

Research Article

Performance Evaluation and Site Application of a Hydrophobic Long-Chain Ester-Based CO₂ Fracturing Fluid Thickener

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Nowadays, there are a wide variety of thickeners developed for dry CO₂ fracturing worldwide, but numerous problems remain during in situ testing. To address problems in CO₂ fracturing fluid operation (high frictional drag, low viscosity, low proppant-carrying capacity, narrow reservoir fractures, etc.), the authors have synthesized the novel hydrophobic long-chain ester thickener, studied viscosity, frictional drag, and proppant-carrying capacity of CO₂ fracturing fluid and core damage by CO₂ fracturing fluid by varying the temperature, pressure, and level of injection of the novel thickener and explored the thickening mechanism for this thickener in CO₂. Based on the study results, as the temperature, pressure, and amount of injected thickener increased, fracturing fluid viscosity increased steadily. In the case of shearing for 125 min under conditions of 170 S⁻¹, 40°C, and 20 MPa, when the thickener level increased from 1% to 2%, fracturing fluid viscosity increased and then decreased, varying within 50–150 mPa·s, and the viscosity-enhancing effect was evident; under conditions of 20°C and 12 MPa, as the flow rate increased, drag reduction efficiency reached 78.3% and the minimal proppant settling speed was 0.09 m/s; under conditions of 40°C and 20 MPa, drag reduction efficiency reached 77.4% and the proppant settling speed was 0.08 m/s; with the increases in temperature, pressure, and injection amount, core damage rates of the thickener varied within 1.77%–2.88%, indicating that basically no damage occurred. This study is of significant importance to the development of CO₂ viscosity enhancers and CO₂ fracturing operation.

1. Introduction

Research on CO₂ dry fracturing technology has been carried out in the world in the past years. Dry CO₂ fracturing technology is more advantageous than conventional hydraulic fracturing technology in that dry CO₂ is water-free and residue-free and flows back more quickly; however, in fracturing practice, liquid CO₂ has such problems as high frictional drag and low proppant-carrying efficiency. To address this issue, we have to add a thickener into CO₂ fracturing fluid. Based on the systematic analysis of the current situation of CO₂ thickeners worldwide, CO₂ thickeners can be divided into fluorinated, siloxane, and hydrocarbon thickeners. Huang et al. [1] obtained polymer polyFAST by copolymerization between styrene and fluorinated acrylate, its CO₂ thickening effect was good, the solubility of polymer polyFAST in CO₂ decreased with increasing polymer

molecular weight, and when n(styrene):n(fluorinated styrene) is about 3:7, the prepared copolymer had the best CO₂ thickening effect. But fluorinated polymers do not apply to real production due to great environmental hazard and high cost; Shi et al. [2] prepared a thickener for dense CO₂ and found that, at thickener concentrations of 2%–4%, the viscosity of liquid CO₂ increased by a factor of 2–3. Cui et al. [3] developed a surfactant-based thickener for liquid CO₂ and simulated the liquid CO₂ thickening process by rheological testing. As the surfactant formed micelles in liquid CO₂, the viscosity of liquid CO₂ increased by a factor of about 86–216 and the maximum viscosity was 21.6 mPa·s. Shen et al. [4] synthesized a polyvinyl acetate telomere through free radical polymerization catalyzed by azodiisobutyronitrile (AIBN) and then the telomere underwent polymerization reaction with styrene to generate a binary copolymer, followed by molecular structure characterization by FTIR

and HNMR. The styrene–vinyl acetate copolymer itself has CO₂-philic groups and styrene thickening groups, and thus, in theory, it can become a high-performance low-cost thickener that is friendly to the environment and causes little damage to the rock core. Bae and Irani [5] prepared a silicon-containing polymer from a siloxane and methane and studied its impact on liquid CO₂ viscosity. The study shows that the viscosity of a mixture of 4% silicon-containing polymer + 20% toluene + 76% CO₂ was 1.2 mPa·s; thus, the viscosity of liquid CO₂ increased by a factor of 30, but to thicken liquid CO₂ with the polymer, a great amount of toluene has to be added; thus, excessive cosolvent consumption leads to poor economics, making the wide application impossible. In summary, even though varieties of CO₂ thickeners have been developed to date, slow dissolution, need of a cosolvent, insignificant viscosity-enhancing effect, environmental pollution of fluorinated thickeners, and other major issues are still present. In contrast, the hydrophobic long-chain ester thickener synthesized in this study, upon dissolution in liquid CO₂, exhibits essential properties of a dry fracturing fluid, eliminating the need of any cosolvent; at room temperature, the novel thickener at a concentration of 1.0%–3.0%, if fully stirred, can be directly dispersed and dissolved in 3 min and viscosity enhancement is evident, with the viscosity varying within 50–150 mPa·s; after dissolution of the thickener, the resulting viscoelastic fluid exhibits good dynamic proppant-carrying capacity, with a proppant concentration of up to 30%, its shear thinning behavior is good, with frictional drag reduction efficiency of over 70%, and its core damage range is 1.77%–2.88%, indicating that it is basically pollution free.

2. Experimental

2.1. Materials

2.1.1. Thickener Samples. The hydrophobic long-chain ester thickener was synthesized from the following chemicals: oil-soluble solvents (petroleum ether and white mineral oil), CO₂-philic solvent (propylene carbonate), highly CO₂-philic monomer (allylmethyl carbonate), structural monomers (styrene, and stearyl acrylate), viscosity-enhancing monomers (methyl methacrylate, and methyl acrylate), dissolution-assisting monomers (n-propyl vinyl ether, and ethyl propenyl ether), oil-soluble chain transfer agents (dodecyl mercaptan and butyl mercaptan), and oil-soluble initiator (azobisisobutyronitrile). The old thickener sample, fluoroacrylate-styrene copolymer (code ZnJ01, supplied by Jilin Oilfield), is a white single-phase fluid product classified as a modified fluorinated polymer.

2.1.2. Gas Sample. Carbon dioxide, purity 99.99%, was from Wuhan Xinxing Gas Co. Ltd.

2.1.3. Proppant Sample. A novel low-density ceramicsite was selected as the proppant, its particle size is ϕ 0.3–0.6 mm or 20–40 mesh, and its bulk density is 1.33 g/cm³.

2.1.4. Experimental Cores. Each of the natural long cores to be used in the experiment was jointed by a few short cores,

a single fracture was artificially crafted on each core, and basic physical parameters of these cores are shown in Table 1.

2.2. Experimental Equipment. A HAAKE RS6000 rheometer, frictional drag test apparatus for CO₂ fracturing fluid, visual high-temperature and high-pressure PVT test system, leak-off and damage test apparatus for CO₂ fracturing fluid, visual dissolubility and dispersibility test apparatus for CO₂, and pco.dimax cs1 high-power microscope were used.

2.3. Methodology

2.3.1. Synthesis of the Hydrophobic Long-Chain Ester Thickener. The hydrophobic long-chain ester thickener was prepared from oil-soluble solvents (10%–15%) and CO₂-philic solvent (45%–65%) as reaction solvents, highly CO₂-philic monomer (1%–3%), structural monomers (3%–5%), viscosity-enhancing monomers (15%–20%), dissolution-assisting monomers (5%–10%) as copolymerization monomers, oil-soluble chain transfer agents (0.5%–1%), and the oil-soluble initiator (0.5%–1%), wherein all the contents are on a mass basis. After completion of the reaction, the resulting copolymer was directly dissolved in the CO₂-philic solvents and the oil-soluble solvent without separation, removal, and other posttreatment processes, making its preparation convenient. The preparation procedure is detailed as follows: (1) adding solvents: while the reactor temperature was kept at 35°C, 18 g of petroleum ether, 18 g of white mineral oil, and 194.1 g of propylene carbonate were added successively into the reactor; (2) adding copolymerization monomers: while stirring was kept in the reactor, 3 g of allylmethyl carbonate, 6 g of styrene, 6 g of stearyl acrylate, 12 g of methyl methacrylate, 24 g of methyl acrylate, 9 g of n-propyl vinyl ether, and 6 g of ethyl propylene ether were added in turn such that the monomers were completely dissolved; and (3) adding the initiator and the chain transfer agents: 1.5 g of azobisisobutyronitrile was added to initiate polymerization reaction for 2 h, then, 1.2 g of dodecyl mercaptan and 1.2 g of butyl mercaptan were added, the reactor was closed and heated to 100°C, followed by 8 h isothermal reaction, and the internal pressure of the reactor was controlled throughout the process to be up to 0.4 MPa. After reaction completion, cooling water was circulated in the reactor jacket to lower the temperature to 30°C, resulting in white emulsion in the reactor; the emulsion was pumped into a plastic bucket to obtain the hydrophobic long-chain ester thickener, which is the novel thickener for site application experiment mentioned in Section 5.2.

2.3.2. Viscosity Test. A rheology test method for CO₂ fracturing fluid was established using a HAAKE RS6000 rheometer: viscosities of liquid/supercritical CO₂ fracturing fluids at variable concentrations were determined after shearing at 170 S⁻¹ for 125 min, the viscosity-enhancing effect of the viscosity enhancer was evaluated, and rheological behavior and viscosity variability patterns of CO₂ fracturing fluids under different influential factors were analyzed. Variations in rheological properties of the fluid under different conditions could be detected using a high-temperature closed

TABLE 1: Natural short core-related physical parameters.

No.	Length (cm)	Diameter (cm)	Permeability (mD)	Porosity (%)	Mean porosity (%)	Mean permeability (mD)
1 [#]	6.664	2.326	0.6938	14.08		
2 [#]	6.508	2.328	0.7608	15.62		
3 [#]	6.756	2.328	0.7713	15.11	15.72	0.7758
4 [#]	7.156	2.326	0.7884	16.48		
5 [#]	6.188	2.326	0.8648	17.34		

system, and the fluid temperature/shear resistance test and pressure versus viscosity relationship test could be performed [6, 7]. Specifically, a liquid CO₂ tank is fully filled with pressurized liquid (supercritical) CO₂ for layer use. A thicker sample at a preset test concentration was put into a mixing tank which was then closed. Thereafter, liquid (supercritical) CO₂ was introduced into the mixing tank till a preset volume. The stirrer was turned on such that the thickener became fully dissolved. The well-dissolved dry fracturing fluid was introduced into the measuring cylinder of the rheometer and sheared at preset temperature, pressure, and shear rate until being stable before data saving.

2.3.3. Frictional Drag Test. On a CO₂ fracturing fluid frictional drag test apparatus, differential pressures of liquid/supercritical CO₂ fracturing fluids in the pipeline subject to thickener addition were determined by high-pressure long-tube flow differential pressure test, where the high-pressure long tube was 10 m long and 10 mm in diameter. And drag reduction efficiency was calculated using $Dr = (\Delta P_1 - \Delta P_2) / \Delta P_1 \times 100\%$ (Dr is the drag reduction efficiency, ΔP_1 is the differential pressure of neat liquid CO₂ when passing through the long tube, and ΔP_2 is the differential pressure of CO₂ fracturing fluid fed with the novel thickener when passing through the long tube). In this experiment, at 20°C/12 MPa and 40°C/20 MPa, drag reduction efficiencies of the fluid fed with the thickener at different concentrations at variable flow rates were determined [8].

2.3.4. Proppant-Carrying Capacity Test. Assisted by a high-temperature high-pressure visual PVT experimental system, this experiment studies the settling patterns of the proppant in liquid and supercritical CO₂ fracturing fluids, determines settling speeds of the proppant in liquid and supercritical CO₂ fracturing fluids versus thickener concentration and proppant concentration as well as their variability patterns, and analyzes the settling speed of the proppant in each CO₂ fracturing fluid. On a proppant settling test apparatus, the experiment was carried out according to a procedure detailed as follows:

- (1) Fill the thickener at a volume ratio into an autoclave and put the ceramsite on top of the visual autoclave
- (2) Heat the autoclave by a water bath surrounding it such that a desired test temperature is achieved
- (3) Open the CO₂ cylinder and fill CO₂ into the autoclave via an air compressor such that within-reactor pressure reaches a desired pressure

- (4) Set the stirrer speed to 1000 rpm such that the thickener can be fully dissolved in CO₂
- (5) Rotate the manual ball releaser on top of the autoclave such that the ceramsite falls inside the autoclave and record the ceramsite settling time
- (6) Calculate ceramsite settling speed

2.3.5. Core Damage Test. The long core leak-off damage evaluation test was performed on a CO₂ fracturing fluid leak-off damage test apparatus, and leak-off quantity Q , leak-off coefficient C , and leak-off velocity V were used to explore the leak-off behavior of liquid/supercritical CO₂ fracturing fluids; by substituting permeability values prior to and after damage of the experimental core into core damage rate calculation formula $D_d = (K_1 - K_2) / K_1 \times 100\%$ (predamage and postdamage permeability values are K_1 and K_2 mD, respectively), the core damage rate can be obtained [9]; hence, the degree of core damage of the CO₂ fracturing fluid was evaluated by the fracturing fluid performance evaluation method according to SY/T 5107-1995 *National Standards for Oil and Gas Industry in the People's Republic of China* (see the flowchart of the apparatus operation in Figure 1).

2.3.6. Explorative Test on the Thickening Mechanism. The visual carbon dioxide dissolution dispersion test apparatus and pco.dimax cs1 high-power microscope were employed to observe the dissolution and dispersion state of the viscosity enhancer in liquid/supercritical CO₂ fluids, and the CO₂ fracturing fluid thickening mechanism was discussed according to the solvent-solute molecular dissolution theory [10].

3. Results and Discussion

3.1. Results of the Viscosity Test. Thickener concentration versus CO₂ viscosity curves and fracturing fluid viscosity versus shear time curves at variable concentrations of the thickener in the fluid were obtained by the HAAKE RS6000 rheometer.

As shown in Figure 2, CO₂ fluid at 20°C/8 MPa was in a liquid state, while at 40°C/15 MPa and 45°C/7.5 MPa, CO₂ fluid was in a supercritical state, as the injection concentration of the thickener increased, the viscosities of both liquid CO₂ and supercritical CO₂ fracturing fluids tended to increase; in particular, when the thickener injection concentration was greater than 1.2%, the viscosity of liquid CO₂ fracturing fluid was always greater than that of supercritical CO₂ fracturing fluid. As shown in Figures 3–5, at

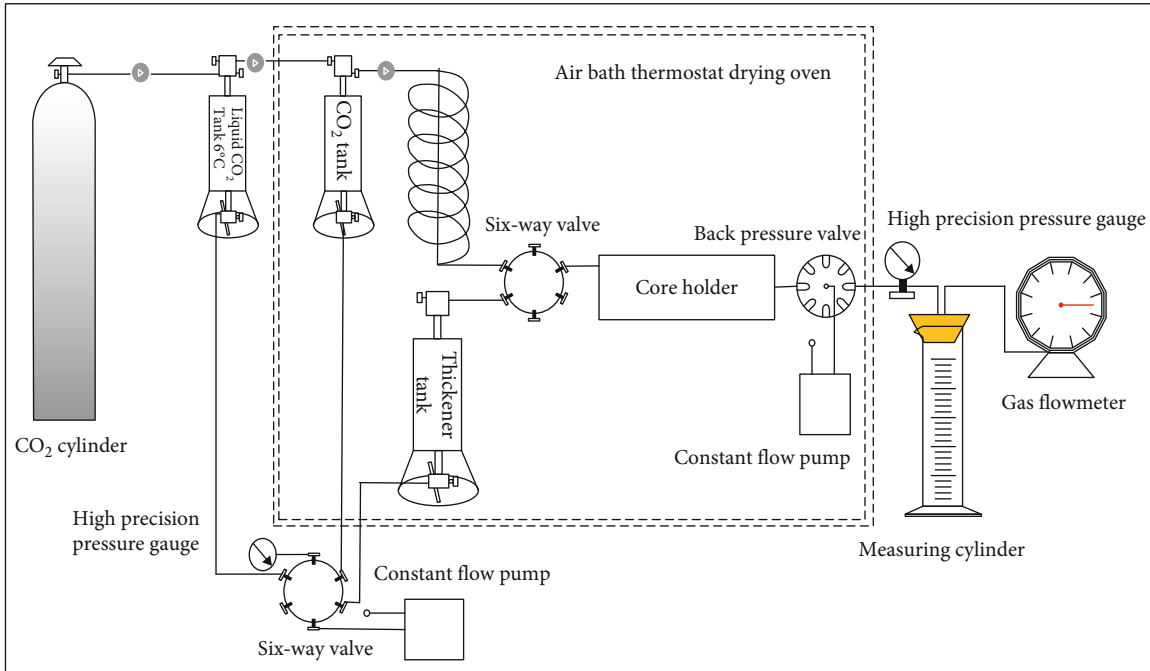


FIGURE 1: Flowchart of the damage test apparatus for CO₂ fracturing fluid.

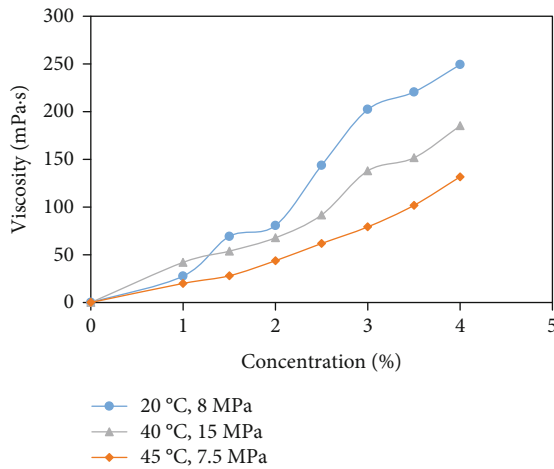


FIGURE 2: Curves of thickener concentration versus CO₂ viscosity.

40°C/20 MPa, when thickener concentration was 1.0%, the viscosity of CO₂ fracturing fluid tended to increase and then decrease over time and remained at 30 mPa·s or so at 30 min till the end of experiment; likewise, when thickener concentration increased to 1.5%, the viscosity remained at 60 mPa·s or so over time; when thickener concentration increased to 2%, the maximum fracturing fluid viscosity was 140 mPa·s, and at the later stage of the experiment, the viscosity decreasing trend was shown but overall viscosity was greater than 100 mPa·s. After shearing at 170 s^{-1} for 125 min, this thickener remained highly stable and had good viscosity-enhancing effect, indicating strong temperature/shear resistance. Given a constant temperature, viscosity of CO₂ fracturing fluid increased with increasing pressure, indi-

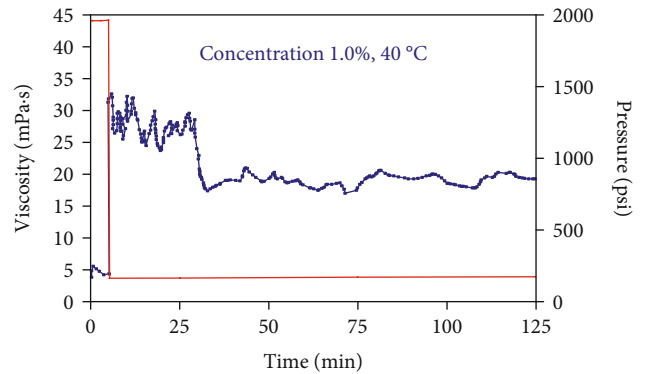


FIGURE 3: Curve of viscosity versus shear time at a thickener concentration of 1%.

cating that pressure variation has indeed significant impact on viscosity of CO₂ fracturing fluid and pressure increase leads to more violent momentum exchange between thickener molecule and CO₂ molecule and higher density of CO₂ fluid such that thickener solute becomes more soluble in CO₂, further increasing viscosity of the fracturing fluid system. Therefore, increasing the thickener concentration and test pressure has important impact on the increase in viscosity of liquid or supercritical CO₂ [11].

3.2. Results of Frictional Drag Test. On a frictional drag test apparatus for CO₂ fracturing fluid, the high-pressure long-tube flow differential pressure test was conducted to determine differential pressures of CO₂ fracturing fluid in a pipeline subject to thickener addition and a formula for drag reduction efficiency calculation was used to obtain drag reduction efficiency; then, drag reduction efficiency

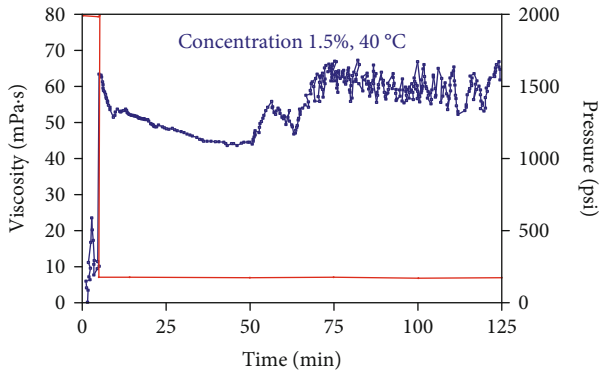


FIGURE 4: Viscosity versus shear time curve at a thickener concentration of 1.5%.

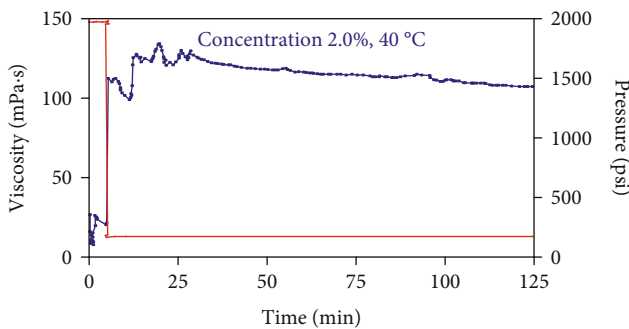


FIGURE 5: Curve of viscosity versus shear time at a thickener concentration of 2.0%.

versus flow rate curves at 20°C/12 MPa and 40°C/20 MPa was obtained through data analysis.

As can be seen in Figures 6 and 7, with the increases in the flow rate and concentration of injected thickener, drag reduction efficiency increased significantly. Given a constant temperature, frictional drag coefficient increased gradually with increasing pressure because higher pressure leads to smaller intermolecular distance and stronger friction force. When the temperature, pressure, and pipe diameter were constant, the faster the flow rate of the fluid in pipeline, the greater the degree of turbulence and the friction loss and drag reduction effect became more significant at higher Reynolds numbers. As temperature and pressure varied, drag reduction efficiency of the thickener ranged within 59.1%–78.3%. When thickener concentration was 2% and flow rate was above 2.0 m/s, drag reduction efficiency reached 78.3%.

3.3. Results of the Proppant-Carrying Capacity Test. Settling times and settling speeds of single-particle proppant and the proppant at a proppant concentration of 5% in liquid/supercritical CO₂ fracturing fluids were determined by a proppant settling test apparatus, as shown in Tables 2 and 3.

As inferred in Tables 2 and 3, supercritical CO₂ is generally superior to liquid CO₂ in proppant-carrying capacity: in the case of a single-particle proppant, the minimum settling speed in liquid CO₂ was 0.09 m/s while the minimum

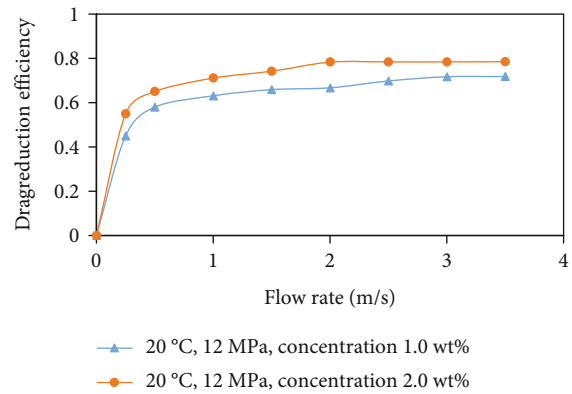


FIGURE 6: Flow rate versus drag reduction efficiency at 20°C/12 MPa.

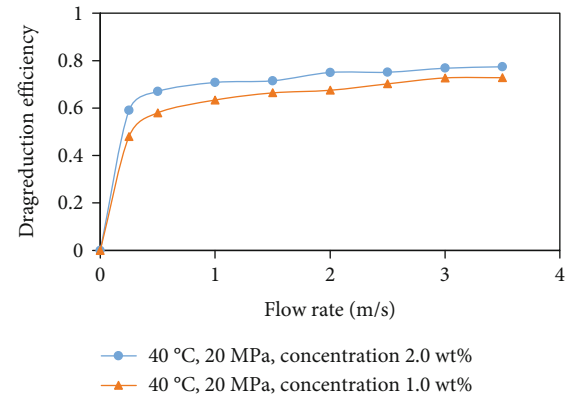


FIGURE 7: Flow rate versus drag reduction efficiency at 40°C/20 MPa.

settling speed in supercritical CO₂ was 0.08 m/s; in the case of 5% proppant concentration, the minimum settling speed in liquid CO₂ was 0.08 m/s while the minimum settling speed in supercritical CO₂ was 0.07 m/s, because the hydrophobic long-chain ester thickener dissolved in CO₂ is markedly viscoelastic and thus has excellent proppant-carrying capacity. Given a constant amount of the injected thickener, increases in temperature and pressure enabled higher fracturing fluid viscosity such that the proppant settling speed became slower. In comparison with single-particle settling, the proppant settling speed at 5% proppant concentration was lower than the free single-particle settling speed due to intermolecular interference and the single-particle settling will cause upward flow of the surrounding liquid which impedes the surrounding fluid from sinking; thus a greater drag will be present at a proppant concentration of 5% and the increase in proppant concentration is, in fact, equivalent to increases in proppant buoyancy and settling drag, manifested as a slower settling speed [12].

3.4. Core Damage Evaluation. The long core leak-off and damage test was carried out on a CO₂ fracturing fluid leak-off and damage test apparatus at a temperature of 55°C and a pressure of 14 MPa. The core leak-off performance

TABLE 2: Settling speeds of single-particle proppant in CO₂ fracturing fluids.

System	Temperature (°C)	Pressure (MPa)	Amount of injected thickener (%)	Settling time (s)	Settling speed (m/s)
Liquid CO ₂	20	8	0	0.47	1.34
	20	8	1.0	3.12	0.20
Thickener + liquid CO ₂	20	8	1.5	4.85	0.13
	20	8	2.0	7.04	0.09
Supercritical CO ₂	40	15	0	0.62	1.02
	40	15	1.0	4.17	0.15
Thickener + supercritical CO ₂	40	15	1.5	5.73	0.11
	40	15	2.0	7.88	0.08

TABLE 3: Settling speeds of proppant at 5% proppant concentration in CO₂ fracturing fluids.

System	Temperature (°C)	Pressure (MPa)	Amount of injected thickener (%)	Settling time (s)	Settling speed (m/s)
Liquid CO ₂	20	8	0	0.64	0.98
	20	8	1.0	3.94	0.16
Thickener + liquid CO ₂	20	8	1.5	5.71	0.11
	20	8	2.0	7.83	0.08
Supercritical CO ₂	40	15	0	0.85	0.74
	40	15	1.0	5.25	0.12
Thickener + supercritical CO ₂	40	15	1.5	6.92	0.09
	40	15	2.0	8.94	0.07

TABLE 4: Core leak-off performance of CO₂ fracturing fluid.

Temperature (°C)	Pressure (MPa)	Mean permeability (mD)	Fracturing fluid system	Leak-off coefficient (10 ⁻² m/min ^{0.5})	Leak-off velocity (m·min ⁻¹)	Cumulative leak-off quantity (mL)
45	10	0.7758	CO ₂	5.328	0.037	11246
45	10	0.7758	Thickener + CO ₂	1.728	0.012	8175

TABLE 5: Parameters of damage evaluation of fracturing fluid.

Fracturing fluid damage rate (%)	None	Weak	Moderately weak	Moderately strong	Strong
Degree of damage	$D_d < 5$	$5 < D_d \leq 30$	$30 < D_d \leq 50$	$50 < D_d \leq 70$	$70 < D_d$

TABLE 6: Core damage performance of CO₂ fracturing fluid.

Fracturing fluid system	Temperature (°C)	Pressure (MPa)	Amount injected (%)	Permeability K_1 (mD)	Permeability K_2 (mD)	Core damage rate D_d (%)	Degree of damage
Thickener + CO ₂	20	8	1.0	0.453	0.445	1.77	Nil
	20	8	1.5	0.447	0.438	2.01	Nil
	20	8	2.0	0.449	0.437	2.67	Nil
	40	15	1.0	0.442	0.434	1.81	Nil
	40	15	1.5	0.456	0.445	2.41	Nil
	40	15	2.0	0.452	0.439	2.88	Nil

of CO₂ fracturing fluid is shown in Table 4, the parameters of damage evaluation of fracturing fluid are shown in Table 5, and the core damage performance of the CO₂ fracturing fluid was shown in Table 6.

As shown in Table 4, under the condition of 45°C/10 MPa, the leak-off velocity of supercritical CO₂ fluid in the long core was 0.037 m·min⁻¹, while the leak-off velocity of supercritical CO₂ fracturing fluid containing a 1.5% viscosity enhancer injected into the long core was 0.012 m·min⁻¹, and in comparison, the leak-off coefficient of CO₂ fracturing fluid into which the viscosity enhancer was injected was markedly lower than that of pure CO₂ fluid, indicating that this viscosity enhancer reduces the leak-off property of supercritical CO₂ fluid to some extent. As CO₂ fluid is residue free, no filter cake will be formed at the front end of the core in a long core leak-off test, indicating a greater leak-off coefficient and a faster leak-off velocity; after a thickener was incorporated, the CO₂ fracturing fluid will form gradually flocculent filter cakes at the front end of the rock core, resulting in lower leak-off coefficient, indicating that CO₂ fluid incorporated with a thickener has pronounced effect of leak-off reduction after entering fractures and thus ensures fracture forming efficiency of a fracturing fluid. And in Table 6, where core damage rate D_d was calculated by substituting the leak-off coefficient into the calculation formula for D_d , it can be found that the CO₂ thickener had low core damage rates ranging within 1.81%–2.88%, and in comparison with the core damage criteria for fracturing fluids in Table 5, its damage to the rock core is almost negligible; moreover, CO₂ is slightly soluble in water and readily soluble in the in-place oil; therefore, the thickened CO₂ fracturing fluid system would be well compatible with the formation.

4. Discussion on the Thickening Mechanism of the Hydrophobic Long-Chain Ester Thickener in CO₂ Fracturing Fluids

The dissolution and dispersion states of the viscosity enhancer in liquid/supercritical CO₂ fluids were examined by visual dissolution and the dispersion test apparatus and the pco.dimax cs1 high-power microscope. The results of the sample dispersion test are shown in Table 7, and the dissolution status of the thickener in CO₂ is seen in Figure 8.

Intermolecular interactions between viscosity enhancer solute and CO₂ solvent include (1) solvent-solute intermolecular interaction: solute-to-solvent aggregates will form due to strong interaction between solute and solvent molecules and (2) solvent-solvent intermolecular interaction: in highly compressible dilute supercritical fluid, apart from solvent-solute aggregates, there are solvent-solvent aggregates. Dissolution and dispersion of the hydrophobic long-chain ester thickener in CO₂ were examined using a pco.dimax cs1 high-frequency microscopic camera, results of the dispersion test of the same amount of thickener injected at different temperatures and pressures are shown in Table 7, and dissolution details are seen in Figure 8. As shown in Figure 8, the hydrophobic long-chain ester

TABLE 7: Results of the sample dispersion test.

Sample	Temperature (°C)	Pressure (MPa)	Amount of injected thickener (wt.%)	Dispersion time (min)
Thickener	20	8	2.0	<2
Thickener	40	15	2.0	<2
Thickener	45	7.5	2.0	<2

thickener dissolves instantly in CO₂; at a thickener concentration of 2%, it can be directly dispersed and dissolved in CO₂ in less than 2 min, so it is readily dispersible and soluble in liquid CO₂ and supercritical CO₂. In terms of synthetic composition, propylene carbonate is a CO₂-philic solvent, white mineral oil and petroleum ether are oil-soluble solvents, allylmethyl carbonate is a strong CO₂-philic monomer, and ethyl propenyl ether and n-propyl vinyl ether are cosolvent monomers, while methyl acrylate and methyl methacrylate are viscosity-enhancing monomers. When the thickener is dissolved in CO₂, it can be quickly dispersed and dissolved due to effects of the CO₂-philic solvent and oil-soluble solvents, as the copolymer components have been directly dissolved in the CO₂-philic and oil-soluble solvents first, making the polymeric molecular chains pre-stretched, and during dissolution, the viscosity-enhancing groups on the molecular chains dissolve to enhance viscosity, meanwhile multiple association effects between them and intramolecular and intermolecular structural groups via the hydrogen bond and dispersion force as well as Lewis acid-base reaction contribute to structural viscosity; thereby, the viscosity-enhancing effect is greatly increased [13–18].

5. Site Application

5.1. Basic Geology of Experimental Well. Well Hong 87-X is located at block M in oilfield J. This block is in the southern part of the Rangzijing structure in the central depression area of the southern Songliao Basin, neighboring the Gudian reverse fault of the Fuxin uplift zone in the east and SW-dipping slope zone of the Xinli structure in the north, and the slope zone is subjected to regional compressive torsional stress and forms a NNW-trending fold zone associated with a number of fault zones parallel axially to the fold zone. The oil reservoir belongs to the fault rock-type oil reservoir in the setting of the westward-dipping slope. The bed of interest is 3300 m deep, the reservoir temperature is 104°C, the gradient of formation pressure is 0.9 MPa/100 m, the calculated Poisson's ratios of the reservoir are 0.20–0.22, the Young's moduli of the reservoir are (2.74–2.82) × 104 MPa, and the closure pressure was 35.4 MPa. The in-place oil has a density of 0.826 t/m³, a viscosity of 5.60 mPa·s, original saturation pressure of 5.1 MPa, a volume coefficient of 1.076, and original solution gas-oil ratio of 27 m³/m³. And porosity values of the pay bed are generally 6.0%–12.0%, averaging 8.7%; permeability values of the pay bed are generally 0.06–2.0 mD, averaging 0.15 mD. In general, the reservoir is characterized in low porosity and ultralow permeability. The

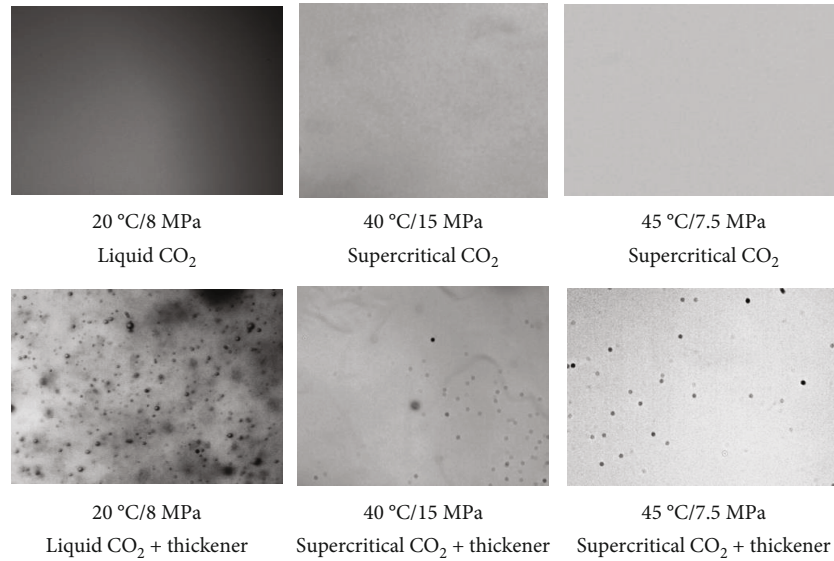


FIGURE 8: Dissolution of the thickener in CO₂.

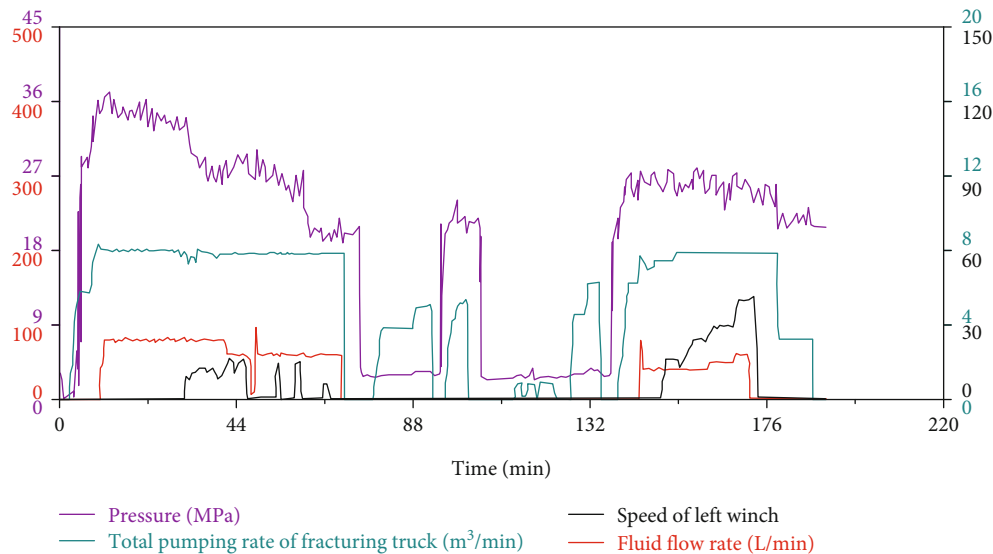


FIGURE 9: Dry fracturing operation curve of Well Hong 87-X.

reservoir lithology is dominated by greyish-brown siltstone and fine sandstone, mainly including lithic arkose or feldspathic litharenite. Particle sizes of the rocks are generally 0.03–0.25 mm, and the clay mineral content is 14.2%.

5.2. Site Operation Process. The fracturing operation of Well Hong 87-X in block M of oilfield J with old thickener Zn_j01 did not get desirable effect. Later, the CO₂ dry fracturing operation with the novel thickener was conducted, where 835 m³ of liquid CO₂ was consumed, ceramsite of 20–40 mm in the size was chosen as the proppant, pumping rates were 5.2–8.2 m³/min, proppant loading was 9 m³, proppant concentration was 4%, operation pressures were 21–37 MPa, and pump-shutoff pressure was 20.8 MPa. Prior

to operation, the pipeline was circulated with CO₂ to test the pressure, ensuring that all the CO₂-related lines are free of liquid buildup; the ratio of liquid CO₂ to the thickener was kept at 100 : 1; the prepad fluid volume and proppant transport program were adjusted based on the results of the pre-fracturing test; the site should support continuous proppant loading and continuous liquid supply. Figure 9 shows the dry fracturing operation curve of Well Hong 87-X.

5.3. Operation Effect Analysis. Based on the comparison between Figures 10 and 11, in the case of the novel thickener, at the stage of proppant loading, the pumping rate was 5.2 m³/min while proppant concentrations were 3%, 4.5%, 5.8%, and 8%, respectively, and after entering the

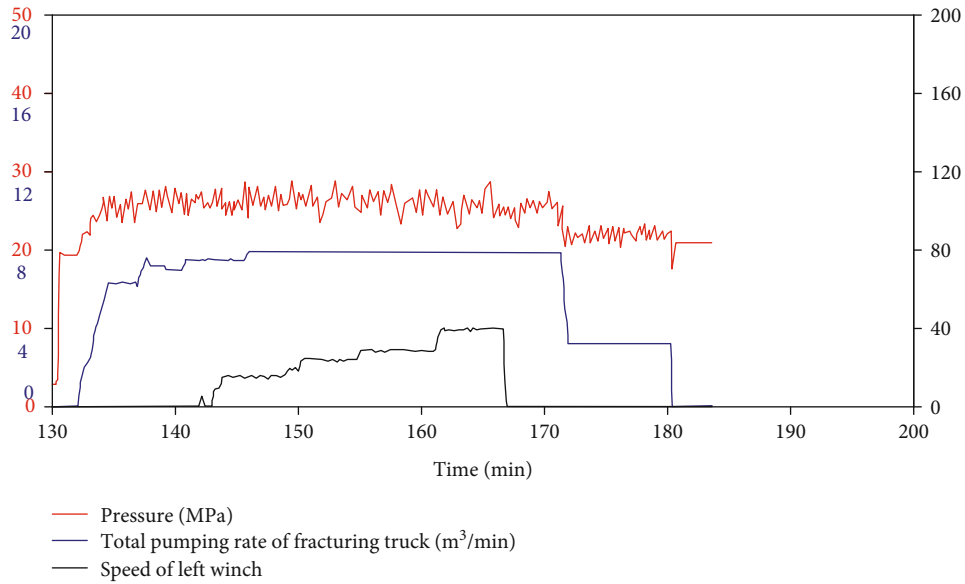


FIGURE 10: Curves of fracturing with the new thickener for Well Hong 87-X at pumping rates of 5–5.2 m³/min.

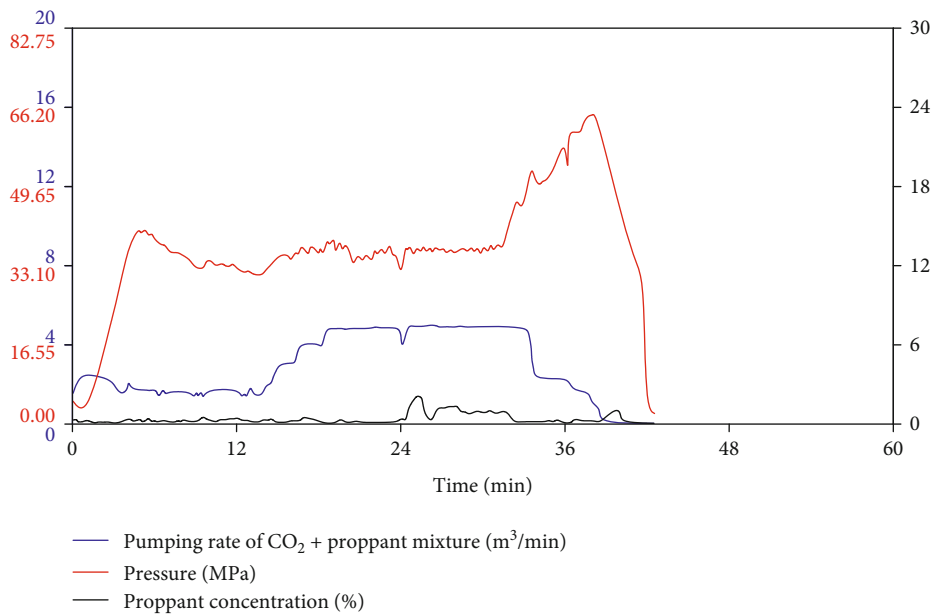


FIGURE 11: Curves of fracturing with old thickener Znj01 for Well Hong 87-X at pumping rates of 4.8–5.1 m³/min.

reservoir, stable pressure and superior proppant-carrying capacity were noted; in the case of the old thickener Znj01, the pumping rate was 5 m³/min and the proppant concentration was 2.5% at the stage of proppant loading, and after entering the formation, the pressure surged and eventually led to sand plug. Given the equivalent pumping rate, compared with the old thickener, the novel thickener had more stable proppant-carrying capacity during proppant loading. As a result of the site application, when the old thickener was used, the daily oil output of this well was up to 3.86 t; while after the novel thickener was used, the maximum daily oil output reached 7.4 t, with an increment of 3.54 t.

6. Conclusions

- (1) The novel hydrophobic long-chain ester thickener synthesized in this study is a linear block copolymer supplied in the form of white emulsion with a molecular weight ranging within about 500,000–800,000. Based on performance testing, its density was 1.05 g/cm³ and its pH was 7.5; the thickener at 2.0 wt% could be dissolved in liquid CO₂ in 3 min to form a fracturing fluid at a viscosity of 80 mPa·s, and its drag reduction efficiency was 78.3%

- (2) The viscosity-enhancing effect, frictional drag, proppant-carrying capacity, and core damage of the novel thickener in CO₂ fracturing fluid were experimentally determined, and the thickening mechanism of this novel thickener in CO₂ was discussed. As a result, with the increase in the amount of the injected thickener, the viscosity of CO₂ fracturing fluid increased gradually, and when the concentration of the injected thickener was greater than 2%, the viscosity-enhancing effect in liquid CO₂ fracturing fluid was superior to that in supercritical CO₂ fracturing fluid; the drag reduction effect was notable when the thickener concentration was 2.0% and the flow rate of the fracturing fluid was more than 2.0 m/s. The thickener, if dissolved in CO₂, could form multiorder structures and become significantly viscoelastic, resulting in higher viscosity; thus, it has excellent proppant-carrying capacity. After the novel thickener was added into CO₂ fracturing fluid, the maximum core damage rate was 2.88%, which is negligible
- (3) After CO₂ dry fracturing of Well Hong 87-X in oil-field J using the novel thickener, the fracturing effect was remarkable and the oil output of the well was substantially elevated; given the equivalent pumping rate, compared with the old thickener, the novel thickener had more stable proppant-carrying capacity during proppant loading, indicating that the novel thickener has better effect of viscosity enhancing and proppant carrying; moreover, the CO₂ dry fracturing technology is of significant importance to CO₂ sequestration and the reduction of greenhouse gas emission; it increases the oil output and protects the environment as well, resulting in a win-win situation in line with the China national strategy of “carbon peak and carbon neutralization”

Data Availability

The raw data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflicts of Interest

The authors declare no competing financial interest.

Acknowledgments

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