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To cite this article: Lijun Zhu *et al* 2018 *IOP Conf. Ser.: Earth Environ. Sci.* **108** 022032

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Screening of Synthesis Conditions of Polymers and the Effects on Viscosity Reduction Performance

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Abstract. The optimum conditions were obtained by optimizing the reaction conditions of the polymerization. Under the conditions of monomer ratio of 1:1, the reaction temperature of 70 °C, the reaction time of 5h, self-polymers and binary copolymers of phenylethyl acrylate and styrene were prepared. By comparing the performance of viscosity reducer to heavy oil, the copolymer with octadecyl acrylate showed the best performance. When the viscosity reduction agent disperse heavy oil molecules, long chain can play a separation of heavy oil micelles, reduce friction, to prevent the combination of heavy oil molecules to achieve the role of viscosity reduction.

1. Introduction

With the increase in oil extraction, the proportion of heavy oil is growing. While the application of heavy oil problems will be placed in front [1]. Heavy oil is the crude oil with viscosity of more than 100mPa·s at the storage temperature of degassing [2]. Heavy oil is rich in colloid, asphaltene, and because of the high molecular weight of the colloid and asphaltene and the polarity is very strong, so they are easy to form hydrogen bonds between molecules, making the molecules have a strong cohesion, resulting in heavy oil cannot flow due to the greater internal friction. These cause the difficulties of mining and transporting of heavy oil [3].

At present, the method of reducing the viscosity of heavy oil is heating, emulsifying and adding viscosity reducing agent. Heating technology is relatively mature, but the energy consumption is too large, the cost is too high. Emulsification costs are lower, the effect is relatively good, but in use exposed some problems, such as dehydration [4]. The most promising technology is to add oil-soluble viscosity reducer, both to reduce the viscosity of heavy oil, the cost is relatively low [5]. There are few reports on oil-soluble viscosity reducers, most of which are reported on the use of a pour point depressant-based fluidity improver for high viscosity and high coagulation crude oil delivery, and the viscosity reduction effect is relatively poor [6-9].

Recently, the research direction of oil-soluble viscosity reducers has been to increase the polarity of the existing ester-type molecular skeleton [10], so that it can be combined with colloid or asphaltene molecules with stronger hydrogen bonding, or Surfactant group [11], the use of its spatial effect and



reduce the interfacial tension of the ability to change the nature of glial and asphaltene to improve the wax, glial, asphaltene dispersion, so as to reduce the viscosity of the purpose [12].

Since most of the viscosity reducer studied was developed on the basis of the pour point depressant, the viscosity reducer was only effective for heavy oil with low wax content, and when the temperature increased, the viscosity reduction effect would change Poor, and even sticky. The fluidity improver has no significant viscosity reduction effect on both heavy and super heavy oils.

Therefore, the development of new molecular structure of the polymer viscosity reducing agent to improve the rate of heavy oil production and reduce the cost of mining and transportation is of great significance. In this paper, the synthesis method of polymer viscosity reducer was studied, and then the viscosity reduction effect of new ethyl acrylate was compared. The development of new viscosity reducer has a reference.

2. Experimental Section

The raw materials and reagents used were of analytical grade and were not further purified. The molecular weight was determined by the gelatin chromatograph (GPC) of Water. The viscosity of heavy oil before and after viscosity reducer treatment was measured by Brookfield R/S plus rheometer.

2.1. Polymerization

The monomers were scaled and accurately weighed and added to a three-necked flask. Install a condenser on a three-necked flask with a rotor. Add toluene as a solvent, from the glass tube to the device through the nitrogen, the reaction in the anaerobic conditions for 30min, you can see the reaction were all dissolved in toluene.

After 30 min of nitrogen, the initiator azobisisobutyronitrile (AIBN) was added (the mass was 1% of the total mass of the reactants). After further nitrogen for 2 min, the device was placed in an oil bath and slowly heated to 70 °C. When the temperature reaches the reaction temperature, turn off the nitrogen. The reaction was carried out at that temperature for 5 h.

2.2. Separation and purification of polymerization products

After the reaction, stop heating. The reaction product was slowly dropped into a large amount of methanol using a dropper and stirred rapidly. The reactor was rinsed with a small amount of toluene and the remaining product was transferred to methanol. After stirring for 2 h, the polymer was completely precipitated. Stirring was stopped, suction filtered by a Buchner funnel, dried and weighed to obtain a polymer.

2.3. Determination of molecular weight

The 10 mg of the polymer was placed in a centrifuge tube and 2 mL of tetrahydrofuran (HPLC) was added. The drug was completely dissolved in tetrahydrofuran and placed in a 5.0 mg / mL sample solution. Match the sample with a needle filter. Measure 150 ~ 200mL filtered sample, into the injector, turn the handle, the instrument began to record the signal. After the test, select the calculation method, the integration area, calculate the molecular weight and record.

2.4. Evaluation method of performance of viscosity reducer []

The 0.4 mL solution of VRA in toluene was transferred into the 25-g dilution oil, which is the mixture of heavy oil and kerosene with ratio of 9:1 (wt), the content of VRA in dilution oil was 500 µg·g⁻¹. A Brookfield r/s plus rheometer with flat part was used for determination of the viscosity of the heavy oil at 60 °C before and after viscosity reduction treatment. The viscosity reduction rate (VRR) was calculated with respect to heavy oil without VRA only [13].

Viscosity reduction rate

$$(VRR)=100\times(\eta_0-\eta)/\eta_0 \quad (1)$$

3. Results and Discussion

In order to obtain the polymer with yield relatively high and large molecule weight, the influence of the reaction conditions on the polymerization reaction is explored, and finally the optimal viscosity reducing agent polymerization conditions are obtained. The polymerization of octadecyl acrylate and styrene was carried out to explore the optimal reaction conditions.

3.1. Effect of Synthesis Time on the Yield of Viscosity Reducer

At the condition of reaction temperature of 70 °C and monomer ratio of 1: 1, change the reaction time, synthesis of a series of polymers, calculate the yield of viscosity reducer, the experimental results in Table 1.

Table 1. Effect of Synthesis Time on the Yield of Viscosity Reducer

Reaction time	Total mass of monomer/g	The amount of product/g	Yield/%
3 h	2.14	0.255	11.94
4 h	2.14	0.590	27.58
5 h	1.07	0.696	64.81
6 h	1.23	0.767	62.33

As can be seen from Table 1, the yield of the polymer in a certain range, with the increase in time, but after 5h, the polymer yields no longer change with time, remained stable. Indicating that after 5h polymerization is basically completed; the product is no longer increased. In terms of reaction yield, the optimum polymerization time was 5 h.

3.2. Effect of reaction temperature on the yield of viscosity reducer

Under the condition of reaction time of 5h and monomer ratio of 1: 1, the reaction temperature was changed, and a series of polymers were synthesized to calculate the yield of viscosity reducer. The experimental results are shown in Table 2.

Table 2. Effect of reaction temperature on the yield of viscosity reducer

Temperature °C	Total mass of monomer / g	The amount of product / g	Yield /%
60	2.04	0.201	9.85
70	1.07	0.696	64.81
80	2.14	1.087	50.81
90	2.14	0.916	42.78

It can be seen from Table 4-2 that the yield of the polymer increases first and then decreases with the increase of the polymerization temperature, reaching its peak at 70 °C. In terms of reaction yield, the optimum polymerization temperature was 70 °C.

3.3. Effect of monomer ratio on the yield of viscosity reducer

Under the condition of reaction time of 5 hours and reaction temperature of 70 °C, change the monomer ratio, synthesize a series of polymers, and calculate the yield of viscosity reducer, the experimental results in Table 3.

Table 3. Effect of monomer ratio on the yield of viscosity reducer

The proportion of the monomer	Total mass of monomer / g	The amount of product / g	Yield /%
1:1	1.073	0.696	64.81
1:2	2.130	0.893	41.90
1:3	1.908	0.589	30.58
1:4	2.221	0.878	39.56

It can be seen from Table 3 that the effect on the yield of the copolymer is different when the polymerization reaction is carried out at different monomer ratios and does not show a certain law. In the case of the reaction yield alone, the optimum polymerization reaction has a monomer ratio of 1: 1.

3.4. Synthesis of homopolymerize of the monomer

In order to investigate the viscosity reduction effect of homopolymer, all the monomers were self-aggregated to calculate their yield. The experimental results are shown in Table 4.

Table 4. Synthesis of monomer homopolymer

Polymer	Monomer	Monomers/g	Product/g	Yield /%	Molecular weight
1	Octadecyl acrylate	2.000	1.515	75.75	32654
2	Styrene	2.000	0.531	26.53	53284

As can be seen from Table 4, when the monomer is self-polymerized, the yield of the octadecyl acrylate self-polymer is higher, while the styrene yield is low, only about 26.53%, the yield is low. The resulting polymer molecular weight gap is larger.

3.5. Synthesis of binary copolymer

In order to investigate the properties of binary polymerization, octadecyl acrylate, phenylethyl acrylate and styrene were copolymerized in two parts, and the yield and molecular weight were calculated. The experimental results are shown in Table 5.

Table 5. Synthesis of polymer monomer binary copolymer

Polymer	Monomer	Monomers/g	Product/g	Yield /%	Molecular weight
3	Octadecyl acrylate, styrene	1.073	0.696	64.81	22971
4	Phenethyl acrylate, styrene	2.021	1.524	75.41	19759
5	Phenethyl acrylate, octadecyl acrylate	2.021	1.618	80.07	7353

As can be seen from Table 5, when the monomer is subjected to binary copolymerization, the yield is high, but the molecular weight is quite different, indicating that the substrate is different when the monomer is different. Under the same conditions, the amount of polymer and the reaction rate of the polymer are different and lead to different molecular weights.

3.6. Performance evaluation of viscosity reducer

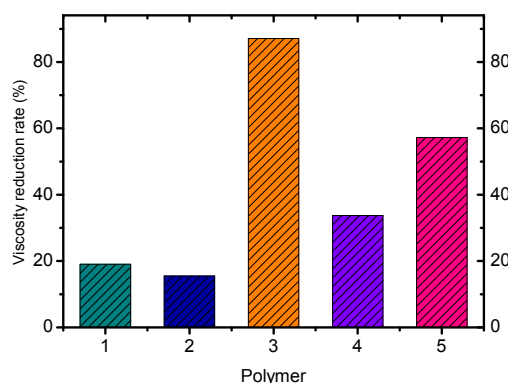


Fig. 1 The viscosity reduction properties of the polymer (1#-5#) to heavy oil

The viscosity reducer was evaluated by the experimental part, and the viscosity reduction was shown in Fig1. From the viscosity reduction performance of the viscosity reducer (Fig. 1), it can be seen that the viscosity reduction of No. 3 polymer (copolymer of octadecyl acrylate and styrene copolymer) is the best, and the No. 5 polymer (opolymer of phenethyl acrylate and octadecyl acrylate) is the second.

From the structural analysis, in octadecyl acrylate monomer, octadecyl alcohol has a long alkyl chain. Therefore, when the viscosity reduction agent **disperses** heavy oil molecules, long chain can play a separation of heavy oil micelles, reduce friction, to prevent the combination of heavy oil molecules to achieve the role of viscosity reduction [1].

4. Conclusion

The optimum conditions were obtained by optimizing the reaction conditions of the polymerization. Under the conditions of polymer monomer ratio of 1: 1, the reaction temperature of 70 °C, the reaction time of 5h, self-polymers and binary copolymers of phenylethyl acrylate and styrene were prepared. By comparing the performance of viscosity reducer to heavy oil, the copolymer with octadecyl acrylate showed the best performance. When the viscosity reduction agent disperses heavy oil molecules, long chain can play a separation of heavy oil micelles, reduce friction, to prevent the combination of heavy oil molecules to achieve the role of viscosity reduction.

Acknowledgments

This work is supported by the Fundamental Research Funds for the Central Universities of China (15CX02029A). The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper. Correspondence to: Zhu Li-Jun (E-mail: zhulj2002@163.com).

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