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Review of fundamental studies of CO$_2$ fracturing: fracture propagation, propping and permeating

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Abstract

CO$_2$ fracturing is one potential technique to relieve environmental issues related to the massive hydraulic fracturing of hydrocarbon reservoirs. We summarize fundamental studies on overall procedures of CO$_2$ fracturing and analyse research progress related to fracturing, the propping of the induced fractures and permeating CO$_2$ into, then recovering hydrocarbons from, the formation. The key controlling characteristics in CO$_2$ fracturing at each stage are defined, together with a definition of their relative dominance. Fractures generated by CO$_2$ fracturing are typically viewed as of superior complexity but increased tortuosity. Proppant transport during CO$_2$ stimulation is evaluated through consideration of particle settling, remobilization and flowing behaviours. New views of permeability evolution in propped fractures as a function of CO$_2$ saturation are presented. Correlations among each procedure are revealed to identify common issues and key technical details illuminated through multidisciplinary efforts. The field case studies of CO$_2$ fracturing are collected for the analysis of hydraulic parameters and then compared against water-based fracturing. The mismatch between pumping rate and CO$_2$ viscosity is highlighted, suggesting that the role of wellbore friction is an important topic requiring resolution. Suggestions for the optimization of CO$_2$ thickening, the usage of fine proppants and injected form of CO$_2$ are discussed and illustrated. Other open questions remain with respect to the nature of CO$_2$-rock interactions and their resultant impact on permeability evolution and fracture generation – key issues are identified for future investigations to promote the popularization of CO$_2$ fracturing for the concurrent and complementary recovery of native hydrocarbons and sequestration of carbon emissions.

Keywords: CO$_2$ fracturing; proppant transport; permeability evolution; pump rate; viscosity

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1. Introduction

The application of CO₂ for the improved recovery of oil and gas (mainly for reservoir stimulation) has a long history for its high performance in enhancing hydrocarbon production (Cao and Gu 2013, Mukherjee and Misra 2018) and concomitantly reducing carbon emissions by the co-sequestration of CO₂ in reservoirs (Godec et al. 2013, Bielicki et al. 2018, Goodman et al. 2019). CO₂ flooding increases oil mobility via CO₂-hydrocarbon interaction (Jia, Tsau and Barati 2019, Martin and Taber 1992, Cao and Gu 2013, Kolster et al. 2017). CO₂ fracturing was initially proposed as early as the 1960s (Crawford et al. 1963) as an alternative to water-based fracturing for environmental issues that were largely sidelined with the popularization of massive hydraulic fracturing. Large scale water consumption for fracturing, in arid areas, such as Shanxi (China), North Dakota, Kansas and Colorado (US), has impacted the widespread granting of fracturing permits (Rahm 2011, Vengosh et al. 2014). For a typical shale gas well, approximately 30000 tons of freshwater and 150 tons of chemicals are injected into the target reservoir (Gallegos et al. 2015, Clark, Horner and Harto 2013, Gregory, Vidic and Dzombak 2011). 30–90 % of the injected material is unrecyclable and trapped underground (Lester et al. 2015, Gregory et al. 2011), including non-degradable chemicals, such as acids, heavy metals and high-molecular polymers, which potentially threaten the underground ecology (Michalski and Ficek 2015, Stringfellow et al. 2017). Therefore, CO₂ fracturing has regained attention and is considered as a potential solution to the current environmental concerns induced by the use of water-based fracturing fluids (Middleton et al. 2015, Mosher et al. 2013, Yu et al. 2015).

CO₂, as a fracturing fluid, exhibits unique advantages. Typically, tensile strength, triaxial compressive strength, and elastic modulus of the rock all decrease with exposure to CO₂, reducing the required operating pressure during fracturing (Ao et al. 2017, Rutqvist, Birkholzer and Tsang 2008, Viete and Ranjith 2006). CO₂-hydrocarbon interactions (i.e. competitive adsorption between CO₂ and CH₄) increase the available mass of free gas and the fluidity of native condensate oils (Liu and Wilcox 2011, Alvarado and Manrique 2010, Stanwix et al. 2018). Field tests of CO₂ fracturing, performed both in China and North America, have achieved higher stimulated production than water-based fracturing (Asadi et al. 2015, Siwei, He and Qinghai 2019). However, the high leak-off of CO₂
constrains its application mainly to unconventional reservoirs with ultra-low permeability, e.g. shale or tight gas and oil (Zhou and Burbey 2014, Busch et al. 2008b). The limited scale (fractured and injected volume of proppant and CO₂) of CO₂ fracturing indicates its imperfection in becoming a regular technique (Asadi et al. 2015, Cui et al. 2017, Fujioka, Yamaguchi and Nako 2010). The low viscosity of CO₂ and resultant limited ability to transport proppant is considered one of the main limitations (Liu et al. 2014, Li et al. 2015, Ha, Choo and Yun 2018).

CO₂ fracturing may be restricted by poor performance at any step in the serial fracturing processes (creating fractures, proppant transport and fracture permeation) or in their coordination (Fig. 1). We summarize fundamental studies on overall procedures of CO₂ fracturing with a focus to (i) analyse current research progress, (ii) reveal associations among each procedure and (iii) propose enhancements and improvements to CO₂ fracturing to realize the true advantages of CO₂ fracturing and promote both the recovery of native hydrocarbons and the sequestration of carbon emissions.

![Fig. 1 Schematic of overall procedures of CO₂ fracturing for reservoir stimulation. (I) Fracturing; (II) Propping; (III) Permeating.](image)

2. Current State-of-the-Art / Practice

The characteristics of CO₂ (acidity, viscosity, diffusivity) and its strong interaction with the host rock (dissolution, adsorption, swelling) result in unique fracturing behaviour of fracture generation, proppant transport and hydrocarbon recovery. The injected CO₂ damages the reservoir and creates an initial fracture network. The following slurry (mixture of CO₂ and proppant) then carries proppant into fractures to prop them. Then ultimately, the final production varies with the evolution of
permeability in this propped fracture and the feeder fractures into the main fluid-driven fracture. A review of fundamental studies on the overall procedure diagnoses the root of bottlenecks in the method and defines correlations among each step within CO$_2$ fracturing.

2.1 Fracture generation by CO$_2$

Mineral dissolution by supercritical CO$_2$ (Sc-CO$_2$), under reservoir conditions, may etch pores and increase the porosity and permeability by orders of magnitude (Yin et al. 2016, Zou et al. 2018, Jia et al. 2018). The removal into solutions of carbonate minerals weakens the fabric of the rock matrix (reduction in tensile and compressive strengths and elastic modulus), decreases the breakdown pressure and enhances the fracability of the targeting formation (Jiang et al. 2016, Qin et al. 2019, Kharaka et al. 2006). The ultra-low viscosity of CO$_2$ promotes complexity of the fracture network, thus increasing the stimulated reservoir volume (SRV) (Zhou et al. 2018, Gan et al. 2015).

2.1.1 Breakdown behaviour

The strength tests on shales soaked in Sc-CO$_2$ exhibit significant reductions in tensile and compressive strengths and elastic modulus, following negative exponential trends with increasing treatment time, as shown in Fig. 2 (Ao et al. 2017, Hol and Spiers 2012). Correspondingly, the breakdown pressure using Sc-CO$_2$ decreases approximately by 15% to 50% when compared with that for liquid CO$_2$ or water fracturing, as shown in Table 1 (Zhang et al. 2017a). Lower breakdown pressures (usually the peak pressure during the fracturing operation) preserves safety margins for higher pump rates that is essential for the subsequent transport of proppant (Barati and Liang 2014b, Cheng 2012). The restrained breakdown pressure also saves on the usage of pumps and related safety at the wellhead, considerably reducing costs to offset the increased expense of CO$_2$ fracturing operations (Middleton et al. 2014).

<table>
<thead>
<tr>
<th>Fracturing fluid</th>
<th>Breakdown pressure / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample #1</td>
</tr>
<tr>
<td>Water</td>
<td>31.79</td>
</tr>
<tr>
<td>Liquid CO$_2$</td>
<td>17.30</td>
</tr>
<tr>
<td>Sc-CO$_2$</td>
<td>15.16</td>
</tr>
</tbody>
</table>

Table 1 Comparison of breakdown pressure for various fracturing fluids (Zhang et al. 2017a).
2.1.2 Morphology of fractures generated by CO₂

The CT scanning of fractures generated by water and CO₂ are compared in Fig. 3 (Ranjith, Zhang and Zhang 2019). The case for water presents a single straight fracture of broad width, while that for CO₂ tends to create multiple narrow fractures with higher tortuosity. The DR scanning results indicate that the fracture surface area created by CO₂ is ~1.24-fold larger (5.87x10⁴ mm²) than that created by water-based fluids, due to the tortuosity and increased number of fractures (Zhang et al. 2017a). The low viscosity and high diffusivity of CO₂ each benefit its entry into micropores and in connecting multiple natural fractures, thus increasing the complexity and connectivity of the fracture network (Li, Li and Dong 2016, Lv et al. 2019, Kim, Cho and Lee 2017).
The resulting fracture width and tortuosity are major differences between water-fracturing and CO₂-fracturing. With the decreasing viscosity of the fluid (CO₂, slickwater and cross-linked guar), the fracture width decreases approximately by half, as shown in Fig. 4 (a). The branching of fractures splits and distributes the fracturing fluid, resulting in narrow fracture networks for low-viscosity injectates (Zou et al. 2018, Perkins and Kern 1961, Montgomery 2013). Meanwhile, fracture tortuosity increases by a factor of ~5–15% when fractured by Sc-CO₂ in Fig. 4 (b) (Jia et al. 2018, Chen, Nagaya and Ishida 2015, Wang et al. 2017a). An incremented tortuosity is also apparent for Sc-CO₂ fracturing comparing with that for liquid CO₂ fracturing by evaluating the change in resulting fractal dimension (Ishida et al. 2012).

![Fracture morphology generated by CO₂ and water-based fracturing fluids. (a) Fracture width created by guar, slickwater and Sc-CO₂ (Zou et al. 2018); (b) Fracture tortuosity of CO₂- and H₂O-created fractures (Jia et al. 2018, Chen et al. 2015, Wang et al. 2017a).](image)

Higher fracture tortuosity, however, hinders proppant transport by increasing proppant settling. Narrower fractures aggravate the difficulty in effective proppant transport (Raimbay et al. 2016, Liu and Sharma 2005). The boosted SRV (Stimulated reservoir volume) resulting from CO₂ injection requires a match in high-efficiency fracture-propping in order to enhance the discharge area for subsequent oil and gas production.

### 2.2 Proppant transport in Sc-CO₂ fracturing

The high viscosity (10² cp level) of gel-based fracturing fluids for conventional reservoirs suspends the proppant for hours to days during slurry injection, largely distributing the proppant uniformly within fractures (Barati and Liang 2014a, Patankar et al. 2002, Novotny 1977). Therefore,
viscosity is commonly used as the criterion in evaluating the proppant transport capacity of a fracturing fluid (Malhotra, Lehman and Sharma 2014). The supercritical state of CO₂ under reservoir conditions is suspected as a key feature in limiting proppant carrying capacity due to its ultra-low viscosity ($10^{-2}$ cp level) (Wang, Li and Shen 2012). The same problem exists for slickwater ($10^1$ cp level) fracturing but is typically solved by increasing the pump rate by a factor of 2 or 3 to carry proppant with the high flow rate (Fink 2020) – a useful technique that could be a reference for CO₂ fracturing. Proppant settles (I) initially in low-viscosity fluids and then maybe remobilized (II) and carried (III) in the form of a migrating dune, as shown in Fig. 5. To restrain dune height (i.e. preventing screen out) and enable the long-range transport of proppant along the fracture, high pump rates and low concentrations of proppant are typically recommended (Hu et al. 2018, Sahai, Miskimins and Olson 2014, Wang et al. 2003).

![Fig. 5 Schematic of proppant transported by low-viscosity fluid within a fracture. (I) Proppant settling (II) Remobilization/entrainment of settled proppant; (III) Proppant transport with the fracturing fluid (Patankar et al. 2002).](image)

### 2.2.1 Particle movements in Sc-CO₂ fracturing

Proppant transport in Sc-CO₂ follows a similar rule to that for the mobilization of proppant in slickwater (Wang et al. 2018, Huo et al. 2017). Particle movement (Fig. 6) may be characterized and compared with that in slickwater transport to identify the relative capacity for proppant transport. Key features of this are:

(I) The equilibrium settling velocity of the transported proppant particles in Sc-CO₂ is closer to the fluid velocity in liquid CO₂ than that in gaseous CO₂ (Table 2) – due to the similarity of forces (drag
force, buoyance, etc.) acting on the particle (Hou et al. 2015, Liangchuan, Zaiming and Zhengsong 2011).

(II) The enhanced driving force (Magnus force generated by particle spin) and reduced resistance force (non-cohesive-force due to the non-interfacial-tension characteristic) results in easier restarting of the particles in Sc-CO$_2$ with an averaged Shields number of 0.0028 (Table 2) – identifying a reduced drag force required to drive particle restarting in Sc-CO$_2$ (Hou et al. 2019).

(III) The measured particle velocity in the flowing direction reaches ~90% of the averaged fluid flow velocity under high flow-rate condition, demonstrating the high particle transport capability of Sc-CO$_2$ (Hou et al. 2016, Hou et al. 2017b). The comparisons of Fig. 7 show the relative performance characteristics for proppant, which is sensitive to the flow rate in the case of Sc-CO$_2$.

**Table 2 Essential kinematic parameters of a particle transported by various fluids**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity $\eta$ cp</th>
<th>Settling velocity $v_s$ m/s</th>
<th>Shields number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supercritical CO$_2$</td>
<td>0.026–0.064</td>
<td>0.13–0.36</td>
<td>0.0015–0.004</td>
</tr>
<tr>
<td>Liquid CO$_2$</td>
<td>0.1</td>
<td>0.11–0.23</td>
<td>N/A</td>
</tr>
<tr>
<td>Gaseous CO$_2$</td>
<td>0.01</td>
<td>3.12–7.21</td>
<td>N/A</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>N/A</td>
<td>0.01–0.1</td>
</tr>
</tbody>
</table>
2.2.2 CO₂ thickening

The application of thickening agents to CO₂ improves proppant transport, restrains the excessive leak-off of CO₂ into the formation and also benefits the sweep efficiency of CO₂ flooding for EOR (enhanced oil recovery) by narrowing the viscosity gap between CO₂ and crude oil (Blunt, Fayers and Orr Jr 1993, Gilfillan et al. 2009). CO₂ is a weak solvent for common polymer thickeners, due to its non-polar nature. Attempts have confirmed the potential of specific polymers (siloxane, fluorinated and hydrocarbon polymer) (O’Brien et al. 2016, Enick et al. 1998, Sarbu, Styranec and Beckman 2000), low-molecular-weight compounds (hydrogen-bonding and organometallic compound) (Shi et al. 1999, Raveendran and Wallen 2002) and surfactants (fluorinated, siloxane and hydrocarbon surfactant) (Harrison et al. 1994, Fink and Beckman 2000, Liu et al. 2001) in thickening fracturing fluids. The potential agents and their thickening efficiencies are summarized in Table 3.

<table>
<thead>
<tr>
<th>Agent</th>
<th>Solution wt %</th>
<th>Thickening result</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl Benzoate / Heptadecafluorodecyl acrylate co-polymers</td>
<td>5</td>
<td>483 times</td>
<td>Sun et al. (2018b)</td>
</tr>
<tr>
<td>P-1-D / Piso-VBE / PVEE</td>
<td>0.81–5</td>
<td>0.07–0.18 cp</td>
<td>Al Hinai et al. (2018)</td>
</tr>
<tr>
<td>Polydimethylsiloxanes</td>
<td>8–18</td>
<td>4–20 times</td>
<td>O’Brien et al. (2016)</td>
</tr>
<tr>
<td>Fluoropolymer &amp; surfactant</td>
<td>0.25–1.5</td>
<td>1.3–9.3 cp</td>
<td>Meng et al. (2016)</td>
</tr>
<tr>
<td>Amphiphilic surfactant</td>
<td>3</td>
<td>8.2–20 cp</td>
<td>Luo et al. (2015)</td>
</tr>
</tbody>
</table>

Fig. 7 The following performance of proppant (ratio between proppant horizontal velocity and fluid velocity) for various fluids (Hou et al. 2016).
Poly (vinyl ethyl ether) and poly (1-decene) | 0.56–0.81 | 13–14 times | Zhang, She and Gu (2011b)
Fluorinated-di-chain-surfactant | 1–10 | 1–2 times | Trickett et al. (2010)

2.3 Permeability evolution in propped fractures with the saturation of CO₂

Fracture permeability or conductivity (fracture permeability times width) governs the final production of hydrocarbons from the reservoir after fracturing (Warpinski et al. 2009). The interaction between fracture surface and fracturing fluid affects the permeability, as well as the distribution of proppant, closure stress, formation temperature and pressure (Arshadi et al. 2017, Zhang et al. 2015b, Wen et al. 2007). With the saturation of CO₂, the phase states (sub- and super-critical), adsorption and resultant embedment and swelling dominate the permeability evolution (Mazumder and Wolf 2008, Busch and Gensterblum 2011).

2.3.1 Embedment and swelling induced by CO₂ adsorption

An approximately 10–60% reduction in fracture aperture caused by proppant embedment is found with a subsequently greater than 50% reduction in oil and gas recovery (Zhang and Hou 2016, Santos, Dahi Taleghani and Li 2018). Proppant embedment may lead to conductivity loss in siltstones of 78.42%, in mudstones of 81.89%, in conglomerates of 91.55% and in shales of 78.05% (Bandara, Ranjith and Rathnaweera 2019). The mineral composition and mechanical characteristics of the formation significantly impact embedment and resulting permeability loss (Tang and Ranjith 2018, Reinicke et al. 2010, Cai et al. 2014). When saturated by CO₂, swelling (induced by CO₂ adsorption in the rock matrix) increases embedment by a factor of 1.84–1.93 (∆b₃/∆b₁), schematically illustrated in Fig. 8. The swelling independently contributes 9–56% ((∆b₂-∆b₃)/(∆b₂-∆b₁)) of the total adsorbing-induced fracture loss, which may be evaluated from the adsorbed mass (Hou, Elsworth and Geng 2020).
The adsorbing CO$_2$ swells the matrix, shrinks the fracture aperture and then leads to a reduction in permeability. This follows the Langmuir isotherm and reaches maximum influence at approximately twice the Langmuir pressure (Wang, Elsworth and Liu 2011, Cai et al. 2014, Liu et al. 2011). The competition between swelling and effective stress results in a typical U-shaped curve for permeability as a function of increasing gas pressure for both integral and split samples (Kumar et al. 2015, Izadi et al. 2011).

2.3.2 Permeability variation with phase states of CO$_2$

Injected as liquids in most cases for fracturing, CO$_2$ experiences a phase transition to supercritical under typical reservoir conditions (exceeding 31 °C and 7 MPa), which is found to significantly impact the evolution of permeability (Buscheck et al. 2016), as shown in Fig. 9. A V-shaped variation around the critical point is observed when gaseous CO$_2$ transforms into supercritical CO$_2$ (Hou et al. 2020, Zhi, Elsworth and Liu 2019). In contrast, the permeation of liquid CO$_2$ remains continuous after phase transition and increases more moderately as the gas pressure also increases. Different mechanisms of permeability variation are discussed between liquid and supercritical transitions – suggested by differences in the subsequent permeability trends at high pressure. The liquid case is explained by the sudden volume change during the phase transition for a relatively stable pressure (Li et al. 2017, Van Der Waals and Rowlinson 2004). The supercritical case may be due to the increasing
adsorbed-phase density (intensifying the swelling that narrows the effective aperture) and resultant swelling stress (counteracting the confining pressure that releases the effective aperture).

Fig. 9 Permeability evolution relative to gas pressure with phase transitions of CO$_2$ from gaseous to liquid (L-CO$_2$) and then to supercritical states (Sc-CO$_2$) (Li et al. 2017, Hou et al. 2020, Zhi et al. 2019).

CO$_2$ in its supercritical state interacts with both organic and inorganic constituents of the permeated rock matrix (Busch et al. 2008a, Karacan and Mitchell 2003, Garcia et al. 2012), which may result in the repeated parabolic evolution of the permeability curve first below and then above the critical point in the propped shale fracture (the Sc-CO$_2$ case with higher permeabilities in Fig. 9). The inorganic interactions are apparent in abnormal increments of permeability recovery for He-repeat tests with penetration of supercritical CO$_2$ compared with the penetration of subcritical CO$_2$ (Fig. 10). The dehydration of clay (competitive adsorption between CO$_2$ and H$_2$O) and dissolution of carbonate (co-existence of released water and CO$_2$) may improve the permeability recovery (Bowers et al. 2017, Weniger et al. 2010, Gaus 2010). The contribution of inorganic adsorption to permeability evolution has an estimated fraction of 60–70% under supercritical condition (Hou and Elsworth 2021).
Fig. 10 Permeability recovery of He before (initial) and after (repeat) the penetration of CO$_2$ (Hou and Elsworth 2021).

2.4 Case studies

CO$_2$ fracturing is usually applied as a candidate strategy in water-sensitive reservoirs or in arid regions where potable water is particularly valuable (Wang et al. 2016, Ribeiro and Sharma 2013). The major difference between CO$_2$ fracturing and water-based fracturing sites is the sealed blinder that mixes proppant with CO$_2$ under pressure - a specialized piece of equipment with high cost and low market maintenance (Liu et al. 2014, Hou et al. 2013). Due to this difficulty, many cases of CO$_2$ fracturing are operated without proppant injection – known as CO$_2$ hybrid fracturing that pumps pure CO$_2$ initially as the pre-pad fluid to create complex fracture networks and then applying water-based fluid for the carrying of proppant (Ribeiro, Li and Bryant 2017, Li et al. 2019b). Stimulation parameters for CO$_2$ fracturing are summarized in Table 4. The targeting formations are tight sands or shales with ultra-low permeabilities that restrain CO$_2$ leak-off (Li and Zhang 2019, Li and Elsworth 2015, Jin et al. 2017). Both the pump rate and sand ratio are much lower than for slickwater- or gel-based fracturing cases. The current scale of fracturing (injected volume of CO$_2$ and proppant) is incomparable with that for water-based fracturing, thus limiting its popularization.
3. Discussions

A summary of current studies reveals correlations among fracturing procedures, from which common issues are extracted to complete the technical details of CO₂ fracturing. Various solutions and relevant research topics are proposed and modified based on current progress. Feasible measures for field practice are also discussed, which may increase the scale of fracturing and stimulated production and lead to its ultimate adoption.

3.1 Mismatch between pump rate and fluid viscosity

The viscosities of guar, slick-water and supercritical CO₂ (three successive generations of fracturing fluid) decrease from ~10² to ~10¹ then to the ~10⁻² cp level (Thomas et al. 2019, Zhang et al. 2017b). Low viscosity leads to high leak-off and potentially poor fluid efficiency in fracture.
generation and proppant transport (Ishida et al. 2004, Shimizu, Murata and Ishida 2011). The success of slickwater-fracturing relies on the enhanced pump rate that can compensate for the low fluid efficiency (Table 5). For CO₂, increasing the pump rate eliminates the slip velocity between the proppant and the carrying fluid (Fig. 7), and boosts proppant transport along the fluid-driven fracture. This also compensates for the fluid loss by leak-off, which may dissipate up to half of the total fluid volume during the pumping (Shiozawa and McClure 2016, Wang et al. 2017b, Lv et al. 2017). A high pump rate cleans proppant settlement in the wellbore, especially in horizontal wells, and controls the height of the evolving proppant dune within the fracture (Fig. 5), thus ensuring continuous proppant injection and preventing proppant plugging and screen-out (Tong and Mohanty 2016, Dontsov and Peirce 2014, Osiptsov 2017).

### Table 5. Hydraulic parameters of gel, slick-water and CO₂ fracturing.

<table>
<thead>
<tr>
<th>Proppant size mesh</th>
<th>Pump rate m³/min</th>
<th>Viscosity cp</th>
<th>Fracturing Scale m³</th>
<th>Proppant ratio %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guar</td>
<td>30–50 &amp; 20–40</td>
<td>~10³</td>
<td>~10³</td>
<td>~50</td>
</tr>
<tr>
<td>Slick-water</td>
<td>100 &amp; 40–80</td>
<td>~10¹</td>
<td>~10¹</td>
<td>~20</td>
</tr>
<tr>
<td>CO₂</td>
<td>100 &amp; 40–80</td>
<td>~10²</td>
<td>~10²</td>
<td>~10</td>
</tr>
</tbody>
</table>

The fracture-entry width, determining the potential for proppant infusion, is sensitive to the injection rate. The maximum fracture width increases by a factor of 60% as the pump rate of CO₂ increases from 3 to 7 m³/min, as shown in Fig. 11 (Wang et al. 2019, Yushi et al. 2017). High pump rates also generate a more complex fracture network that increases the stimulated reservoir volume (Hou et al. 2014, Zou et al. 2016). With the lowest viscosity of these three fluids, CO₂ fracturing may require even higher injection rates. However, the mismatch between viscosity and pump rate during CO₂ fracturing may result in low fluid efficiency for fracturing and subsequent proppant carrying capacity even at the smallest fracturing scale and proppant ratio (Table 5).
3.2 Friction reducers for CO₂

The friction of pure CO₂ decreases with increasing Reynolds number. The friction factor is proportional to CO₂ viscosity (temperature) and inversely proportional to injection rate and CO₂ density (pressure) – thus, liquid CO₂ generates higher friction than does Sc-CO₂ (Wang et al. 2014, Brkić 2011). Approximately 5–20 MPa of pressure loss per kilometre is observed in pipe-flow tests (Jinqiao et al. 2015). The pressure lost by friction in CO₂ is comparable (slightly lower) to that loss by friction in pure water (Li et al. 2019c). Theoretically, a ~70% reduction in friction should be achieved, similar to that the friction reducer achieves in slickwater, to elevate the pump rate and make up the mismatch between pump rate and viscosity (Table 5). A fluoropolymer is presented to reduce the frictional pressure of liquid CO₂ by a factor of 13.3–45% (Scharmach and Kelly 2019, Kelly, Scharmach and Renz 2017). Besides, few studies are reported on the friction reducer for CO₂.

3.3 Sc-CO₂ thickening

3.3.1 Targeting viscosity optimization

The appropriate usage of thickener benefits costing control and environmental protection. The evaluation of the enhancement in proppant transport by thickener suggests that the effect of Sc-CO₂ viscosity is significant at its low-value range, while the increased density of CO₂ also makes a contribution (Fig. 12). An optimum value of enhanced Sc-CO₂ viscosity is proposed of ~0.001 Pa·s,
about 50 times higher than the original value (Hou et al. 2017a). Besides, higher viscosity of CO\textsubscript{2} also restrains leak-off and benefits the growth in fracture width, an important consideration in the optimization of viscosity.

![Viscosity and Density Graph](image)

Fig. 12. Effects of CO\textsubscript{2} density and viscosity on enhanced proppant transport in the thickened CO\textsubscript{2} (Hou et al. 2017a).

### 3.3.2 Shear resistance of thickened CO\textsubscript{2}

An increasing pump rate requires higher shear resistance of the thickened CO\textsubscript{2}. The shear viscosity of the thickened CO\textsubscript{2} is often left undefined during the thickener investigations that measure zero shear viscosity by falling-ball viscometer (Sun et al. 2018a, O’Brien et al. 2016). However, the capillary viscometer, measuring the pressure drop of the flowing CO\textsubscript{2} mixture in a tube, is able to quantify both the shear viscosity and friction, and thus is suitable for evaluating the mixture system with both reducer and thickener (Enick et al. 2012, Zhang, She and Gu 2011a, Li et al. 2019a). The thickened viscosity of CO\textsubscript{2} decreases approximately by half of the initial value with increasing shear rate (Fig. 13). Meanwhile, the friction coefficient also drops with increasing flow rate (Luo et al. 2015). The temperature, pressure and contents of agents may also evolve the shear viscosity of the thickened CO\textsubscript{2}, which should be better defined.
3.4 Permeability evolution in fractures generated by CO₂

Permeability evolution in unpropped samples shows similar trends to those with the propped case – due to the swelling stress in forcing the closure of fractures and in depressing the potential for permeation (Wang, Liu and Elsworth 2015, Wang, Elsworth and Liu 2013). The injection of adsorbing CO₂ aggravates such phenomena and may result in rapid depletion of production with the decreasing pore pressure (Fig. 9). Therefore, proppant is crucial in CO₂ fracturing to maintain effective apertures. #100 mesh proppant may be an alternative when larger sizes of proppant encounter problems entering narrow and tortuous fractures, as well as ultra-lightweight porous ceramic proppants (Rickards, Brannon and Wood 2013, Ely et al. 2014, Alotaibi and Miskimins 2015).

The smaller size of proppant mitigates embedment since the embedment depth is proportional to the proppant diameter, as shown in Fig. 14 (Kewen Li 2015, Alramahi and Sundberg 2012, Zhang et al. 2015a), thus mitigating effective aperture loss with the saturation of CO₂. Besides, fine proppant also blocks natural fractures and macropores and enhances the fluid efficiency for fracture propagation (Dahi-Taleghani and Olson 2013, Gale et al. 2014). CO₂-rock interactions revealed in permeability tests may also influence the fracturing procedure, especially the swelling stress that may counteract the confining pressure (Zhang et al. 2018), reduce the difference between max- and min-stress and enhance the complexity of the fracture network (Hoek and Bieniawski 1965, Soliman, East and Augustine 2010).
Fig. 14. Reduction of fracture aperture versus proppant diameter with various elastic modulus of proppant (Kewen Li 2015).

4. Recommendations

Despite abundant fundamental studies on overall procedures for CO₂ fracturing, several essential issues remain to be resolved, and are discussed as follows (Fig. 15):

i. **Fracturing:** Increasing pump rate promotes the evolution of high pressure within fractures. The addition of thickener and fine proppant both enhance fluid efficiency by restraining CO₂ leak-off, thus boosting the growth in fracture width and in improving subsequent proppant transport, especially for larger sized proppant.

ii. **Propping:** Pump rate appears to dominate the CO₂ capacity of proppant transport, especially when CO₂ is thickened to an optimal viscosity. The higher tortuosity of fractures generated by CO₂ may require higher pump rates and smaller sizes of proppant than water-based fracturing.

iii. **Permeating:** Permeation behaviour of CO₂ in propped fractures with fine proppants should be further defined. The definitions of CO₂-organic and CO₂-mineral interactions and the resultant swelling stresses improve predictions of permeability and production. The effect of swelling stress on fracture propagation requires further definition.

iv. **Agents for CO₂:** Developing friction reducers for CO₂ should take top priority over other agents. Relevant thickeners may be tested for optimization or used as the cosolvent. The shear
resistance of thickened CO₂ should be investigated, as well as the effects of temperature, pressure and relative proportions of agents.

v. **Field practice**: Hybrid CO₂ fracturing may be an option in developing CO₂ fracturing, although the ratio of CO₂ in the mixture needs to be optimized. #100 mesh proppant may be necessary for propping tortuous and narrow fractures. Injecting CO₂ in its supercritical state may reduce the friction loss over that for liquid CO₂.

vi. **Multidisciplinary breakthroughs**: Breakthroughs in CO₂ fracturing may be achieved in fundamental studies of additive agents and CO₂-rock interactions, which involve interdisciplinary fields of Sc-CO₂ extraction, CO₂ flooding, CO₂ adsorption and CO₂ sequestration.

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**Fig. 15. Schematic of fundamental studies and suggestions on overall procedures of CO₂ fracturing and their associations.**

5. **Conclusions**

Fundamental studies on overall procedures for CO₂ fracturing (fracture-propagation, propping and permeating) are summarized and analysed to disclose gaps between field practices and nascent research. The major conclusions may be generalized as follows:

1. Higher tortuosity and narrower width of fractures generated by CO₂ enhance the stimulated reservoir volume as a result of the low viscosity and high diffusivity of CO₂, yet also aggravate the
difficulty of subsequent proppant transport by hindering proppant entry into the fracture and in increasing proppant settlement, thus limiting fracturing scale in field tests.

(2) The mismatch between pump rate and CO₂ viscosity is apparent in comparing hydraulic/pumping parameters apparent in field cases. Increasing the pumping rate in CO₂ injection simultaneously improves fracture generation and proppant transport. A higher pump rate expands fracture width by making up for CO₂ leak-off and thereby boosting the effective pressure within fractures. It also eliminates the slip velocity between proppant and the proppant-carrying CO₂, cleans the settled proppant from the wellbore and controls the evolving and maximum dune height in fractures.

(3) Reductions in rock strength that accompany saturation by CO₂ lower the breakdown pressure to fracturing, which reserves a safety margin against raising pump rate. Research on friction reducers for CO₂ modification is insufficient and should take top priority. Relevant thickeners may be optimized or used as cosolvents. Besides, injecting CO₂ in a supercritical state automatically reduces the friction loss relative to that for liquid CO₂.

(4) Thickeners for CO₂ may target a lower enhanced-viscosity due to the contribution of CO₂ density. The shear resistance of thickened CO₂ becomes more crucial with an increase in the injection rate. Fine proppant (i.e. #100 mesh) may be an alternative when larger sizes of proppant are inapplicable. This will prop tortuous and narrow fractures, mitigate against embedment and control leak-off by blocking natural fractures and macropores.

(5) Other open research questions persist, including the effect of swelling stress on fracture propagation, the definition of CO₂-organic and CO₂-mineral interactions and resultant effects on permeability evolution, the optimization of CO₂ usage for the hybrid fracturing.

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