

Urea Enhanced Aquathermolysis of Heavy Oil Catalyzed by Hydroxamic Acid-Co(II) Complex at Low Temperature

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Abstract. To develop effective water-soluble catalyst for aquathermolysis, a phenyl hydroxamic acid-Co(II) complex was synthesized using hydroxamic acid and CoCl₂. The effects of water content and catalyst concentration on aquathermolysis were investigated. The effect of adding urea as fortifiers was investigated. The crude oil samples before and after aquathermolysis were fully characterized by SARA and elemental analysis. With the catalyst and urea, the viscosity of the product was also substantially reduced from 470000 mPa•s to 120000 mPa•s at 15 °C. Finally improved the flow properties better and upgrade the quality of heavy oil.

Keywords: heavy oil; catalyst; viscosity reducing; catalytic aquathermolysis

1 Introduction

To keep the increase in crude oil production, we must increase the heavy oil resource development and utilization [1-2]. Changing the chemical composition and characteristics of heavy oils and bitumen in-situ and before loading into pipelines is attractive because it helps improve production and saves the cost of purchasing and transport of diluents, and the processing operations for their recovery and reuse. In 1982, Hyne, Clark and their collaborators demonstrated that metal complexes can accelerate the thermal degradation of large organic molecules such as asphaltenes in the presence of water, a reaction they termed aquathermolysis [3-5]. There are interests in the reaction within reservoirs when steam is injected and in the development of catalysts that promote the reaction.

Catalysts may be classified in terms of the phase within which they are active. A catalyst may be dissolved in the oil, suspended as particles in the oil or dissolved in the water. The oil soluble and dispersed catalysts are reported to be slightly more active than the water-soluble catalyst [6-8], but the costs are significantly higher than for water soluble catalysts. Identifying an effective water-soluble catalyst and the reaction conditions that promote decomposition of large hydrocarbon molecules to lower the oil viscosity is a motivation for

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this study. The conditions are different from catalytic cracking processes in refineries at elevated temperatures. Aquathermolysis of heavy oil, catalyzed by water-soluble catalysts, occurs at relatively mild conditions (160-280°C; 10-25 MPa) and short durations (24-240 hours), but the viscosity reduction is only about 60% [9,10] and the product is still viscous.

In this study, water-soluble catalyst (a phenyl hydroxamic acid-Co(II) complex), to achieve a significant reduction the viscosity of heavy oil at 180°C. Such catalyst was soluble in water, didn't introduce other organic solvents and didn't cause secondary pollution for oil. Meanwhile, it could directly inject into stratum with the water, which could significantly reduce the difficulty and cost of exploitation of heavy oil [11]. Furthermore, urea was also found can reduce the viscosity further in the aquathermolysis.

2 Results and Discussion

2.1 The effect of water on efficiency of the aquathermolysis

The effect of mass ratio of water to oil on the viscosity are shown in Figure 1. The presence of water is demonstrated to cause the reacted oil to have a lower viscosity, and the more water, the greater the reduction within the range of investigation [12]. The changes were not significant once the water to oil ratio reached 0.3. This will be used as a reference concentration. The data also showed that as the temperature rose, a more dramatic lowering of viscosity is observed. The oil viscosity is much more sensitive to temperature changes than to the amount of water present for the reaction[13].

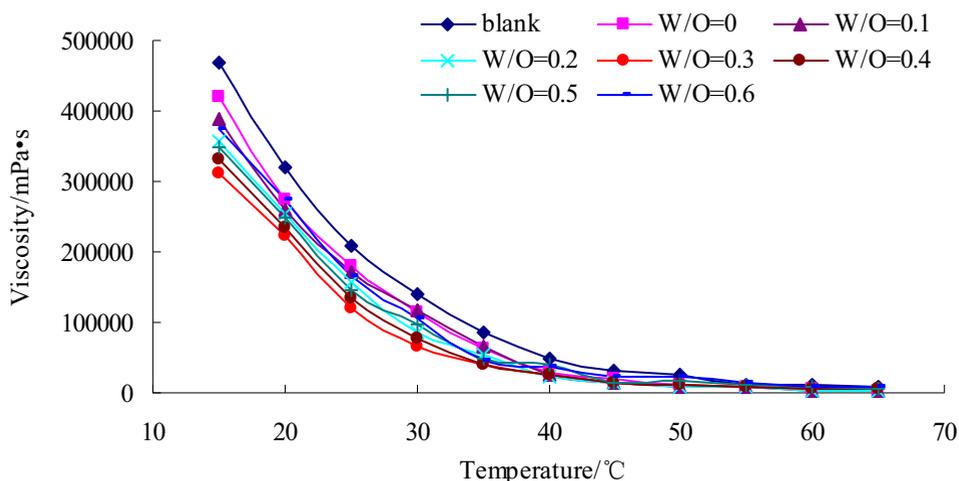


Figure 1 The influence of water on the viscosity of heavy oil after aquathermolysis reaction

2.2 The effect of catalyst concentration on catalytic aquathermolysis

Using phenyl hydroxamic acid-Co(II) complex (PHC) as catalyst, water/oil (mass ratio) of 0.3, the effect of catalyst concentration on aquathermolysis reaction of heavy oil was investigated, and the results were shown in Figure 2. It was found from the result, the viscosity was reduced along with the increase of catalyst. With 0.15% PHC, the viscosity reduction rate comes to the highest, 82% (25°C), as the concentration of catalyst exceeds

0.15%, the efficiency becomes weaker. Hence, the optimum amount of the catalyst (PHC) was 0.15%.

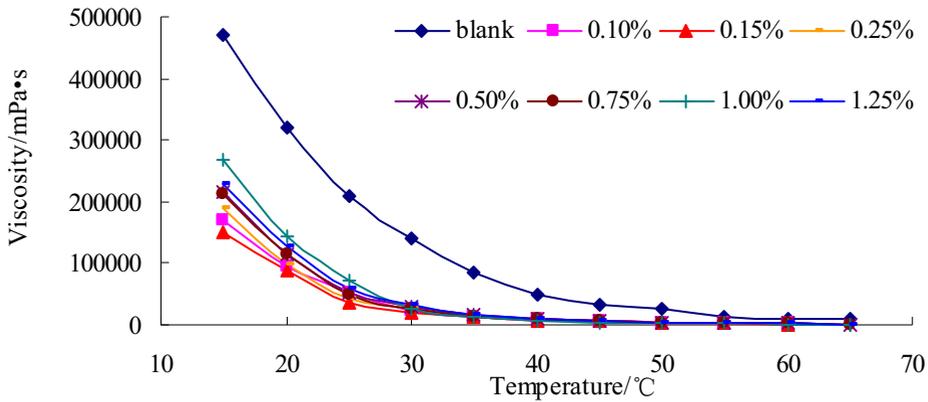


Figure 2 Effect of catalyst (PHC) concentration on the viscosity

2.3 Effect of urea to aquathermolysis

Using the optimized catalyst PHC with the concentration of 0.15%, the effect of the additives, urea, was investigated under the same reaction condition. The results were shown in Figure 3. Figure 3 shows that the viscosity of the crude oil can be further reduced at the present of urea, and the viscosity can be reduced from 470000 mPa·s to 120000 mPa·s at 15°C, and from 320000 mPa·s to 65600 mPa·s at 20°C. Compared with the aquathermolysis reaction just with water and PHC, the viscosity was reduced from 150000 mPa·s to 120000 mPa·s at 15°C, and from 89800 mPa·s to 65600 mPa·s at 20°C when 1.5% urea was introduced in this reaction, which indicates urea can reduce the viscosity further. The reason can be contribute to the viscosity reduction of CO₂ from the decomposing of urea under the high temperature.

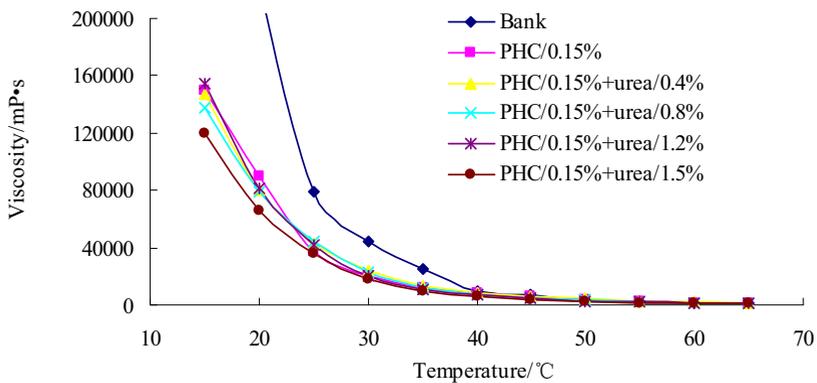


Figure 3 Effect of different concentrations of methanol on the aquathermolysis

2.4 Group composition analysis

The heavy oil was further analyzed for structural changes and group compositions. Four compound groups, namely, saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (SARA), were separated by the column chromatography-based method according to industrial standard of China Petroleum SY/T 5119[13]. Each test run was repeated three times to check repeatability and the maximum errors of the product distribution fell within 2.0%. Only the average data were reported hereinafter in Table 1.

TABLE 1 THE GROUP COMPOSITIONS OF OIL SAMPLE BEFORE AND AFTER REACTION

Oil sample	Saturated HC (%)	Aromatic HC (%)	Resin (%)	Asphaltene (%)
Before reaction	48.85	21.51	26.86	2.78
After reaction without catalyst	50.64	23.23	23.68	2.45
After reaction with PHC	59.16	27.59	12.23	1.02
After reaction with PHC & urea	60.22	26.52	11.75	1.51

After the reaction without catalyst, the saturated hydrocarbons and aromatic hydrocarbons have increased by 1.79% and 1.72%, respectively, while the resins and asphaltene have decreased by 3.18% and 0.33%. After the aquathermolysis with catalyst (PHC), the saturated hydrocarbons and aromatic hydrocarbons have increased by 10.31% and 6.08%, whereas the resins and asphaltene have decreased by 14.63% and 1.76%, respectively. However, the saturated hydrocarbons and aromatic hydrocarbons have increased by 12.59% and 6.95%, while the resins and asphaltene have, respectively, decreased by 17.74% and 1.80% after the catalytic aquathermolysis with catalyst (PHC) [14]. But at the present of urea, the group compositions of crude oil does not change significantly, which indicates urea does not contribute to the viscosity reduction chemically.

2.5 Paraffin crystal morphology study

As shown in Table 1, the saturated HC content increases after aquathermolysis, which can improve the fluid ability of the crude oil. The change of the compositions will lead to the change of the status under low temperature, so the morphology of paraffin crystal in saturated HC was investigated, and the photographs were shown in Figure 4. From the figure, the paraffin crystals with larger size in the saturated HC are found before aquathermolysis (left). For the sample after aquathermolysis (right), the paraffin crystals are smaller and less than the left one, which indicates the aquathermolysis can reduce the tendency of crystals to form three-dimensional network, so as to reduce the viscosity and depress the pour point of the heavy oil [15].

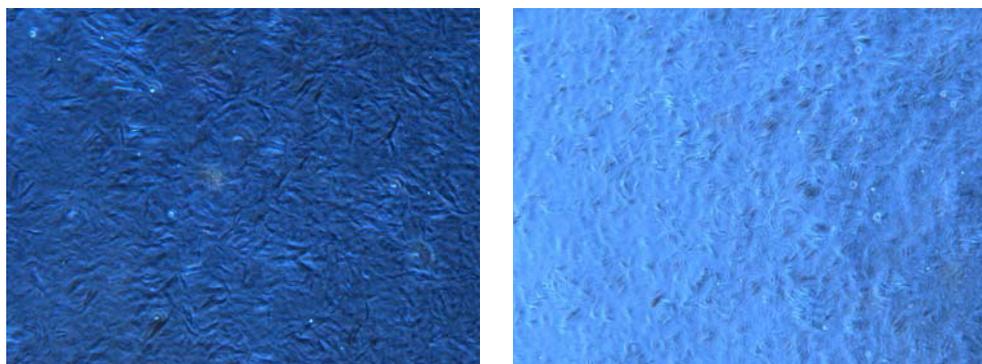


Figure 4 Photography of paraffin crystal in saturated HC of the crude heavy oil before (left) and after (right) aquathermolysis

3 Materials

Petroleum ether, toluene, ethanol, phenyl hydroxamic acid and metallic chloride were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (at AR reagent grade) and were used without further purification. The heavy oil used for evaluations was Huabei crude oil with no suspended sand particles.

3.1 Synthesis of catalysts

Phenyl hydroxamic acid and CoCl_2 were added in a 100ml flask with molar ratio of 2:1, and appropriate amount of methanol was added as solvent. The mixture was refluxed for 4h with stirring, then cooled to room temperature. The solvent was evaporated to get the crude product. After recrystallization, the pure product was obtained as catalyst. The synthesis, structures and the names of catalyst (PHC) were shown in Figure 5.

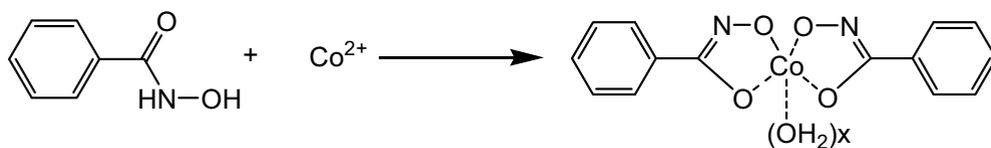


Figure 5 Synthesis of phenyl hydroxamic acid-Co(II) complex (PHC)

4 Catalyzed aquathermolysis of heavy oil

Experiments were carried out by introducing pre-determined mass ratios of water to heavy oil, with a catalyst to crude oil mass ratio, into the reactor. Each mixture was heated to and maintained at $180\text{ }^\circ\text{C}$ for 24 hours. The reactor and the mixture were cooled to about $50\text{ }^\circ\text{C}$ in a water bath. The mixture was then poured into a beaker and the oil decanted for transport properties and compositional tests.

The viscosity of the treated heavy oil was determined using a BROOKFIELD DV-II + programmable Viscometer at known temperatures. Viscosity reduction for the oil, $\Delta\eta\%$, was calculated from $((\eta_0 - \eta)/\eta_0) \times 100$, where η_0 and η ($\text{mPa}\cdot\text{s}$) are respectively the viscosities of the oil before and after the reaction.

Furthermore, the heavy oil was further analyzed for structural changes and group compositions. Four compound groups, namely, saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (SARA), were separated by the column chromatography-based method according to industrial standard of China Petroleum SY/T 5119. The paraffin crystal in the saturated HC of the heavy oil before and after aquathermolysis was investigated using a BX41-P OLYMPUS polarizing microscope under 15 °C.

5 Summary

In this work, a phenyl hydroxamic acid-Co(II) complex (PHC) was synthesized and used in the catalytic aquathermolysis of heavy oil. Under the optimized reaction condition at 180 °C for 24 h catalyzed by the complex, the viscosity of heavy oil was reduced by 82%. With the catalysis, the asphaltene and resin were partly pyrolysed into small molecules, and the heteroatom contents were also decreased. All of these changes were unregressed, and finally led to the viscosity reduction. Furthermore, urea was also found can reduce the viscosity further in the aquathermolysis, which has great potential for further applications in catalytic aquathermolysis of heavy.

Acknowledgements

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