



Research Article

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Study on Hydrogen Donors Catalytic Upgrading of Heavy Oil Using Ultradispersed Catalyst

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ABSTRACT

Based on high pressure reactor as simulator of conditions in heavy oil recovery, use self-made Mo ultra-dispersed catalyst to carry out aquathermolysis of heavy oil with formamide as hydrogen donor. Investigated effects on heavy oil viscosity, group composition and elements content by adding hydrogen into these moments before and after the catalytic aquathermolysis reaction, and employ infrared spectrum and gas chromatography to analyse changes in the structures and composition of heavy oil at these moments before and after the catalytic aquathermolysis reaction with hydrogen donor. The results showed that, with the increase of mass fraction of hydrogen donor, heavy oil viscosity reduction rate increased, saturated hydrocarbon and aromatic hydrocarbon accrued, at the same time, contents of resin and asphaltene reduced. Under the synergy of catalyst and hydrogen donor, carbon content in the crude oil reduced, hydrogen content increased, and H/C atomic ratio increased, content of sulfur also decreased. The results of infrared spectrum and gas chromatography analysis showed that, after hydrothermal catalytic pyrolysis, the number of aromatic rings reduced, the content of light components increased, and the content of heavy components decreased, after oil upgraded, oil was further diluted by light hydrocarbon, which reduces the viscosity of crude oil system.

Keywords: Ultradispersed catalyst, hydrogen donor, heavy oil, aquathermolysis, upgrading

INTRODUCTION

Due to the shortage of conventional light crude, the production of heavy oil will continue to increase in the next few years. However, heavy oil has the drawbacks of high viscosity, poor liquidity and even unable to flow under the condition of the reservoir. So only a small amount of oil can be extracted adopting conventional technology. As a result, some researchers begin to investigate how to reduce the viscosity of heavy oil to make it easy to transport. In this respect, steam stimulation method is often used. By adding superheated water into reservoir well, viscosity of crude oil is reduced. It is believed that this process of adding superheated water into reservoir would probably lead

to some asphaltene molecules decomposition^[1-3].

Catalytic aquathermolysis has become the important area to solve some problems in the process of heavy oil extraction. Hyne et al pointed out that some metals can accelerate aquathermolysis^[4,5]. Since then, researchers conduct experiments to study the effect of some catalysts in the reaction. It is found that superheated water can transfer heat to warm hydrocarbon, which can pyrolyze some asphaltene molecules to small molecules. It can further improve high viscosity and poor liquidity of heavy oil. In addition, the increase of heat can provide a driving force to make the viscosity of crude oil flows easily, and improve its crude oil output as well. When there are catalysts in reaction system, the viscosity of crude oil falls to low level^[6-11]. The catalysts commonly used in aquathermolysis are water soluble, oil soluble and dispersed catalysts. According to the effects of viscosity, it can be ordered in the following sequence: water soluble catalysts < oil soluble catalysts < dispersed catalysts.

In order to improve the dispersion effect of catalyst, it is necessary to develop high dispersible catalysts that can conduct upgrading reaction of heavy oil under a relatively low temperature. Due to super dispersed catalysts' unique structure and surface characteristics, its catalytic activity and selectivity are obviously higher than those of traditional catalysts. With the decrease of the catalyst particle size, its surface area increases gradually, along with its adsorption capacity and catalytic performance. These unique effects make the dispersed catalysts can not only control the reaction velocity and greatly improve the reaction efficiency, but also make the original reaction.

Super dispersed catalysts have high potential economic value in upgrading and viscosity reduction. It is a new way of the future efficient exploitation of heavy oil. By improving the grade of the heavy oil, there comes high profits. On the other hand, heavy oil upgrading and viscosity reduction in the underground reduce the cost of mining and gathering, as well as the burden of the refinery processing heavy oil.

EXPERIMENTAL SECTION

Experimental instrument and chemical substance

Instrument: CWYF-I strong magnetic, high temperature and high pressure reaction kettle (Jiangsu Haian Huada oil factory), HAAKE RS6000 (Germany HAAKE Company), Nicolet iS10 infrared spectrum (American Nicolet Company), Clarus500 gas chromatograph (American PE corporation) etc.

Chemical substance: base oil (initial boiling point 623 K), n-hexane, methylbenzene, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, nickel sulfate, caustic soda, formamide, petroleum ether, diethyl ether etc. and silica gel, neutral alumina (100~200 mesh), above all are analytically pure.

Catalyst preparation

Molybdenum super dispersed catalyst preparation: Choose water soluble transition metal salt and take on-ionic surfactant sorbitan mono-oleic acid ester water/oil emulsion, lubricating oil base oil (initial boiling point 340°C) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ as catalyst precursor, because its cost is lower than the oil soluble transition metal salts and distilled water flash evaporation and decomposition preparation. Microemulsion preparation experiment is conducted under atmospheric pressure using the mixture of base oil 150g, water 16.8g and surfactant 9g to reduce the interfacial tension between oil-continuous phases and water droplets. To form stable micellar microemulsion, it needs to mix for 10 minutes with the high speed of 4000 rpm. The catalyst particle size is 1800nm measured by dynamic light scattering method.

Experimental method

Filter samples of heavy oil in 80°C with pore size 0.045 mm stainless steel screen mesh, and dehydrated below 120°C until it is qualified when the moisture content is less than 0.5%. Put a certain amount of heavy oil, water and super dispersed catalyst at high temperature and high pressure reaction kettle, do aquathermolysis and viscosity reduction process under certain temperature and reaction time. Inject N₂ to the high pressure reaction kettle before heating and maintain pressure in 8 ~10 mpa. After the completion of the reaction, cool to room temperature and collect sample oil to set aside.

Test method analysis

Crude oil family compositions use silica gel and the alumina as adsorbent to be examined according to the relevant provisions of the SY/T5119-1995. Carbon and hydrogen analysis is carried out in accordance with the national standard GB/T19143-2003 method. Oxygen analyzer is applied in oxygen determination. High temperature pyrolyzing samples in cracking tubes. Chromatographic column is used to pyrolyze gaseous mixture. Thermal conductivity detector is used to examine carbonic oxide or infrared detector to check directly carbonic oxide in gaseous mixture pyrolyzing. The content of elemental sulphur is examined by tube stove method in accordance with GB/T 387-1990. While the determination of nitrogen content is based on the sample of carbon, hydrogen, sulfide and oxygen content data, using the differential method to obtain.

Use HAAKE RS6000 rheometer to measure viscosity. Below 50°C, calculate viscosity reduction rate by the heavy oil viscosity before and after reaction when shear rate is 10s⁻¹. Viscosity reduction rate can be calculated by formula $\Delta\mu = (\mu_0 - \mu) / \mu_0 \times 100\%$. Among them, $\Delta\mu$ refers to viscosity reduction rate, μ_0 refers to viscosity reduction rate before reaction and μ refers to viscosity reduction rate after reaction.

Using Nicolet iS10 fourier transform infrared spectrometer analyzes heavy oil infrared spectrogram hydrogen catalytic aquathermolysis before and after reaction. Dissolve before and after reaction heavy oil in CCl₄, apply little on the KBr tablets, remove CCl₄ and get the sample by drying in the infrared oven, obtain infrared spectrogram with Nicolet iS10 infrared spectrometer.

According to SY/T 5779-1995 “crude oil whole hydrocarbon gas-chromatography analytical method”, it adopts Clarus500 gas chromatograph to conduct whole hydrocarbon gas-chromatography analysis to study the effect of hydrothermal catalytic pyrolysis reaction of heavy oil before and after. Analysis conditions: temperature of the injection port is 260°C, chromatographic column HP-1 (30m×0.25mm×0.25μm). Temperature programmed: 40°C constant temperature for 10 min, 3°C / min to 320°C, constant temperature for 10 min, FID detector, detector temperature 320°C, carrier gas is nitrogen, flow rate of 1 ml/min, diversion ratio of 1:100.

RESULTS AND DISCUSSION

The heavy oil used in this experiment was taken from Liaohe Shuguang Oilfield and the 50 °C dehydrated and degassed heavy oil had a viscosity of 15420 mPa·s. Figure 1 shows the stock tank oil viscosity-temperature curve.

Viscosity is an important parameter reflecting the flowing performance of fluid and has a close relationship with temperature. Non-Newtonian fluid at a certain temperature will be transformed into Newtonian fluid. It is generally believed that after being transformed into Newtonian fluid continuous seepage can occur to heavy oil within the formation. Therefore, oil extraction engineering design requires injection of steam to heat the formation to the temperature above that certain temperature for conversion. Conventional heavy oil exhibits characteristics of Newtonian fluid generally at 40~50 °C or even lower temperatures, but the extra and ultra heavy oil requires about 70~80 °C or even higher temperatures to be transformed into Newton fluid.

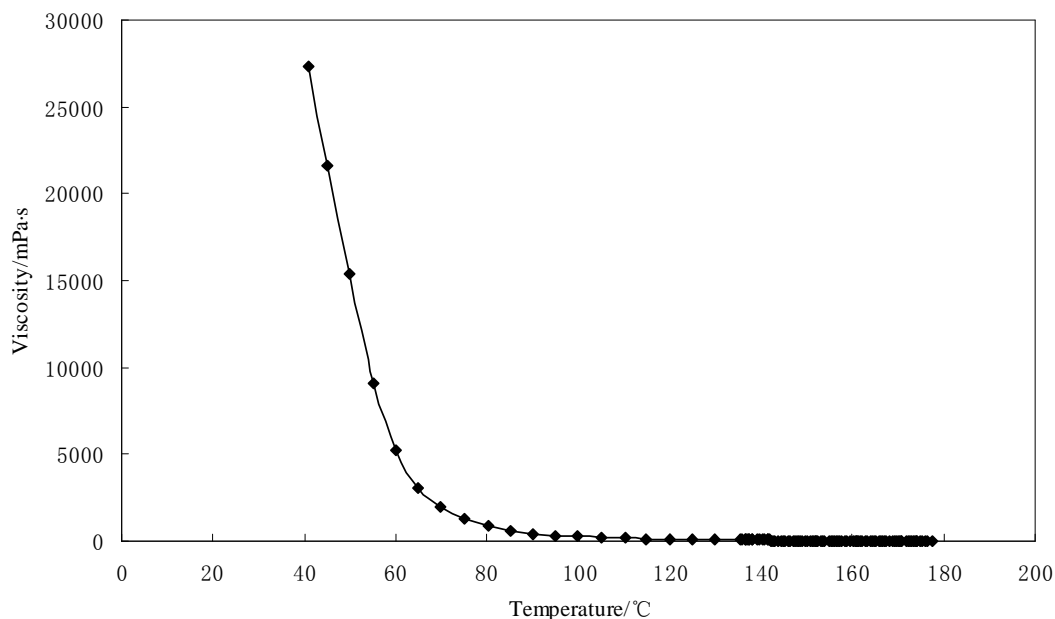


Fig.1 Viscosity-Temperature Curve of Crude oil from Liaohe

Figure 1 shows that Liaohe Oilfield's heavy oil has a strong thermo-sensitivity and its viscosity sharply declines with the rise of temperature. This is because the heavy oil is multiphase liquid mixture, where the size, distribution, and concentration of solid particles of macromolecules (e.g., asphaltenes) in the liquid, resin content, as well as momentum exchange, link to growth, and arrangement of such components as saturated hydrocarbons have a greater impact on its viscosity. Most crude oil is a relatively stable colloidal dispersed structure. Its dispersion phase with asphaltene as the core and attached to its resin as solvable layer constitutes micelles. Its dispersion medium is mainly composed by oil and some resin. From the center of micelles to the dispersion medium its composition gradually changes and transits. Connection or split of these micelles makes heavy oil's internal structure becomes loose, internal cohesion lower, which is the substance of heavy oil viscosity-temperature relationship changes [12-14]. The Liaohe heavy oil viscosity-temperature curve shown in Figure 1 was treated with regression analysis and the equation was $\eta = 78477E^{-0.0513T}$.

Heavy oil viscosity change before and after hydrogen donor catalytic aquathermolysis reaction

Reaction temperature was 280 °C, reaction time 24h, oil-water ratio 4: 1, and ultradispersed catalyst dosage was 0.1% of heavy oil mass. Hydrogen donor of different mass fractions of heavy oil was added. After the reactor was filled with N₂ the original pressure was 9.0MPa. After undergoing Hydrogen Donor Catalytic Aquathermolysis Reaction the heavy oil received dehydration treatment, and the measured viscosity is shown in Table 1.

Table 1 Heavy oil viscosity change before and after hydrogen donor catalytic aquathermolysis reaction

Hydrogen donor content /%	0	1	3	5	7
Heavy oil viscosity after the reaction /Pa·s(50°C)	1565.13	1267.524	1090.194	1033.14	909.78
$\Delta\mu$ viscosity reduction rate /%	89.85	91.78	92.93	93.3	94.1

Table 2 shows that under other conditions remaining unchanged, with the addition of hydrogen donor formamide content increased. After heavy oil underwent hydrogen donor catalytic aquathermolysis reaction, viscosity reduction rate increased. When the hydrogen donor content reached 7%, the heavy oil viscosity reduction rate reached 94.1%. Compared with the viscosity without addition of hydrogen donor to catalyze aquathermolysis, the heavy oil viscosity reduction rate increased 4.25%.

Heavy oil group composition change before and after hydrogen donor catalytic aquathermolysis reaction

According to chromatographic analysis of group composition, SARA analysis was done on the heavy oil group composition before and after Hydrogen Donor Catalytic Aquathermolysis Reaction. See the experimental results in Table 2. As can be seen from Table 2, with the increase of hydrogen donor addition, contents of saturated

hydrocarbons and aromatic hydrocarbons in the heavy oil increased, while resin and asphaltene content decreased. By contrast, it can be seen that after aquathermolysis caused by addition of catalyst, contents of saturated hydrocarbons and aromatic hydrocarbons in the heavy oil increased from 22.92%, 25.44% before the reaction to 26.12%, 36.93% respectively. Compared with heavy oil samples before the reaction, resin and asphaltene content decreased by 11.91%, 2.78%. After aquathermolysis by adding catalyst and different mass fractions of hydrogen donor, contents of saturated hydrocarbons and aromatic hydrocarbons in the heavy oil continued to increase, resin and asphaltene content decreased more obviously. When the hydrogen donor of 7% mass fraction was added, compared with the heavy oil samples before the reaction, contents of saturated hydrocarbons and aromatic hydrocarbon increased by 8.16%, 15.32%, while the resin and asphaltene content decreased by 17.51% and 5.97%.

This shows that the heavy oil after undergoing hydrogen donor catalytic aquathermolysis reaction saw light components increase and heavy components decrease significantly. This also shows that in hydrogen donor catalytic aquathermolysis reaction, some naphthenic hydrocarbons were aromatized into aromatic hydrocarbons; long alkyl chain on aromatic ring fused in resin and asphaltene molecular structure broke and generated small-molecule hydrocarbons; and alkyl bridge connecting the two aromatic rings or an aromatic ring and an naphthenic ring fractured, causing resin and asphaltene content to reduce and aromatic content to increase.

Table 2 Heavy oil group composition analysis after hydrogen donor catalytic aquathermolysis reaction

Hydrogen donor content /%		Original heavy oil	0	1	3	5	7
Post-reaction SARA/ wt%	Saturated hydrocarbons	22.92	26.12	27.41	28.91	30.13	31.08
	Aromatic hydrocarbons	25.44	36.93	38.52	39.82	40.15	40.76
	Resin	40.81	28.9	26.59	25.03	24.33	23.3
	Asphaltenes	10.83	8.05	7.48	6.24	5.39	4.86

Heavy oil element analysis before and after the reaction

The elemental composition of heavy oil before and after hydrogen donor catalytic aquathermolysis reaction is shown in Table 3. As seen from Table 3, after the addition of ultra dispersed catalyst and hydrogen donor, compared to the pre-reaction heavy oil samples, after hydrogen donor catalytic aquathermolysis reaction the heavy oil's H/C atomic ratio rose from 1.559 before the reaction to 1.969, an increase of 0.41, S content decreased from 0.24 before the reaction to 0.08, a decrease of 0.16. H/C atomic ratio is an important parameter of heavy oil upgrading and also a sign of heavy quality improvement. Activation reactants can accelerate the hydrogenation reaction rate and improve the conversion rate for the hydrogen-based heavy oil reforming. Catalyst and hydrogen molecules form chemisorption bond, change fragmentation pathway of hydrogen molecules, reduce the activation energy of hydrogen molecules and free radicals, and accelerate the hydrocracking reaction of heavy oil's organic molecules. Meanwhile, the catalyst may promote the C-C bond cleavage of organic matter in heavy oil, conducive to cleavage reaction between organic matter in heavy oil and initial pyrolysis products, prompting heavy oil structural changes, thereby reducing the viscosity of heavy oil.

Table 3 Heavy oil element composition before and after hydrogen donor catalytic aquathermolysis reaction

Name	C	H	S	O	N	H/C atomic ratio
Original heavy oil element composition /wt%	86.13	11.19	0.24	1.76	0.68	1.559
Heavy oil element after viscosity-reducing hydrogen donor catalytic upgrading /wt%	84.89	13.93	0.08	0.5	0.6	1.969

Heavy oil structural change before and after hydrogen donor catalytic aquathermolysis reaction

The reaction conditions for hydrogen donor catalytic aquathermolysis included the reaction temperature 280 °C, reaction time 24h, oil-water ratio of 4:1, ultradispersed catalyst addition 0.1wt%, and hydrogen donor formamide addition 7wt%. The heavy oil received IR analysis using Fourier transform infrared spectrometer before and after the reaction of and the results are shown in Figure 2 and Figure 3.

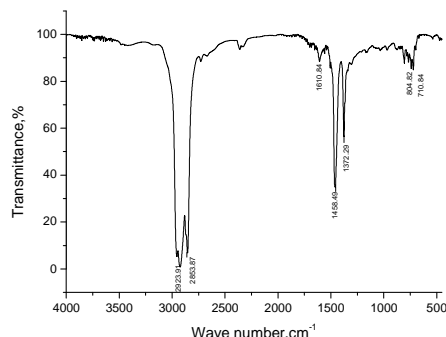


Fig.2 Infrared Spectrogram before the Reaction

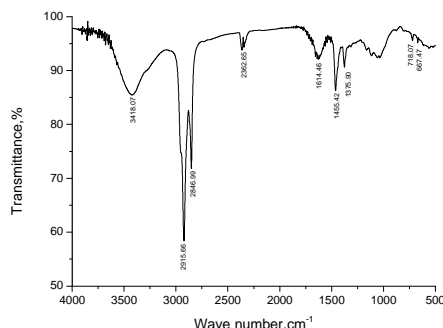


Figure 3 Infrared Spectrogram after the Reaction

Figure 2 shows the infrared spectrogram of the original heavy oil samples, and Figure 3 shows the infrared spectra of heavy oil samples after hydrogen donor catalytic aquathermolysis reaction.

As can be seen from the infrared spectrum in Figure 2, the strong absorption peaks at the vicinity of 2853cm⁻¹ and 2923cm⁻¹ were stretching vibration absorption peaks of naphthenic and paraffinic methylene C-H, and the peak at the vicinity of 1610cm⁻¹ was also contributed by framework vibration of aromatic conjugate double bond C=C bond; the strong absorption peaks near 1455cm⁻¹ and 1375cm⁻¹ were caused by C-CH₃ asymmetric bond and -CH₂-symmetric bond, while the absorption at the vicinity of 710cm⁻¹ was related to the bending vibration of long-chain alkyl (CH₂)_n (n ≥ 3).

In Figure 3 the absorption peak near 1614cm⁻¹ after the reaction enhanced, indicating a decrease in the number of aromatic rings after the reaction of the sample, which is due to that heavy oil contains more heteroatoms, such as S, O and N, which are mainly located in the heavy oil ring structure. In aquathermolysis reaction these heteroatoms underwent hydrogenation and de-heteroatomation, resulting in a reduction in the total number of rings. After hydrogen donor catalytic aquathermolysis reaction, some side alkyl chains were removed from heavy oil, and thus its aromatic content increased.

Crude oil total-hydrocarbon chromatographic analysis before and after hydrogen donor catalytic upgrading reaction

The total hydrocarbon gas chromatographic analysis was done before and after ultra dispersed catalyst and hydrogen donor-based aquathermolysis reaction according to SY / T 5779-1995 "Crude Oil Total Hydrocarbon Gas Chromatography". The crude oil was measured using PE 6890 chromatograph before and after the upgrading. See the results in Figures 4 and 5 and Table 4.

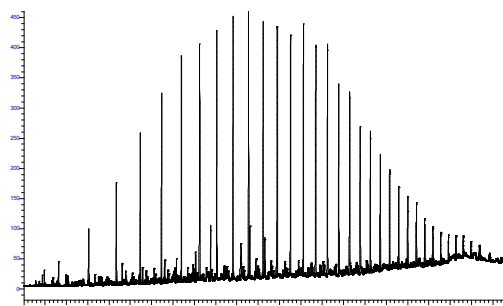


Fig.4 Total hydrocarbon chromatogram of original heavy oil samples

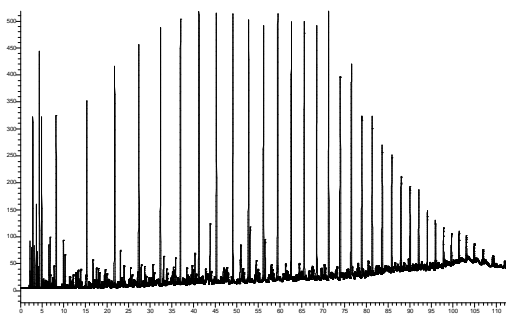


Fig.5 Total Hydrocarbon chromatogram of heavy oil after hydrogen donor catalytic aquathermolysis upgrading reaction

Table 4 Crude oil total hydrocarbon distribution after hydrogen donor catalytic aquathermolysis upgrading reaction

Distribution of hydrocarbons	Percentage of hydrocarbons before viscosity reduction (%)	Distribution of hydrocarbons	Percentage of hydrocarbons after viscosity reduction (%)
<C10	1.71	<C10	7.64
C10-C14	16.55	C10-C14	19.4
C15-C20	35.45	C15-C20	28.91
C21-C25	25.67	C21-C25	23.46
C26-C30	14.15	C26-C30	14.08
C31-C35	7.04	C31-C35	6.96
>C35	0	>C35	0

Table 4 shows that before catalyst and hydrogen donor-based aquathermolysis upgrading the heavy crude oil had a large content of C15 ~ C25 hydrocarbons distributed mainly in C15 ~ C25, and after the upgrading the crude oil saw C10 ~ C14 increase obviously, hydrocarbon substances less than C10 increase 5.93%. As can be inferred from Figure 4 and Figure 5, in heavy oil, the more high-carbon-number hydrocarbons, the stronger the dispersion force between molecules, the greater the force, the higher the viscosity of heavy oil; after catalyst and hydrogen donor-based aquathermolysis upgrading the existence of low-carbon-number hydrocarbons had a significant impact on reducing the viscosity of heavy oil, which may further dilute the heavy oil as a solvent, so that the guarant viscosity of crude oil can be reduced.

CONCLUSION

(1) The viscosity of heavy oil was improved by adding ultra-dispersed catalyst and formamide, compared with catalytic aquathermolysis without the hydrogen donor formamide, when the mass fraction of hydrogen donor is 7%, viscosity reduction rate is 94.1%, heavy oil viscosity reduction rate increased by 4.25%.

(2) Based on catalytic aquathermolysis of heavy oil with different mass fraction, the content of saturated hydrocarbons and aromatic hydrocarbons increased, the content of resin and asphaltene decreased. When the mass fraction of hydrogen donor is 7%, compared with heavy oil before the reaction, saturated hydrocarbons and aromatic hydrocarbons, respectively, increased by 8.16%, 15.32%, but the resin and asphaltene decreased by 17.51% and 5.97%, respectively. The content of sulfur decreased from 0.24(before reaction) to 0.08(after reaction), H / C atomic ratio of heavy oil increased from 1.559(before reaction) to 1.969(after reaction).

(3) After hydrogen donor catalytic aquathermolysis, IR spectra of heavy oil showed that hydrogenation and heteroatom removal reactions happened in the process of aquathermolysis, and the number of aromatic rings reduced after aquathermolysis.

(4) After hydrogen donor catalytic aquathermolysis, gas chromatography of heavy oil showed that, after upgrading, compositions of crude oil have a series of changes, light components of crude oil increased, and heavy components decreased, at the same time, oil was further diluted by light hydrocarbon, making viscosity of crude oil

lowered.

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REFERENCES

- [1]Fajun Zhao, Yongjian Liu,Xin Zhao, et al. *Chemistry and Technology of Fuels and Oils*, **2015**, 51(1): 33-40.
- [2]Fajun Zhao, Yongjian Liu, Yongbin Wu, et al. *Chemistry and Technology of Fuels and Oils*,**2012**,48(4):273-282
- [3] Jianyi Hu, Jiayu Niu. *Mar. Petrol. Geol.*, **1999**, 16:85–95.
- [4] Hyne J B, Greidanus J W, Tyrer J D. Aquathermolysis of heavy oil[C].Proceedings of the 2nd international conference on heavy crude and tar sands. Caracas, Venezuela: **1982**: 25-30.
- [5]Hyne J B. Synopsis Report No.50,Aquathermolysis[R].AOSTRA Contracts No.11103103B/C,**1986**.
- [6] Weissman J G, Kessler R V, Sawicki R A, et al. *Energy & Fuel*, **1996**,10(4): 883-889.
- [7] Ovalles C, Filgueiras E, Morales A, et al. *Fuel*, **2003**,82:887-892.
- [8] Ovalles C, Vallejos C, Vasquez T, et al. *Petroleum Science and Technology*,**2003**, 21(1-2):255-274.
- [9] Akstinat M H. *Petroleum Geology*,**1983**,5:363-388
- [10] Shengjian Jiang, Xilin Liu, Yongjian. Liu, et al. In situ upgrading heavy oil by aquathermolytic treatment under steam injection conditions[C]. SPE International Symposium on Oilfield Chemistry, February 2-4; Houston,USA,**2005**.
- [11] Yongjian. Liu, Liguang Zhong, Shengjian Jiang, et al.. *J. Fuel. Chem. Tech*, **2004**, 32,117-122.
- [12]Bing Qin, Study on the Relationship between the Composition and Performance of Viscosity-Reducing Agent Used in the Viscous Crude Oil Recovery[D].Doctoral Thesis.Research Institute of Petroleum Processing. Beijing ,**2001**.
- [13] Pierre C, Barré L, Pina A ,et al. *Oil & Gas Science and Technology*,**2004**, 59(5):489-501.
- [14] Bazyleva Ala B, MD Anwarul Hasan, Michal Fulem, et al. *Journal of Chemical & Engineering Data*, **2010**, 55 (3):1389–1397.