

Viscosity Reduction of Heavy Oil by Aquathermolysis with Coordination Complex at Low Temperature

Hua-rui Hao¹, Hui-jun Su¹, Gang Chen^{*2}, Jing-rui Zhao³ and Li Hong⁴

¹School of Chemistry and Chemical Engineering, Yulin University, Yulin 719000, China

²College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, 710065, China

³Shaanxi Yanchang Petroleum Oilfield Chemical Technology Co., LTD, Yan'an, 717400, China

⁴Jiangsu Santacc Co., Ltd. Zhengjiang, 212200, China

Abstract: To seek for new catalysts for the aquathermolysis of crude oil under relatively low temperature, in this paper, a series of Mannich base-transition metal coordination complexes was synthesized and used in aquathermolysis of heavy oil as catalyst. The results show an evident viscosity reduction by 84.2% for the heavy oil reacted at 180 °C for 24 h catalyzed by the Ni(II) coordination complex. The group compositions, the element content of the heavy oil and paraffin crystal morphology before and after the aquathermolysis reaction were analyzed, which are consistent with the viscosity reduction of the heavy oil. Besides the catalysts were also found to be widely applicable.

Keywords: Aquathermolysis, catalyst, coordination complex, heavy oil, viscosity reduction.

1. INTRODUCTION

The reserves of crude oil account for more than 70% of the total quantity of petroleum all over the world. However, due to the high viscosity and density, it is very difficult to handle heavy crude oils. Therefore, many researchers are devoting to reduce viscosity of heavy oil for the production and transportation [1, 2]. It was reported that metals can catalyze the aquathermolysis, and thereafter the uses of catalysts in this reaction have been screened [3]. Now, the catalytic aquathermolysis has been applied to solve the viscosity problem during exploration of heavy crude oil. The research has proved that superheated water (240-300 °C) can heat the hydrocarbon leading asphaltene and resin molecules to break down to small molecules, therefore the viscosity is reduced [4, 5], and if some catalyst is employed in this reaction, the viscosity can be reduced deeply. Commonly, after aquathermolysis, the amount of saturate and aromatics will increase, while the amount of asphaltene and resin will decrease [6-9]. Generally, the catalysts for aquathermolysis include mineral, water soluble, oil soluble, and dispersed catalysts. In fact, the oil soluble catalysts and dispersed catalysts are more active than the water-soluble catalyst. But the cost of the two former types of catalysts is much higher than that of simple water soluble catalysts. Hence, more research is focusing on making this process more economical. Another problem is the reaction condition of these catalysts when used in the oil field. The activity of the catalysts is affected by the temperature obviously. In the indoor experiments, the temperature can be controlled under a certain temperature, but during the oil field application

, when the superheated water is injected into the oil reservoir, the oil surface temperature is higher, however, temperature is gradually lower on the depth of the oil floor, and hence the catalyst loses its activity. So, further research should address the catalysts' activity under low temperature. Several groups have investigated the heavy oil aquathermolysis catalyzed by water-soluble catalysts under relative low temperature (160-280 °C, 10-25 MPa, 24-240 h), but the viscosity reduction is only about 60% [9, 10].

In our previous work, a series of transition metal coordination complex was prepared from *p*-chlorophenol Mannich base and transition metal chloride and applied as catalyst in the aquathermolysis of heavy oil at relatively low temperature. In this work, the most effective one can reduce the viscosity by more than 70% under the relatively low reaction temperature of 180 °C [11]. But *p*-chlorophenol is poisonous for human beings during the preparation and application. To seek more human-friendly and effective catalyst for the aquathermolysis of heavy oil, a series of Mannich base-transition metal complex was prepared and evaluated.

2. EXPERIMENTAL

2.1. Materials

Petroleum ether, toluene, ethanol, formaldehyde, *p*-methylphenol, and piperazine were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (at AR reagent grade) and were used without further purification. The heavy oil samples (1#, 2#, and 3#) used for evaluations were obtained from Yumen Oilfield, whose properties are shown in Table 1.

*Address correspondence to this author at the College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, 710065, China; Tel/Fax: 086-029-88382693; E-mail: gangchen@xsyu.edu.cn

Table 1. The physical parameters of heavy oil from Yumen oil field.

Oil Sample	η^{50} (mPa·s)	Pour Point (°C)	ρ^{20} (g·cm ⁻³)	Saturated HC (%)	Aromatic HC (%)	Resin (%)	Asphaltene (%)
1#	12500	41.2	0.901	51.83	9.66	23.92	14.6
2#	25530	46.5	0.907	48.37	13.55	25.50	12.58
3#	30510	51.2	0.912	50.87	5.58	19.95	23.60

2.2. Synthesis and Characterization of the Complexes [12, 13]

The complexes were synthesized as shown in Fig. (1) and the corresponding names are listed in Table 2. A amount of *p*-methylphenol (2 mmol), formaldehyde (2.2 mmol) and piperazine (1 mmol) was dissolved in ethanol and refluxed for 4 h under stirring. A methanol solution of MCl_n (1 mmol) was added dropwise and stirred for another 2 h. The mixture was cooled to room temperature and filtrated, the solution was kept at room temperature for 7 d, and the natural evaporation gave crystals for the further use. The IR spectra of a selected complex were recorded in KBr pellets with a Bruker Tensor 37 spectrometer in the 400–4,000 cm⁻¹ region.

Table 2. The composition and the name of the complexes.

M	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
Name	MPC-1	MPC-2	MPC-3	MPC-4	MPC-5

2.3. Catalytic Aquathermolysis Reaction of the Heavy Oil by the Complexes [13-15]

All the experiments were carried out by adding heavy oil, water and catalyst in a designed mass ratio of the crude oil quality into a reactor. Then the reactants were heated to 180 °C for aquathermolysis reaction for 24 h. After the reaction, the mixture was cooled to about 50 °C in a water bath and dumped into a baker, thereby the oil sample was obtained by decant the water for test and analysis. The reaction conditions and catalysts screening were carried out using 1# heavy oil.

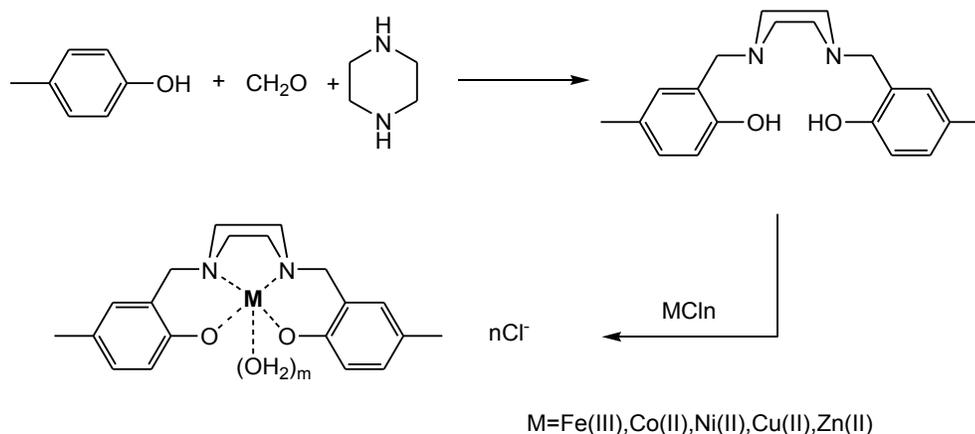
The viscosity of the heavy oil was evaluated by a

BROOKFIELD DV-II Viscometer at different temperature. The viscosity reduction rate $\Delta\eta\%$ was calculated as follows: $\Delta\eta\% = ((\eta_0 - \eta)/\eta_0) \times 100$, where $\Delta\eta(\%)$ is the viscosity reduction rate, $\eta_0(\text{mPa}\cdot\text{s})$ is the viscosity of the oil before the reaction, and $\eta(\text{mPa}\cdot\text{s})$ is the viscosity of the oil after the reaction. Three readings were made on each sample to check repeatability and to obtain an average value and the relative standard deviation was within 2.0%. The pour point was tested according to the ASTM-97 procedure. The initial temperature is set at 2.5 °C above the temperature at which the oil became solid and the detection limit is 0.1 °C [14]. Three readings were made on each sample to check repeatability and to obtain an average value and the relative standard deviation was within 2.0%, and the changed pour point (ΔP) was calculated as follows: $\Delta P = P - P_0$. Furthermore, the structural changes and group compositions of the heavy oil before and after reaction were further analyzed. The four composition groups, asphaltenes, resins, saturated hydrocarbons and aromatic hydrocarbons were separated by the column chromatography-based SARA method according to the standard of China Petroleum SY/T 5119 [15]. Elemental analysis of the heavy oil before and after reaction was performed on an elemental analyzer (vario EL). 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.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalyst

In order to study the binding mode of the Mannich base to the metal ion in the complexes, the IR spectrum of the free ligand (Mannich base) was compared with the spectra of the Ni(II) complex, as shown in Fig. (2). The IR spectra of the

**Fig. (1).** Preparation of *p*-methyl-phenol Mannich base-transition metal complexes.

complex show a wide and deep band in the region of 3300 cm^{-1} , which are assigned to coordination H_2O of the complex. The bands in ligand spectra due to $\nu(\text{C}-\text{O})$ is located in the regions 1130 cm^{-1} . In the spectra of complex, the $\nu(\text{C}-\text{O})$ mode of the free ligand moves to 1086 cm^{-1} indicating the enolization of C-O followed by deprotonation and complexation with metal ions. The bands in the region of 1599 cm^{-1} and 1499 cm^{-1} , which are assigned to $\nu(\text{Ph})$ of the ligand, which move to 1614 cm^{-1} and 1513 cm^{-1} respectively in the complex. It is concluded that the ligand acts as a monobasic tetra-dentate manner in the complex [16].

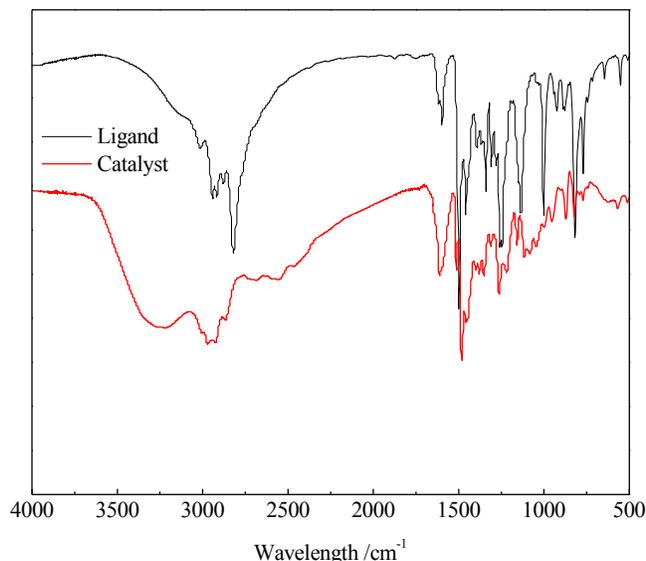


Fig. (2). The IR spectrum spectra of the ligand and the catalyst-Ni(II) complex.

3.2. Aquathermolysis Reaction Condition Screening

From the beginning, 1# heavy oil was used for the reaction conditions and catalyst screening. The effect of mass ratio of water to oil on the viscosity in the reaction was investigated, under the settled temperature and reaction time, $180\text{ }^\circ\text{C}$ and 24 h, and the results are summarized in Fig. (3). It is quite clear that water addition to the heavy oil can help to reduce the viscosity, depending on the mass ratio. This decreased tendency is quite clear as the water content

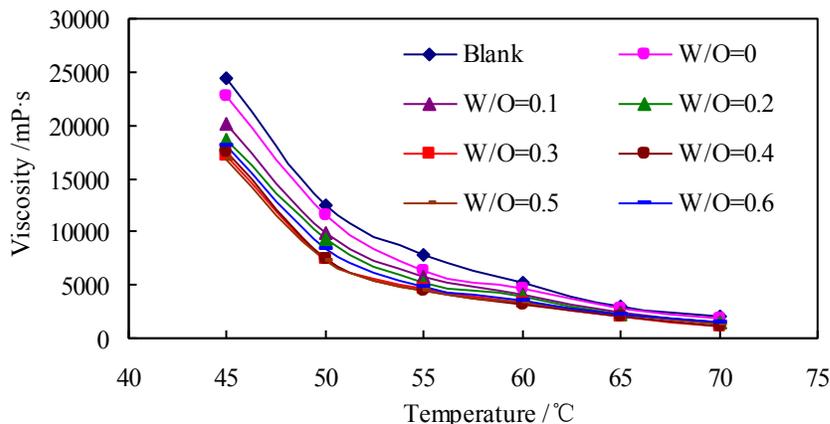


Fig. (3). The influence of water on the viscosity of crude oil after aquathermolysis reaction.

increases before the mass ratio of water to oil reaches to 0.3. With the ratio varying from 0.3 to 0.5, the viscosity reduction is almost in the same level, and when the mass ratio reaches 0.6, it presents a slightly ascending tendency. So the mass ratio of water to oil was settled as 0.3 in the following experiments [11].

3.3. Catalyst Screening

This series of coordination complex was used in the aquathermolysis reaction as catalyst with the concentration of 0.5%, and the results are summarized in Table 3 (the viscosity was tested at $50\text{ }^\circ\text{C}$). As shown in this table, not all the complexes are effective in this reaction, only MMC-1, MMC-3 and MMC-5 can catalyze the reaction, among which MMC-3 is the most effective one with the 84.2% viscosity reduction rate and $10.3\text{ }^\circ\text{C}$ pour point depression. On the contrary, MMC-2 and MMC-4 cannot help to reduce the viscosity and pour point, but lead to some increase. Therefore, MMC-3 (Ni(II) complex) was selected as the catalyst in the further study.

Table 3. The aquathermolysis reaction results using coordination complexes as catalysts.

Catalyst	$\Delta\eta$ (%)	ΔP ($^\circ\text{C}$)
MMC-1	33.4	4.2
MMC-2	-8.5	-0.8
MMC-3	84.2	10.3
MMC-4	-8.3	-1.2
MMC-5	12.5	2.3

3.4. Effect of Catalyst Concentration on the Aquathermolysis Reaction

The catalyst plays the most important role in this reaction, so the effect of catalyst concentration on the aquathermolysis reaction was investigated in the following study. Fig. (4) shows that the viscosity reduction efficiency depends on the catalyst concentration. The viscosity keeps dropping as the concentration increases from 0.1% to 0.5% with the viscosity dropping from $18700\text{ mPa}\cdot\text{s}$ to $3720\text{ mPa}\cdot\text{s}$, and it dose not change obviously as the concentration

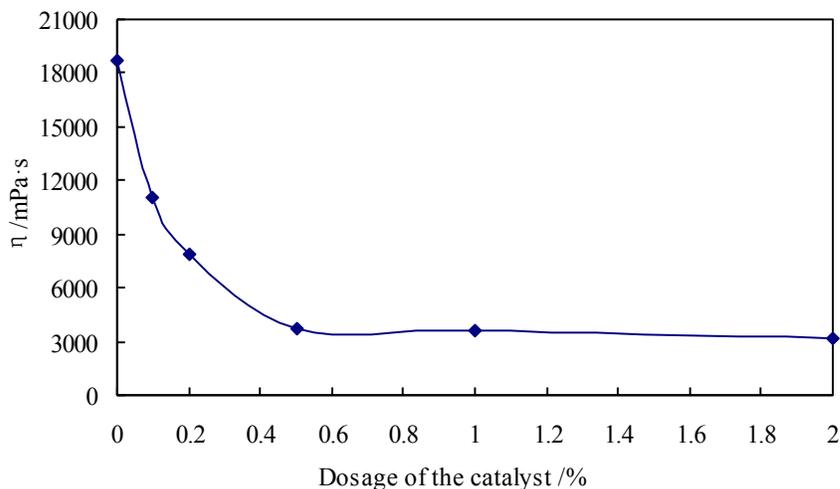


Fig. (4). Effect of catalyst concentration on the viscosity.

beyond 0.5%, so the optimum concentration should be 0.5%.

3.5. Group Compositions Analysis

Theoretically, there is a chemical reaction during the process, so the compositions should change to some degree. The contents of the group compositions of heavy oil before and after reaction are listed in Table 4. It can be found that the saturate HC and aromatic HC increase, as resin and asphaltene decrease after reaction. The original SARA compositions of feedstock are 51.83%, 9.66%, 23.92% and 14.59%, respectively. When MMC-3 and water are in coexistence in heavy oil, the saturate increased to 55.75%, aromatic increased to 11.67%, resin decreased to 21.25% and asphaltene decreased to 11.33% after reaction. It reveals that the reduced part of resin and asphaltene depolymerized to aromatic and saturated HC.

Table 4. Group compositions of heavy oil before and after reaction.

Oil Sample	Saturated HC (%)	Aromatic HC (%)	Resin (%)	Asphaltene (%)
before reaction	51.83	9.66	23.92	14.59
after reaction	55.75	11.67	21.25	11.33

3.6. Element Analysis

The change of the compositions can surely cause the change of element ratio in the oil. Element analysis results of oil samples are listed in Table 5. It was found that the amount of heteroatoms in oil samples is 8.3% before reaction, which reveals that many free radicals can generate during the aquathermolysis by the cleavage of C-R (R= N, O, S) bonds [17]. After reaction, the contents of C and H increase, and the contents of N, S and other elements are depressed to 7.20% totally. It can be attributed to the cleavage of C-R to produce some water-soluble compounds, such as some small molecular amine, alcohol and sulphide [18, 19].

3.7. Paraffin Crystal Morphology Study

As shown in Table 5, 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 are shown in Fig. (5). 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 that 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 [20].

Table 5. Element content of oil sample before and after reaction.

Oil Sample	Composition (%)				
	C	H	N	S	Other
before reaction	81.31	10.39	0.45	0.42	7.43
after reaction	82.25	10.55	0.25	0.33	6.62

3.7. Application in Other Heavy Oils

As the reaction conditions and catalyst have been screened with using 1# heavy oil, other heavy oil samples

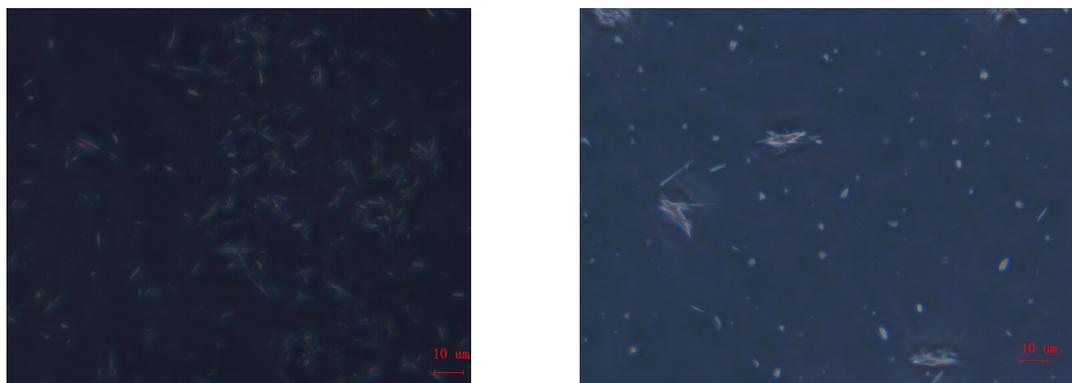


Fig. (5). Photography of paraffin crystal in saturated HC of the 1# heavy oil before (left) and after (right) aquathermolysis.

Table 6. The aquathermolysis results of 2# and 3# heavy oil.

Oil Sample	Catalyst	Viscosity (mPa·s)						
		40 °C	45 °C	50 °C	55 °C	60 °C	65 °C	70 °C
2#	-	67322	43900	25530	13577	7820	5350	3455
2#	MMC-3	24335	12597	6003	3875	2550	2235	2010
3#	-	85070	60303	30510	18560	9020	6155	3896
3#	MMC-3	17902	11580	5859	3776	2011	1977	1884

were investigated in such conditions with 0.5% MMC-3, and the results are shown in Table 6. From the results, it can be found that the viscosity of the two heavy oil samples can be decreased effectively by 70-80% at lower temperature, which means the reaction conditions and the catalyst are widely applicable.

CONCLUSION

In this work, a series of Mannich base-transition metal coordination complexes 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 Ni(II) coordination complex, the viscosity of heavy oil was reduced by 84.2%. With the catalysis, the asphaltene and resin were partly pyrolyzed into small molecules, and the heteroatom contents were also decreased. All of these changes were unregressed, and finally led to the viscosity reduction. This type of coordination complex is widely applicable and has great potential for further applications in catalytic aquathermolysis of heavy.

CONFLICT OF INTEREST

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

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