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

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Summary: To develop effective water-soluble catalysts for aquathermolysis of heavy oil, in this paper, a series of complex was synthesized using phenyl hydroxamic acid and metallic chloride. The Ni(II) complex was characterized, and all the complexes were screened in aquathermolysis of heavy oil. The effects of water content and Ni(II) complex concentration on aquathermolysis were investigated. The effect of adding methanol as a reactant was examined and interpreted. With the catalyst and methanol, the reaction occurred at temperatures as low as 180℃. The viscosity of the product was also substantially reduced by the decomposition of the large hydrocarbon molecules.

Key words: Heavy oil; Catalyst; Viscosity reducing; Catalytic aquathermolysis, Water-soluble.

Introduction

With prospects of light crude oil supplies running out in the not too distant future, heavy oil and bitumen are gaining prominence as reliable sources for satisfying the increasing global demand for fuels and petrochemical feedstock. Heavy oil and bitumen reserves are estimated to account for 70% of the total recoverable petroleum in the world. However, the viscosities are high, between 10 and 10^7 mPa·s, and with densities between 7 and 26 °API, they present challenges for production and transportation. Flow through pipelines are currently achieved through the use of diluents, primarily condensates, which are mixed with the crude oil produced or extracted or heat tracing of pipes. Now, exploration and development of heavy oil are increasing [1, 2], in which changing the chemical composition and characteristics of heavy oils and bitumen in-situ before loading into pipelines is attractive. 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]. The catalysts for aquathermolysis 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. Water-soluble catalysts don't introduce other organic solvents and don't cause secondary pollution for oil. Meanwhile, it could directly inject into reservoir with the water, which could significantly reduce the difficulty and cost of exploitation of heavy oil. Aquathermolysis of heavy oil, catalyzed by water-soluble catalysts, occurs at relatively mild conditions (160-280℃; 10-25MPa) and long durations (24-240h), but the viscosity reduction is only about 60% [9, 10], so that the product is still viscous. It has been suggested that a hydrogen donor additive such as tetralin helps to further lower the viscosity [11], however, tetralin is expensive and the oxide product is toxic.

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 this study. A series of transition metal complex was synthesized using phenyl hydroxamic acid and metallic chloride, and then they were evaluated for reducing the viscosity and pour point of heavy oil at 180℃. Furthermore, the chemical change of the heavy oil was fully characterized.

Experimental

Materials

Petroleum ether, toluene, ethanol, phenyl

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

Synthesis of catalysts

Phenyl hydroxamic acid and metallic chloride 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, and 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 catalysts were shown in Fig. 1. All the complexes were synthesized under the same condition.

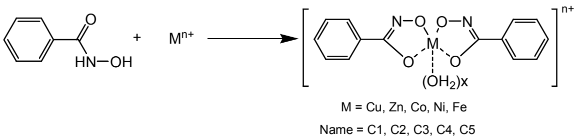

Fig. 1: Synthesis, structures and the names of catalysts.

Characterization of the complex

Electronic spectra were recorded in the range 200–400 nm, with spectral on as standard, on a UV-2600 spectrophotometer. FTIR spectra were recorded in KBr pellets with a Bruker Tensor 37 spectrometer in the 400–4,000cm^{-1} region. FTIR spectrometer was calibrated by 1.5 mil and 55 micron thick polystyrene (PIKE Technologies) as reference standard before the analysis.

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 180℃ and maintained for 24 hours. The reactor and the mixture were cooled to about 50℃ in a water bath. The mixture was then poured into a beaker and the oil decanted for transport properties and compositional tests.

Product evaluation

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 $((\eta_0-\eta)/\eta_0)\times100$, where $\eta0$ and η (mPa·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 [12]. 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.

Elemental analyses of the heavy oil before and after reaction were performed on an EL-2 elemental analyzer. The paraffin crystals in the saturated hydrocarbons of the heavy oil before and after aquathermolysis were examined under a BX41-P OLYMPUS polarizing microscope at temperature of 5 ^{o}C.

Gas chromatography analysis of saturated hydrocarbon before and after reaction was carried out as follows: HP-5 capillary column (30m×0.32mm, 0.25m); the nitrogen gas was as carrier and its flow rate of 20 ml/min, the hydrogen flow rate 40ml/min, air flow rate 360 ml/min. Inlet temperature of 320℃, the detector temperature 280℃, the program automatically temperature: initial temperature of 75℃, kept 0.5 min; to 50℃/min heating rate to 100℃, kept 0.5 min; then 10℃/min heating rate to 80℃, kept 2.00 min. Split injection (split ratio 5:1) with volume 2μL.

Results and discussion

IR and UV Characterization of catalyst

The IR spectra of the free ligand (Phenyl hydroxamic acid) was compared with the spectra of the Ni(II) complex (C_4), Fig. 2. It was easy to see from Fig. 2 that the characteristic absorption peaks increased in the range of 3250-3500 cm^{-1} after coordinating with Ni(II). Moreover, the absorption peaks at 3100 cm^{-1} and 1360 cm^{-1} had shifted to 2750 cm^{-1} and 1400 cm^{-1}, respectively and became stronger. Besides, the characteristic absorption peaks also appeared at 1170 cm^{-1}, 1000 cm^{-1} and 720 cm^{-1}. The peaks above indicate that the ligand has chelated with the cobalt. As a result, the prepared complex (C_4) agrees well with what we have designed [13]

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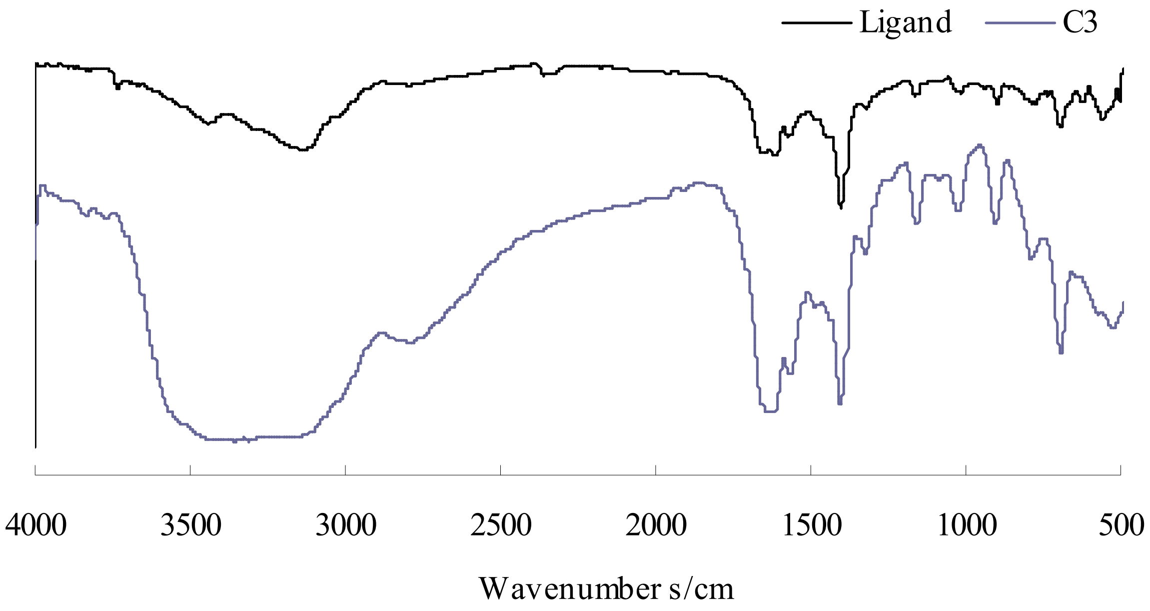

Fig. 2: Infrared spectra of catalyst and its ligand.

Electronic spectra of the ligand and C_4 in methanol are presented in Fig. 3. The absorption peaks have shifted from 201 and 223 nm to 193 and 215 nm, and the intension enhances significantly, which proves that the ligand with metal ion to form a stable cobalt complex.

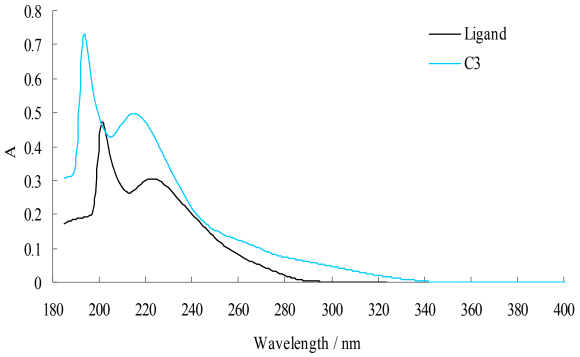

Fig. 3: Electronic spectra of catalyst and ligand

The effect of water on the aquathermolysis

The effect of mass ratio of water to oil on the viscosity is shown in Fig. 4 [14]. It demonstrates that the presence of water causing heavy oil to lower viscosity, and the more water, the greater the reduction within the range of investigation. The effect becomes not so significant once the water to oil ratio reaches to 0.3, which will be used as a reference ratio. The data also shows that as the temperature rises, a more dramatic lowering of viscosity is observed. It means the oil viscosity is much more sensitive to temperature changes than to the amount of water presented in the reaction[15].

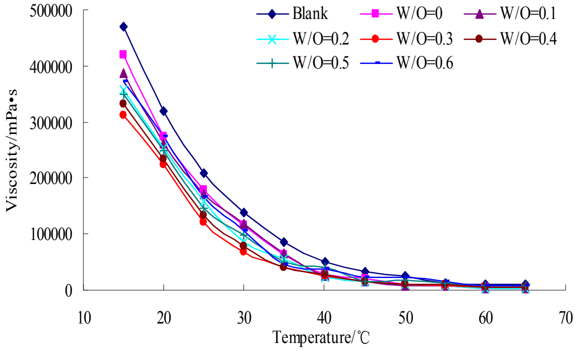

Fig. 4: The influence of water on the viscosity of heavy oil after aquathermolysis.

Evaluation of catalyst

Effect of catalysts on aquathermolysis

The catalysts were screened under the optimized condition above with a 1.0% mass ratio to crude oil, and the results were summarized in Fig. 5. The results show that not all the five catalysts are effective for this aquathermolysis reaction, and only

C_3 and C_4 are effective. In the following work, Ni (II) complex (C_4) was investigated as the catalyst in detail.

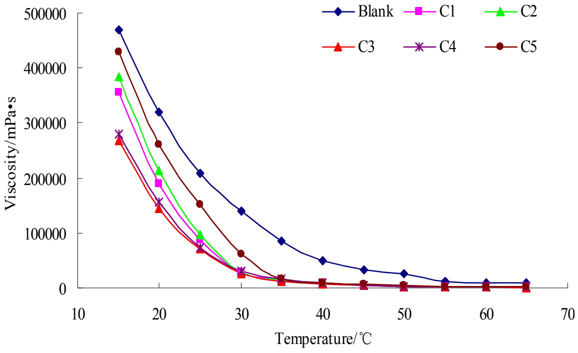

Fig. 5: Effect of different catalyst on viscosity of heavy oil.

Effect of catalyst concentration on aquathermolysis

With a water/oil mass ratio of 0.3, the effect of catalyst concentration on aquathermolysis reaction of heavy oil was investigated, and the result was shown in Fig. 6. It was found from the result that the viscosity was reduced along with the increasing of catalyst concentration. With 0.15%C_4, the viscosity reduction rate comes to the highest, 60.3% (20℃), as the concentration of catalyst is more than 0.15%, the efficiency does not change obviously. Hence, the optimum concentration of the catalyst was selected as 0.15%.

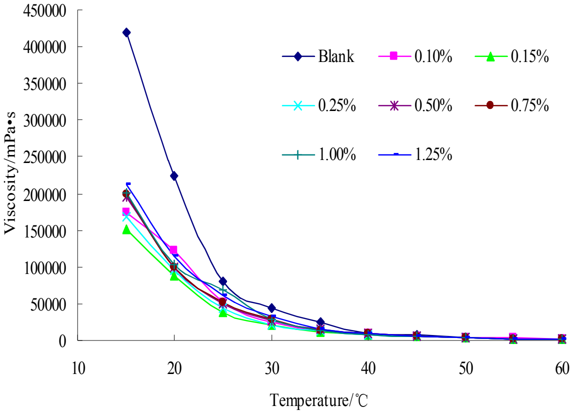

Fig. 6: Effect of Ni(II) complex concentration on the aquathermolysis.

Effect of methanol on aquathermolysis

Using the selected catalyst C_4 with the concentration of 0.15%, the effect of the additives, methanol, was investigated under the same reaction condition. The results were shown in Fig. 7. It is clear that 0.15% C_4+MeOH can reduce the viscosity further compared with 0.15% C_4 at low temperature. Using 0.15%C_4+ 15%MeOH, the viscosity was reduced by 71.3% compared with the blank, while the higher dosage of MeOH (20%) does not help to reduce the viscosity obviously.

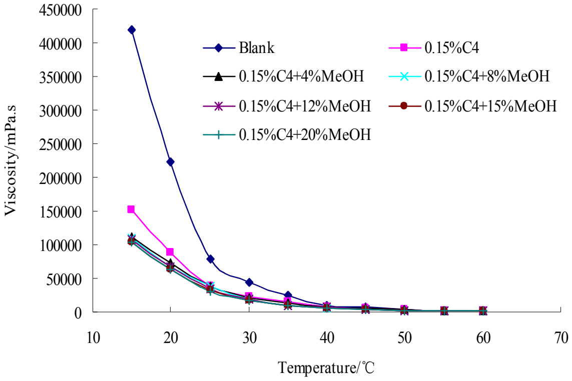

Fig. 7: Effect of methanol on the catalytic aquathermolysis.

Aquathermolysis is represented by the following reactions (1-3):

In aquathermolysis, C-S and C-O bonds in oils components, particularly resins and asphaltenes, may be cleaved to form radical chains. Active hydrogen produced in equation 2 is at low concentrations and the amount is not sufficient to terminate all of the radical chains formed from heavy oil components. In the absence of a hydrogen donor, the active chains can react with each other and produce higher molecular weight components. Addition of a hydrogen donor, such as methanol, leads to the decomposition reaction (Equation 4) and production of free radical hydrogen in substantial quantities to terminate radical chains (Equation 5).

$$\text{heavy oil} + \text{water} \longrightarrow \text{light hydrocarbon} + \text{gas}\,(CH_4, CO, H_2) + \text{active chains} \tag{1}$$

$$CO + H_2O \longrightarrow CO_2 + \text{active H} \tag{2}$$

$$\text{active chains} + \text{active H} \longrightarrow \text{active chains termination (with low molecular weight)} \tag{3}$$

$$CH_3OH + H_2O \longrightarrow CO_2 + CO + \text{active H} \tag{4}$$

$$\text{active chains} + \text{active H} \longrightarrow \text{active chains (with low molecular weight)} \tag{5}$$

Group composition analysis

The heavy oil was further analyzed for group compositions and chemical changes. The 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 [12], and the results were shown in Table-1. Each test 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.

Table-1: The group compositions of oil sample before and after reaction.

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 C_4	**57.22**	**27.15**	**14.38**	**1.25**
After reaction with C_4 & MeOH	**62.05**	**28.26**	**8.74**	**0.95**

After the reaction without catalyst, the saturated hydrocarbons and aromatic hydrocarbons have increased by 1.79% and 1.72%, respectively, and the resins and asphaltene have decreased by 3.18% and 0.33% at the same time. After the aquathermolysis with catalyst (C_4), the saturated hydrocarbons and aromatic hydrocarbons have increased by 8.37% and 5.64%, whereas the resins and asphaltene have decreased by 12.84% and 1.53%, respectively. Furthermore, the saturated hydrocarbons and aromatic hydrocarbons have increased by 13.20% and 6.75%, while the resins and asphaltene have, respectively, decreased by 18.12% and 1.83% after the catalytic aquathermolysis with catalyst (C_4) and MeOH. The result certifies that the catalyst can cause the heavy components (resin and asphaltene) to decompose to light components (saturated hydrocarbon and aromatic hydrocarbon) by catalytic pyrolysis [16]. Hereby, it has a significant efficiency for reducing viscosity and depressing pour point of heavy oil.

Elemental analysis

The change of element contents (C, H, N and S) of heavy oil before and after aquathermolysis reaction was detected by elemental analyzer, in which the content of oxygen was calculated by difference. The results were displayed in Table-2. It can be found that the change of elements content is slight after aquathermolysis without catalyst, and they changed greatly as C_4 was employed in, furthermore, they changed sequentially when MeOH was added. The content of carbon increased from 80.55% to 83.85%, and the reaction also caused the decrease of O element obviously from 6.01% to 3.12%, which elucidates that most of C-O bonds in resins and asphaltenes of heavy oil have been broken [17, 18].

Table-2: Element content of heavy oil before and after reaction.

Sample	Composition (%)				
	C	H	N	S	O
Before reaction	**80.55**	**10.56**	**0.85**	**2.03**	**6.01**
After reaction without catalyst	**81.12**	**10.98**	**0.63**	**1.95**	**5.32**
After reaction with C_4	**82.43**	**11.51**	**0.41**	**0.99**	**4.66**
After reaction with C_4 & MeOH	**83.85**	**11.82**	**0.36**	**0.85**	**3.12**

Paraffin crystals

Below the pour point of the crude and processed oils, paraffin crystals will deposit and tend to plug flow lines and filters. Visual observations suggest that paraffin crystals are larger size and more numerous in the crude heavy oil than after being processed, as shown in Fig. 8. This may suggest that some of the longer paraffinic chains were also decomposed in the aquathermolysis reaction.

Gas chromatograph analysis

The change of saturated hydrocarbon component before and after the aquathermolysis of heavy oil was analyzed by gas chromatograph, as shown in Fig. 9 and 10. From the two figures, the intension of peaks has increased obviously at 10.26833, 13.56833, 16.68167, 19.43583, 19.11833, 23.76417, 23.87757, 27.02083 and 30.09083 min after catalyzed aquathermolysis, which is consisted with the increase of saturated hydrocarbon component as shown in TGA and composition analysis. The increased saturated hydrocarbons, as a solvent, can reduce the viscosity, depress the pour point and improve the quality of heavy oil.

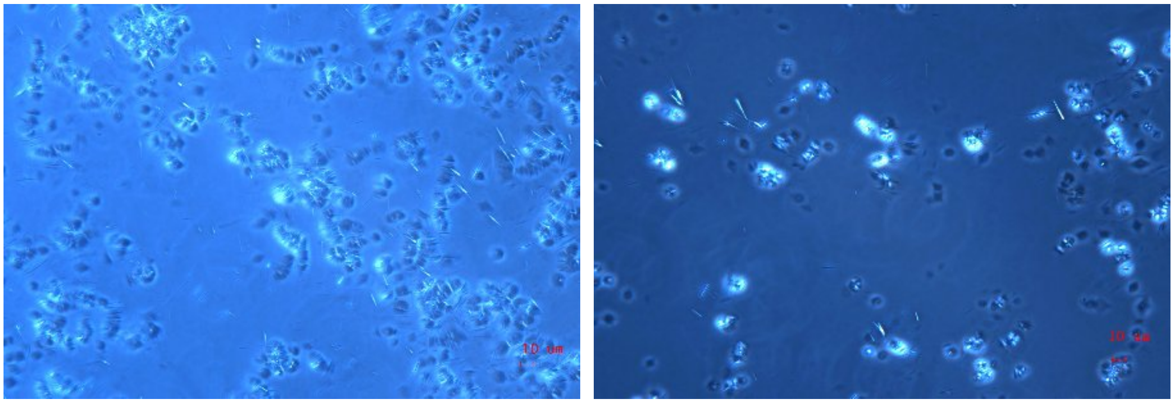

Fig. 8: Photography of paraffin crystal in saturated HC of the heavy oil before (left) and after (right) aquathermolysis.

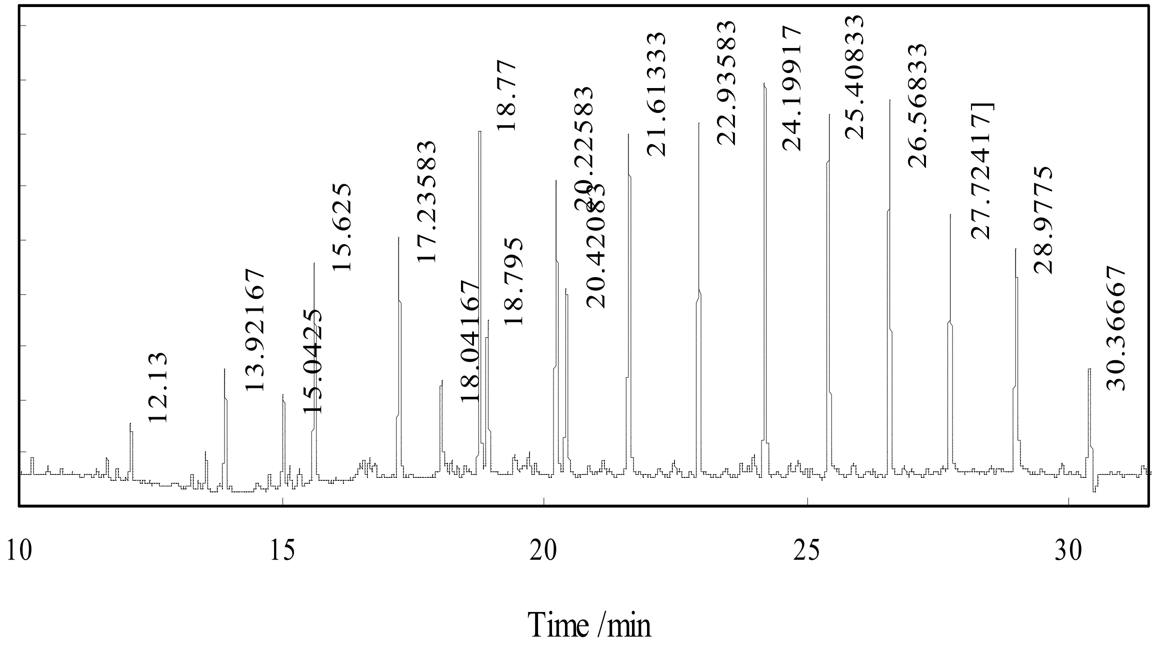

Fig. 9: Gas chromatograph of saturated hydrocarbon before aquathermolysis.

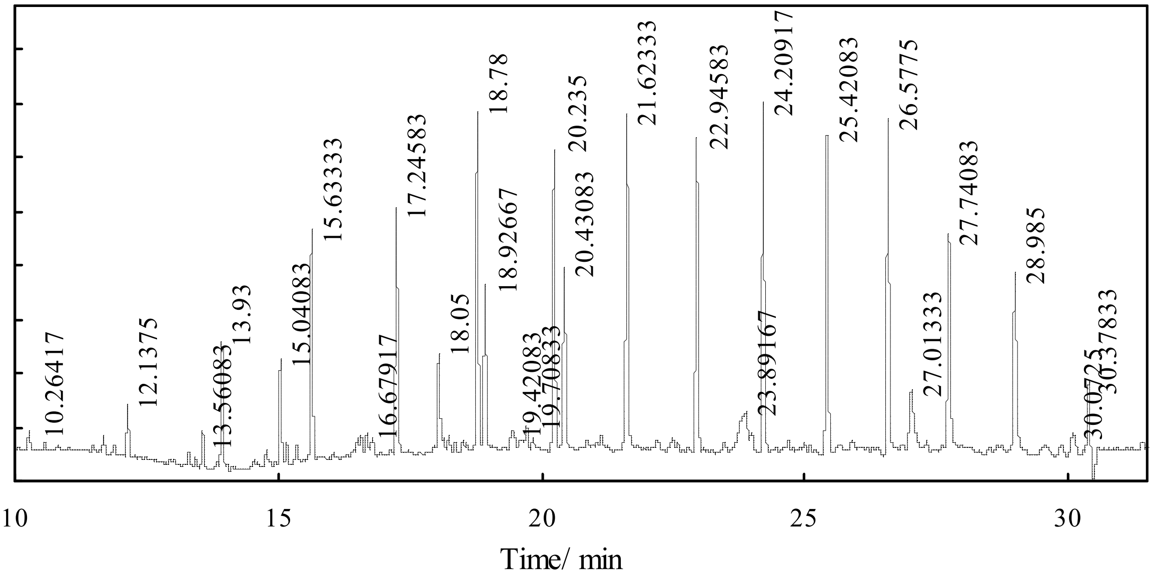

Fig. 10: Gas chromatograph of saturated hydrocarbon after catalytic aquathermolysis.

Conclusion

A water soluble catalyst, hydroxamic acid-Ni(II) complex, was prepared for aquathermolysis of heavy oil. Using 0.15% catalyst and 15% methanol at 180℃ for 24 h, the viscosity of heavy oil was decreased by 71.3% (20℃). Further investigation indicate that the catalysis aquathermolysis could not only enhance the visbreaking of heavy oil, but also improve its pyrolysis and remove some heteroatoms (S, O and N), and finally make the flow properties better and the quality upgraded, which indicates that it has great potential for further applications. The paraffin crystals and gas chromatograph analysis all indicate the composition change after aquathermolysis.

Conflict of interest

The authors confirm that this article content has no conflict of interest.

Acknowledgements

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