



Research of a novel double cross-linking fracturing fluid

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Abstract

A kind of JDL-1 thickener for betaine hydrophobic association polymer was prepared by aqueous solution polymerization of mixed micelles, AM, AA, AMPS and DM16 were used as raw materials, which was synthesized by redox initiator system. Friction tester and high-temperature rheometer were used to evaluate the resistance reduction and temperature and shear resistance of the thickener. The results show that the viscosity average molecular weight of the polymer prepared with AM, AA, AMPS and DM16 mass ratio of 70:20:5:5 was higher than 12 million, and the dissolution time of the polymer was less than 3 min. When the surfactant is used for physical cross-linking, the apparent viscosity of the cross-linked fracturing fluid is larger than that of 60 mPa·s at 90 °C, 170 s⁻¹ sheared 1 h; when metal cross-linking agent is used for coordination cross-linking, the apparent viscosity is larger than that of 80 mPa·s at 120 °C, 170 s⁻¹ sheared 1 h. The drag reduction rate was 73%, the anti-swelling rate was higher than 70%, and the damage rate was less than 10%. The field trial was successful and confirmed the multifunctional effect of betaine-type hydrophobic associating polymer.

Keywords Thickener · Physical cross-linking · Coordination cross-linking · Multifunctional effect

Introduction

Fracturing fluid is a very important fluid for fracture and sand carrying during fracturing. Traditional fracturing fluid is mainly guar gum fracturing fluid (Li et al. 2019; Elkattatny et al. 2018). However, guar gum is becoming more and more expensive. Meanwhile, with the development of unconventional oil and gas such as shale gas, tight gas and shale oil, new requirements are put forward for its the performance (Allison 2016; Wallace and Fritsch 2009; Bi et al. 2013; Zhao and Dong 2016). In order to meet the fracturing requirements of complex formations, the fracturing fluids should be reformed and strengthened. Therefore, it is necessary to study new fracturing fluid system (Qun et al. 2020; Yang and Hou 2020; Mpelwa et al. 2020; Cai Bo and Yun 2018; Yang et al. 2015; Wang et al. 2019).

The main way to exploit shale gas is volume fracturing, which is characterized by large displacement and large liquid volume. In order to meet the requirements of “large volume reconstruction” and “high filling rate”, large-scale horizontal well volume fracturing of shale gas reservoir is usually carried out by using slippery water and gel fluid system. At present, the slick water and gel fluid system are prepared separately, and each section needs to be prepared in advance. The process is complex, the operation is difficult, and the fracturing efficiency is low. Generally, the drag reducer for slippery water is linear anionic polymer of polyacrylamide, which can quickly dissolve and increase viscosity, and can realize on-line mixing; the thickener for glue liquid is anionic hydrophobically associating polyacrylamide copolymer, which has slow dissolution speed and poor friction reduction effect, and cannot be used as drag reducer for slippery water. For a fracturing fluid system, thickener and cross-linker are the functional main agents. The properties of fracturing fluid depend not only on the molecular structure of thickener, but also on the cross-linking structure formed by polymer and cross-linking agent. In this paper, in order to improve the efficiency of field operation and solve the problem of single effect of traditional thickener, a thickener was prepared by aqueous solution polymerization method. What we focus on is the viscosity of the fracturing fluid system which is

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different by using surfactants and metal cross-linkers. It proves that one dose of thickener is multi-purpose.

Materials and methods

Experimental materials

All reagents were used without further purification. Acrylamide (AM) was purchased from Zhejiang Xinyong Biochemical Co., Ltd.; acrylic acid (AA), 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and dimethyldiallyl ammonium chloride (DM16) were purchased from Hangzhou Yinhu Chemical Co., Ltd. Sodium hydroxide, potassium persulfate (KPS), sodium bisulfite and water-soluble azo (V50) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The rheological properties of the liquid were determined by the Rheostess-6000 rheometer from Thermo Haake, Germany (www.thermo.com). The friction of the pipeline was determined by mz-iv fracturing fluid friction tester (sykyyq.uooioo.com). The viscosity of Newtonian fluid and non-Newtonian fluid was observed using the Znn-D6B electric six speed rotary viscometer (<http://www.tongchunhunsy.com/>).

Synthesis of thickener

The thickener was synthesized by aqueous solution polymerization. Firstly, added the monomer and additives into the beaker according to the design amount, then added appropriate amount of pure water to make the total monomer concentration of 26%, neutralized with NaOH to pH = 7 and stirred until completely dissolved. When the temperature of the solution was cooled to 20 °C, the oxygen was completely removed by injecting nitrogen for 30 min. Secondly, the redox initiator composed of potassium persulfate (KPS) and sodium bisulfite was slowly added, and it was fully stirred until the solution was evenly mixed, and then continued to ventilate nitrogen for 5 min. After sealing the beaker and holding for a period of time, the colloidal polymer was obtained. Thirdly, removed the polymer and cut it with scissors, washed it with anhydrous ethanol, soaked it for 24 h and then dry it in a 50 °C oven for constant weight. Finally, it was crushed and passed through 60 mesh sieve to obtain a white granular thickener.

Viscosity average molecular weight

According to the national standard, the intrinsic viscosity of polymer was measured by glass capillary viscometer, and the average molecular weight of polymer was calculated.

Drag reduction rate

Drag reduction was measured using a friction tester. The test pipeline system consists of screw pump, mixing tank and test pipe section. During the experiment, the fracturing fluid was put into the mixing tank, pumped into the test pipe section by a screw pump at a certain flow and then returned to the mixing tank for circulation. If necessary, a closed loop can also be performed. The flow rate was controlled by the frequency converter, and the inlet and outlet pressure of the test pipe section could be automatically collected by the computer. The drag reduction rate η was computed by

$$\eta = \frac{\Delta P_{\text{water}} - \Delta P}{\Delta P_{\text{water}}} \times 100\% \quad (1)$$

where ΔP_{water} was the pressure drop of water passing through the test pipeline, MPa; and ΔP was the pressure drop of fracturing fluid passing through the test pipeline at the same flow rate, MPa.

Temperature resistance and shear resistance

The rheometer started at 70 °C, the temperature rising speed was controlled to 3 °C/min \pm 0.2 °C/min, the shear rate of the rotor was adjusted to 170/s, and the fracturing fluid was continuously sheared under heating. Record the change of fracturing fluid viscosity with the increase in temperature.

Apparent viscosity

According to the industry standard “SY/T 5107–2016 performance evaluation method of water-based fracturing fluid” (SY, T5107–2016 performance evaluation method of water-based fracturing fluid. xxxx), the base fluid was prepared and its viscosity was measured by six speed viscometer at 100 rpm.

Anti-dilatation property

By simulating the real situation of the reservoir, the anti-dilatation property was measured by the anti-dilatation test tube method. After gel breaking and cooling, the multi-functional double cross-linking fracturing fluid is filtered. Took 3 anti-dilatation test tubes (No. 1, 2 and 3) and 1 g of formation core powder (accurate to 0.01 g) was added, respectively. Then, added 5 ml of kerosene to No.1, added 5 ml of filtered gel breaker to No.2, added 5 ml of distilled water to No.3, stirred well with a glass rod for 5 min, put it in an oven at 50 °C for 24 h and read settling volume the anti-dilatation test tube. The evaluation procedure of 70 °C fracturing fluid was the same. Finally, it was placed in an

oven at 70 °C for 24 h, and then, the sedimentation volume in the anti-dilatation test tube was read. The anti-dilatation property B was computed by

$$B = \frac{V_2 - V_1}{V_2 - V_0} \times 100\% \quad (2)$$

where V_2 was the average settlement volume of core powder in No.3 anti-dilatation test tube, ml; V_1 was the average settlement volume of core powder in No.2 anti-dilatation test tube, ml; and V_0 was the average settlement volume of core powder in No. 1 anti-dilatation test tube, ml.

Core damage experiment

According to the industry standard “SY/T 5107–2016 performance evaluation method of water-based fracturing fluid”(SY, T5107–2016 performance evaluation method of water-based fracturing fluid. xxxx), the damage rate was evaluated with gel breaker at 50°C and 70°C.

Results and discussion

Optimization of monomer ratio for thickener synthesis

On the basis of conventional aqueous solution polymerization process, a series of monomer compositions and ratios were designed according to the performance requirements of fracturing fluid for quick dissolution, drag reduction, cross-linking and sand carrying, so as to ensure that the relative molecular weight (molecular chain length) of the thickener can be controlled in an appropriate range, and the polymer has “linear main chain, proper side chain, slightly rigid and hydrophilic strong” molecular structure. In this work, we studied the influence of monomer ratio on the relative molecular weight, dissolution time and cross-linking property of the synthesized thickener. Table 1 shows that the content of AA has an effect on both cross-linking and molecular weight. When the degree of hydrolysis was 30%, although the thickener had strong hydrophilicity

and dissolved quickly, there were too many cross-linking groups, which would easily cause structural collapse and white flocculation when zirconium cross-linking agent was used. In addition, when the contents of AMPS and DM16 were too high, the relative molecular weights of 1, 4 and 5 were less than 10 million due to the high steric hindrance of AMPS and DM16. The viscosity increasing ability and salt resistance of thickener could be improved by increasing the amount of DM16. However, when DM16 was excessive, it had a strong shielding effect on carboxylic acid group, which caused the solution not to be cross-linked by zirconium cross-linker. The comprehensive experimental results show that the best thickener is obtained when the mass ratio of AM, AA, AMPS and DM16 is 70:20:5:5. Its viscosity average molecular weight can reach more than 12 million, and it can be completely dissolved in less than 3 min. Moreover, it can be cross-linked and hung with zirconium cross-linking agent.

Measurement results of drag reduction rate

As can be observed in Fig. 1 that displays the relationship between the drag reduction rate and Reynolds number. With the increase in Reynolds number, the drag reduction rate increases to 73%, and there is still a rising trend. It is higher than the industry standard that the drag reduction rate is more than 50% (SY, T6376–2008. Low friction is required in large displacement fracturing operation. From the experimental results, the fracturing fluid not only meets the requirements of construction, but also reduces the difficulty of construction and the requirements of construction equipment.

Measurement results of the temperature resistance and shear resistance

Figures 2, 3 show the viscosity curve of multifunctional double cross-linked fracturing fluid with temperature. The physical cross-linking of surfactant is given in Fig. 2, and the thickener concentration is 0.35%. The curve shows that when the temperature is less than 80 °C, the viscosity of fracturing fluid decreases slowly with the increase in temperature;

Table 1 Results of monomer ratio optimization in thickener synthesis reaction

Serial number	Monomer mass ratio /%				Viscosity average molecular weight / ten thousand	Dissolution time /min	Cross-linking state
	AM	AA	AMPS	DM16			
1	55	30	10	5	760	<3	White catkins
2	65	20	10	5	1065	<3	Weak cross-linking
3	70	20	5	5	1280	<3	Pick and hang
4	65	20	5	10	885	<10	Non-cross-linking
5	65	20	10	5	976	<3	Weak cross-linking

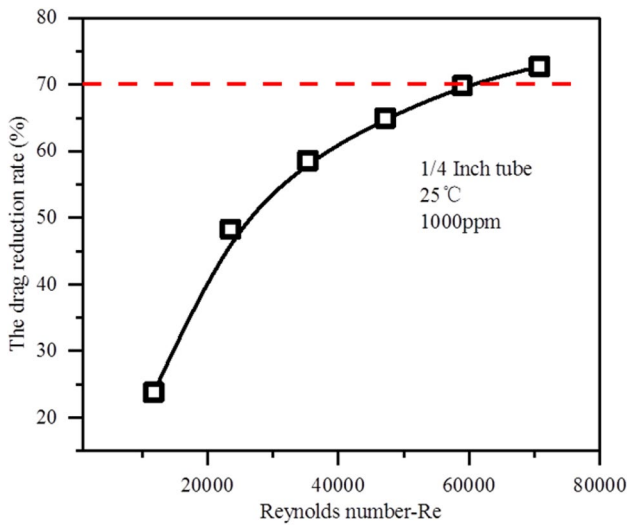


Fig. 1 Variation curve of drag reduction rate with Reynolds number

when the temperature is higher than 80 °C, the viscosity decreases relatively quickly; but when the temperature rises to 90 °C, the viscosity is still greater than 60 mPa.s. This is mainly due to the physical cross-linking with surfactants, and the long molecular chains in the solution are entangled with each other to form a network structure. In Fig. 3, a metal cross-linking agent is added along with changing concentration. The thickener concentration is 0.4%. It shows that the viscosity decreases with the increase in temperature. When the temperature is 120°C, the viscosity is still higher than 80 mPa.s. Because after adding metal cross-linking agent to the solution, the carboxyl groups have coordination reaction with metal cation to enhance the temperature resistance of fracturing fluid (Kalganekar and Patil (2012); Sokhanvrian et al. 2019).

Property measurement results of 50 °C and 70 °C multifunctional double cross-linked fracturing fluid

At 50 °C and 70 °C, the multifunctional double cross-linked fracturing fluid was evaluated according to various industry standards. Tables 2, 3 shows that the apparent viscosity

Fig. 2 Variation of viscosity with temperature by physical cross-linking

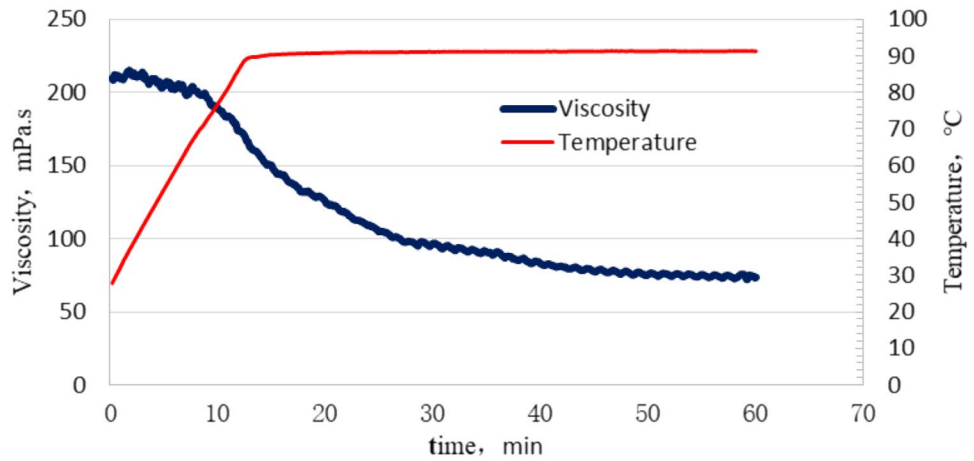
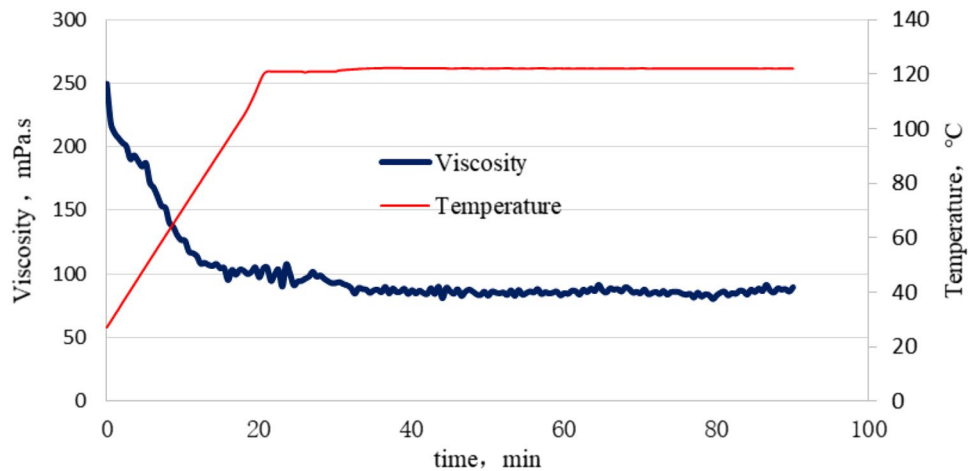


Fig. 3 Variation of viscosity with temperature by metal cross-linking



is 3 mPa·s, the anti-dilatation rate is 78% and 79%, it was increased by about 9% over the standard, and the core damage rate is about 10%. Evaluation results of the apparent viscosity, damage rate and anti-dilatation property of the fracturing fluid show that all meet the industry index.

Application to real construction

The construction section of Jin 5 Well is 2080.3–2085.4 m, and the thickness of "Materials and methods" Section is 4.2 m. According to the previous use of conventional fracturing fluid in this area, the reservoir natural fractures are more developed in this area, the fracturing fluid filtration is relatively large in the process of fracturing, the fracture width is not enough, and it is easy to sand plug. Multifunctional double cross-linking fracturing fluid was used. In the process of field application, low viscosity system is used to prepare drag reducing agent, and high viscosity system is used to prepare sand carrying fluid, which avoids

repeated switching during construction. According to the construction curve in Figs. (1, 4), the results showed that the construction displacement is 3~4 m³/min, the construction pressure is 40~50 MPa, and the highest sand carrying ratio is about 40%; 2) the average drag reduction rate is 72.5%, and the whole construction process is successfully completed without sand plugging, and the stable production capacity is good after fracturing; 3) the field trial was successful and confirmed the fracturing fluid can one agent multi-purpose.

After fracturing of Jin 5 Well, the well was opened immediately to drain fluid. After 140 m³ of fluid was discharged (the natural drainage rate could reach 55%), the formation pressure dropped to zero, and the micelle-breaking was well. Therefore, the multifunctional double cross-linked fracturing fluid was easy flowback and no residue after the micelle-breaking, which did low damage to the formation and achieved the effect of increasing oil and gas production.

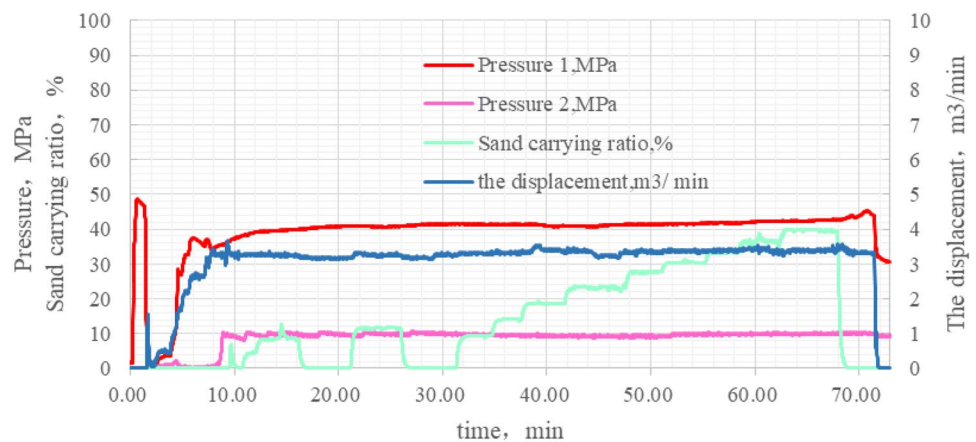
Table 2 Test results of 50°C multifunctional double cross-linked fracturing fluid

Serial number	Test project	Test execution standard	Performance index	Test result	Evaluate
1	Apparent viscosity, mPa·s	SY/T 5107–2016	≤5	3	Meet the standard
2	Anti-swelling rate, %	SY/T 5107–2016	≥70	78	Meet the standard
3	Core damage rate, %	SY/T 5107–2016	≤15	8.6	Meet the standard

Table 3 Test results of 70°C multifunctional double cross-linked fracturing fluid

Serial number	Test project	Test execution standard	Performance index	Test result	Evaluate
1	Apparent viscosity, mPa·s	SY/T 5107–2016	≤5	3	Meet the standard
2	Anti-swelling rate, %	SY/T 5107–2016	≥70	79	Meet the standard
3	Core damage rate, %	SY/T 5107–2016	≤15	9.1	Meet the standard

Fig. 4 Fracturing operation curve of well Jin 5



Conclusions

In this work, a betaine-type hydrophobic associating polymer JDL-1 thickener was synthesized in the laboratory. Due to its hydrophobic side group, the thickener could meet all of requirements of instant dissolution, drag reduction, cross-linking and sand carrying. Combined with laboratory evaluation and field application, the fracturing fluid system composed of JDL-1 thickener has the following advantages:

1. With the increase in Reynolds number, the drag reduction rate increases to 73%, and there is still a rising trend. It was increased by 23% over standard treatments. The apparent viscosity, damage rate and anti-dilatation property of the fracturing fluid show that all meet the industry index. The anti-dilatation rate was increased by about 9% over the standard
2. It has the dual functions of association and coordination. In the laboratory, when the surfactant is used for association, the viscosity of the system was kept above 60 mPa·s after continuous sheared for one hour under the condition of 170 s^{-1} at $90 \text{ }^\circ\text{C}$; when metal cross-linking agent is used for coordination, the viscosity of the system was kept above 80 mPa·s after continuous sheared for one hour under the condition of 170 s^{-1} at $120 \text{ }^\circ\text{C}$.
3. In the process of field application, low viscosity system is used to prepare drag reducing agent, and high viscosity system is used to prepare sand carrying fluid, which avoids repeated switching during construction and realizes one agent multi-purpose. The field trial was successful and confirmed the multifunctional effect of betaine-type hydrophobic associating polymer.

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Author contributions Yanrong Ge and Zhongcong Zhao designed and supervised the experiments. Xiaoliang Cheng, Tao Liu and Tengfei Chen carried out the field application. Yanrong Ge synthesized the thickener. Xiupeng Guo performed the monomer optimizational experiments. Yanrong Ge and Zhongcong Zhao evaluated the performance of fracturing fluid. All authors contributed to analyze and discuss the data. Yanrong Ge and Zhongcong Zhao wrote and edited the manuscript. All authors reviewed and approved the final manuscript.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Allison E (2016) United States Experience Regulating Unconventional Oil and Gas Development. Society of Petroleum Engineers
- Bi HB, Wang YX, Wu GG, Zhang J, Duan XW, Sun GB (2013) Discussion on unconventional petroleum reserves classification and evaluation in China. *Int Petrol Technol Conf*. <https://doi.org/10.2523/IPTC-17193-MS>
- Cai Bo Xu, Yun WX et al (2018) A new high temperature polymer fracturing fluid. *IOP Conf Series: Earth Env Sci* 186(4):012028
- Elkatatny S, Mahmoud M, Abdelgawad K (2018) Reaction of chelating agents with guar gum polymer for completion fluid. *Arab J Sci Eng* 43(11):6481–6491
- Kalgaonkar RA, Patil PR (2012) Performance enhancements in metal-crosslinked fracturing fluids. *Soc Petrol Eng*. <https://doi.org/10.2118/152040-MS>
- Li Y, Guo J, Wang S (2019) The damage mechanisms of fracturing fluid on production in tight gas reservoirs. *Energy Procedia* 158:5988–5993
- Mpelwa M, Zheng Y, Tang S et al (2020) Performance optimization for the viscoelastic surfactant using nanoparticles for fracturing fluids. *Chem Eng Commun* 207(10):1474–1482
- Qun LEI, Dingwei WENG, Baoshan GUAN et al (2020) A novel approach of tight oil reservoirs stimulation based on fracture controlling optimization and design. *Petrol Explor Dev* 47(3):632–641
- SY/T 5107–2016 performance evaluation method of water-based fracturing fluid
- SY / t6376–2008 general specification for fracturing fluids
- Sokhanvrian K, Nasr-El-Din HA, Harper TL (2019) Effect of ligand type attached to zirconium-based crosslinkers and the effect of a new dual crosslinker on the properties of crosslinked carboxymethylhydroxypropylguar. *Soc Petrol Eng*. <https://doi.org/10.2118/194204-PA>
- Wallace J, Fritsch JW (2009) Expanding solutions for unconventional oil and gas recovery. *Soc Petrol Eng*. <https://doi.org/10.2118/123598-MS>
- Wang J, Yao E, Qiu Y, Zhou F, Wang Z, Zhang L, Wang R (2019) Research and evaluation of a novel low friction, high density and high temperature resistance fracturing fluids system. American Rock Mechanics Association
- Yang J, Cui W, Duan Y, Yang Z, Qiu X, Guan B, Bai J (2015) Successful application of a new fracturing fluid with supramolecular

complex structure. Soc Petrol Eng. <https://doi.org/10.2118/174753-MS>

Yang J, Hou J (2020) Synthesis of erucic amide propyl betaine compound fracturing fluid system. Coll Surf A: Physicochem Eng Asp 602:125098

Zhao B, Dong S (2016) Progresses and challenges in oil and gas exploration in China. Society of Exploration Geophysicists

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