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Laboratory experiment on a toluene-polydimethyl silicone thickened supercritical carbon dioxide fracturing fluid

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ABSTRACT

Supercritical carbon dioxide (SCCO$_2$) fracturing fluid is an excellent application in CO$_2$ re-use. It has many advantages than water-based fracturing fluids. However, the low viscosity hinders its application in unconventional oil and gas reservoirs. Therefore, we tried to improve the property of SCCO$_2$ fracturing fluid by increasing the viscosity. A thickened SCCO$_2$ fracturing fluid was constructed and the fracturing property of the fracturing fluid was investigated. The fracturing fluid consisted of toluene (cosolvent), polydimethyl silicone (thickener) and SCCO$_2$. In SCCO$_2$, toluene and polydimethyl silicone obtain low miscible pressure at 42 °C. In addition, the constructed fracturing fluid system obtains higher viscosity value (as high as 1.5 mPa·s), which can be 40 times high than the viscosity of pure SCCO$_2$ at 42 °C and 20 MPa. These features match the viscosity requirement as a fracturing fluid. Molecular dynamics (MD) simulations were carried out to study the solubility parameter of the fracturing fluid system in molecular level. These MD simulation results show that, as a cosolvent, toluene helps polydimethyl silicon dissolve in SCCO$_2$, which is consistent with laboratory experiment results. Moreover, the studied fracturing fluid obtains good properties as a fracturing fluid in terms of high proppant carrying capability, low fluid leakoff coefficient, and low formation damage rate.

1. Introduction

Unconventional reservoirs are generally poor in reservoir properties and cannot be explored with conventional methods under current technical conditions (Cao et al., 2016; Ge et al., 2016; Jia et al., 2012). In order to effectively exploit unconventional reservoirs, reservoir stimulation techniques are required (Zhou et al., 2016; Holditch, 2006). Hydraulic fracturing technique is the most widely used reservoir stimulation method for unconventional reservoirs (Kissinger et al., 2013; Gordalla et al., 2013; Reinicke et al., 2010; Guo et al., 2015; Liu and Mostaghimi, 2017). However water-based fracturing fluid systems have some shortages, such as huge waste of water resources, damages to reservoir induced by clay swelling and fluid residual, groundwater contamination caused by incomplete flowback, and expensive sewage treatment fee (Gordalla et al., 2013; Estrada and Bhamidimarri, 2016; Liu and Mostaghimi, 2016; Liu et al., 2017). In order to avoid these disadvantages, scientists and engineers turns to carbon dioxide (CO$_2$) fracturing especially supercritical carbon dioxide (SCCO$_2$) fracturing techniques.

Fracturing with CO$_2$ is a rising non-aqueous fracturing technique, which has been widely used in unconventional reservoirs. It is firstly used in northern America in the 1980s (Harris et al., 1998; Yost, 1994). CO$_2$ can reach its supercritical state ($T_C > 31.1$ °C, $P_C > 7.38$ MPa (Cummings et al., 2012)) under reservoir conditions. In this study, we used a temperature of 42 °C and a pressure of 20 MPa, for a reservoir about 1000 m deep underneath. As a supercritical fluid, SCCO$_2$ obtains some unique properties, such as high density close to liquid, lower viscosity (1×10^{-3}~1×10^{-2} mPa·s) close to gas (Michels et al., 1957), low surface tension nearly to zero, and higher miscibility with hydrocarbons (Liu et al., 2014). SCCO$_2$ fracturing technique helps enhance oil and gas production by deceasing oil and gas blockage (He et al., 2015; Wang et al., 2013). However, the low viscosity of SCCO$_2$ leads to poor proppant carrying capacity, and high fluid loss while fracturing, which will limit its

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application in low permeability oil or gas reservoirs (Liu et al., 2014; Lancaster et al., 1987). Thus, how to thicken the $SCCO_2$ viscosity is becoming an important issue for $SCCO_2$ fracturing. Many researchers has done some effort trying to solve this problem. According to the previous report, there are mainly two methods enhancing the viscosity: use direct thickeners and thickener-cosolvent system. Hydrocarbon liquids, polymers, telechelic ionomers, and surfactants can all be used as thickeners (Enick et al., 2001). The research results indicate that none yields satisfactory results, mainly due to the low solubility of these compounds in $SCCO_2$. J. P. Heller and his coworkers made some efforts searching for polymers enhancing the viscosity of $SCCO_2$. Though they were not successful, they provided that polymer may increase $SCCO_2$ viscosity (Heller et al., 1985; Dandge and Heller, 1987; Gullapalli et al., 1995). For the thickener-cosolvent system, the organic liquids, regarded as cosolvent, help increase the solubility of thickener compounds, which is a good method (Enick et al., 2001). Recently, in order to enhance the viscosity, R. M. Enick and E. J. Beckman did a lot of work and they successfully synthesized some fluoro-polymers to enhance the $SCCO_2$ viscosity. These fluoro-polymers can effectively increase the viscosity, but these materials are not used in field works during fracturing as they are expensive and also damage the environment (Lee et al., 2014; Zhang et al., 2011).

Our objective of this work is to construct a high viscosity $SCCO_2$ fracturing fluid system and study their properties. We established a $SCCO_2$ fracturing fluid system by measuring minimum miscible pressure (MMP) (Yellig and Metcalfe, 1980) and viscosity. The value of MMP represents the soluble property of the chemical in $SCCO_2$. This system is made up of toluene, polydimethyl silicone (PDMS) and $SCCO_2$. It has reasonable MMP and higher viscosity. We calculated solubility parameter with the help of materials studio (MS) by molecular dynamics (MD) simulations method, in order to better understand the function of cosolvent in the $SCCO_2$ fracturing fluid. In addition, we studied $SCCO_2$ fracturing fluid properties for unconventional reservoirs, such as proppant carrying ability, fluid leakoff test, and formation damage rate. Through this work, we hope to gain more understanding of $SCCO_2$ fracturing fluid.

2. Experimental section

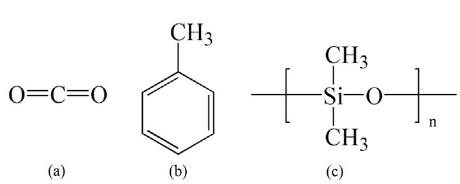
2.1. Materials

Toluene (99.5%) was purchased from Sinopharm Chemical Reagent CO., Ltd (Shanghai, China). PDMS (viscosity 350 mPa·s) was purchased from Aladdin Chemical Reagent CO., Ltd (Shanghai, China). Toluene was used as a cosolvent and PDMS was used as a thickener for $SCCO_2$. Carbon dioxide (99.9%) was purchased from Tianyuan Gas Co., Ltd (Qingdao, China). The structure of toluene, PDMS, and CO_2 are shown in Scheme 1.

2.2. Methods

2.2.1. Minimum miscible pressure measurements

Fig. 1 shows the $SCCO_2$ phase equilibrium reactor. The reactor has a windowed variable volume cell. MMP values were determined by isothermal compressions and expansions of mixed fluid at 42 °C. The process is shown as following. First, we add a certain amount of cosolvent and thickener into the high-pressure cell, the cell is flushed with pure CO_2 and sealed. After that, CO_2 is pumped into the cell with the help of a CO_2 booster pump. Then, the CO_2/cosolvent/thickener system is compressed and stirred until achieving a single phase, and finally the system is expanded until unstable.



Scheme 1. Chemical structure of toluene (a), PDMS (b), and CO_2 (c).

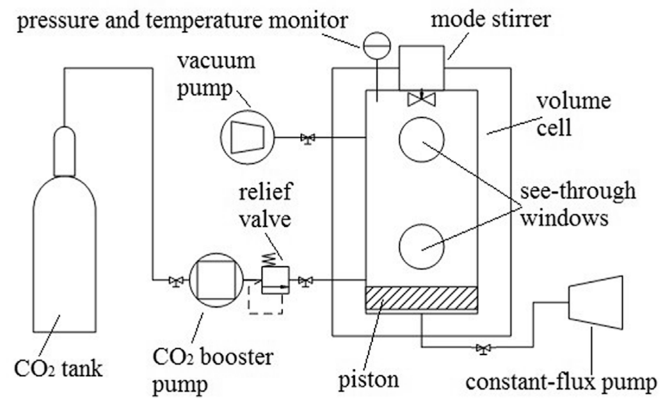


Fig. 1. Diagram of $SCCO_2$ phase equilibrium reactor.

2.2.2. Viscosity measurements

Under the condition of 42 °C and 20 MPa, the viscosity of the single phase CO_2-cosolvent-thickener system can be determined with the help of a falling sphere viscometer. The viscosity was calculated with the help of Navier-Stokes equation (Calvignac et al., 2010). The terminal velocity reduction revealed the viscosity increase in fluids of a falling sphere:

$$\mu = C\frac{(\rho_c - \rho_f)}{V_t} \tag{1}$$

where, μ is the viscosity of the fluid, ρ_c is the density of falling sphere, ρ_f is the density of the fluid, V_t is the terminal velocity of the falling sphere, C is the viscometer constant, which can be determined from a known fluid.

2.2.3. Molecular dynamics simulations

MD simulations were conducted with Materials Studio 8.0 (Accelrys). We employed an ab initio COMPASS force field for simulations (Gupta et al., 2011; Rigby et al., 1997). Temperature and pressure were controlled by Anderson thermostat and barostat, and simulated temperature is 42 °C. In equilibration phase, cells were allowed to relax for 100 ps under NVT. In production phase, the equilibration structure was processed via the NPT ensemble for 400 ps. The density and solubility parameter of $SCCO_2$ were simulated as a function of system pressure in this section. The pressure ranged from 8 to 30 MPa. In order to investigate the cosolvent concentration effect on the fracturing fluid system, the density and solubility parameter simulation as a function of toluene concentration were conducted.

2.2.4. Proppant carrying ability measurement

Proppant carrying ability can be determined by proppant fall rate (Montgomery, 2013a). This test was carried out at 42 °C and 20 MPa. An aluminous sphere was used to test the fall rate. The falling length is 600 mm.

2.2.5. Fluid leakoff coefficient measurement

Fluid leakoff coefficient (Crowe et al., 1989) test was carried out at 42 °C using a fluid leakoff facility as shown in Fig. 2. Cores were treated according to SY/T 5336-1996, and were added into the high-pressure core-holder. Cores employed in this test were cylindrical and 50 mm in length, 25 mm in diameter. The gas permeability of these cores were $5.3 \times 10^{-3}\ \mu m^2$. The inlet pressure was 20 MPa. Confining pressure was always maintained at 4 MPa higher than the inlet pressure of the core-holder, and back pressure was maintained at 2 MPa lower than the inlet pressure. A gas flow meter was used to measure the cumulative produced gas volume.