VARIOUS TECHNOLOGIES

Using Hydrogen Donor with Oil-soluble Catalysts for Upgrading Heavy Oil*

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Received August 10, 2014

Abstract—With self-made oil-soluble organic cobalt salt as catalyst and formamide as hydrogen donor, we studied the aquathermolysis reaction of heavy oil through simulating the condition of thermal recovery of oil reservoir with autoclave. In the paper, we explored the effect of the hydrogen donor added into catalytic aquathermolysis reaction on the viscosity of heavy oil, group composition and component contents. Moreover, FTIR spectrum was employed to analyze the structural change of heavy oil after hydrogen donor catalytic aquathermolysis. The obtained data are validated that when the mass fraction of added hydrogen donor was increased, the viscosity reduction rate and the contents of saturated hydrocarbons and aromatic hydrocarbons were increased and the contents of resin and asphalt were decreased. Under the synergic action of catalysts and hydrogen donor, the content of carbon in heavy oil was decreased and the content of hydrogen was increased. Thus, the ratio of H/C rose and the content of sulfur was reduced. Analysis result of infrared spectrum validated that hydrogen donor catalytic aquathermolysis underwent decarboxylation and that the number of aromatic rings was reduced.

DOI: 10.1134/S1070427214100164

INTRODUCTION

As conventional oil production declines, currently worldwide development of the oil industry mainly focuses on the exploration of heavy oil and bitumen. These resources have a reservoir of 6000 billions barrels in global scale, most of which are in Venezuela and Canada. China has 1.8×10^{11} barrels of heavy oil resources [1].

Heavy oil usually refers to the crude oil with a high viscosity and density and high contents of resin and asphaltene. Heavy oil with higher viscosity is also called bitumen or tar sand oil. Because of the high viscosity and high flow resistance of heavy oil in the reservoir, it is difficult to develop heavy oil effectively with conventional techniques [2, 3].

Thermal exploration is one of the main methods to improve the oil recovery, such as steam stimulation and steam flooding. In the process of steam injection, steam, heavy oil, and organic matters undergo a series

of chemical reactions [4–6], known as "Aqua thermolysis" Reaction."

As an irreversible way of viscosity reduction, catalytic aquathermolysis of heavy oil is drawing the attention of scholars domestic and abroad. A suitable catalyst is the key to achieve the upgrading and viscosity reduction of heavy oil. In modern petrochemical industry, heavy oil pyrolysis process and corresponding catalyst have been developed. In the process, the reaction temperature is generally at least above 400°C. In contrast, temperature in thermal recovery of heavy oil is lower. However, if the catalyst with high dispersion and high activity is injected into the reservoir, the activation energy will be dramatically reduced. In this way, it is possible to achieve pyrolysis of heavy oil in the reservoir at a relatively low temperature.

Previous studies mainly deal with water-soluble metal salt catalyst. The catalyst has certain lipophilicity at high temperature and poor contact extent with heavy oil compared with oil-soluble catalyst. The higher the water

^{*} The text was submitted by the authors in English.

content of the system, the stronger the dilution effect of water-soluble catalyst. Metal catalyst components are difficult to obtain at high dispersion in heavy oil, so the utilization rate is low and catalyst can not be fully exerted. Thus, the degree of aquathermolysis reaction is reduced. In addition, water carried by the catalyst must be removed, thus the cost of post-processing increases $[7-15]$.

In contrast, oil-soluble catalyst has unparalleled advantages. Taking metal compounds containing organic groups as dispersed catalysts, the dispersing effect in heavy oil is obviously improved, for it is soluble in oil and can dissolve with oil. The catalyst has great influence in upgrading and viscosity reduction reaction and the organic groups do not require addition water separation operation. Since the high dispersive oil-soluble catalyst can be dissolved in raw material to give high dispersion degree in raw material and provides highly catalytic activity, the high conversion rate of heavy oil upgrading may be achieved. Thus, in the preparation of oil-soluble catalyst for aquathermolysis viscosity reduction, cobalt is selected as the active center [16–18].

Moreover, in the view of Hyne [5], in the aqua thermolysis reaction, the break of C–S bond of sulfides in heavy oil will decrease the molecules with high molecular weight and the content of asphaltene. $H₂$ is generated in Water-Gas Shift Reaction (WGSR), which can be used for hydrodesulphurization and the generation of hydrocarbons together with other unstable groups in heavy oil. Little $H₂$ is generated in aquathermolysis reaction through WGSR, which can not meet the requirements of hydrodesulphurization, thus reduces the level of heavy oil upgrading and viscosity reduction. Ovalles et al. [19] reported the use of Tetralin as hydrogen donor and natural minerals as the catalyst. Tetralin and the catalyst was mixed with water for the reaction at 280–315°C for at least 24 h. Experimental results were as follows: compared with original oil, heavy oil API increased by 4°; viscosity decreased by 50%; mass fraction of asphaltene is reduced by about 8%. Hewgill et al. [20] described the process of injecting organic hydrogen donors during steam flooding, and hydrogen donors included formic acid, formic ether, and formamide. The heavy oil is upgraded through the removal of asphaltene and hydrogenation.

Based on these aforementioned contributions and analyses, we can conclude that the quality of heavy oil will be improved evidently during the aquathermolysis reaction once the oil-soluble catalyst and hydrogen donor are added. Thus, in this paper we carried out some experiments to investigate the upgrading of Liaohe heavy oil using hydrogen donor and self-made oil-soluble catalyst. The experiments dealt with the efficiency of viscosity reduction, the rate of flow resistance reduction, and the changes in chemical composition, group composition and structure of the heavy oil before and after the reaction.

EXPERIMENTAL

Main Chemical Materials and Equipment Setup

Main reagents: formamide (AR, Tianjin Chemicals, China), heptane (AR, Shenyang Chemicals, China), petroleum ether (AR, Shenyang Chemicals, China), benzene (AR, Shenyang Chemicals, China), ethyl ether (AR, Shenyang Chemicals, China), ethanol (AR, Shenyang Chemicals, China), alumina for chromatography (74–165 μm, Shanghai Chemicals, China), silica gel for chromatography (165–245 μm, Guoyao Chemicals, China), *n*-hexane (AR, Tianjin Chemicals, China), 2-ethylhexyl acid (AR, Tianjin Chemicals, China), CoCl₂ (AR, Tianjin Chemicals, China) and sodium hydroxide (AR, Shenyang Chemicals, China).

Main instruments: dehydration instrument, HAAKE VT550 rotational viscometer, extractor, alumina absorbed chromatographic column, electronic balance, IR spectrophotometer), DTA–TGA analyzer, etc.

Main raw materials: oil sample from Liaohe oil field. The density of heavy oil sample is 0.9680 g cm⁻³ (20 $^{\circ}$ C), and the viscosity is 3.716 mPa s (50°C). The content of saturated hydrocarbon is 24.32 wt %. The content of resin is 30.27 wt % and that of asphaltene is 8.52 wt %. H/C atomic ratio is low. The sulfur content is 0.56 wt %. The oil sample belongs to low sulfur heavy oil.

Preparation of Catalyst

Preparation process of oil-soluble organic acid cobalt catalyst was as follows. Firstly, 2-ethylhex anoic acid and 12% (m/m) NaOH were put into a three-neck flask with a molar ratio of 1 : 0.98–0.998. Gasoline no. 200 was used as solvent. The mixture was heated to 50–70°C for 0.5 h. Then CoCl₂ (molar ratio of 2-ethylhexanoic acid and $CoCl₂·6H₂O$ was 2 : 0.98) was dropped slowly to the stirring saponification liquor. The temperature should be maintained at 80–90°C for 0.5 h. The reaction can be ended after another 1.5 h. Then the mixture was washed

Fig. 1. Viscosity–temperature curve of crude oil from Liaohe.

for 2 to 3 times with water and the organic phase was collected. The oil-soluble catalyst to be used in thermal recovery of heavy oil will be obtained after distillation, dehydration, and sedimentation. The catalyst is purple viscous liquid. The chemical structure of the catalyst obtained was:

Experimental Method

At 80°C, the heavy oil sample was filtered by 0.045 mm-diameter stainless steel mesh filter and dehydrated at the temperature below 120°C, until the moisture content was less than 0.5%. Then a certain quantity of heavy oil, water and oil-soluble catalyst was put into a high-temperature autoclave to carry out aquathermolysis viscosity reduction treatment at a certain temperature for different reaction time. Before heating, $N₂$ was charged into the autoclave. The pressure was maintained between 8–10 MPa. After the reaction was completed, the oil sample was cooled to room temperature and collected for use.

Analytical Methods

Group components in crude oil were tested according to SY/T5119-1995 relevant regulations and silica gel and aluminum oxide were taken as adsorbents. For the analysis of carbon and hydrogen content, National Standard GB/T19143-2003 method was applied. And oxygen was tested by an oxygen analyzer. When the sample was undergoing pyrolysis, cracked gaseous mixture was separated by a chromatographic column. Carbon monoxide was tested by a thermal conductivity detector or carbon monoxide in the cracked gaseous mixture was directly inspected by an infrared detector. According to the National Standard GB/T387-1990, the content of carbon was inspected by tube oven process. According to the content data of carbon, hydrogen, sulfur and oxygen, nitrogen content was obtained by the subtraction method.

HAKKE VT550 viscometer was used to measure the viscosity of the oil. With 44.08 s⁻¹ shearing rate, the viscosity of heavy oil after the reaction process was determined at 50°C. Then the viscosity reduction ratio was calculated in accordance with the formula: $\Delta \mu = (\mu_0$ μ)/μ₀ × 100%. In the formula, Δμ refers to the viscosity reduction ratio; μ_0 is the viscosity of heavy oil before the reaction; μ is the viscosity of heavy oil after the reaction.

Spectrum One infrared spectrometer was used to analyze the FTIR spectrum of heavy oil before and after the hydrogen donor catalytic aquathermolysis. Heavy oil was dissolved in CCl_4 . Then oil was sampled with KBr tablet and put into infrared drying oven to remove $CCl₄$ with obtaining the sample for FTIR spectrum.

RESULTS AND DISCUSSION

Heavy oil (from Liaohe Oil Field) used in the experiment was undergone dehydration and degasification at 50°C with the viscosity of 3716 mPa s. Figure 1 was the viscosity-temperature curve of heavy oil after degasification.

As a crucial parameter indicating the fluid mobility, viscosity is closely related to temperature. At certain temperature, the non-Newtonian fluid would be converted into Newtonian fluid. Based on the fact that the continuous flow of heavy oil can only be found after its transition into Newtonian fluid, the Oil Extraction Engineering Design was required to increase the formation temperature up to value, which would be higher than the conversion temperature with injecting steam. Though the property of Newtonian fluid could be observed in heavy oil at 40–50°C or even lower temperature, it is necessary to heat to 70–80°C or higher temperature for extra-heavy oil and super-heavy oil.

As shown in Fig. 1, heavy oil from Liaohe oilfield is highly temperature-sensitive so that the viscosity sharply

Mass fraction of hydrogen donor, %			
Maximum pressure in reactor (before the reaction), MPa		16.9	
Maximum pressure in reactor (after the reaction), MPa		89	

Table 1. Pressure differences after hydrogen donor catalytic aquathermolysis reaction

Table 2. Viscosity changes before and after hydrogen donor catalytic aquathermolysis reaction

declines with the rising temperature. Regression analysis of the heavy oil viscosity-temperature curve of Liaohe in Fig. 1 reveals a formula of $\eta = 68.375E^{-0.062T}$.

The Pressure and Viscosity Differences before and after Hydrogen Donor Catalytic Aquathermolysis Reaction

Reaction temperature is 280°C. The reaction duration is 24 h. The mass ratio of oil to water is 4 : 1 and the added mass of catalyst is 0.1% of the mass of heavy oil. Then hydrogen donor with varied mass fractions is added. After injecting N_2 into the reactor, the original pressure is 8.0MPa. With the progress of catalytic aquathermolysis reaction, the pressure in the reactor is also changed, as shown in Table 1. After the hydrogen donor catalytic aquathermolysis reaction is completed, heavy oil is dehydrated. The determined viscosity is shown in Table 2.

According to Table 1, without hydrogen donor formamide, the maximum pressure in the reactor is 15.0 MPa. When the mass fraction of hydrogen is up to 7%, the maximum pressure in the reactor is 17.8 MPa. That indicates besides the influence of the saturated vapor pressure of H₂O and light hydrocarbon vapor pressure caused by aquathermolysis, formamide join the reaction under the high temperature and generate CO and NH₃, which are the main factor of the exaltation in the reactor.

As shown in Table 2, when other conditions remain unchanged, with the increase in a mass fraction of added hydrogen donors, an increase in the viscosity reduction rate is obtained after the aquathermolysis reaction. When the mass fraction of hydrogen donors is 7%, the viscosity reduction rate of heavy oil is up to 89.5%. Compared with the reaction without hydrogen donor, the viscosity reduction rate of the reaction with hydrogen donor increases by 21.71%.

The Content Changes in Group Compositions after Adding Hydrogen Donor to the Catalytic Aquathermolysis

According to group composition chromatographic analysis, group compositions of heavy oil before and after hydrogen donor catalytic aquathermolysis were analyzed. As shown in Table 3, with the increase of hydrogen donor mass fraction, the mass fraction of saturated hydrocarbons and aromatic hydrocarbons in heavy oil rises and a mass fraction of resin and asphaltene is reduced. Through the comparison, it can be seen that the contents of saturated hydrocarbons and aromatic hydrocarbons increase after adding catalyst and the aquathermolysis reaction. Then the contents of saturated hydrocarbons and aromatic hydrocarbons rise, respectively, from 24.32% to 26.58 and from 36.89% to 38.26%. Compared with oil sample before reaction the contents of resin and asphaltene are, respectively, reduced by 2.22% and 1.41%. After adding hydrogen donors with different mass fraction of aquathermolysis, the contents of saturated hydrocarbons and aromatic hydrocarbons increased continuously and the contents of resin and asphaltene were significantly reduced. When the mass fraction of hydrogen donor was 7%, saturated hydrocarbons and aromatic hydrocarbons, respectively, increased by 7.13% and 4.69% and the mass fractions of resin and asphaltene were, respectively, reduced by 6.4% and 5.42%. The above change indicated that light constituents in heavy oil were increased and heavy constituents were decreased after hydrogen donor catalytic aquathermolysis. It also shows that, in hydrogen donor catalytic aquathermolysis reaction, partial cyclane

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Mass fraction of hydrogen donor, %	Group composition after reaction, wt $\%$					
	saturated hydrocarbon	aromatic hydrocarbon	resin	asphaltene		
Original heavy oil	24.32	26.58	27.52	29.63		
$\mathbf{0}$	30.76	31.45	36.89	38.26		
	39.95	40.56	41.1	41.58		
3	30.27	28.05	25.96	24.92		
5	24.08	23.87	8.52	7.11		
	6.57	4.89	4.06	3.1		

Table 3. Group composition analysis after adding hydrogen donors with different mass fractions for catalytic aquathermolysis reaction of heavy oil

is converted into aromatic hydrocarbon, the long alkyl chains on the aromatic ring of resin and asphaltene molecule s are broken into small molecule hydrocarbons (Fig. 2). And the alkyl bridges connecting two aromatic rings or one aromatic ring with a naphthenic ring are broken. Thus, the contents of resin and asphaltene decreased and the content of aromatic hydrocarbon increased. These changes are mainly responsible for viscosity reduction of heavy oil after hydrogen donor aquathermolysis reaction.

Analysis on Chemical Composition of Heavy Oil before and after Reaction

Chemical compositions of original heavy oil are shown in Table 4 and the components after hydrogen donor catalytic aquathermolysis viscosity reduction reaction is shown in Table 5. As shown in Table 5, with the increase in the mass fraction of hydrogen donor, C content decreased and H content increased. Atomic ratio of H/C increased and the heteroatom and C atomic ratio

Fig. 2. The broken of long alkyl chains in the asphaltene during hydrogen donor catalytic aquathermolysis reaction.

Component of original heavy oil, wt %					H/C	
	Н				atomic ratio	
85.48	11.61	0.57	1.71	0.61	1.63	

Table 4. Chemical composition of original heavy oil

decreased. When the mass fraction of hydrogen donor was 7%, H/C atomic ratio increased by 0.37 (from 1.63 to 2.0) after hydrogen donor catalytic aquathermolysis. A content decreased by 0.5 (from 0.57 to 0.07). H/C atomic ratio is an important parameter of viscosity reduction as well as the indicator of the quality upgrading. Activated reactant can accelerate the hydrogenation reaction rate and improve the conversion rate of upgrading of heavy oil. Catalysts and hydrogen molecules form chemical adsorption key, which changes the fragmentation pathway of hydrogen molecules, reduces activation energy of hydrogen molecules and free radicals, and accelerates hydrocracking reaction of organic molecules of heavy oil. Meanwhile, the catalyst can also promote the C–C bond breaking in organic matter of heavy oil, which is conductive to the pyrolysis of organic matter in heavy oil and products from initial pyrolysis reaction. Component change after reaction further validates that heavy oil undergoes hydrogen donor catalytic aquathermolysis under the action of hydrogen donor. And the reaction changes the structure of heavy oil and further reduces its viscosity.

Structural Change of Heavy Oil after Hydrogen Donor Catalytic Aquathermolysis

Reaction conditions for hydrogen donor catalytic aquathermolysis reaction are as follows: reaction temperature is 280°C; reaction time is 24 h; water–oil ratio is 4 : 1; dosage of catalyst is 0.1 wt %; and dosage of formamide is 7 wt %. Heavy oil before and after the reaction was analyzed by FTIR spectrum. The results are shown in Fig. 3.

Figure 3 shows the FTIR spectrum of heavy oil after catalytic aquathermolysis and hydrogen donor catalytic aquathermolysis. In the FTIR spectrum, the OH bond in the absorption band of 3450 cm^{-1} is weakened.

According to the FTIR spectrum shown in Fig. 3a, the strong absorption peak in the vicinity of 2850 and 2920 cm⁻¹, is the stretching vibration absorption peak

Table 5. Chemical composition of heavy oil before and after hydrogen donor catalytic aquathermolysis

Component of original heavy oil, wt $\%$	Mass fraction of hydrogen donor, wt %					
	0	1	3	5		
C	85.48	11.61	0.57	1.71	0.61	
H	12.24	12.76	13.2	13.65	14.08	
S	0.33	0.31	0.25	0.14	0.07	
O	1.42	1.22	1.08	0.98	0.82	
N	0.61	0.61	0.61	0.61	0.6	

of naphthenic and alkyl chain methylene CH and the absorption peak at 1707 cm–1 is the characteristic absorption peak of open-chain C=O structure. The absorption peak in the vicinity of 1700 cm–1 and 1600 cm–1 deals with C=C skeleton vibration of conjugated double bonds of aromatic hydrogen. Strong absorption peak in the vicinity of 1457 and 1376 cm–1 is caused by the asymmetric bond of $C-CH_3$ and symmetric bond of $-CH_2$ –. The absorption peak in the vicinity of 869, 812, and 745 cm–1 represents deformation, vibration, and absorption of aromatic proton in the off-plane of C–H and indicates the vibration of aromatic hydrogen on the aromatic proton. The absorption peak in the range from 720 to 730 cm–1 is related to bending vibration of longchain alkyl $(CH_2)_n$ ($n \geq 3$).

Through the comparison between Fig. 3a and Fig. 3c, it can be seen that in Fig. 3c the absorption peak in the vicinity of 1610 cm^{-1} increases after the hydrogen donor is added to catalyst aquathermolysis reaction, indicating that the number of aromatic rings are reduced after reaction. It is due to the heteroatoms contained in heavy oil, such as S, O, and N. These heteroatoms are mainly contained in the fused ring structure of heavy oil. The hydrogenation and removal of impurity atoms of fused ring structure during aquathermolysis reaction results in the reduction in the total number of rings. This can also be confirmed by the position of absorption peak, for the absorption peak extends along the increasing wave length direction when the conjugated length in aromatic ring increases. In Fig. 3a the absorption peak appears at 1615 cm–1 before hydrogen donor catalytic aquathermolysis reaction and appears at 1606 cm–1 after the reaction. The absorption peak at 1606 cm–1 is stretching vibration peak of phenyl C=C. The results indicate that the number of polycyclic aromatic ring is significantly reduced. The heavy oil

Fig. 3. (a) The FTIR spectrum of original crude oil sample; (b) The FTIR spectrum of crude oil sample after catalytic aquathermolysis reaction; (c) The FTIR spectrum of crude oil after hydrogen catalytic aquathermolysis reaction in which dosage of hydrogen donor is 7 wt %.

has undergone the reaction of dealkylation of side chain during hydrogen donor catalytic aquathermolysis reaction and the content of aromatic hydrocarbon increased.

MECHANISM OF VISCOSITY REDUCTION IN HYDROGEN DONOR CATALYTIC AQUATHERMOLYSIS REACTION

As an irreversible way, upgrading and viscosity of heavy oil reduction has drawn the attention of domestic

and foreign scholars. Chemical-induced pyrolysis method is selected. The molecular structure of heavy oil component is the long chain linked by aromatic series and aliphatic group, in which at least some parts are connected by S atom. Thus it is necessary to seek for a suitable additive system in steam injection oil reservoir environment, which can selectively break S bonds in macromolecules.

 The right catalyst is the key to achieving viscosity reduction in the aquathermolysis of heavy oil. Under

Fig. 4. The broken of C–S bond in the heavy oil during hydrogen donor catalytic aquathermolysis reaction.

the condition of high temperature and high pressure, oil-soluble organic transition metal cobalt catalyst is added to the reaction system for hydrogen donor catalytic aquathermolysis reaction. Probably through the combination of cobalt metal ions and S atoms, binding site is activated to react with water molecules.

In the structure of molecular of the heavy oil, as electronegativity of S is greater than that of C , H^+ from the system attacks S in heavy oil while OH– attacks on C. And C–S electron cloud deviates and the C–S bond energy is reduced. Therefore, at 280°C, under the synergic action of organic metal cobalt salt and formamide, S interacts with high-temperature and high-pressure water, leading to the C–S bond breaking in ultra heavy oil. The appropriate chemical structure is shown in Fig. 4.

In the process of catalytic aquathermolysis upgrading, formamide can not only significantly improve the viscosity of heavy oil, but also works as solvent to dilute hydrocarbon molecule free radicals, reduce opportunities for the collision of free radicals, and inhibit the polymerization of heavy oil. Formamide is conducive to C–S bond cleavage and puts forward the aquathermolysis reaction towards the direction of the hydrodesulphurization reaction. Thus, the contents of saturated hydrocarbon and aromatic hydrocarbon increased and the mass fractions of resin and asphaltene decreased. In this way, the viscosity of heavy oil is reduced. Meanwhile, cobalt metal ion can be hydrolyzed easily, which is helpful to bring the hydrogen and water molecules in hydrogen donors to the position of reaction. Transition metal cobalt ions can accelerate the generation of the heavy oil modifier, hydrogen.

Decarboxylation in aquathermolysis reaction may produce CO and water-gas shift reaction (WGSR) [5] occurs. Decomposition product CO generated by formamide in the reactor is helpful to put forward the water gas shift reaction (WGSR) toward the positive reaction to generate more $CO₂$ and $H₂$ for hydrogen donor supply in hydrodesulfurization reaction. In addition, the production of $CO₂$ and NH₃ will help to improve the viscosity of heavy oil and enhance oil recovery.

Hydrogen donor, as the reactants of in-situ upgrading, is the important factor of aquathermolysis and upgrading. The upgrading technology with hydrogen donor has been tested and verified. Ovalles et al. [15] summarized the reaction between the hydrogen donor (tetralin), and the super heavy oil as follows:

Without any hydrogen donors, the active chain generated from aquathermolysis will undergo the reaction below. Therefore, the viscosity of heavy oil after aquathermolysis will rise again.

$$
As^{\dagger} + As^{\dagger} \longrightarrow As - As
$$

CONCLUSIONS

By adding hydrogen donor formamide in catalytic aquathermolysis reaction, the maximum pressure in the reactor is higher and the viscosity of heavy oil has been improved. The ratio of saturated hydrocarbons and aromatic hydrocarbon increased, while the ratio of resin and asphaltene decreased after the catalytic aquathermolysis reaction. When the mass fraction of hydrogen donor was 7%, the contents of saturated hydrocarbons and aromatic hydrocarbons respectively

increased by 7.13% and 4.69%, while the contents of resin and asphaltene, respectively, decreased by 6.4% and 5.42%. The content of sulfur decreased by 0.5% and the H/C atomic ratio increased from 1.63 to 2.0 compared with the heavy oil used in experiment from Liaohe Oil Field.

The mechanism of hydrogen donor catalytic aquathermolysis viscosity reduction is proposed on the basis of the experimental results. The hydrogen donor formamide is added to dilute free radicals of hydrocarbon macromolecules, reduce collision opportunities of free radicals, provide active hydrogen atoms, and inhibit aggregation of heavy oil, which is helpful to the hydrodesulfurization and viscosity reduction of heavy oil.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China, (project no. 2146002), Major National Special Projects for Oil and Gas (project no. 2011ZX05012-003) and the Opening Foundation of key laboratory of the Educational Ministry for Improving Oil and Gas Recovery.

REFERENCES

- 1. Liu, W.Z., *Beijing*: *Petroleum Industry Press*, 1998.
- 2. Hu, J.Y., Niu, J.Y., *Mar. Petrol. Geol.*, 1999, vol. 16, pp. 85–95.
- 3. Zhong, W.X. and Chen, M.S., *Oil Forum*, 2008, vol. 28, no. 5, pp. 18–23.
- 4. Akstinat, M.H., *J. Petrol. Geol.,* 1983, vol. 5, pp. 363–388.
- 5. H yne, J. B., *Synopsis Report no. 50, Aquathermolysis. Alberta: AOSTRA Contracts* 1986, no. 11103103B/C,
- 6. Clark, P.D., and Hyne, J.B., *AOSTRA J. Res.*, 1990, vol. 29, pp. 29–39.
- 7. Hyne, J.B., Greidanus, J. W., Tyrer, J.D., Verona, D., Rizek, C., Clark, P. D., Clarke, R. A. and Koo, J., *Chapter IX in Proc. 2nd Int. Conf. on Heavy Crude and Tar Sands held in Caracas*, Venezuela, 1982, vol. 1, pp. 25–30.
- 8. Clark, P.D., Hyne, J.B., and Tyrer, J.D., *Fuel*,1984, vol. 63, no. 7, pp. 1649–1655.
- 9. Monin, J.C., and Audlbert, A., *SPE Reserv. Eng.*, 1988, vol. 3, pp. 1243–1250.
- 10. Rivas, O.R., Campos, R.E., Borges, L.G., and Intevep, S.A., SPE 18076, *SPE Annual Technical Conference and Exhibition*, Houston:1988,October,.
- 11. US Patent 5482118, 1989.
- 12. Clark, P.D., Clarke, R.A., Hyne, J.B., and Lesage, K.L., *AO STRA J. Res*, 1990, vol. 6, pp. 53–64.
- 13. Clark, P.D., and Kirk, M.J., *Energ. Fuels*, 1994, vol. 8 , pp. 380–387.
- 14. Richard, P.D., William, C.M., and Murray, R.G., *Energ. Fuels*, 2000, vol. 14, pp. 671–676.
- 15. Fan, H.F., Liu, Y.J., Zhao, X.F., and Zhong, L.G., *J. Fuel Chem.Tech.*, 2001, vol. 29, pp. 430–433.
- 16. Chen, R.Y., Liu, Y.J., Liang, M., Wu, H.Y., and H, C.L., *J. Daqing Petroleum Institute*, 2010, vol. 34, no. 6, pp. 68–71.
- 17. Qin,W.L., Su, B.Y.,and Pu,C.S., *Acta Petrolei Sinica (Petroleum Processing Section)*, 2009, vol. 25, no. 6, pp. 772–776.
- 18. Wu, C., Chen Y.L., Wang, Y., and Yang, C., *J. Oil & Gas Tech.*, 2007, vol. 29, no. 3, pp. 267–269.
- 19. Ovalles, C., Vallejos, C., Vasquez, T., Martinis, J., Perez-Perez, A,. Cotte, E., Castellanos, L., and Rodriguez, H., SPE69692, *SPE International Thermal Operations and Heavy Oil Symposium*, Margarita Island:2001,March.
- 20. US Patent 5105887, 1992.