduces quickly at a higher temperature. This may be due to thermolysis of crude oil at high temperatures.

Fig. 5 Effect of reaction temperature on the viscosity of 1[#] oil sample

3.5 Reversion of decreased towards original value on ageing

The reduction in viscosity after aquathermolysis is not fully sustained. The viscosity of reacted oil 1[#] gradually increased back towards its original higher viscosity, as shown in Fig. 6. The oil which had been subject to aquathermolysis for a longer time (72 h vs. 24 h) retained more of its viscosity reduction (7.1%) on ageing for about two weeks than did the oil reacted for only 24 hours (3.5% reduction).

During aquathermolysis, a number of active chains may be produced due to side-chain dealkylation and alteration of some heteroatomic functional groups (Zhao et al, 2002). These active chains can polymerize to form large molecular compounds, thus leading to the increase in viscosity with time.

Fig. 6 Stability analysis of viscosity reduction

4 Conclusions

1) The reactions between conventional heavy oil and superheated steam were investigated for the first time. Experimental results demonstrated that aquathermolysis did take place. The content of high carbon number hydrocarbons decreased and light hydrocarbons increased. The viscosity of conventional crude oil reduced and the oil was upgraded after aquathermolysis.

2) After 48 hours, the aquathermolysis reached a state of chemical equilibrium for conventional crude oil. After reaction equilibrium, aquathermolysis was not sensitive to reaction time.

3) The main mechanisms of aquathermolysis between conventional heavy oil and superheated steam included hydrogenization, desulfuration reaction of resin and asphaltenes, etc.

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