

Synthesis and evaluation of an oil-soluble viscosity reducer for heavy oil

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Abstract: To reduce the viscosity of highly-viscous oil of the Tahe oilfield (Xinjiang, China), an oil-soluble polybasic copolymer viscosity reducer for heavy oil was synthesized using the orthogonal method. The optimum reaction conditions are obtained as follows: under the protection of nitrogen, a reaction time of 9 h, monomer mole ratio of reaction materials of 3:2:2 (The monomers are 2-propenoic acid, docosyl ester, maleic anhydride and styrene, respectively), initiator amount of 0.8% (mass percent of the sum of all the monomers) and reaction temperature of 80 °C. This synthesized viscosity reducer is more effective than commercial viscosity reducers. The rate of viscosity reduction reached 95.5% at 50 °C. Infrared spectra (IR) and interfacial tensions of heavy oil with and without viscosity reducer were investigated to understand the viscosity reduction mechanism. When viscosity reducer is added, the molecules of the viscosity reducer are inserted amongst the molecules of crude oil, altering the original intermolecular structure of crude oil and weakening its ability to form hydrogen bonds with hydroxyl or carboxyl groups, so the viscosity of crude oil is reduced. Field tests of the newly developed oil-soluble viscosity reducer was carried out in the Tahe Oilfield, and the results showed that 44.5% less light oil was needed to dilute the heavy oil to achieve the needed viscosity.

Key words: Oil-soluble, viscosity reducer, heavy oil, synthesis, evaluation

1 Introduction

Heavy oil makes up a fairly large proportion of oil resources around the world. Reserves of heavy oil, extra-heavy oil and natural asphalt all over the world are about 100×10^9 t (Lv et al, 2005; Dai et al, 2004). With the depletion of light oil reserves and the improvement of oil production technology, the proportion of the heavy oil recovery will increase in the 21st century (Sun and zhang, 2005; Liu et al, 2005). The heavy oil recovery technology in China has been developing rapidly since 1960s. Up to now, technologies for heavy oil thermal recovery including steam stimulation and steam drive methods, and technologies for heavy oil cold production including alkaline drive, polymer drive and miscible flooding, have been developed and widely used (Fan et al, 2007; Zhou et al, 2007). Most of the technologies have been widely applied in heavy oil development and achieved good results. Because of the high viscosity, high density and poor fluidity of heavy oil, reducing viscosity has become the key in heavy oil exploitation, transportation and

refining. At present, the main ways to reduce the viscosity of heavy oil are thermal recovery (by means of heating cables, electric heating oil-pumping rod, and heat-conducting oil), dilution method by using light oil, viscosity reduction by emulsification and so on. Among these methods, the thermal recovery is relatively mature and has better effect, but because of its high electricity consumption the cost is high (Chang and Zhang, 2006; Chen et al, 2004). The thin oil dilution method has no effect on the post-treatment of recovered fluid, however, it can cause a waste of thin oil and its production cost is high (Zhang et al, 2006). The density of Tahe crude oil is between 0.9950 g/cm^3 and 1.099 g/cm^3 , with an average value of 1.0094 g/cm^3 . The kinematic viscosity (50 °C) of Tahe crude oil is between 48,170 mPa·s and 1,800,000 mPa·s, and the freezing point is between 8 °C and 60 °C, with an average value of 33 °C. So the crude oil of Tahe oilfield is heavy oil. The oil-soluble viscosity reducer can be added directly, avoiding post-processing problems which occur in viscosity reduction by emulsification. However, the rate of viscosity reduction of heavy oil by the existing commercial oil-soluble viscosity reducers is not satisfactory, and the study of oil-soluble viscosity reducers is rarely reported abroad and in China work has progressed slowly (Wu and Guo, 2003).

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In addition, the oil-soluble viscosity reducer can work well only when it interacts well enough with colloid and asphalt molecules of heavy oil, and the conditions at the bottom of the wells have great effect on its application. Up to now, we have not found reports of heavy oil recovery by viscosity reduction with only oil-soluble viscosity reducer (Zhang, 2006; Wang, 2006). So it was urgent to develop a suitable oil-soluble viscosity reducer for Tahe heavy oil. In this paper, an oil-soluble viscosity reducer was synthesized and its properties evaluated, and it was found that the synthesized oil-soluble viscosity reducer is more efficient than commercial ones. Field testing of the new developed oil-soluble viscosity reducer was carried out in the Tahe Oilfield of Xinjiang.

2 Experimental

2.1 Reagents and instruments

TK1074 and TK1232 crude oil were from the Tahe oilfield (Xinjiang, China), and formation water was from the 21/5 well station of Tahe oilfield; Methyl stearate, ethyl stearate and vinyl acetate were all analytically pure. Kerosene (with an interfacial tension of $46.61 \text{ mN}\cdot\text{m}^{-1}$) was treated by silica gel, and pentane, benzene, ethanol, petroleum ether (90-120 °C) were all analytically pure.

TK1074 Tahe model oil was made by using the kerosene as solvent and TK1074 Tahe crude oil as solute with a mass fraction of 10%.

Instruments: MAGNA-IR 560 Infrared spectrometer (Nicolet Co., USA), Dataphysics DCAT-21 interfacial tensiometer (Dataphysics Co., Germany), SVR-S interfacial viscoelastic meter (Kyowa Kagaku Co. Ltd., Japan), and Haake RV2 viscometer (HAAKE Co., Germany).

2.2 Synthesis of oil-soluble viscosity reducer

Using the four factors and three levels orthogonal test method (see Table 1), the monomer ratio, initiator amount, reaction temperature and reaction time were all optimized and oil-soluble viscosity reducers (terpolymer, quadripolymer 1, quadripolymer 2 and quadripolymer 3) were synthesized under the optimum conditions. In this section, the quadripolymer's monomers are 2-propenoic acid, docosyl ester, maleic anhydride, styrene and acrylamide, respectively, while the terpolymer's monomers are 2-propenoic acid, docosyl ester, maleic anhydride and styrene. The initiator is ADMVN and the solvent is methylbenzene.

2.3 Determination of interfacial tension

The influence of different concentrations of oil-soluble viscosity reducer on the interfacial tension between TK1074 Tahe model oil (with a mass fraction of 10%) and formation water was determined at 25 °C with Dataphysics DCAT-21 interfacial tensiometer.

2.4 Determination of interfacial shear viscosity

The interfacial shear viscosity of TK1232 crude oil in formation water was measured with SVR-S interface viscoelastic meter.

Table 1 Orthogonal test table

Levels	Factors			
	Monomer ratio	Temperature °C	Initiator dosage, wt%	Reaction time h
Level 1	3:1:1	70	0.6	8
Level 2	3:2:1	80	0.8	9
Level 3	3:2:2	90	1.0	10

2.5 Evaluation of oil-soluble viscosity reducer

The viscosity of heavy oil from Tahe oilfield was measured according to China petroleum industry standard SY/T 5767-2005 "Technical specification for practice of transporting crude oil treated with pour point depressants through pipeline" and SY/T 0520-2008 "Viscosity determination of crude petroleum—Equilibrium method by rotational viscometer". The measurement is carried out at 50-90 °C. The rate of viscosity reduction is calculated as follows:

$$\varepsilon_{\mu} \% = \frac{\mu_1 - \mu_2}{\mu_1} \times 100$$

where $\varepsilon_{\mu} \%$ is the rate of viscosity reduction; μ_1 is the apparent viscosity of crude oil, mPa·s; μ_2 is the apparent viscosity of viscosity-reduced crude oil, mPa·s.

3 Results and discussion

3.1 Results of orthogonal tests

Oil-soluble viscosity reducers were synthesized under different reaction conditions shown in Table 1. The rate of viscosity reduction of TK1232 crude oil was studied at different conditions (w (mass of light oil): w (mass of heavy oil)=0.4:1, and the amount of viscosity reducer was 1% of the total mass of thin and heavy oils) to get the optimum reaction conditions. The results are shown in Table 2. The initiator amount is the percentage of the the total mass of monomers (except solvent).

Table 2 Orthogonal test results

Project	Monomer ratio	Temperature (T), °C	Initiator wt%	Time (t) h	Rate of viscosity reduction at 50 °C %
1	3:1:1	70	0.6	8	56.7
2	3:1:1	80	0.8	9	72.0
3	3:1:1	90	1.0	10	57.3
4	3:2:1	70	1.0	10	73.3
5	3:2:1	80	0.8	8	74.7
6	3:2:1	90	0.6	9	65.3
7	3:2:2	70	1.0	9	78.7
8	3:2:2	80	0.6	10	73.3
9	3:2:2	90	0.8	8	76.0

According to the above Table, analyzing the experimental results. In Table 3, K_1 , K_2 , K_3 respectively stand for the sum of corresponding rate of viscosity reduction of the four factors and three levels of experiments; k_1 , k_2 , k_3 is the average value of K_1 , K_2 and K_3 , respectively.

Table 3 Analysis of orthogonal test results

Project	Monomer ratio	Temperature (T), °C	Initiator wt%	Time (t) h
K_1	186.00	208.7	195.3	207.3
K_2	213.3	220.0	221.3	216.0
K_3	228.0	198.7	210.7	203.9
k_1	62.0	69.6	65.1	69.1
k_2	71.1	73.3	73.8	72.0
k_3	76.0	66.2	70.2	67.9
Range of k	14.0	7.1	8.7	3.9

Table 3 shows that the influence of each factor on the rate of viscosity reduction in view of the range is in the order of monomer ratio>amount of initiator>reaction time>reaction temperature. The optimum conditions for synthesizing the viscosity reducer are as follows: molar ratio of monomers of n (2-propenoic acid, docosyl ester): n (maleic anhydride): n (styrene)=3:2:2, the reaction temperature of 80 °C, the amount of initiator ADMVN of 0.8 wt% and the reaction time of 9 hours.

3.2 Influence of solvent amount on viscosity reducer

According to the optimum reaction conditions obtained from orthogonal experiments, we fixed the monomers ratio, and changed the proportion of monomer and solvent (methylbenzene) to obtain w (light oil): w (heavy oil)=0.4:1 and the amount of viscosity reducer of 2% in the total mass of thin and heavy oil. The effects of solvent on viscosity reducer at different temperatures on TK1232 were investigated and the results can be seen in Table 4.

Table 4 Effect of solvent amount on viscosity of Tahe TK1232 crude oil

Mass ratio of monomer to solvent	Rate of viscosity reduction at 130 °C, %	Rate of viscosity reduction at 90 °C, %	Rate of viscosity reduction at 50 °C, %
1:1	50.0	71.3	76.6
1:2	62.5	90.3	95.5
1:3	68.7	90.3	94.0
1:4	62.5	87.9	90.7

Table 4 shows that the weight ratio of monomer to solvent of oil-soluble viscosity reducer has a great effect on viscosity reduction of heavy oil. In the experiment range, when the weight ratio of monomer to solvent was 1:2, the oil-soluble

viscosity reducer had the best viscosity reducing result.

3.3 Evaluation of oil-soluble viscosity reducer

Under the same conditions, the viscosity reducing effects of the synthesized terpolymer and, quadripolymer viscosity reducers and commercial terpolymer on TK1232 crude oil was investigated at 90 °C and 50 °C, and the results are shown in Table 5. The viscosity of TK1232 crude oil without viscosity reducer at 90 °C and 50 °C is 1,416 mPa·s and 12,881 mPa·s, respectively.

Table 5 The viscosity reducing effects of different copolymers on TK1232 crude oil

Viscosity reducer	90 °C		50 °C	
	Viscosity mPa·s	Rate of viscosity reduction, %	Viscosity mPa·s	Rate of viscosity reduction, %
Commercial terpolymer 1	249	82.4	1511	88.3
Commercial quadripolymer 2	429	69.7	3721	71.1
Synthesized terpolymer	137	90.3	585	95.5
Synthesized quadripolymer 1	274	80.6	1319	89.2
Synthesized quadripolymer 2	515	63.6	1717	86.7
Synthesized quadripolymer 3	283	80.0	4293	66.7
Synthesized quadripolymer 4	549	61.2	6354	50.7

Table 5 shows that the synthesized terpolymer viscosity reducer is better than commercial viscosity reducers and the quadripolymer viscosity reducers. At 50 °C, the viscosity of TK1232 crude oil fell from 12,881 mPa·s to 585 mPa·s, and the rate of viscosity reduction is 95.5%, after adding the synthesized terpolymer viscosity reducer.

3.4 IR spectra of TK1074 heavy oil with and without viscosity reducer

IR spectra of TK1074 heavy oil with and without viscosity reducer are shown in Fig. 1. It can be seen that the intensity of the absorption peak of the hydroxyl O-H decreased at 3,500 cm^{-1} after using viscosity reducer. The peak of carbonyl C=O appeared at 1,736 cm^{-1} after using viscosity reducer. The structure of TK1074 crude oil had changed after using viscosity reducer.

3.5 Influence of oil-soluble viscosity reducer on oil-water interfacial tension

Viscosity reducer was added to 10% TK1074 Tahe model oil (the amount of viscosity reducer being 1 wt% of the model oil) and stirred to make the oil phase, and formation water was used as aqueous phase, to study the oil-water interfacial

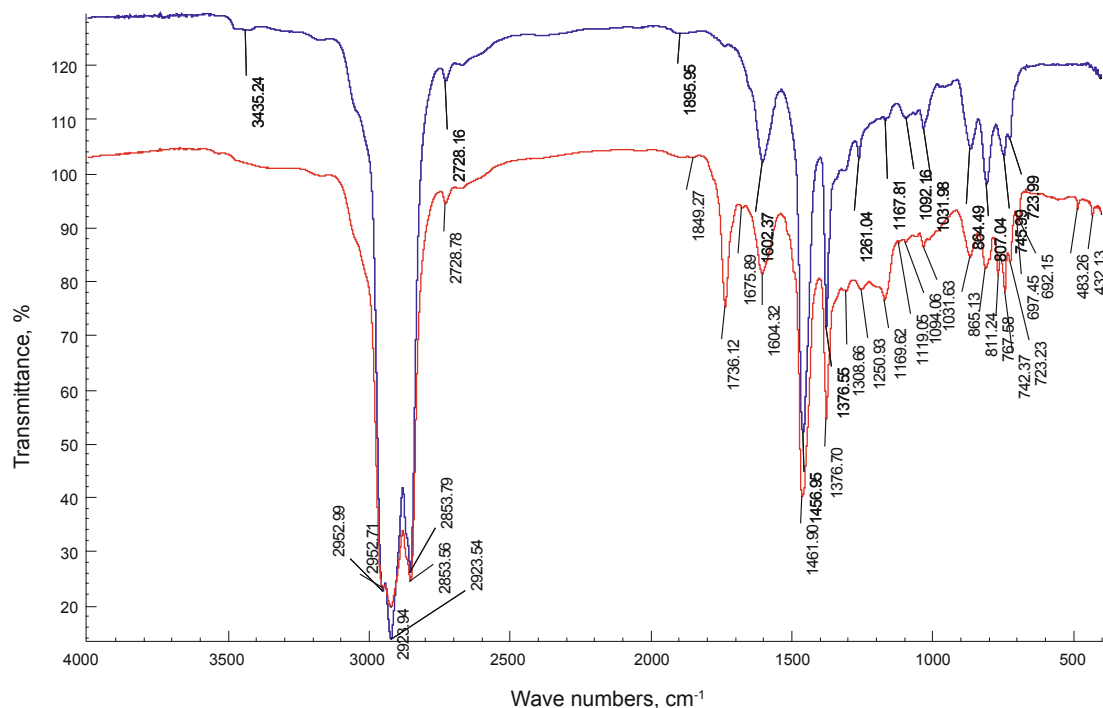


Fig. 1 IR of TK1074 crude oil with or without viscosity reducer (Blue: IR of TK1974 heavy oil, red: IR of TK1074 heavy oil with viscosity reducer)

tension with and without viscosity reducer(see Fig. 2).

Fig. 2 shows that the interfacial tension between crude model oil and formation water system decreased dramatically when using the viscosity reducer, indicating that the viscosity reducer has a high interfacial activity. The viscosity reducer can spread from the oil phase to the oil-water interface replacing macromolecular active substances from the crude oil, so a new interfacial film is formed and the interfacial tension is greatly reduced.

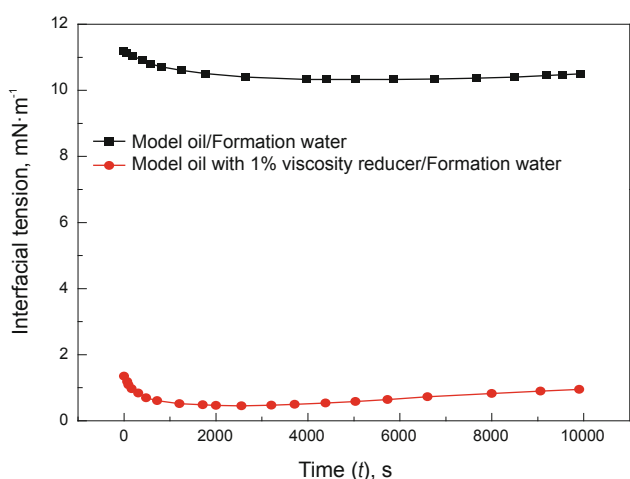


Fig. 2 Effect of viscosity reducer on interfacial tension between TK1074 crude model oil and formation water

3.6 Field test of the oil-soluble viscosity reducer

The field test of the developed oil-soluble viscosity reducer was carried out for two months in well TH12510

(machine pumping well) and TH12210 (flowing well) of the second oil production plant of the Tahe oilfield. Results are as follows: (1) For well TH12510, during the test, the light oil dilution ratio was reduced from 0.83 to 0.49. In normal production conditions, the light oil needed for heavy oil dilution was decreased by 44.5%, after using oil-soluble viscosity reducer, with an average saving rate of 21.0% , and a maximum 6.1 t/d of light oil was saved per day , with an average saving amount of 4.5 t/d. (2) For well TH12210, during the test, the light oil dilution ratio was reduced from 1.42 to 0.99 after using oil-soluble viscosity reducer. In normal production conditions, the light oil used for heavy oil dilution was decreased by 30.4%, and a maximum 12.3 t/d of light oil was saved per day, with an average saving amount of 9.0 t/d.

4 Conclusions

1) The synthetic conditions of oil-soluble viscosity reducer are as follows: under the protection of nitrogen, reaction 9 h, mole ratio of raw material monomer 3:2:2, amount of initiator is 0.8%, reaction temperature is 80 °C. In the scope of $w(\text{monomer}):w(\text{solvent})=1:1\sim 1:4$, when $w(\text{monomer}):w(\text{solvent})=1:2$, there is the best viscosity reducing effect.

2) The synthetic terpolymer viscosity reducer is better than the commercial viscosity reducers and the synthesized quadripolymers. At 50 °C, viscosity reduction rate is 95.5%.

3) When viscosity reducer is added, molecules of viscosity reducer interact with the molecules of heavy oil altering the original intermolecular structure of heavy oil, weakening its ability to form hydrogen bonds with hydroxyl or carboxyl groups, and hence the viscosity of the crude oil is reduced.

4) The results of field test showed that the relative savings rate of light oil was up to 44.5% after adding viscosity reducer, achieving good results.

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