Experimental research of heavy oil aquathermolysis on the synergistic effect of ultradispersed catalyst and reservoir minerals

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Abstract. Based on high pressure reactor as simulator of conditions in heavy oil recovery, we use self-made Mo ultra-dispersed catalyst to carry out aquathermolysis of heavy oil with reservoir minerals, The results indicate that in contrast with simple AT, the addition of reservoir minerals leads to lower average molecular weight ,higher contents of saturated and aromatic hydrocarbon fractions and lower contents of resin and asphaltene fractions, and the viscosity reduction ratio of heavy oil samples increases from 27.42% to 72.54%. Reservoir minerals can catalyze the AT of heavy oil. With the addition of reservoir minerals into the reaction system, the average molecular weight of the reaction products decreases further, the contents of saturated and aromatic hydrocarbon fractions in group composition increase further and the contents of resin and asphaltene fractions decrease further, the viscosity decreases greatly with a reduction ratio as high as 74.76%.

Keywords: ultradispersed catalyst, reservoir minerals, heavy oil, aquathermolysis, viscosity reduction.

1. Introduction

Catalytic aquathermolysis has become the important area to solve some problems in the process of heavy oil extraction. Hyne et al pointed out that some metals can accelerate aquathermolysis. Since then, researchers conduct experiments to study the effect of some catalysts in the reaction. It is found that superheated water can transfer heat to warm hydrocarbon, which can pyrolyze some asphaltene molecules to small molecules. It can further improve high viscosity and poor liquidity of heavy oil. In addition, the increase of heat can provide a driving force to make the viscosity of crude oil flows easily, and improve its crude oil output as well. When there are catalysts in reaction system, the viscosity of crude oil falls to low level. The catalysts commonly used in aquathermolysis are water soluble, oil soluble and dispersed catalysts. According to the effects of viscosity, it can be ordered in the following sequence: water soluble catalysts < oil soluble catalysts < dispersed catalysts.

For the catalytic effect of the oil reservoir, American mineralogist Grim and chemist Brooks firstly found the reaction that organic materials produce hydrocarbon has catalytic effects. In the process of steam injection in heavy oil extraction, researchers over the world have found that reservoir minerals have catalytic effects on heavy oil cracking. However, for the heavy oil aquathermolysis in condition of steam injection, the catalytic potential of reservoir mineral remains explored. In order to understand the catalytic effects of reservoir mineral on heavy oil aquathermolysis in condition of steam injection, we conduct the research of the catalytic properties of reservoir mineral and ultradispersed catalyst on heavy oil aquathermolysis.

2. Experimental Section

2.1 Experimental instrument and chemical substance

Instrument: CWYF-I strong magnetic, high temperature and high pressure reaction kettle (Jiangsu Haian Huada oil factory), HAAKE RS6000 (Germany HAAKE Company).

Chemical substance: base oil (initial boiling point 623 K),reservoir mineral from Liaohe oil sand, n-hexane, methylbenzene, $(NH_4)_6Mo_7O_{24}$, ammonium molybdate, caustic soda, petroleum ether, diethyl ether etc. and silica gel, neutral alumina (100~200 mesh), above all are analytically pure.

2.2 Catalyst Preparation

Molybdenum ultradispersed catalyst preparation: Choose non-ionic surfactant sorbitan mono-oleic acid ester water/oil emulsion, lubricating oil base oil (initial boiling point 340 ℃) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as catalyst precursor, choose water soluble transition metal salt because its cost is lower than the oil soluble transition metal salts and distilled water flash evaporation and decomposition preparation. Microemulsion preparation experiment is conducted under atmospheric pressure using the mixture of base oil 150g, water 16.8g and surfactant 9g to reduce the interfacial tension between oil-continuous phases and water droplets. To form stable micellar microemulsion, it needs to mix for 10 minutes with the high speed of 4000 rpm. The catalyst particle size is 1800nm measured by dynamic light scattering method.

2.3 Experimental Method

Filter samples of heavy oil in 80℃ with pore size 0.045 mm stainless steel screen mesh, and dehydrated below 120℃ until it is qualified when the moisture content is less than 0.5% Put a certain amount of heavy oil, water and ultradispersed catalyst at high temperature and high pressure reaction kettle, conduct aquathermolysis and viscosity reduction process under certain temperature and reaction time. Inject N_2 to the high pressure reaction kettle before heating and maintain pressure in 8-10 MPa. After the completion of the reaction, cool it to room temperature and collect sample oil to set aside.

2.4 Test Method Analysis

Crude oil group compositions use silica gel and the alumina as adsorbent to be examined according to the relevant provisions of the SY/T5119-1995. We adopt VPO method. Using pyridine as solvent, use VPO in 45℃ to measure the average MW of heavy oil and bitumen before and after reaction. Use HAAKE RS6000 rheometer to measure viscosity. Below 50℃, calculate viscosity reduction rate by the heavy oil viscosity before and after reaction when shear rate is $10s^{-1}$. Viscosity reduction rate can be calculated by formula $\Delta\mu = (\mu_0-\mu)/\mu_0\times100\%$. Among them, $\Delta\mu$ refers to viscosity reduction rate, μ_0 refers to viscosity reduction rate before reaction and μ refers to viscosity reduction rate after reaction.

Table 1 Reservoir mineral properties and content analysis of Liaohe oilfield

Minerals classification	Minerals name	Content /wt%
Rock minerals	quartz	54.5
	potash feldspar	18.2
	plagioclase	13.9
	calcite	1.3
	dolomite	1.2
	link feldspar	0
	rhodochrosite	1.4
Clay minerals	Total content	9.5
Clay minerals relative content	montmorillonite	91.9
	illite	4.5
	kaolinite	1.7
	chlorite	1.9

3. Result and Discussion

3.1 mineral composition, content and properties in experiment

The data in this experiment is from the purpose reservoir of Liaohe oilfield, which represents the reservoir condition of the oil used in experiment. Smash rock core is in size of 100-300μm. Its mineral composition and content analysis was seen in Table 1.

3.2 Changes of viscosity caused by reservoir mineral

Put a certain amount of crude oil in the reaction kettle, adding 30 wt% water in the temperature of 240℃ for 24 h, and then add into 0.1wt% catalyst and 10 wt% reservoir mineral. For the heavy oil before and after reaction, we use HAAKE RS6000 rheometer to measure its viscosity in 80℃, the result was seen in Table 2. We can observe from Table 2 that after the aquathermolysis, the viscosity of heavy oil decreases by 27.42%, and its viscosity decreases by 74.76% after adding the catalyst and reservoir mineral, which shows that reservoir mineral has catalytic effect on the heavy oil aquathermolysis.

Table 2 Changes of the viscosity of heavy oil and its rate of viscosity reduction before and after reaction

Name	Viscosity before reaction/mPa s	Viscosity after reaction/mPa s	Viscosity reduction ratio/%
Aquathermolysis	11000	7984	27.42
Catalytic aquathermolysis		3021	72.54
Catalytic aquathermolysis on the effect of reservoir minerals		2776	74.76

3.3 Changes of heavy oil group composition caused by reservoir mineral

Put heavy oil into the reaction kettle to prepare ultradispersed catalyst as the catalyst used in catalytic upgrading and viscosity reduction reaction. Add into a certain amount of crude oil, 30 wt% water in 240℃ for 24 h, and then add into 0.1wt% catalyst, 10 wt% reservoir mineral. And then analyse the composition changes of oil sample.

Table 3 Reservoir mineral’s effect on heavy oil group composition

Name	Before reaction SARA/wt%				After reaction SARA/wt%			
	S	A	R	A	S	A	R	A
Aquathermolysis	22.3	26.4	42.6	8.7	27.9	30.5	36.2	5.4
Catalytic Aquathermolysis					28.1	30.6	36	5.3
Catalytic aquathermolysis on the effect of reservoir minerals					29.3	31.8	33.7	5.2

According to chromatographic analysis of group composition, SARA analysis was done on the heavy oil group composition before and after reaction. And we assume the weight of reservoir mineral remain constant in process of reaction, thus we should exclude the amount of reservoir mineral added in the experiment when calculate the content of bitumen. Results was seen in Figure 1 and Table 3. We can see from Figure 1 and Table 3, after adding reservoir mineral, contents of saturated hydrocarbons and aromatic hydrocarbons in the heavy oil continued to increase, resin and asphaltene content decreased, saturated hydrocarbons increase from 22.3wt% to 29.3 wt%, aromatic hydrocarbons increase from 26.4wt% to 31.8 wt%, and resin decreases from 42.6wt% to 33.7wt%, asphaltene decreases from 8.7 wt% to 5.2wt%. This shows that the presence of reservoir mineral has catalytic effect on heavy oil aquathermolysis. Meanwhile, compared the catalytic aquathermolysis with no reservoir mineral, the content of saturated hydrocarbons and aromatic hydrocarbons further increase, while resin and asphaltene content further decreased in the aquathermolysis with reservoir mineral and catalyst, which suggests that reservoir and catalyst have synergistic effect on heavy oil aquathermolysis during the aquathermolysis reaction.

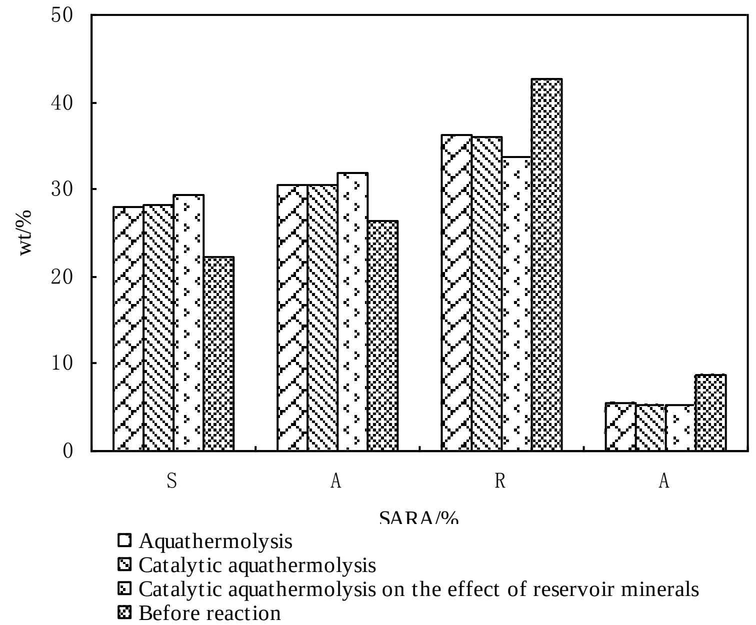

Fig.1 Changes of heavy oil group composition in different condition

3.4 Reservoir mineral's effects on heavy oil average molecular weight

Using pyridine as solvent, we adopt VPO to measure the average molecular weight (MW) of asphaltene of heavy oil before and after reaction in 45 ℃, and the results was seen in Table 4. Put a certain amount of crude oil in reaction kettle, add into 30 wt% water in 240℃ for 24 h, then add into 0.1 wt% catalyst and 10wt% reservoir mineral, and measure the average MW of oil sample after reaction.

Table 4 Reservoir mineral's effects on average MW of heavy oil and asphaltene

Name	Heavy oil average MW	Asphaltene average MW
Before reaction	636	5318
Aquathermolysis	493	5027
Catalytic aquathermolysis	352	3692
Catalytic aquathermolysis on the effect of reservoir minerals	337	3607

We can observe from Table 4 that the average MW of heavy oil didn't change obviously after aquathermolysis, while after catalytic aquathermolysis, the MW of heavy oil decrease from 636 to 352, and afer adding reservoir mineral, the MW of heavy oil decrease to 337 after aquathermolysis, which suggests that reservoir mineral accelerates heavy oil aquathermolysis in condition of steam injection, and when catalyst and reservoir mineral co-exsist, the MW of heavy oil decrease to 337. This further shows that reservoir mineral has catalytic effect on heavy oil aquathermolysis. Meanwhile, the measurement results of the MW of asphaltene extracted from heavy oil after reaction, the MW of heavy oil decrease after aquathermolysis, and after adding reservoir mineral and catalyst, the MW of asphaltene decrease greatly. This trend shows that at the time of catalytic aquathermolysis, reservoir mineral inhibit the aggregation of asphaltene, and cause the reduction of its average MW. This theoretically explains the reduction of viscosity of heavy oil after aquathermolysis. Because viscosity is the indicator of flowability, it shows the inner resistence caused by friction between molecules when molecules move relatively. The bigger the molecules are, the bigger the interaction between them are, and the more energy the flow will need, so the viscosity will be higher.

4. Conclusion

(1) Addition of ultradispersed catalyst and reservoir mineral improve the viscosity of heavy oil, compared with aquathermolysis with no reservoir mineral and catalyst, the rate of reduction of viscosity of heavy oil reach 74.76%, which increase by 47.43%.

(2) After heavy oil catalytic aquathermolysis with 10wt% reservoir mineral, the content of saturated hydrocarbons and aromatic hydrocarbons increase, while the content of resin and asphaltene decrease, saturated hydrocarbons increase from 22.3wt% to 29.3 wt%, aromatic hydrocarbons increase from 26.4wt% to 31.8 wt%, and resin decreases from 42.6wt% to 33.7wt%, asphaltene decreases from 8.7 wt% to 5.2wt%.

(3) the average MW of heavy oil didn’t change obviously after aquathermolysis, while after catalytic aquathermolysis, the MW of heavy oil decrease from 636 to 352, and afer adding reservoir mineral, the MW of heavy oil decrease to 337 after aquathermolysis, which suggests that reservoir mineral accelerates heavy oil aquathermolysis.

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