ISSN 0965-5441, Petroleum Chemistry, 2017, Vol. 57, No. 12, pp. 1018–1023. © Pleiades Publishing, Ltd., 2017.
Published in Russian in Neftekhimiya, 2017, Vol. 57, No. 6, pp. 639–644.

Experimental Study on Homogeneous Catalytic Upgrading of Heavy Oil[1]

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Received January 3, 2017

Abstract—Four catalyst precursors were prepared to assess the performance on the upgrading process of heavy oil. It has been showed that viscosity of Lukeqin heavy oil was decreased significantly, which revealed a viscosity reduction ratio of up to 99.28% with a catalyst precursor concentration of 0.12 wt %, reaction temperature of 365°C and reaction time of 40 min. Analysis of the oil after upgrading showed an obviously change in the composition of hydrocarbon components. The increase of light fractions after reaction improved the properties of heavy oil which is benefit to the pipeline transportation and downstream refining. Meanwhile, the mechanism of upgrading was also investigated. This work proved that heavy oil can be effectively upgraded with the catalyst precursor of petroleum acid iron.

Keywords: heavy oil, catalytic upgrading, viscosity reduction, catalyst precursor, petroleum acid

DOI: 10.1134/S0965544117120143

INTRODUCTION

With the shortage of light crude oil resources and the increasing demand for energy resources, heavy oil, an important hydrocarbon resource, plays a more important role in global economy and has attracted worldwide interest [1]. However, the exploitation was impeded by its high viscosity and solidification [2–4]. Thus, many effective technology of thermal recovery [5] such as steam flooding, cyclic steam stimulation, steam assisted gravity drainage (SAGD) [6] and in-situ combustion (ISC) [7] have been developed and adopted for its recovery.

The thermal process of in-situ combustion that generate the thermal energy efficiently through combustion in the reservoir [8], which applicable to a wide range of heavy oil fields and heavy oil types, it encourage the mobility of heavy oil by heating, vaporization of fluids and thermal cracking [9].

The effect of transition metal catalyst on in-situ combustion process has been investigated. The effect of additives of the metallic salt on the in-situ combustion at the temperature range of high temperature oxidation has been investigated by He et al. [10]. The metallic salt additives (Fe^{3+}) decreased the activation energy and enhanced fuel deposition and the complete combustion was produced broadly. Ramirez-Garnica et al. studied the nickel ionic solution on the in-situ recovery technique by combustion tube experiment which conforming that the nickel catalyst enhanced the oil upgrading in in-situ combustion process [11].

As for the complicity of hydrocarbon mixture and its consecutive reaction of heavy oil reactions in porous media, the method of ISC is economically more feasible that compared to other steam-based techniques. But this method has its own shortcomings that the deposited coke block the pore which could reduce the permeability of the reservoir and decrease the consequently oil production [12]. High temperature process of heavy oil with catalytic is desirable to process the heavy oil or super heavy oil.

Since the high relative amount of resin and asphaltene, its difficulty to produce and process the heavy hydrocarbon feedstock [13], one of the important aspects of viscosity reduction during upgrading process is the removal of heteroatoms such as O, N and S. Besides, Clark found that reducing carbon numbers and cracking of heavy oil molecules can reduce the viscosity of heavy oil [14]. The most appropriate catalysts are those containing strong active sites that can effectively break the C–C, C–S, C–O and other related bonds in resins and asphaltenes, which leading to a net increase of saturates and aromatic hydrocarbons. The viscosity reduction was attributed to the breaking of C–C, C–S, C–O bonds of resin and asphaltene during the pyrolysis reaction.

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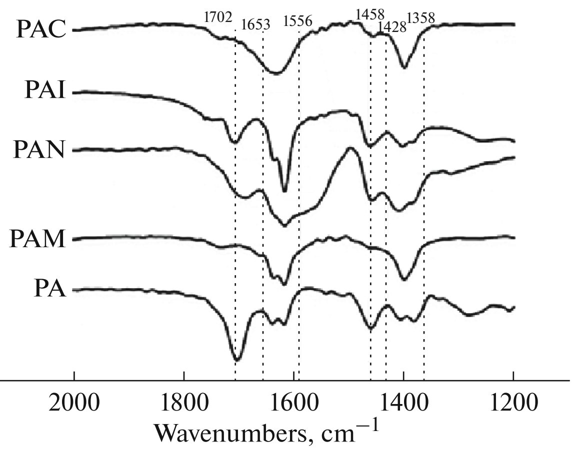

Fig. 1. FT-IR spectra of petroleum acids and catalysts.

Generally, thermal cracking processes is carried out at moderate pressure, the hydrogen is transferred from large molecules to light molecules and accompanied by carbon or coke. Thermal processes have disadvantages in producing a large amount of low value by-products that require further treatment. Therefore, the thermal processes are less efficient than catalytic upgrading that can remarkable reduce the viscosity of heavy oil and improve the flow property without hydrogen.

The purpose of this study is to determine the viscosity reducing effect of four catalyst precursors and optimal experimental conditions for catalytic upgrading reaction in heavy oil from Lukeqin (China), mechanism of catalytic pyrolysis of heavy oil was also studied, the marked effects show the importance of the catalytic pyrolysis in the process of transportation and refining of heavy oil.

EXPERIMENTAL

Synthesis and Characterization of the Catalysts

According to Wang [15], 0.1 mol sodium hydroxide was prepared to saturated aqueous solution at 80°C, a portion of excess naphthenic acid was added into solution, then, excessive naphthenic was removed by separating funnel after saponification, excess sodium naphthenate was added into cupric nitrate, ferric nitrate, nickel nitrate and manganese nitrate solution, respectively, precipitant was formed. And then, the precipitation was vacuum filtered and washed with water to keep the pH value at 7. Finally, the catalyst precursors were synthesized by grinding after the precipitation was dried under 105–110°C for 30 min. The catalyst precursor was characterized by FT–IR using the KBr disc method.

The heavy oil of Lukeqin with a viscosity of 17460 mPa s (50°C), a water content of less than 1% and a density of 0.9585 g/cm^{-1} (20°C), its pyrolysis with/without catalyst precursor were applied in an autoclave (the volume is 500 mL), 100 g heavy oil and a given dosage of catalyst precursor were added into the autoclave. After purging with nitrogen, the reactor was sealed, all experiments were carried out at temperature of 350–400°C for 10–40 min, the reaction was ceased by exposing the autoclave in air cooling and collect the oil sample in a 150 mL beaker, its viscosity was recorded by the NDJ-8SN digital display viscometer at 50°C, the VRR ($\Delta\eta$) was determined by the method as below:

$$\Delta\eta = \frac{\eta_0 - \eta}{\eta_0} \times 100\%,$$

where η, η_0, and η are the rate of viscosity reduction, viscosity before and after reaction, respectively.

The contents of SARA (saturate, aromatic, resin and asphaltene) before and after reaction of heavy oil with/without catalyst precursor were separated from the samples by a column chromatography. The gas chromatography analyses with mass spectroscopy detector for saturate before and after reaction were implemented, the elemental analysis of oil sample were detected by an elemental analyzer, in which the oxygen content was calculated by difference.

RESULTS AND DISCUSSION

Characterization of the Catalysts

The FT-IR spectra of petroleum acid (PA), petroleum acid copper (PAC:Cu^{2+}), petroleum acid iron (PAI:Fe^{3+}), petroleum acid nickel (PAN:Ni^{2+}) and petroleum acid manganese (PAM:Mn^{2+}) was shown in Fig. 1. The band at 1702 cm^{-1} is assigned to the stretching vibration of C=O of petroleum acid, with a strong absorption peak of PA [16]. The peaks at 1653–1580 cm^{-1} and 1428–1358 cm^{-1} in spectra of PAC, PAI, PAN and PAM are enhanced, which are the –COO– anti symmetric stretching vibration peaks and symmetric stretching vibration peaks, respectively. Besides, the peak at 1702 cm^{-1} disappears or weaken obviously, which indicates that the carboxylic acid combines with metal ions, showing that –COO– increases. These evidenced that transition metal ions have combined with petroleum acid.

Figure 2a shows that heavy oil viscosity and VRR after reaction with 4 different catalyst precursors at the temperature of 370°C for 30 min. The VRR has reached to 90.92% without catalyst precursor, however, the viscosity of the heavy oil was 1586 mPa·s, which cannot meet the requirements of pipeline transportation. The VRRs of PAC, PAI, PAN and PAM were 97.8, 98.68, 99.24, and 98.39%, respectively. In addition, PAI and PAN show a greater performance on heavy oil upgrading reaction and the viscosity was decreased from 17460 mPa s to 231 and 132 mPa s, respectively. In consideration of the VRR and eco-

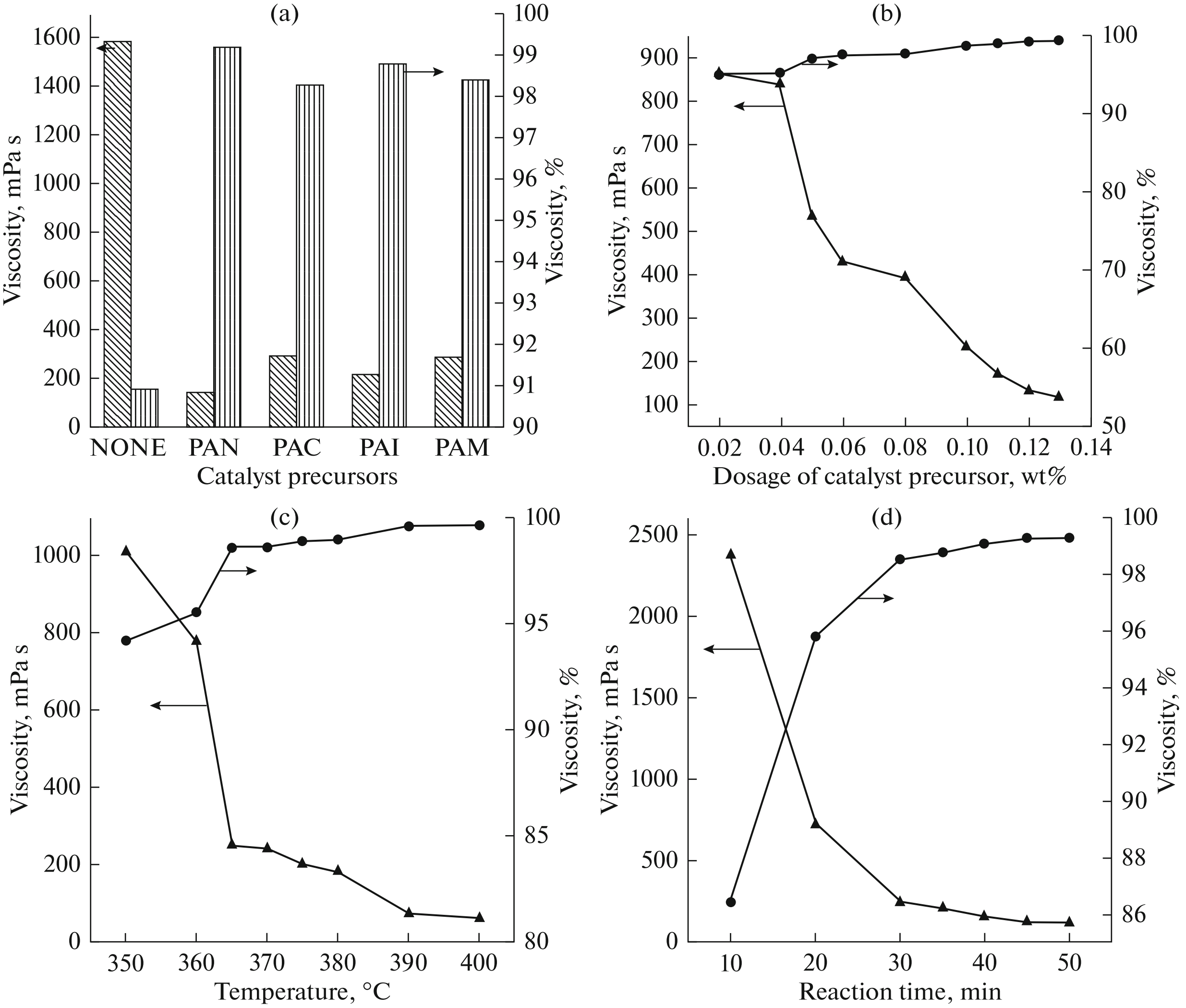

Fig. 2. Effect on viscosity and viscosity reduction of heavy oil: (a) different catalyst precursors, (b) dosage of catalyst precursor, (c) reaction temperature, (d) reaction time.

nomic factors, PAI was more favorable than either of the three catalysts precursors for upgrading reaction.

The effect of dosage of catalyst precursor on upgrading of heavy oil was discussed (temperature: 370°C, time: 30 min), the addition of PAI increased the VRR. As shown in Fig 2b, with the dosage of PAI increasing from 0.02 to 0.13 wt %, the viscosity of oil samples decreased greatly. The viscosity of oil samples changed slowly when the dosage of PAI less than 0.04 wt %. The viscosity of heavy oil decreased to 124 mPa s with 0.12 wt % catalyst precursor concentration, But with the dosage of PAI increasing to 0.13 wt %, the viscosity of heavy oil changed not significantly. So the optimal dosage of PAI is 0.12 wt %.

The effect of reaction temperature on viscosity of heavy oil was discussed under the condition (dosage of PAI: 0.12 wt %, time: 30 min) and the results were shown in Fig. 2c. With the increasing of temperature, the viscosity of oil sample decreased from 1006 to 243 mPa s with the VRR from 94.24 to 98.6% in the temperature region 350–365°C. The increasing of reaction temperature was promoted the depolymerization and polymerization, besides high temperature is of benefit to small molecular to form heavy hydrocarbon and aggravate the coking of oil, when the temperature reached 365°C, viscosity decreased slowly. When the temperature was above 370°C, toluene insoluble components appeared in upgraded oil, and coke will plug the pipe. In conclusion, 365°C was the optimal upgrading reaction temperature.

The reaction time for the pyrolysis of heavy oil are illustrated in Fig. 2d, under the condition (dosage of PAI: 0.12 wt %, reaction temperature: 365°C). When it came to 40 min, the viscosity of heavy oil was 125 mPa s after reaction, which meet the line transportation.

The contents of SARA of heavy oil before and after reaction with/without catalyst precursor were also

Table 1. Element and SARA composition of oil before and after upgrading reaction with PAI (temperature: 365°C, time: 40 min, PAI concentration: 0.12 wt %)

Sample	Element composition, %					SARA, %			
	C	H	O	N	S	saturates	aromatics	resins	asphaltenes
Initial oil	87.03	9.985	1.881	0.85	0.254	34.82	29.98	33.88	1.32
Oil without PAI	87.17	10.472	1.325	0.79	0.243	42.68	27.13	24.47	5.72
Oil with PAI	87.4	11.007	0.746	0.62	0.227	52.43	24.03	15.33	8.21

measured and shown in Table 1. After upgrading reaction, the contents of saturate and asphaltene had been increased from 34.82% and 1.32% to 52.43% and 8.21% when the PAI catalyst precursor was charged, while the contents of aromatic and resin hydrocarbon were reduced by 5.95 and 18.55%, respectively. During the catalytic upgrading process, there are two reaction pathways that are cracking reaction and condensation reaction. On the one hand, a large amount of resin was break into small molecular hydrocarbon fractions leading to the increase of saturates that makes for efficient pipeline transportation. On the other hand, polymerization reaction with a portion of free radicals come from the cleavage of C—S and C—N bonds occurred, which can polymerize to heavy hydrocarbon molecules, in the upgrading process, resulting in the an increase in the content of asphaltene by 6.89%.

The elemental analysis results of oil before and after reaction with/without catalyst precursor are listed in Table 1. It can be easily observed that the elemental contents of sulfur and nitrogen are all reduced substantially which implying that desulfurization and denitrogenation process occur during upgrading reaction with PAI that due to the Fe^{3+} in PAI works on C—S and C—N bonds compare to thermal cracking without catalyst precursor. The bond energies of C—S and C—N is 272 and 305 kJ/mol, respectively, they are both weaker than the C—C bond's with 346 kJ/mol [17, 18], which enable the cleavage of C—S and C—N bonds more easily. The increase of atomic ratio H/C after reaction indicates the most efficient pyrolysis of heavy hydrocarbons. The viscosity of oil sample is 1585 mPa s without PAI, the content of saturate and aromatics increased by 6.65%, which contributing to the catalytic cracking of the resin with PAI.

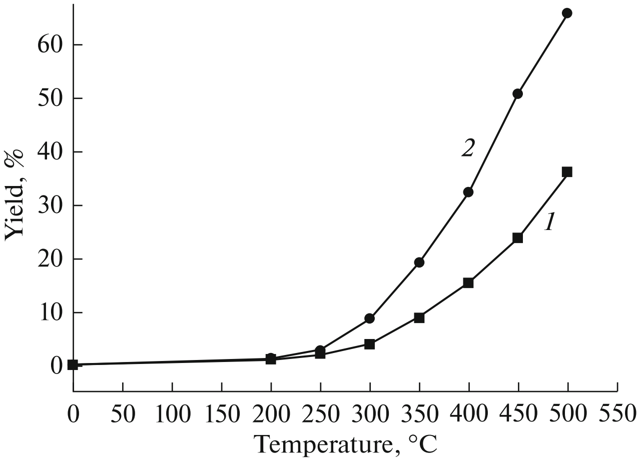

Fig. 3. TBP distillation curve of heavy oil before and after reaction. (*1*) Heavy oil; (*2*) upgraded oil

The result of TBP distillation of heavy oil before and after reaction was shown in Fig. 3 (temperature: 365°C, time: 40 min, PAI concentration: 0.12 wt. %). It is clearly to see that portions below 500°C has been increased from 36.18 to 65.89% after reaction, which once again conformed that the upgrading process leads to the more crucial VRR of the heavy oil when PAI was employed. Additionally, the component at a temperature under 250°C changed slightly, whereas, there is an obvious increase of fraction within the range 250 to 500°C. Heavy hydrocarbons are pyrolyzed to low carbon number alkanes with a lower boiling point. It further proved that the PAI catalyst precursor can accelerate the cracking of large molecules and decrease the molecular weight of heavy oil.

Figure 4 shows the GC-MS spectra of saturate before and after upgrading reaction (temperature: 365°C, time: 40 min, PAI concentration: 0.12 wt %), It is easy to see that additional peaks of C_{10}—C_{12} appear and the peak intensity in the C_{25}—C_{31} region markedly decreases after upgrading reaction, which indicates that some parts of heavy hydrocarbons with long chain had broken into small alkanes that could have been caused by pyrolysis and ring opening of resin and asphaltene molecules. Meanwhile, a distinctly increase occurs of the peak intensity of C_{13}—C_{22}, the condensation reaction of fragments after cleavage of heavy components makes the long-chain alkane increased, still, the cracking reaction is dominant in the upgrading reaction process. The above significant changes reduced the viscosity and thus make the treated heavy oil own a preferable quality.

Obviously, the viscosity of upgraded oil is strongly time dependent, which might make the viscosity increase close up to the initial value in a few days after upgrading process [19, 20]. The viscosity regression was investigated at different time periods after upgrading process and the result is shown in Fig 5, from which we can observe that the viscosity of upgraded oil

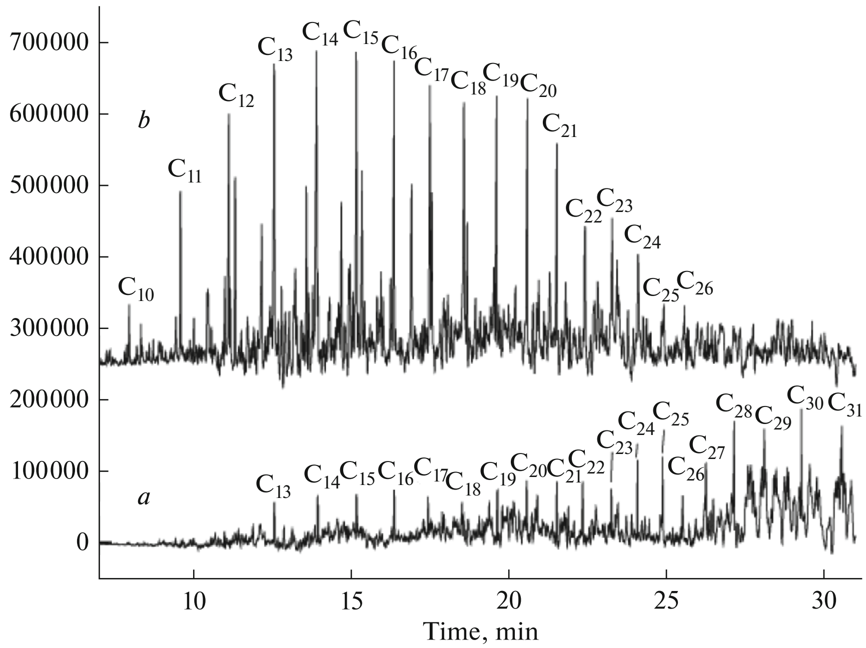

Fig. 4. The selected ion mass chromatograms of saturate ($m/z = 57$): (a) before reaction with PAI; (b) after reaction with PAI.

has increased from 125 to 186 mPa s after 10 days, even though the viscosity of oil sample increased by about 57.6% after 25 days, it could still meet the requirement of pipeline transportation, which conforming that the thermal cracking with PAI exhibit a satisfied effect that deal with the one of the great problem in upgrading heavy oil, to a certain degree, the mechanical and thermal oil treatment reduced the viscosity of crude oil, but the chemical reactions that break the heteroatom group dominate in the upgrading process.

The homogeneous reaction between oil-solute catalytic precursor and organic sulfide such as thiophene, dibenzothiophene and terahydrothiophene with a low activation energy and leads to the formation of intermediate, i.e., Fe-organosulphur , which the coordination of the iron cation to the organic sulfide that weaken the C—S bonds that caused the desulfurization reaction, According to P. D. Clark [14], the small molecule hydrocarbon fragments, H_2S and iron sulfide were produced by the thermolysis of Fe-organosulphur, the target product of iron sulfide act as catalytic that works on C—O and C—N bonds, the dynamic polarization between the polycyclic aromatic hydrocarbons and polar bonds such as C—O and C—N in resin and asphaltene, which decrease the activation energy and make it easily to crack, the inductive effect was transmit to C—C bonds which are adjacent to polycyclic aromatic hydrocarbons leading to the change of its electron cloud, as a consequence, the polarity of C—C bonds was increased that makes the C—C bonds cracked more easily, fragment was obtained and the cracking reactions were accelerated so that increased the content of small molecular hydrocarbon.

CONCLUSIONS

Compare to other three kinds of catalyst precursors: PAC, PAN and PAM, the PAI shows more economy with a supreme VRR of 99.28% at the temperature of 365°C, the reaction time of 40 min and the PAI concentration of 0.12 wt %, the content of heteroatoms reduced and 18.55% of resin was converted to light fractions during the upgrading reaction. It is worth mentioning that light fractions boiling away at temperatures below 350 and 500°C, increased by 9.82 and 29.45% respectively, through TBP stimulated

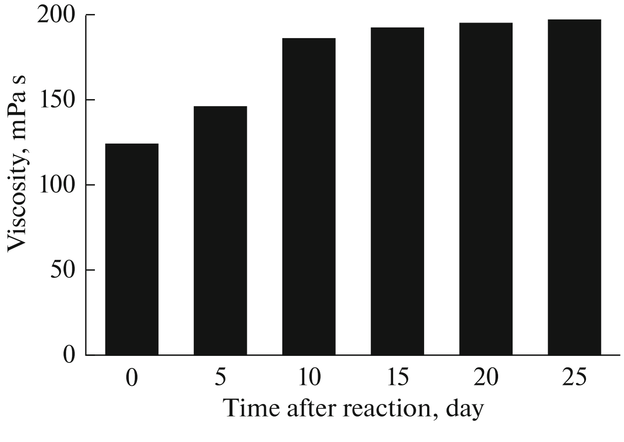

Fig. 5. The viscosity regression of upgraded oil.

distillation. The above remarkable changes of heavy hydrocarbons reduced the viscosity of heavy oil obviously, which is benefit to the pipeline transportation and downstream refining, and the increase contents of asphaltene can improve the quality of asphalt products.

ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by National Science and technology major special project ("12th Five Year Plan") "the mechanism and method of the thermal recovery of heavy oil thermal recovery" (2011ZX05024-005-008). We also thank the editors and anonymous reviewers for the suggestions on improving our manuscript.

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