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A New Thickener for CO_2 Anhydrous Fracturing Fluid

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Abstract. CO_2 dry fracturing technology is well-known for its advantages. Little water is used in this technology, which is able to ease the pressure of consumption on water resources. Many abroad theoretical researches, laboratory experiments and field tests have been taken to explore the yield mechanism, the adaptability and the technology of pure liquid CO_2 fracturing. These achievements have been applied to a variety of reservoirs transformation and improven the effectiveness of stimulation treatment in a degree. The researches and studies in the domestic didn't get popular until recent years. Thus, this article firstly introduces the main development and application about pure CO_2 anhydrous fracturing technology, and sums up the effect and evaluation of its fluid through application examples both in the domestic and abroad. However, although this technology has many excellent qualities, but systematic studies indicate that its proppant-carrying capacity is less competitive because of the low viscosity of pure CO_2 liquid and other reasons. In a consequence, it is necessary to develop an appropriate thickener for CO_2 anhydrous fracturing fluid to improve its carrying capacity. Then this article describes some studies of previous scholars about CO_2 thickener. Then we put forward our own research ideas and transform it into actual experiments. Thanks to the valid performances of these tests, we successfully develop a thickener X and cosolvent B.

1 INTRODUCTION

Supercritical CO_2 has many unique properties, and there are many advantages to replace the conven –tional water-based gel fracturing fluid with supercritical CO_2 fracturing fluid to create fractures and carry proppants[1]. This technique doesn't contain water and is easy to flow back with little residue left. It can not only improve the effectiveness of stimulation treatment but also reduce environmental pollution and the consumption of water resources. In the early 1860s, liquid CO_2 began to be used in the oil and gas industries and attract some people to conduct a number of studies[2-3]. Its exploration and application in the domestic start in the recent years[4-7]. According to American and Canadian studies and applications[8-12] in recent decades, taking pure CO_2 liquid as the fracturing fluid is many times more efficient than other fracturing fluids; nevertheless, it also has some conspicuous drawback.
The viscosity of supercritical CO_2 liquid is only about 0.02MPa • s, which is a negative factor for carrying proppants, generating a much width fracture and reducing the amount of fracturing fluid loss. Therefore, it is necessary to develop an economic and efficient thickener for supercritical CO_2 anhydrous fracturing fluid to improve its prop-carrying capacity. There are many researches in this area[13-15] at home and abroad. Although every of them does have certain effects, some of them have high requirement to pressure, temperature, concentration and other conditions, some costs are too high, and some even have a certain toxicity. The development of CO_2 thickener has always been the challenge to the scientific community. It currently seems like that ionic surfactant and block copolymer have their potential applications.

2. The Development of the Thickener for Liquid CO_2 Fracturing Fluid

2.1 The molecular structure design of the thickener's main agent

Since the viscosity of a non-Newtonian fluid changes with the shear rate, the rheological properties of these fluids cannot be accurately predicted by common methods like capillary tube technique, a method to

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measure the viscosities. In fact, we usually make use of a rotary viscometer to measure the viscosity of a non-Newtonian fluid.

The main mechanism of CO_2 Thickener is to assemble polymers or surfactants with the molecules of CO_2 into a three-dimensional network structure. Moreover, the polymers or surfactants must contain the functional groups that can react with CO_2 molecules through bonding connections. As a result, in order to develop an efficient modifier for the viscosity of CO_2 liquid, the design of effective functional groups of the polymers and the surfactants, which can be miscible with CO_2, and the three-dimensional self-assembled structures become the key points.

The most valid design proposal to increase the viscosity of supercritical CO_2 liquid is to add chemicals which have good intermiscibilities with CO_2. When dissolved in the liquid of supercritical CO_2, some super-polymers can increase the viscosity of the solvent greatly by twining their special molecular structure, like a hair, among different polymers' chains. But the CO_2 liquid is a very stable solvent, and it has a very low dielectric constant, viscosity and surficial tension, the normal solvent cannot get matched with it. Though, glycol and other solvents may be miscible, the changes of the CO_2 liquid in physical and chemical properties are very limited. That's why we need to design the ionic or polar chemical additives with the functional group connecting CO_2. With the strong inter-reaction force among different molecular groups of the chemical agent, its physical and chemical properties will get improved.

Considering the pros and cons of a thickener, we devised a new thickener named X, which show its merits in three advantages. It contributes for a more environmentally friendly fracturing fluid. And its molecular amphiphilic structure will form vermicular micelles in a CO_2 liquid. So it can greatly increase the viscosity without too much loss of dissolving capacity. What's more, it has a oil wettability so that its vermicular micelles will break up in the oil, thereby reducing the viscosity, stimulating its flowback and curtailing the damage to reservoir.

2.2 Basic materials

Agent A (chemically pure), Agent C (chemically pure), Xylene (chemically pure), Co -solvent B (AR), Azobisisobutyronitrile (AIBN, chemically pure), Solvent oil 120 # ,

All the raw materials are purchased from Sinopharm Chemical Reagents Co. Ltd.

2.3 Synthesis Procedure

(1) Fill each of four reagent bottles with 50g agent A, 45g agent C and 95g xylene, then stir well.

(2) Import nitrogen continually for 1hour, and improve the temperature to 70℃.

(3) Drop a mixture solution containing 1g azobisisobutyronitrile and 10g cosolvent B in 2 hours.

(4) After dropwise finishing, raise the temperature to 85℃ and keep the reaction continuing for 4 hours. Then you will get a transparent viscous liquid.

(5) Cool down the liquid and input 95g solvent oil 120 # in the liquid. Then stir well.

Finally, you can get the finished product - the thickener.

2.4 The co-solvent for the thickener

The solubility parameter is defined as the square root of the cohesive energy density, reflecting the degree of molecular cohesion (the intermolecular force). It is widely used to explain and predict the thermodynamic behavior of the solution. Two materials with similar solubility parameters are more prone to be miscible. Maybe, the solubility parameter of supercritical CO_2 liquid can reach that of liquid alkanes, aromatics, benzene and toluene by adjusting the temperature and the pressure, but it is still far lower than the solubility parameters of methanol, ethanol, acetone, formic acid and other polar solvents. Thus, it is difficult to significantly improve the solubility parameter of CO_2 liquid by simply increasing the pressure and the temperature greatly. The study results have shown that adding a small amount of cosolvent in supercritical CO_2 liquid can not only maintain continuous adjustment of the solubility parameter of the fluid, but also improve the solubility parameter of the mixed fluid. This impact is more particularly obvious in polar solvents which have higher solubility parameters than CO_2 liquid, such as methanol and ethanol. It is more likely to form a special force between the polar solutes and the polar cosolvents, which can increase the solubility and selectivity of the solute. Considering various factors, the cosolvent B is more appropriate for the experiments.

3. The Testing of the X-Thickener's Performance

The solubility experimental results show that, X-thickener is insoluble in water and has a significant stratification phenomenon in water but is fusible in kerosene and crude oil and can be completely miscible in them.

Besides, X-Thickener does a few damages to low permeable sandstone cores. Its average damage rate is low, only 0.98%, indicating that the CO_2 thickener has good compatibility with the formation.

In addition, the viscosity experimental results indicate that X-thickener has a very high viscosity at a low temperature. Although the viscosity of X-thickener gradually decreases with the increasing temperature, it is still above 1500mPa • s.

According to the rheological studies of X-thickener, HAAKE6000 rheometer is taken to measure rheological parameters n and K of X-thickener at different temperatures. The results is shown in Figure 1. From the experimental results, we can find that when the temperature of the liquid is between 40℃ and 90℃, the shear stress is in a linear relation with the shear rate and the curve passes through the origin, which indicates that the X-thickener to CO_2 liquid is Newtonian fluid at this moment. But when the temperature reaches 100℃, X-thickener presents shear thinning.

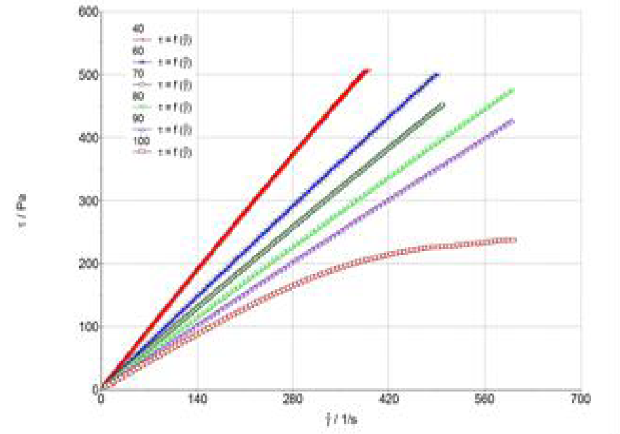

Fig.1 The rheologies of X-thickener at different temperatures

4. The Rheology Experiments of CO_2 Anhydrous Fracturing Fluid

4.1 Laboratory reagents

In this experimental phase, thickener X and co-solvent B are the main agents.

4.2 Laboratory apparatuses

The core apparatus of this experiment is a MARS II modular rheometre made by Thermo HaaKe Company in Germany. The rheometer can tolerate a high temperatures up to 200 ℃ and withstand a maximum pressures of 40MPa. It adopts a software system called D400/ 300 and an external magnetic system named D400/300. Of course, besides the rheometre, a piston container and a hand pump are necessary.

4.3 Experimental run

The mechanism of the experiment is to utilize a piston container to elevate the pressure of CO_2 to the required pressure and then take the rheometre to test the CO_2 liquid's rheology. The specific installation of the system is as follows. CO_2 cylinders, the piston container, and the rheometre measuring cup are connected with each other through a six-way valve. And there is a pressure gauge and an air bleeding valve installed on the top of the rhometre measuring cup. When you open the valve, CO_2 will enter into the piston container from the cylinders, draining away the water at the bottom of the piston container. Then, close the CO_2 cylinder's valve and push the water into the bottom of the piston container by the hand pump. The piston will move toward and compress the CO_2 gas until the pressure of the gas hits the required value. Then CO_2 can go into the measuring cup if the release valve of the rheometer measuring cup opens. Finally, turn off the air bleeding valve and test the CO_2 liquid's rheology.

4.4 Laboratory data

Mix up the thickener X with co-solvents B at a ratio of 1: 9. The gelling agent occupies 2.5% of the total liquid which accounting for 25% of the rheometre measuring cup. After installing the whole test system, choose the 35th rotors to test. With the assistance of the hand pump, adjust the pressure of CO_2 in the cup upward to 23MPa, and keep the testing temperature at 60℃. The shear rate over the experiments is 100/S and comparatively stable. The pressure curve and the rheological diagram during this experiment are shown in Figure 2 and Figure 3 respectively. Over the experiment do the system pressure keep stable around 28~29MPa, and the viscosity is relatively stable, with an average of 13.76 mPa • s.

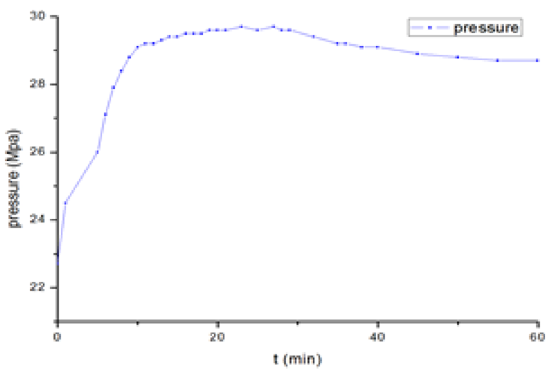

Fig.2 Pressure - Time Curve

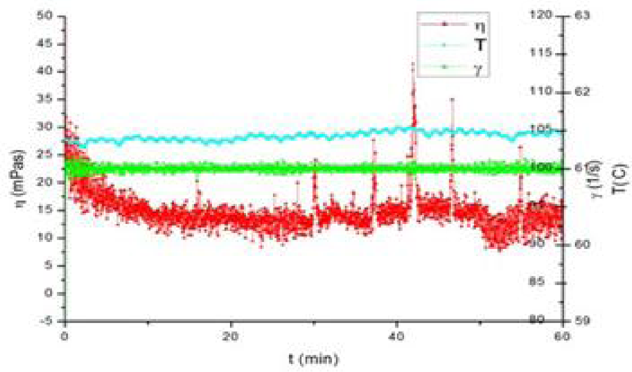

Fig.3 Temperature (blue) / the Shear Rate (green) / the viscosity (red) - Time Curve

According to the same principle, by changing the reagent concentration, the mass ratio, the pressure, the temperature and other conditions, we test the viscosities under different conditions, which are summarized in Table 1. Taking the cost and thickening effect factors into account, we focused on the parameters around the mass fraction of the thickener X of 1%, 28 MPa, 60 ℃.

Table.1 Rheological Experimental Data

No.	P (MPa)	T(℃)	MX (g)	MB (g)	∝	η (%)	Μ (mPa•s)
1	28	60	0.18	0.28	2:3	0.2 45	1.27
2	28	60	0.41	0.60	2:3	0.5 2	4.13
3	28	60	0.75	3.01	1:4	1	7.36
4	28	60	0.85	1.27	2:3	1.1 3	9.56
5	28	60	1.12	1.69	2:3	1.5	11.23
6	28	60	1.5	2.25	2:3	2	12.87
7	28	60	1.88	16.92	1:9	2.5	13.76
8	28	90	0.73	1.13	2:3	1	5.20
9	28	75	0.74	1.12	2:3	1	6.52
10	28	45	0.73	1.12	2:3	1	7.74
11	28	30	0.74	1.13	2:3	1	8.82
12	24	60	0.74	1.13	2:3	1	6.81
13	20	60	0.74	1.14	2:3	1	5.73
14	15	60	0.75	1.13	2:3	1	3.77
15	10	60	0.76	1.14	2:3	1	2.21

Note: P — Pressure, T — Temperature, MX — X-thickener's Mass, MB—Co-solvent B's Mass,

∝—The Mass Ratio of Thickener X and Cosolvent B,

η—The Mass Fraction of X-Thickener,

μ—Viscosity

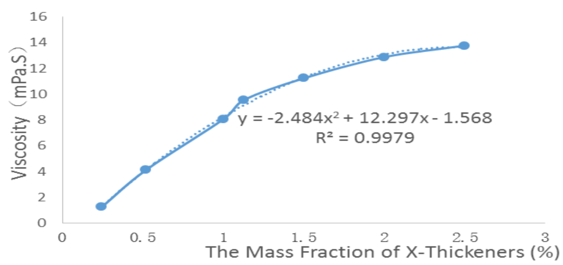

Fig.4 The Impact of X-Thickener's Mass Fraction on Viscosity (60 ℃, 28 MPa)

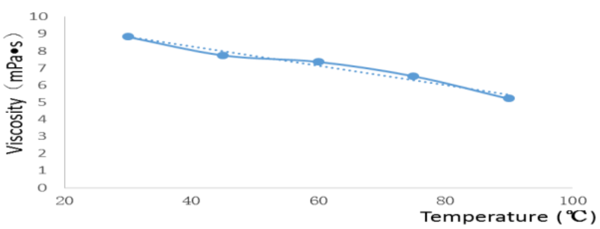

Fig.5 The Impact of Temperature on Viscosity (1% Mass Fraction of X-thickener, 28 MPa)

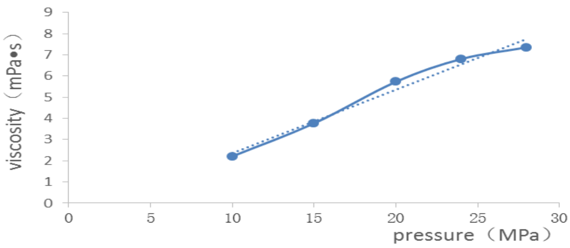

Fig.6 The Impact of Pressure on Viscosity (1% Mass Fraction of X-thickener, 60℃)

(1) Under conditions of 60℃ and 28 MPa, when the mass fraction of X-Thickener rises to 2.5% from 0.245%, the viscosity of the solution correspondingly rises from 1.27 mPa • s to 13.76 mPa • s. As is shown in Figure 4, the mass fraction of X-Thickener plays a major role to the solution's viscosity. The viscosity of the solution is continuously adjustable so that it is able to meet the needs of the carrying fracturing in applications.

(2) Under conditions of 28 MPa and 1% mass fraction of X-Thickener, as is shown in Figure 5, when the temperature rises from 30℃ to 90 ℃, the viscosity of the fracturing fluid decreases from 8.82 mPa • s to 5.20 mPa • s. To draw a conclusion, the viscosity of the fracturing fluid was negatively correlated with temperature.

(3) Under conditions of 60℃ and 1% mass fraction of X-Thickener, as is shown in Figure 6, when pressure rises from 10MPa to 28MPa, the viscosity of the fracturing fluid also rises significantly from 2.21 mPa • s to 7.36 mPa • s. In this case, the viscosity of the fracturing fluid has a significant positive correlation with pressure.

5. Conclusions and recommendations

This project mainly studies supercritical CO_2, utilizing a designed and assembled CO_2 viscosity testing device. By selecting various thickeners, it develops and optimizes a gelling agent system, including thickener X and cosolvent B, and thickener X has a good intermiscibility co-solvent B. Then it conducted many relevant experiments to test corresponding rheological properties of the CO_2 and drew the following conclusions.

(1) The unique molecular amphiphilic structure of X-thickener is miscible well in the supercriticle CO_2 liquid by forming vermicular micelles. It can greatly increase the viscosity of the fracturing fluid. From the results of the experiments, the testing viscosity can reach 13.76 mPa • s, which is hundreds of times bigger than the original one and basically meet the capacity requirements for carrying proppants.

(2) Under the corresponding conditions of this experiment, when the mass fraction of the thickener X increases, a corresponding viscosity rises in the solution. Considering the cost and thickening effect factors, it is recommended that the mass fraction of X-Thickener about 1% can basically meet the demand.

(3) Under the corresponding conditions of this experiment, the viscosity of the fracturing fluid was negatively correlated with the temperature but have a significant positive correlation with the pressure. In order to get better thickening effects, it would be better by mixing injection at a low temperature but a high pressure as much as possible. In addition, it need further testing researches at low temperatures and high pressures conditions.

(4) Due to the laboratory testing equipments and safety aspects, the project doesn't measure the parameters at a higher pressure. It proposes to continue the measurement of parameters and the variation of its viscosity at other temperatures and pressures. The new kind of thickener for CO_2 anhydrous fracturing fluid needs to be tested about other features, like friction parameters.

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