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Research Article

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The catalytic aquathermolysis of heavy oil in the presence of a hydrogen donor under reservoirs conditions

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ABSTRACT

Under the condition of high pressure reactor simulating oil reservoirs thermal recovery, with the catalyst of self-made organic oil-soluble salt, with the hydrogen donor of formic acid, the study of catalytic aquathermolysis of heavy oil has been carried out. The effects of adding hydrogen donor on the viscosity, group composition and sulfur content of heavy oil have been investigated and the thermal conversion behavior of the asphaltene of heavy oil have been analyzed by the method of TG-DTA analysis before and after the catalytic aquathermolysis reaction. It turns out that, with the increase of the mass fraction of hydrogen donor, the viscosity reduction ratio, the contents of saturated hydrocarbons and aromatic hydrocarbons are going up while the contents of resin and asphaltenes are reducing after the hydrogen donor catalytic aquathermolysis reaction. Then under the combined effect of catalysts and hydrogen donor, the amount of carbon and sulfur dropped, the amount of hydrogen increased, so the proportion of H/C atomic number becomes higher. According to the TG-DTA curve of asphaltenes in the heavy oil, the weight loss of asphaltenes in the heavy oil after the hydrogen donor catalytic aquathermolysis reaction is higher than that of before the reaction, which means the stability of the asphaltene in heavy oil has been weakened after the hydrogen donor catalytic aquathermolysis reaction.

Keywords: Aquathermolysis; Hydrogen donor; Catalytic; Asphaltene; Pyrolysis

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INTRODUCTION

With the increasing demand and the continuous exploitation of oil in China, the oilfield exploitation has is in a later period, the crude oil reserves which have good quality and are easy to exploit have been in shortage critically are seriously in short supply, so the trend is clear that the oil is becoming heavier than ever. At present, the recovery efficiency of most of the oil recovery is lower than 50% and most of the domestic oil exploration is in the second or third stage, which makes the heavy crude oil a major exploitation target. As it is called heavy oil and asphalt internationally, heavy oil has two features-high content in resin with asphaltene and low amount of wax. Consequently, its oil viscosity is high and is difficult to flow, so it is hard and unable to be exploited in a long time in the past. In China, the content of resin in heavy oil is as high as 20%~40%, while that of asphaltenes is relatively lower,with only 0~5% in general. Therefore, heavy oil in China has higher oil viscosity and lower relative density than that abroad[1]. Due to the high oil viscosity and the poor fluidity, the heavy oil even can not flow under the condition of reservoir, only a small amount of oil can be exploited with conventional technology. So it is of great significance to investigate pertinent EOR methods. Researchers all over the world have started some relevant researches on improving the heavy oil exploitation, including steam flooding[2], steam stimulation[3], steam-assisted gravity drive[4], conventional in-situ combustion[5], Toe-to-Heel Air Injection process[6], and process of aquathermolysis and downhole catalytic upgrading[7,8], in which steam stimulation and steam flooding are the most widely used methods in the world currently. Though sound efficiency has witnessed the common heavy oil, they have limited efficiency of exploitation for the extra-heavy oil. Inspired by the catalytic cracking technology applied in petrochemical production, researchers proposed the aquathermolysis method to reduce the viscosity of heavy oil. By injecting proper catalysts, hydrogen donors and other additives with the steam to the heavy oil, the heavy component of heavy oil is in the process of catalytic cracking under the hydrothermal condition, so the viscosity of the oil is reduced and it is easier to be exploited.

Aquathermolysis refers to the chemical interaction occurred through the contact with hot water which is in vapor or liquid form or vapor-liquid two-phase coexistence form, resulting in pyrolysis of some components.According to Hyne[9], the most critical step in the aquathermolysis of heavy oil is the hydrolysis of sulfide bond in sulfides and thiophenes. The break of C-S bond in sulfides will reduce the amount of molecule with higher molecular and decrease the content of asphaltene so that the viscosity of heavy oil decreases. After adding a new amount of transition metal catalyst and hydrogen donor to the system, the conversion rate of aquathermolysis reaction inicreases tremendously.

EXPERIMENTAL SECTION

1 Laboratory Instruments and Drugs. Instruments:
CWYF-Ⅰ high temperature and high pressure reactor with strong magneto (Haian Huada Petroleum Instrument Factory, Jiangsu), HAAKE VT550 of Germany, Diamond TG/DTA (PerkinElmer Company, Amercia), and WAY-2S Abbe Refractometer, etc.

Drugs: Formic acid, hexane, toluene, organic acid, nickel sulphate and sodium hydroxide are of analytical grade, as well as silica gel, neutral alumina (100-200 mesh), etc.

2 Catalyst Preparation.
Add a certain percentage of organic acids and alkali liquor that are required by the reaction to a flask with three necks and mix them intensively, then heat the flask up to 60~65℃, with reaction time 2~3h. Then add the nickel salt into the saponified liquor drop by drop, and start the blender at temperature 90~95℃ and dropping time 1~1.5h. After dropping finished, two more hours is needed before stopping the reaction. Then it is to be washed by water for 2~3 times before separating the aqueous phase and organic phase by a separating funnel. Having eliminated the water layer, the organic phase is to be distilled, dehydrated and sedimentated, now here comes the catalysts. According to WAY-2S Abbe Refractometer, the determined refractive index is $n_D^{25℃}=1.4737$. The catalyst is a kind of transparent viscous green liquid which is insoluble in water and soluble in alcohol, ether, benzene and other organic solvents.

3 Experimental Methods.
Weigh a certain amount of heavy oil, add it at a 4:1 oil-water ratio to 300mL of intermittent high-temperature and high pressure autoclave and add oil-soluble catalysts and a certain amount of hydrogen donors. Before heating, inject N_2 to the autoclave and keep the pressure between 8~10MPa till the reactor temperature rises to 280℃， with reaction time 24h. After the reaction, cool it down to room temperature, the oil sample is collected for further analysis.

4 Analytical Methods.
Group components in crude oil are tested in accordance with SY/T5119-1995 relevant regulations, while silica gel and aluminium oxide are taken as adsorbents. For the analysis of carbon and hydrogen content, National Standard GB/T19143-2003 method is used and oxygen is tested by oxygen analyzer. According to the National Standard GB/T 387-1990, the content of carbon is inspected by tube oven process. The content of nitrogen is calculated by subtraction method.HAKKE VT550 viscometer is used to test the viscosity of the oil. By the Pyris Diamond TG/DTA, the thermal properties of asphaltene before and after the hydrogen donor catalytic aquathermolysis reaction are tested.

RESULTS AND DISCUSSION

1 The Viscosity Change before and after Adding Hydrogen Donor Catalytic Aquathermolysis Reaction. Reaction temperature is 280℃, the reaction duration is 24h, the mass ratio of oil to water is 4:1, and the added mass of catalyst is 0.1% of that of the heavy oil, then add hydrogen donors with varied mass fraction. Dehydrate the heavy oil after it completes the hydrogen donor catalytic aquathermolysis reaction, and the determined viscosity is indicated in Table 1.

In Table 1, it is easy to see that as other conditions remain unchanged, when the mass fraction of the added hydrogen donors increases, the heavy oil viscosity reduction rate gradually rose after catalytic aquathermolysis reaction, and reaches 87.02% when the mass fraction of the added hydrogen donor is 7%.

Table1.The viscosity change of heavy oil before and after the hydrogen donor catalytic aquathermolysis reaction

Mass fraction of hydrogen doner/%	μ_0 Viscosity before the reaction/mPa·s	μ Viscosity after the reaction/mPa·s	$\Delta\mu$ Viscosity reduction ratio/%
0	3716	1312	64.69
1		1146	69.16
3		1050	71.74
5		870	76.58
7		482	87.02

2 The Content Changes of Group Composition and Sulfur in Heavy Oil before and after the Hydrogen Donor Catalytic Aquathermolysis Reaction. On the basis of chromatography analysis of group composition, the group composition of heavy oil (SARA components) before and after the adding hydrogen donor catalytic aquathermolysis reaction is analyzed and the experimental result is revealed in Table 2.

Table2.The test result of group components before and after the heavy oil catalytic aquathermolysis reaction by adding hydrogen donor with different mass fraction

Items		Original heavy oil	Adding hydrogen donor				
Mass fraction of hydrogen donor/%			0	1	3	5	7
SARA after reaction / %	Saturated hydrocarbons	24.32	26.12	27.37	29.02	30.51	31.12
	Aromatic hydrocarbons	36.89	38.08	39.68	40.12	40.89	41.26
	Resin	30.27	28.27	26.29	25.78	24.54	24.12
	Asphaltene	8.52	7.53	6.66	5.08	4.06	3.50

As shown in Table 2, the mass fraction of saturated hydrocarbon and aromatic hydrocarbon increase as the amount of the mass fraction of hydrogen donors increases, but that of resin and asphaltene declines. After adding catalyst, the contents of saturated hydrocarbon and aromatic hydrocarbon increase from the previous 24.32% and 36.89% to 26.12% and 38.08% respectively after the aquathermolysis reaction. Compared with the heavy oil sample before the reaction, the contents of resin and asphaltene reduce by 2% and 0.99% respectively. After adding hydrogen donors with different mass fraction to the catalytic aquathermolysis, the contents of saturated hydrocarbon and aromatic hydrocarbon in heavy oil increase, and that of resin and asphaltene have a clear decline. Compared with the heavy oil sample before the reaction, when the hydrogen donor is added at 7% mass fraction, the contents of saturated hydrocarbon and aromatic hydrocarbon increase by 26.12% and 38.08% respectively, and that of resin and asphaltene reduce by 6.15% and 5.02%. It implies that with the hydrogen donor catalytic aquathermolysis reaction, the light group composition becomes higher while that of heavy composition becomes lower. At the same time, it indicates that some parts of naphthenic hydrocarbon have aromatized into aromatic hydrocarbon in the process of hydrogen donor catalytic aquathermolysis reaction. The hydrocarbons produced by the broken of a long alkyl chain which is condensed on the aromatic hydrocarbon in the molecular structure of resin and asphaltene combine with the broken of alkyl group that connects two aromatic hydrocarbons or between one aromatic hydrocarbon and one naphthenic ring system, results in the reduction of resin and asphaltene contents but the increase of aromatic hydrocarbon content. It is also the main reason of the viscosity reduction of heavy oil after the hydrogen donor catalytic aquathermolysis reaction.

The fact can be testified by comparing the TG-DTA curve of the asphaltene after 280℃ hydrogen donor catalytic aquathermolysis reaction with that of original oil. In accordance with Figure 2, the weight loss resulted from the asphaltene in heavy oil after the hydrogen donor catalytic aquathermolysis reaction, the asphaltene before the hydrogen donor catalytic aquathermolysis reaction is more heat-resistant.

3 The Change of Elements Contents before and after the Hydrogen Donor Catalytic Aquathermolysis Reaction. Following the optimal condition determined by the hydrogen donor catalytic aquathermolysis reaction, the reaction temperature is 280℃, the reaction duration is 24h, the mass ratio of oil to water is 4:1, and the added mass of catalyst is 0.1% of that of the heavy oil. The hydrogen donor catalytic aquathermolysis reaction of heavy oil is conducted when the added amount of hydrogen donor formic acid is 7%. In accordance with the Analytical Method of Elements, the elements of content in heavy oil before and after the hydrogen donor catalytic aquathermolysis reaction are studied, and the result is revealed in Table 3.

Table 3.Analysis of elements content in heavy oil before and after the hydrogen donor catalytic aquathermolysis reaction

Item	C(wt%)	H(wt%)	S(wt%)	O(wt%)	N(wt%)	H/C (atomic ratio)
Before the aquathermolysis reaction	85.78	11.62	0.565	1.61	0.425	1.63
Catalytic aquathermolysis reaction	85.03	13.36	0.336	0.86	0.414	1.89
Hydrogen donor catalytic aquathermolysis reaction	84.94	13.78	0.074	0.8	0.406	1.95

The experimental result of Table 3 reveals that under the function of the catalysts and the hydrogen donor, the elements composition of heavy oil have been changed significantly--- mainly after the reaction, the C content in heavy oil gets lower, H contents increase, H/C atomic number ratio is higher and the ratio of heteroatom containing to C is lower. Some chemical changes in heavy oil distillates are also visible, as the added catalyst and hydrogen donor lead to the broken-down of the lateral chains of aliphatic alkane and some weak bonds, which makes some lighter and smaller hydrocarbon molecules become the fluid phase. The higher H/C atomic number ratio is a symbol of the improved quality of the heavy oil, because the content of sulfur is reduced in heavy oil with more light hydrogen components. Compared with the condition before the hydrogen donor catalytic aquathermolysis reaction, sulfur in heavy oil drops by 0.262%, and the reduction of sulfur atom is more obvious. All the said proves the fact that under the coactions of the catalysts and the hydrogen donor, the heavy oil has a hydrogen donor catalytic aquathermolysis reaction which causes the change of the heavy oil structure, leading to a reduction of heavy oil viscosity and the improvement of heavy oil quality.

4 The Change of Thermal Property of Heavy Oil Asphaltene before and after the Catalytic Aquathermolysis Reaction. The reaction temperature is 280□, the reaction duration is 24h, the (mass) ratio of oil to water is 4:1, and the added mass of catalyst is 0.1% of that of the heavy oil. Dehydrate the heavy oil after it completes the catalytic aquathermolysis reaction and extract asphaltene from the heavy oil to conduct the thermal analysis.

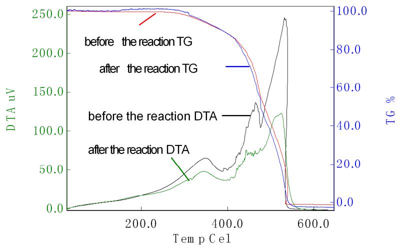

Fig. 1 Analysis of the asphaltene TG-DTA in heavy oil before and after the catalytic aquathermolysis reaction

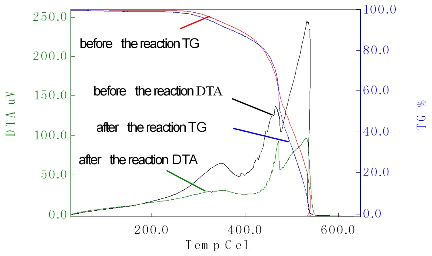

Fig. 2 Analysis of the asphaltene TG-DTA in heavy oil before and after the hydrogen donor catalytic aquathermolysis reaction

The TG-DTA curves of the asphaltene in heavy oil before and after the catalytic aquathermolysis reaction are shown in Figure 1. As expressed in the TG curve in Figure 1, the TG curves of asphaltene before and after the catalytic aquathermolysis reaction are typically smooth thermal weightlessness curves which remain relatively stable when the temperature is lower than 260℃ and no great change of weightlessness has been found. Compared with the TG curves before the reaction, when it exceeds 260℃, the ones of asphaltene in heavy oil after the catalytic aquathermolysis reaction have moved into the low temperature area. After it reaches 550℃, the weight remains unchanged, and the amount of weightlessness of the asphaltene in heavy oil after the catalytic aquathermolysis reaction is clearly higher than that before the reaction.In contrast, the DTA curves reveal that there is a broad endothermic peak in the low temperature area with 380℃ and a narrow endothermic peak in the high temperature area with 470℃, which are taken as two reaction areas according to the curves of the asphaltene in heavy oil before the aquathermolysis reaction,. After adding catalyst and the aquathermolysis reaction, the absorption peak in the high temperature area of the asphaltene in heavy oil becomes less obvious.

5 The Change of Thermal Property of Asphaltene in the Heavy Oil before and after the Hydrogen Donor Catalytic Aquathermolysis Reaction. The reaction temperature is 280℃, the reaction duration is 24h, the (mass) ratio of oil to water is 4:1, the added mass of catalyst is 0. 1% of that of the heavy oil, and the added hydrogen donor is 7% of that of the heavy oil. Dehydrate the heavy oil after it completes the hydrogen donor catalytic aquathermolysis reaction and extract asphaltene to conduct the thermal analysis as shown in Figure 2.

According to the Figure 2, the TG analysis curves of the asphaltene in heavy oil before and after the hydrogen donor catalytic aquathermolysis reaction remain relatively stable when the temperature is lower than 260℃ and no great change of weightlessness has been found. Compared with the TG curves before the reaction, when it exceeds 260℃, the ones of asphaltene in heavy oil after the catalytic aquathermolysis reaction has moved into the low temperature area. After it reaches 550℃, the weight remains unchanged, and the amount of weightlessness of the asphaltene in heavy oil after the catalytic aquathermolysis reaction is higher than that before the reaction.In contrast, the DTA curves, before and after the hydrogen donor catalytic aquathermolysis reaction, reveal that before the catalytic aquathermolysis reaction there is a broad endothermic peak in the low temperature area and a narrow endothermic peak in the high temperature area, which are taken as two reaction areas. After adding catalyst and the hydrogen donor, the absorption peak in the low temperature oxidation area of the asphaltene DTA curves disappears after the aquathermolysis reaction.With regard to the above analysis, the stability of the asphaltene in the heavy oil has been reduced after going through hydrogen donor catalytic aquathermolysis reaction. The phenomenon means that the structure of asphaltene is a possible factor besides the composition of asphaltene in the heavy oil.

CONCLUSION

Steam injection is one of the enhanced measures for oil recovery. The transition of the process together with the spot evaporation and the reduction of asphaltene quantity make the oil lighter.

Adding formic acid as hydrogen donor has improved the viscosity of heavy oil. Compared with the catalytic aquathermolysis reaction without formic acid as hydrogen donor, the viscosity reduction rate of the heavy oil increases by 22.33% when the mass fraction of hydrogen donor is 7%.

After the catalytic aquathermolysis reaction of the heavy oil with hydrogen donor formic acids of different mass fractions, the amount of saturated hydrocarbons and the aromatic hydrocarbons is higher while that of the resin and asphaltene gets lower. Compared with the heavy oil samples before the reaction, the volume of saturated hydrocarbons and the aromatic hydrocarbons has increased by 6.8% and 4.37% respectively adding the hydrogen donor with 7% mass fraction, while that of the resin and asphaltene has dropped by 6.15% and 5.02%.

TG-DTA method implies that the structure and composition of asphaltene in the heavy oil have been changed after the hydrogen donor catalytic aquathermolysis reaction, and the thermal stability of the asphaltene in the heavy oil has been weakened after the reaction.

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