Laboratory study of the Non-Newtonian behavior of supercritical CO₂ foam flow in a straight tube

Dongxing Du, Yingge Li, Kun Chao, Chengcheng Wang, Dexi Wang

PII: S0920-4105(18)30081-0
DOI: 10.1016/j.petrol.2018.01.069
Reference: PETROL 4656

To appear in: *Journal of Petroleum Science and Engineering*

Received Date: 6 September 2017
Revised Date: 12 January 2018
Accepted Date: 30 January 2018


This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Laboratory Study of the Non-Newtonian Behavior of Supercritical CO$_2$ Foam Flow in a Straight Tube

Dongxing Du$^{1,2,*}$, Yingge Li$^{1,3}$, Kun Chao$^{1,2}$, Chengcheng Wang$^{1,2}$, Dexi Wang$^{1,2}$

$^1$College of Electromechanical Engineering, Qingdao University of Science and Technology, Qingdao, 266061, China
$^2$Geo-Energy Research Institute, Qingdao University of Science and Technology, Qingdao, 266061, China
$^3$College of Automation and Electronic Engineering, Qingdao University of Science and Technology, Qingdao, 266042, China

*Corresponding Author. Email: du-dongxing@163.com

ABSTRACT

Rheological properties of supercritical CO$_2$ (ScCO$_2$) foam fluids are essential to understand foam displacement mechanisms in the research & development of efficient CO$_2$-EOR and CO$_2$ geological storage technologies. In this paper, a systematic laboratory study concerning non-Newtonian CO$_2$ foam flow characteristics in a straight tube was carried out under different gas-liquid ratios. Through modifying experimental pressure and temperature conditions, comparative studies on liquid phase CO$_2$ and gaseous CO$_2$ foam rheology were also carried out. The experimental results show obvious shear-thickening behavior for the scCO$_2$ foam (45°C and 8.0MPa) with flow behavior index increasing from 1.03 to 1.76 with increasing foam quality. And the apparent viscosity of scCO$_2$ foam could reach up to 140 times of the single-phase water. The liquid phase CO$_2$ foam (25°C and 8.0MPa) also exhibits clearly the shear-thickening characteristics with flow behavior index ranging from 1.56 to 1.88. The gaseous CO$_2$ foam, on the other hand, behaves in a shear-thinning or pseudo-plastic manner with flow behavior index of 0.70<n<0.76. Due to the decreased interfacial tension and less bubble coalescence rate, much finer foam textures are observed for ScCO$_2$ and liquid CO$_2$ bulk foam, which mainly contributes to the shear thickening behavior for ScCO$_2$ and liquid CO$_2$ foam fluid.

Keywords: Supercritical CO$_2$, liquid CO$_2$, gaseous CO$_2$, foam, rheology, non-Newtonian behavior
1. INTRODUCTION

“Gas Flooding”, typically including CO₂, N₂ or natural gas, has become one of the leading enhanced oil recovery (EOR) technologies for extracting residual oil stranded or trapped in the reservoirs.¹,² However, due to the less viscous, lighter density and higher mobility, the gas flooding technologies frequently suffer from poor displacement efficiency due to viscous fingering, gravity override, gas channeling problems, etc.³,⁴ Foam technology, therefore, has been introduced to improve the sweep efficiency of the gas flooding process by drastically increasing the gas phase apparent viscosity.⁵–⁹ In addition, as one of the important carbon resourceful usages and geological storage enhancement technology in the Carbon Capture, Utilization and Storage (CCUS) chain, CO₂ foam has attracted worldwide interest for its potential application not only in CO₂-EOR processes, but also in geological carbon storage practices as well.¹⁰–¹⁴

Detailed investigations on the foam rheological properties are substantial to understand the mechanism of foam displacement process in underground formations. As one aspect of the foam rheological studies, researchers have reported fairly lot results concerning moving foam lamellae in straight capillary tubes to capture the foam flow characteristics in porous media. Bretherton¹⁵ has analyzed the motion of long bubbles in tubes and pointed out the pressure drop for long bubbles moving steadily in a tube at small Reynolds number, which is given by the equation as follows,

\[ \Delta \rho \equiv 3.58 \left( \frac{3 \mu U}{\sigma} \right)^2 \frac{\sigma}{r} \]  

(Where \( \mu \) is the surfactant solution viscosity, \( U \) is the speed, \( \sigma \) is the surface tension and \( r \) is the capillary tube radius). Following this idea, Hirasaki et al.¹⁶ successfully predicted the pressure drop across the foam film by taking account into two radii of curvature and surface tension gradient. Xu et al.¹⁷ concluded the effective viscosity of foam in periodically constricted tubes by accounting for the
drag on lamellae along pore walls and capillary forces, and found that the drag on the lamella increase
the pressure gradient above the quasi-static limit by a factor scaling roughly as the 2/3 power of
velocity. Nguyen et al.\textsuperscript{18} have investigated the motion of foam film in diverging and converging tube
by taking into account the influence of dynamic surface tension effects, proved that the surface tension
effects give rise to a difference between the dynamic and static pressure drops across a single foam film
at diverging segment, but the surface elasticity has limited effect on pressure drop at converging
segment. Du et al.\textsuperscript{19} experimentally investigated gaseous CO\textsubscript{2} and N\textsubscript{2} foam lamellae foam flow
characteristics in a vertical tube. They found both CO\textsubscript{2} and N\textsubscript{2} lamellae show clear linear relationships
between non-dimensional parameters of $\Delta p d/\sigma$ and $(3\mu U/\sigma)^{2/3}$ with nearly the same slope but different
threshold values, indicating a startup pressure to mobilize the bubble train in a straight tube. Their
mechanistic models for CO\textsubscript{2} and N\textsubscript{2} foam lamellae predict similar trend however much higher flow
resistance compared to Bretherton and Hirasaki models, for which the authors contributed to viscous
forces. Besides experimental works, some researchers have also reported their numerical studies. Du et
al.\textsuperscript{20-21} have employed the Surface Evolver\textsuperscript{22} software to study the lamellas flow behavior in a vertical
straight and converging-diverging tubes. They found that the physical model with viscous force can
adequately describe the initiating pressure for mobilizing foam lamellae flow in a straight tube, which
is in consistent with their experimental observations.\textsuperscript{19} Without taking into account the viscous force of
the moving liquid layer on the tube wall, on the other hand, they observed the lamellae accelerate and
decelerate with the periodically varying cross sections and the pressure of each bubble varies
periodically as the section converges and diverges. The pressure fluctuations increase as the bubble
number increases, however, the fluctuation can not produce positive pressure drops along the duct.

All above researchers treated foam rheology based on the analysis of foam lamellae or bubble
train, which are sophisticated and may lack of practical conveniences. In practices, foam may move not only in the form of lamellae train but also as bubble clusters, which could be more practically treated with specific non-Newtonian fluid correlations. Therefore as another aspect of foam rheology studies, the method of dealing foam as a bulk non-Newtonian fluid always keeps active accompanying its application potentials in EOR and greenhouse gas geological storages. Reidenbach et al. experimentally studied the N₂ and liquid CO₂ foam in laminar and turbulent region based on a yield pseudo-plastic model. Without taking foam generators, they observed the foam flow in laminar flow shows Bingham pseudo-plastic behavior while the turbulent foam exhibits shear thickening behavior with flow index varying among 1.23 to 1.8. Lee et al. measured foam mobility during simultaneous flow of the dense CO₂ and surfactant solutions through core samples. They found foam mobility decreased steadily as surfactant concentration increased until a minimum mobility was attained at some particular concentration well above the conventional critical micelle concentration (CMC). The effect of foam volume fraction showed that mobility decreases with increasing fraction of surfactant solution. They also observed foam shear-thinning behavior under conditions of low surfactant availability in the total (Darcy) velocity range of 3-11 ft/day. Sun et al. studied the rheology of CO₂ foam fracturing fluid under downhole condition on a large scale flow-loop experiment system, and they found the foam fluid showed power-law shear thinning behavior with the apparent viscosity proportional to the increment of foam quality and pressure. Gu et al. investigated the rheology of polymer-free foams in a recirculating pipe rheometer up to 155 °F and 2000 psi. They observed all of studied foam fluids exhibit power-law rheological behavior with the increasing pressure corresponding to increasing foam viscosity and quality. Lv et al. carried out systematical investigations concerning the CO₂ and N₂ foams behaviors both in bulk and porous media by static foam tests and core flood experiments, and
they concluded that CO₂ bubbles are relatively larger, wider size distribution and unstable than N₂ bubbles in the static foam tests, but in porous media, their foam stability are similar and exhibited different non-Newtonian flow characteristics at different foam qualities. Very recently, Kahrobei et al. investigated the effects of injection velocity and surfactant concentration on foam generation and hysteresis behavior as a function of foam quality. They found that the transition from coarse-foam to strong-foam is almost independent of flowrate, surfactant concentration, and foam quality. They also observe that the rheological behavior of foam is strongly dependent on liquid velocity, say, at very low and high velocities foam is shear-thinning, while at intermediate velocities the behavior is shear thickening.

It is deduced from above literatures that the rheology studies concerning CO₂ foam fluid are becoming more and more popular relating to its potential applications in CO₂ EOR and carbon geological storage practices, however most laboratory works reported up to now focus on the rheological performance of CO₂ in gas phase, the rare documented liquid phase CO₂ foam rheology result don’t agree well with each other. Under practical conditions of oil reservoirs, which are usually deeper than 750 m with temperature higher than 50°C, the CO₂ fluid is always in the supercritical phase (the critical point of CO₂ is T=31.04°C & P=7.38MPa), therefore more efforts should be devoted on the Supercritical CO₂ (ScCO₂) foam rheology studies. Herein, we report a systematic laboratory study on bulk ScCO₂ foam rheology based on non-Newtonian fluid assumptions. Pressure drops were measured for the flowing foam fluid in a straight tube and the foam apparent viscosities were obtained by employing constitutive equations of a power-law non-Newtonian fluid. Effect of foam quality was investigated through employing various surfactant solution flow rates. In particular, the comparative laboratory studies on liquid and gaseous CO₂ foam rheology were also carried out to deepen
understanding of scCO$_2$ foam flow mechanism in porous media.

2. EXPERIMENTAL SECTION

2.1 Experimental materials

In this study, sodium dodecyl sulfonate (AR, Sinopharm Chemical Reagent Co., Ltd., “SDS” for short with molecular weight of 288.38) is selected as the surfactant, and is dissolved in deionized water to make the surfactant solution. The employed surfactant concentrations is 5g/L, which is well above the CMC of 8.02 mmol/L or 2.31g/L. As the characteristic time for foam rheology measurement is 10~60s, which is much shorter than the reported CO2 foam half-life time of 4.7min, the instability and degradation of surfactant solution could be reasonably neglected.

2.2 Experimental setup and procedure

The experimental setup system is schematically depicted in Figure 1.

In the experiment, the pressurized CO$_2$ out of the gas cylinder is firstly cooled (~4°C) to liquid phase, and then is pumped with the high-precision piston pump into the high pressure foam generator in the hot water bath (~45°C), where the liquid CO$_2$ changes the phase to Supercritical CO$_2$ and mixes with the SDS solution to generate ScCO$_2$ foam. Foam fluid flows through a horizontal quartz glass tube with inner diameter of 4mm, and expels through rear buffer tank and back-pressure control system. The transparent quartz glass tube could meet the requirements of bearing the high experimental pressure without sacrificing clear foams morphology observations. To obtain stable ScCO$_2$ foam in the straight tube, the system pressure is well maintained at 8.0MPa and the forepart of tubing system, including the foam generator and quartz glass tube, is immersed in the hot water bath with temperature of 45°C. The flowing foam pressure difference between the inlet and outlet of the quartz glass tube is measured by the precision differential pressure gauge. Through manipulation of the system pressure and temperature,
the phase of CO$_2$ fluid could be varied among supercritical, liquid and gas. Through modifying the flow rate of SDS surfactant solution, the influence of foam quality on the foam rheology could be scrutinized.

The structure of the foam generator, which is essential for generating pre-mixed foam fluids, is described in Fig.2. The co-injected CO$_2$ fluid and surfactant solutions are pushed from the right side of the generator, then through the consolidated quartz sand plate to make well mixed foam fluid. The detailed side view and front view of the high pressure quartz tube unit, which is the most important component in the setup, are described in Fig.3. With proper sealing measures and 4 fastening stainless steel pull rods, the quartz tube unit could stand high pressure up to 15Mpa, which ensures the safe measurement and clear observation of the supercritical CO$_2$ foam flow behaviors.

It has to be mentioned the experimental conditions of 8Mpa and 45°C is well above the critical point of CO$_2$. At this pressure and temperature, a water-rich liquid phase coexists with a CO$_2$-rich dense phase, where a distinction between the vapor and liquid phases disappears.$^{31}$ The mixture fluid formed with dense CO$_2$ as the internal phase is strictly emulsion$^{30}$ sometimes referred to as foamulsion.$^{32}$ However, for the sake of consistency we still use the term of “foam” to represent such a mixture fluid in this paper. Actually, fairly lot researchers employed the term of “foam” as well in the cases where the CO$_2$ fluid lies in the supercritical or liquid phase region.$^{24, 27, 33-36}$

2.4 Power-law constitutive equations and data processing method

By treating flowing foam as a non-Newtonian fluid with power-law constitutive equations, the relationship between shear stress and shear rate can be correlated with Eq.(1)

$$\tau = K \gamma^n$$

(1)

Where $K$ is the flow consistency coefficient and $n$ is the flow behavior index (When $n<1$, fluids...
exhibit the decrease of apparent viscosity with increasing shear rate, named as shear-thinning fluids; when $n > 1$, fluids show the increase of apparent viscosity with increasing shear rate, named as shear-thickening fluids). Eq. (1) can be rearranged in the same shape as Newtonian fluid in engineering applications, such as,

$$\tau = \mu_a \gamma$$

(2)

Where $\mu_a = K \gamma^{n-1}$, is the apparent viscosity of the power-law fluid, and is a function of shear rate.

The shear stress $\tau$ and shear rate $\gamma$ for bulk foam flow can be calculated with the following equation,

$$\tau = \frac{\Delta P}{l \frac{d}{4}} , \quad \gamma = \frac{8U}{d}$$

(3)

Where $d$ is the tube diameter, $\Delta P$ is the pressure drop along the tube, $l$ is the length of the tube, $U$ is the average flow velocity, and its relationship with volumetric flow rate $Q$ is $U = 4Q/(\pi d^2)$.

Therefore, plotting measured $\frac{8U}{d}$ and $\frac{d\Delta P}{d\ell}$ in natural logarithmic scale will give a straight line for power-law type of Non-Newtonian fluid, and experimentally obtained $n$ and $K$ values determine the rheology characteristics of the flowing foam fluid.

3. RESULTS AND DISCUSSION

3.1 Rheology characteristics for scCO$_2$ foam in a straight tube

At the constant surfactant concentration of 5g/L and surfactant flow rate of 1.0ml/min, rheology characteristics for ScCO$_2$ foam fluid were investigated through measuring foam flow pressure drops along the tube at different flow rates of scCO$_2$ fluid. The experimentally obtained data of $\ln \left(\frac{8U}{d}\right)$ vs. $\ln \left(\frac{\Delta P d}{4l}\right)$ are displayed in Figure 4(a), and the clear linear tendency validates the assumption of power-law model for the bulk foam fluid. The linear relationship between
\[ \ln\left(\frac{8U}{d}\right) \text{ vs. } \ln\left(\frac{\Delta Pd}{4I}\right) \text{ could be fit as,} \]

\[ \ln\left(\frac{\Delta Pd}{4I}\right) = 1.34 \ln\left(\frac{8U}{d}\right) - 3.48 \tag{4} \]

It is obtained from Eq.(4) that the flow consistency coefficient \( K \) for ScCO\(_2\) foam fluid is 0.031(\( K = e^{-3.48} \)), while the flow behavior index \( n \) is 1.34, demonstrating obvious shear-thickening Non-Newtonian behavior. Also shown in Fig. 4(a) are the error bars for experimental data and the standard error for the fit line of Eq.(4). Based on the error estimation described in Section 3.6, the error bars lies in the range of ±5.67 for measured shear stress of \( \tau \), and the standard errors for the linear fit line of Eq.(4) are 0.19 (5.5%) for intercept and 0.05 (3.73%) for slope respectively.

To show clearly the non-Newtonian behavior of flowing ScCO\(_2\) foam fluid, the apparent viscosities, as calculated through Eq.(2), are displayed in Fig. 4(b) based on experimentally obtained values of \( K = 0.031 \) and \( n = 1.34 \). It can be clearly observed the apparent viscosity of ScCO\(_2\) bulk foam exhibits a typical shear-thickening behavior, showing higher apparent viscosities at higher shear rates. It is also noticed that although the foam is made of above 80% of ScCO\(_2\) phase in quality, as indicated in Fig.7 in later section, its apparent viscosity is remarkably higher than 0.001 \( Pa \cdot s \) of single phase water. The apparent viscosities for ScCO\(_2\) foam flow in the measured shear rate range of \( \gamma = 20 \sim 80 \text{s}^{-1} \) are 0.08\text{--}0.14 \( Pa \cdot s \), which are 80\text{--}140 times larger than the single phase water. Actually, the unique rheological characteristics of high apparent viscosity indicate ScCO\(_2\) foam could contribute potentially as a mobility control agent in modern petroleum and environmental industries.

Through modifying surfactant flow rates, foams with various qualities, or flow gas fractions, could be generated. Fig. 5 (a)-(c) depicts ScCO\(_2\) foam flow characteristics at different surfactant flow rates of 2.0ml/min, 1.5 ml/min and 0.5ml/min respectively. In accordance with the results on surfactant rate of 1.0ml/min, Fig. 5 also reveals obvious shear thickening behavior with flow behavior index n all
above 1 at other surfactant rates.

The comparisons of ScCO$_2$ rheology properties at different surfactant flow rates are displayed in Fig. 6 based on the experimentally obtained correlations between shear stress and shear rate in natural logarithmic scales. It could be clearly observed from Fig. 6 that lower surfactant flow rates always produce high pressure drops and are correspondence to higher flow behavior index values in the studied region.

With reference to Fig. 7, which displays various foam qualities corresponding to different shear stresses for surfactant flow rates of 2.0ml/min, 1.5 ml/min, 1.0 ml/min and 0.5ml/min respectively, it is clearly observed lower surfactant rate always corresponds to higher foam quality at the same bulk flow rate. Therefore it could be concluded the higher foam quality leads to higher flow resistance at the same shear rate for ScCO$_2$ foam flow in a straight tube.

The exception for the fit line of surfactant rate of 0.5 ml/min, which touches the line of 1.0ml/min at ln$\tau$=2.7, could be reasonably contributed to the foam instability at lower water saturation region, where the high foam quality accompanying slow flow rate may leads to unsatisfactory foam generation and therefore produces a similar pressure drop as the higher flow rates of 1.0ml/min.

The detailed discussions on the shear-thickening rheological behavior for ScCO$_2$ foam fluid are carried out in later section of 3.4.

### 3.2 Rheology characteristics for liquid CO$_2$ foam in a straight tube

Keeping the system under the condition of high pressure of 8.0MPa and normal room temperature of 25℃, the rheological properties of liquid phase CO$_2$ foam have been studied at various surfactant rates of 0.5ml/min, 1.0ml/min, 1.5ml/min and 2.0ml/min and the logarithmic values of $\Delta pd/4l$ vs. $8U/d$ are plotted in Fig. 8 (a)-(d) respectively. It could be clearly observed from Fig.8 (a)-(d) that the liquid
CO₂ foam also shows obvious shear-thickening behavior, with flow index number $n$ varying between 1.56 and 1.88, which are relatively larger compared to ScCO₂ foam.

The experimentally obtained fitting curves for liquid CO₂ foam rheology properties are displayed in Fig. 9, from which the effect of foam quality could be clearly observed. Similar to the rheology behavior of ScCO₂ foam, liquid CO₂ foam also gives the highest flow resistance at highest gas flow fractions corresponding to the lowest surfactant rate of 0.5ml/min, whereas the effect of foam quality becomes non-obvious when surfactant rate increases above 1.0ml/min.

3.3 Rheology characteristics for gaseous CO₂ foam in a straight tube

Under the conditions of atmospheric pressure and room temperature, gaseous CO₂ foam rheology was experimentally investigated at different gas-liquid ratios through varying surfactant flow rates from 0.2ml/min to 2.0ml/min. Fig. 10 (a)-(d) depict the logarithmic values of $dΔp/4l$ vs. $8U/d$ at surfactant rate of 2.0ml/min, 1.5ml/min, 0.5ml/min and 0.2ml/min respectively, together with the fitting lines and standard error analysis sheets. It could be read from Fig.10 that, in obvious contrast with ScCO₂ and Liquid CO₂ foam, the gaseous CO₂ foam shows shear thinning, or pseudo-plastic rheological behavior, with flow behavior index $n$ ranging between 0.70 to 0.76, which are much less than the unity. The shear thinning behavior for bulk gaseous CO₂ foam is in consistence with other reported works on aqueous foams 39-41 including gaseous CO₂ foam lamellae flowing in vertical straight tubes. 42 In particular, the experimental obtained $n$ values are close to the theoretical value of 2/3 for foam lamellae flows. 15

Fig.11 compares the gaseous CO₂ foam rheology at different surfactant solution flow rates. As revealed in Fig.7 that various surfactant rates are correspondence to various foam qualities, it could be concluded from Fig.11 that the foam quality affects the gaseous CO₂ foam rheology in a similar way to ScCO₂ and Liquid CO₂ foam, that is, higher quality foams (lower surfactant flow
rates) produces higher shear stresses at the same shear rate values.

3.4 Comparisons of CO₂ foam rheology properties under different phase conditions

Figure 12 depicts the colored data blocks, which cover all the rheological data at various surfactant rates, in the logarithmic graph of Δ⁴ℓ/d₄ vs. 8U/d for SC₂O, liquid CO₂ and gaseous CO₂ foam, respectively. With higher flow consistency coefficient K and flow index behavior n, the liquid CO₂ foam always shows larger apparent viscosities in contrast to ScCO₂ foam at the studied shear rate range of 2.4<ln γ <4.2, whereas the gaseous CO₂ foam shows higher shear stress values than ScCO₂ foam at lower shear rate ranges of 2.0<ln γ <3.0. Due to the higher flow behavior index numbers, the flow resistance for ScCO₂ foam increases quickly with shear rate than gaseous CO₂ foam and surpasses the gaseous CO₂ at ln γ >3.5.

To understand the distinctively different foam rheology properties at various phase states, visualized typical foam textures for ScCO₂, Liquid CO₂ and gaseous CO₂ bulk foam fluid are displayed in Figure 13 under the steady flow conditions. It is clearly observed much finer foam (emulsion) textures in the cases of ScCO₂ and liquid CO₂ foam, while less dense bubble distribution for gaseous CO₂ foam. The relationship between foam texture and its rheology has been discussed in detail by other researchers. Herzhaft 43 measured changes in foam texture (bubble-size distribution) vs. foam viscosity in a recirculating pipeline viscometer. He found foams are shear-history-dependent fluids, and although the viscous properties of foam fluids are determined primarily by quality (internal-phase volume) and liquid-phase properties, the foam textures also has un-negligible influences. Li et al. 44 also declares besides air volume fraction, the two phase aqueous foam rheology is governed by the bubble size too. Air volume fraction has a positive correlation with foam rheology, while bubble size influences foam rheology negatively. Li et al. 30 revealed through
experimental results that the foam volume and half-life increase sharply when CO$_2$ changes from gas to liquid phase (4 MPa to 6 MPa at 22 °C) and from liquid phase to supercritical phase (6 MPa to 8 MPa at 40 °C) and the strong relationships between interface properties and state properties. They concluded the decreased interfacial tension and increased viscoelastic modulus contribute to the foam rheology improvement under liquid and supercritical states. Their observations also comply with other researchers' works$^{45-47}$, which reported the interfacial tension of supercritical CO$_2$/surfactant could be much lower than the surface tension of gaseous CO$_2$/surfactant at elevated temperature and pressure conditions.

Therefore, it could be deduced the shear thickening behavior for ScCO$_2$ and Liquid CO$_2$ foam mainly comes from the finer textures or much dense bubble distributions. With shear rate increases, the foam texture becomes much finer due to easier bubble generations and less bubble coalescences at lower interfacial properties. Under nonlinear generation of bubble densities, it is easy to understand the force to keep foam flowing would become more significant rather than linear increment with increasing shear rates, which is reflected as the shear-thickening behavior of supercritical and liquid CO$_2$ foam fluids. For the gaseous CO$_2$ foam, on the other hand, the pressure drop increment at higher shear rate becomes smaller due to high bubble coalescence rates, therefore shows the shear-thinning, or pseudo-plastic behavior. Under the same shear rate values, foam quality dominates the shear stress values, namely, higher foam quality corresponds to higher shear stresses. However, the foam shear-thickening or shear-thinning behavior with changing shear rates could be more reasonably contributed to the distinctively foam texture evolution histories accompanying the shear rates variations.

Foam quality may also influence the bubble generation and coalescence process with varying shear rates, as supercritical CO$_2$ foam exhibits different slopes at different surfactant rates.
3.5 Discussion on upscaling considerations

As there is no constriction, pores throat and pore body in tube flow experiments, clarification on how to upscale the results on tube foam flow rheology to the foam flow characteristics in porous media is essential for highlighting this work. Actually, tube flow rheological investigations always play an important role to relate the foam apparent viscosity with its flow velocity, which is substantial for predicting foam flow behavior in porous media.

The population balance model, which describes foam transport in a way similar to mass conservation equation, relies heavily on foam texture (bubble populations) and the relationship between foam apparent viscosity and foam flow velocity. Kovscek et al.\textsuperscript{48-49} predicted the foam apparent viscosity $\mu_f$ in the following formula as,

$$
\mu_f = \mu_s \left(1 + \alpha \frac{n_f}{\mu_f^*} \right)
$$

(5)

where the power-law exponent of $d$, which explicitly relating the foam apparent viscosity with foam flow velocity, is put to be close to $1/3$. Authors declared this relation is consistent with the classical result of Bretherton\textsuperscript{15} for slow bubble flow in capillary tubes. Afterward foam modelling works\textsuperscript{37, 50-54} also employed the same exponent for relating foam apparent viscosity to its flow velocity. To reveal the connection between bulk foam and lamellae trains, Reinelt et al.\textsuperscript{55} developed a microscopic model for the rheology of bulk foams by considering small deformations of an idealized material with two-dimensional spatially periodic cell structure. The quasi-steady asymptotic analysis of the flow is developed for small capillary numbers $Ca$ based on the macroscopic deformation rate and the effective stress is calculated through involving the volume average of either local stress or stress power to clarify the role of viscous flow and surface tension. They conclude the viscous contribution to the effective stress in bulk foam, is $O(Ca^{2/3})$, which is the same as the classic foam lamella works of Bretherton\textsuperscript{15}. 
Weaire et al. \textsuperscript{56} reviewed recent progress concerning an understanding of the rheological properties of foams, both in bulk form and confined in narrow channels, including the problem of foam sliding along a solid wall. They declared the classic Bretherton results could apply to situations of 2D or 3D bulk foam that involve wall effect. They conclude the proper interpretation of rheological data could help the coupling of foam drainage and rheology. Actually, the flow behavior index for gaseous CO\textsubscript{2} bulk foam flow, as experimentally obtained in this work, lies in the range of 0.70-0.76, which locates in the region of 15\% to the Bretherton theoretical value of 2/3. The bulk foam results also complies with the tube lamellae research results \textsuperscript{19-20}, which validates again the positive relationship between bulk foam and lamellae foam rheological properties.

Therefore in this work, the flowing bulk foam rheology is scrutinized with the expectation to reveal the foam flow mechanism in porous media in relation to the flow velocity. Through detailed investigations on the flowing foam rheology which reflects the substantial effect of foam quality and bubble distributions, we expect to make contributions on understanding of supercritical and liquid phase CO\textsubscript{2} foam flow behavior in porous media and on elaboration of the future foam modeling works.

### 3.6 Error analysis

The errors for measured direct parameters, including pressure drop, tube diameter, tube length and volumetric flow rate, are shown in Table 1.

Based on it, the measurement error for indirectly obtained apparent viscosity can be analyzed as follows,

1. The error for shear rate can be calculated by Eq.(6),

\[
Er(\dot{\gamma}) = \pm \left| \frac{\Delta \dot{\gamma}}{\dot{\gamma}} \right| = \pm \left( \left| \frac{\Delta V}{V} \right| + 3 \left| \frac{\Delta d}{d} \right| + \left| \frac{\Delta t}{t} \right| \right) = \pm 1.67\%
\]  

2. The error for shear stress can be determined through Eq.(7).
(3) The error or apparent viscosities can be obtained to be 7.34% by Eq.(8).

\[ \text{Error} = \pm \left( \frac{\Delta \mu}{\mu} \right) = \pm \left( \frac{\Delta \rho}{\rho} + \frac{\Delta d}{d} + \frac{\Delta l}{l} \right) = \pm 7.34\% \]  

4 CONCLUSIONS

In this paper, the rheology properties for CO\textsubscript{2} foam fluid under different phase states were experimentally investigated. Through varying pressure and temperature, the relationship between shear stress and shear rates for supercritical CO\textsubscript{2}, liquid phase CO\textsubscript{2} and gaseous CO\textsubscript{2} foam were measured in a straight tube under different gas-liquid ratios or surfactant flow rates. Foam rheological properties were presented in non-Newtonian power-law correlations and the following results were obtained,

(1) The ScCO\textsubscript{2} foam (under the system condition of T=45°C, P=8.0MPa) shows obvious shear thickening non-Newtonian behavior with flow behavior index \( n \) ranging from 1.03 at surfactant rate of 2.0ml/min to higher value of 1.76 at lower surfactant rate of 0.5ml/min. Clear dependence of ScCO\textsubscript{2} foam rheology on the foam quality has been observed. In accordance with shear thickening non-Newtonian behavior, the apparent viscosity for ScCO\textsubscript{2} foam increases with increasing flow rates and could reach 80~140 times of the single-phase water viscosity.

(2) The liquid phase CO\textsubscript{2} foam (under the system condition of T=25°C, P=8.0MPa) also clearly shows the shear thickening behavior with measured flow behavior index \( n \) varying between 1.56 and 1.88. Similarly, higher foam quality achieved under lower surfactant rates of 0.5ml/min leads to higher flow resistance for CO\textsubscript{2} foam in liquid phase, whereas the foam quality effect becomes not obvious with increasing surfactant rates above 1.0ml/min.

(3) The gaseous CO\textsubscript{2} foam (under the system condition of T=25°C, P=atmospheric), on the other hand, behaves in a clear shear-thinning, or pseudo-plastic non-Newtonian manner with measured flow...
behavior index values of 0.70 ~ 0.76, which are much less than the unity. Foam quality shows the similar influences on gaseous foam rheology as ScCO$_2$ foam, with lower surfactant flow rate (higher foam quality) corresponding to higher pressure losses.

(4) Comparisons on shear stress in the studied shear rate region have been performed for ScCO$_2$, liquid CO$_2$ and gaseous CO$_2$ foam respectively. It is observed the liquid phase CO$_2$ foam gives the highest shear stress in the studied shear rate region of $2.4<\ln \gamma <4.2$, whereas the gaseous CO$_2$ foam has higher shear stress values than ScCO$_2$ foam at lower shear rate ranges of $2.0<\ln \gamma <3.0$. With more quickly increasing of shear rate with shear stress, the flow resistance for ScCO$_2$ foam surpasses the gaseous CO$_2$ foam at $\ln \gamma >3.5$.

(5) The shear thickening manner of ScCO$_2$ and liquid CO$_2$ foam fluid in contrast to the shear thinning behavior of the gaseous CO$_2$ foam were investigated based on visualizing the foam fluid under different phase states. It is deduced that, owing to the much lower interfacial tension of supercritical & liquid CO$_2$/surfactant than the surface tension of gaseous CO$_2$/surfactant system, the shear thickening rheological behavior of supercritical CO$_2$ and liquid CO$_2$ foam fluid could be reasonably contributed to the evolved finer foam textures accompanying with the increasing shear rates.

(6) The detailed foam rheology works could help to understand the supercritical and liquid phase CO$_2$ foam displacement behaviors in porous media.

**ACKNOWLEDGEMENTS**

The authors would like to thank the financial support from National Natural Science Foundation of the People’s Republic of China (NSFC No.51476081).
REFERENCES


[45] Bachu S, Bennion D B. Interfacial tension between CO$_2$, freshwater, and brine in the range of pressure from 2 to 27 MPa, temperature from 20 to 125°C, and water salinity from 0 to 334000mg/L. J. Chemical & Engineering Data. 2009, 54(3):765-775.


[49] Kovscek A R, Patzek T W, Radke C J. Mechanistic Foam Flow Simulation in Heterogeneous and


Table 1 Experimental error

<table>
<thead>
<tr>
<th>physical quantity</th>
<th>accuracy</th>
<th>minimum value</th>
<th>Maximum relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>10Pa</td>
<td>200Pa</td>
<td>±5.0%</td>
</tr>
<tr>
<td>D</td>
<td>0.02mm</td>
<td>4.0mm</td>
<td>±0.50%</td>
</tr>
<tr>
<td>L</td>
<td>0.5mm</td>
<td>300mm</td>
<td>±0.17%</td>
</tr>
<tr>
<td>t</td>
<td>0.1s</td>
<td>10s</td>
<td>±1.0%</td>
</tr>
</tbody>
</table>
Figure 1. Schematic diagram of the experimental setup

1. Upper body; 2. Pressure cap; 3. O-type ring; 4. Lower body; 5. Consolidated quartz sand plate

Figure 2 Structure of the foam generator

(a) Side view
(b) Front view


Figure 3 The detailed description of the high pressure quartz tube unit
Figure 4. Rheological properties of ScCO\textsubscript{2} foam at surfactant flow rate of 1.0ml/min

(a) Experimental logarithmic curve

(b) Apparent viscosity

\[ \ln\tau = -3.48 + 1.34\ln\gamma \]

\[ \mu_a = K\gamma^{n-1} \]

K=0.031, n=1.34
Figure 5: Rheological properties of ScCO$_2$ foam fluid at different surfactant flow rates

(a) 2mL/min

(b) 1.5mL/min

(c) 0.5mL/min

Exp. data

ln(τ) = -2.86 + 1.03lnγ

ScCO$_2$, Surf rate: 2ml/min

Exp. data

ln(τ) = -3.52 + 1.29lnγ

ScCO$_2$, Surf rate: 1.5ml/min

Exp. data

ln(τ) = -4.65 + 1.76lnγ

ScCO$_2$, Surf rate: 0.5ml/min

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Std. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-2.86442</td>
<td>0.10511</td>
</tr>
<tr>
<td>Slope</td>
<td>1.02857</td>
<td>0.03217</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Std. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-3.51522</td>
<td>0.16557</td>
</tr>
<tr>
<td>Slope</td>
<td>1.28744</td>
<td>0.04832</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Std. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-4.65055</td>
<td>0.22079</td>
</tr>
<tr>
<td>Slope</td>
<td>1.75590</td>
<td>0.06347</td>
</tr>
</tbody>
</table>
Figure 6. Rheological properties of ScCO$_2$ foam at different surfactant rates based on fit curves in the studied shear stress regions.

Figure 7. Correspondence of foam qualities and shear rates for different surfactant rates in the studied shear stress regions.
Figure 8. Rheological properties of liquid CO\(_2\) foam at various surfactant flow rates

(a) 2.0ml/min

(b) 1.5ml/min

(c) 1.0ml/min

(d) 0.5ml/min

Figure 9. Rheological properties of liquid CO\(_2\) foam at different surfactant rates based on fit curves in the studied shear stress regions.
Figure 10. Rheological properties of liquid CO$_2$ foam at different surfactant rates.

Figure 11. Rheological properties of gaseous CO$_2$ foam at different surfactant rates based on fit curves in the studied shear stress regions.
Figure 12. Comparisons of rheological properties of ScCO\textsubscript{2} foam, liquid CO\textsubscript{2} foam and gaseous CO\textsubscript{2} foam in the studied shear stress regions.
(a) scCO$_2$ foam (t=45$^\circ$C, P=8.0MPa)  (b) liquid CO$_2$ foam (t=25$^\circ$C, P=8.0MPa)

(c) gaseous CO$_2$ foam (t=25$^\circ$C, atmospheric pressure)

Figure 13. Visualization of flowing CO$_2$ foam under different phase states
Highlights

The highlights of our work are listed as follows,

1) One of the pilot systematic laboratory studies focusing on CO$_2$ foam rheology under different phase states.

2) Supercritical CO$_2$ (scCO$_2$) foam (45°C and 8.0MPa) shows obvious shear-thickening behavior with flow behavior index n ranging from 1.03 to 1.76.

3) Liquid phase CO$_2$ foam (25°C and 8.0MPa) exhibits clear shear-thickening behavior with flow behavior index n ranging from 1.56 to 1.88.

4) The gaseous CO$_2$ foam behaves in a shear-thinning or pseudo-plastic manner with flow behavior index of 0.70<n<0.76.

5) Combined effects of foam texture and foam quality contribute to the distinctively different rheological behaviors of CO$_2$ foam under different phase states.