Rheology of Diluted Heavy Crude Oil Saturated with Carbon Dioxide

Ruien Hu, John P. Crawshaw, J. P. Martin Trusler and Edo S. Boek*

Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), Dept. of Chemical Engineering, South Kensington Campus, Imperial College London, London SW7 2AZ, United Kingdom.

KEYWORDS

Viscosity, Shear Rate, Heavy Crude Oil, Carbon Dioxide

ABSTRACT

The viscosity of heavy crude oils strongly affects their producibility and recovery from oil reservoirs. Thus, the viscosity of heavy crude oils with dissolved gases at different shear rates is valuable knowledge for heavy crude oil exploitation. However, most publications only present the viscosity measurements at one specific shear rate, and only few papers in the literature have reported the rheological measurements. In this study, viscosity measurements of CO_2 saturated heavy crude oils were performed as a function of shear rate, at a temperature of 25 °C and pressures up to 220 bar. The experimental apparatus is a unique circulation system which is able to measure the viscosity of CO_2 saturated mixtures. A novel high pressure rheometer with a flow-through Couette geometry was developed to measure the viscosity at a range of shear rates. The

experimental results show that the addition of CO_2 to heavy crude oil at the given temperature and pressures reduces the viscosity significantly, but the pressure dependence of the mixture viscosity changes at the phase transition of the CO_2 rich phase. A modified Arrhenius equation, accounting for the effect of CO_2 composition on viscosity, is applied to correlate the viscosity data.

Introduction

Carbon dioxide (CO_2) is one of the most important greenhouse gases, due to large emissions to the atmosphere from chemical and transportation processes. It has a significant contribution to global warming and climate change [1]. Thus the technologies to reduce CO_2 emission in the atmosphere have continuously drawn attention from governments and industry. Recently, the concept of carbon capture, utilization and storage (CCUS) has been developed, in order to provide an economically feasible strategy to reduce CO_2 emissions in the short to medium term. Among all the technologies within the CCUS concept, CO_2 flooding for Enhanced Oil Recovery (EOR) is one of the most promising ways to provide the opportunity to offset the cost of carbon storage in oil fields by improving oil recovery.

CO_2 flooding requires a fundamental understanding of the thermodynamic and transport properties of CO_2 and reservoir fluids under reservoir conditions. Measuring and predicting the transport properties of mixtures of reservoir fluids with CO_2 under these extreme conditions is crucial for developing predictive models that can then be used to design the most cost-efficiency recovery strategy. The viscosity of the crude oil-CO_2 mixture, which is a key parameter for mobility control, is fundamental for designing and managing the CO_2 flooding productivity. This research project addresses the measurement the viscosity of crude oil-CO_2 mixtures. However, apart from the effect of pressure and oil-CO_2 composition on the mixture viscosity, this study also reveals the effect of

shear rate. Given that CO_2 dissolution in crude oil could give rise to asphaltene precipitation and deposition [2], the resulting mixture could have both solid and liquid phases present. From a rheological point of view, the precipitated solid particles could create a structural network, which would give rise to a shear rate dependence of the mixture viscosity - *i.e.* non-Newtonian behavior [3].

In the literature, many studies have focused on how the phase behavior and viscosity of crude oil-gas mixtures are affected by temperature, pressure and gas composition. Kariznovi et al. give a good review about experimental set-ups and the measurements each can provide [4]. However, these early studies were not capable of detecting any non-Newtonian behavior of the fluid. Only recently, Behzadfar et al. have reported rheological measurements for CO_2-bitumen mixtures [5]. These measurements were performed in a high pressure cell mounted on a rheometer. The CO_2 saturation took place by diffusion with a gentle mixing process in the pressure cell. Complete saturation was indicated by stable viscosity and pressure measurements.

In this work, a circulation system has been built to saturate the crude oil with CO_2. In this system, the mixing process and rheological measurement take place in two different units. The measurements were performed at 25 ℃ and at various pressure and shear rate. The viscosity data were correlated with a modified Arrhenius equation.

Experiments

Materials

Pure squalane and squalane saturated with CO_2 were used to test the system performance. The squalane sample used in the test was sourced from Sigma-Aldrich with purity of 99%, and the

CO_2 (mole fraction purity $x \geq 0.99995$) was obtained from BOC. Both were used without further purification. Then two different diluted crude oil samples were studied. The diluted crude oils are mixtures of different amounts of toluene and a heavy crude oil sample provided by Shell, Netherlands, with an *n*-heptane asphaltene content of 18.8 wt%. The density (at 15°C) was measured to be 0.983 g/cm^3 and the kinematic viscosity (at 40°C) was 20020 mm^2/s [6]. Other key properties of the crude oil sample are listed in Table 1. As illustrated in Table 1 the viscosity of the crude oil is extremely high such that the gear pump in the circulation system was not powerful enough to circulate the crude oil even at elevated temperature. Therefore the crude oil was diluted by toluene to reduce its viscosity into the range that the circulation system could handle. The toluene used was sourced from Sigma-Aldrich with a purity of 99.8%. The crude oil and toluene were used without further treatment. The compositions of the diluted crude oil samples are shown in Table 2.

Viscosity Measurement

The system designed and built to allow the viscosity measurement of gas-saturated crude oils is a circulation system, which contains four off-the-shelf pieces of equipment: a syringe pump, mixer, gear pump and rheometer, as shown in Scheme 1. The measurement procedure was as followings. First, the crude oil sample was loaded into the mixer and then the whole system was primed. The remaining volume in the system was evacuated for 30 minutes to remove air and the system brought to the set point temperature. CO_2 was then introduced into the mixer via the syringe pump that controls the system pressure. Inside the mixer, a stirrer coupled with a rotating magnet was used to enhance the mixing between the crude oil and CO_2. The mixture was circulated into the pressure cell of the rheometer by the gear pump. Once the pressure cell was completely full, the mixture was recycled back to the mixer and the circulation continued for more than 24 hours to

ensure equilibrium. During the circulation, the stirrer was kept rotating in order to ensure the liquid had a uniform composition. The suction tube in the mixer removed fluid from close to the bottom of the mixer, sampling the liquid and not the vapor phase. After reaching equilibrium, the circulation was stopped and the viscosity measured in the rheometer. The saturation of the crude oil and CO_2 was confirmed by no further reduction in pressure and viscosity was observed.

The mixer is a Parr Instruments 4651 reactor with a vessel volume of 250 ml, mounted on a Series 4923EE benchtop heater with a Series 4838 temperature controller. The mixer, manufactured in 316 stainless steel, is sealed with a PTFE flat gasket and split ring arrangement, operated at a maximum working pressure of 410 bar and up to 350 °C. Stirring of the mixture is done by a stirring bar placed at the bottom of the vessel, which is driven by a rotating magnet set. The benchtop heater is modified to install the rotating magnet set via an electric motor, which provides stirring speeds adjustable from 0 to 1700 rpm.

The viscosity measurement was performed in a high-pressure cell mounted on the Anton Paar MCR301 rheometer. The high pressure cell had a concentric cylinder geometry with a 0.5 mm gap; it could be pressurized up to 400 bar and operated in a temperature range from 25 to 300 °C. The sample volume was 18 ml. The design of the pressure cell allows high shear rates to be applied to viscoelastic samples without encountering problems such as the Weissenberg effect or the sample escaping from the gap [7]. Also, as the pressure cell is completely sealed and entirely flushed with the sample, there is no room for loading errors and the sample loading is repeatable. For every experiment an Air Check test was performed, in which the torque applied on the cylinder geometry in an empty cell is measured at the rotation speed of 0.3 min^{-1}. Such torque is mainly caused by the friction on the sapphire bearings that contact with the cylinder geometry. The torque measured in Air Check was compared with the limits set by rheometer manufacturer to judge

whether the pressure cell is working in good conditions. All the experiments that have performed showed a positive result in the Air Check. Also, the motor adjustment for the pressure cell was done manually. In the beginning of each experiment, the viscosity in an empty cell was measured at the interested shear rate values. Then, performed at the same share rates as in the empty cell, the viscosity measurements with samples was subtracted by that with empty cell, and the resulted viscosity values were the true measurement values. The uncertainty of the viscosity measurements was estimated by measuring the UKAS certified viscosity standards N35 and S600 (100% hydrocarbons, from Paragon Scientific Ltd). The agreement with the standards in the certified temperature range 25 – 80 °C was better than ±3.5%. The repeatability of the rheological measurements was better than 1%.

The gear pump circulating the fluid was a model GAH X21 suction shoe gear pump from Micropump. The pump was a rotating positive displacement pump which can be operated up to 345 bar and 120 °C. The main body of the gear pump was fabricated of stainless steel, while the gears and suction shoes were made of carbon. The pump was magnetically coupled to a drive motor.

Measuring the mass of CO_2 injected into the mixer

Although the system was designed to measure the viscosity, using the syringe pump and the mixer the amount of CO_2 injected can also be measured, which indicates the dissolution and phase behavior of the mixture.

Scheme 2 shows the measurement principle as follows. A known amount of crude oil was preloaded into the mixer. The air remaining in the system was then removed by evacuation,CO_2 was introduced into the pump and the mixer, and the syringe pump was set to operate in constant

pressure mode. At this stage, the CO_2 had contacted the crude oil and would start to dissolve into it at a rate controlled by diffusion. However, the diffusion coefficient of CO_2 in such crude oil is very small [8] and hence the rate of dissolution under diffusion control was very low and was assumed to be negligible. When the temperature and pressure reach the desired values, the stirrer was turned on to start the mixing. The now rapid dissolution of CO_2 in the oil resulted in a volume change, ΔV, in the syringe pump which was recorded. Given that the temperature and pressure inside the syringe pump were kept constant, the density of the CO_2, ρ_{CO2}, inside the pump could be determined from an equation of state [9] and hence the mass of CO_2 injected into the vessel could be determined as $m_{CO_2} = \rho_{CO_2}\Delta V$.

Results and Discussion

The viscosity measurement of pure squalane was performed at 25 °C and 1 bar, at shear rates from 80 to 500 1/s. As shown in Figure 1, the viscosity of pure squalane is independent of the shear rate, behaving as a Newtonian fluid as expected. When CO_2 was mixed with squalane at 25 °C and 4.3 bar, the saturated mixture had a lower viscosity than pure squalane, but also behaved as a Newtonian fluid. Compared to the literature values, the measurement errors for pure squalane and CO_2 + squalane mixture are 2.4% and 3.8%, respectively. The literature value of pure squalane viscosity was obtained from Ciotta et al. [10] while that of the CO_2 + squalane mixture was calculated based on the data from Tomida et al. [11] and Chai et al. [12]. In addition, the pressure cell gives a good measurement at shear rate of 500 1/s. It indicates that shear rate up to 500 1/s does not cause any flow instabilities in the pressure cell, and the measurement is reliable.

Figure 2 and Figure 3 illustrate the viscosity of the toluene/crude oil mixture at various shear rates. The measurements at atmospheric pressure represent the viscosities of the diluted crude oils

without CO_2 dissolved at 25 °C. The horizontal line demonstrates that the viscosities of both diluted crude oils are independent of shear rate, *i.e.* both samples behave as a Newtonian fluid. When the pressure increases, more and more CO_2 dissolves into the crude oil and reduces the mixture viscosity significantly. However the addition of CO_2 does not cause a change from Newtonian behavior, as the viscosity is constant for various shear rates at a specific pressure level. Therefore, although the dissolved CO_2 could cause the precipitation of asphaltene, the dispersed particles do not appear to form an interacting network with each other for these crude oil mixtures.

Figure 4 summarizes the viscosity measurements at different pressures for the CO_2 saturated mixtures of a crude oil sample at two different dilutions. The dissolved CO_2 causes the diluted crude oil mixtures to have an exponential decrease of viscosity with pressures up to about 50 bar, and then the viscosities increase very slightly with pressure. We believe this change of pressure dependence of the viscosity is a consequence of the phase behavior change for the CO_2 and crude oil mixtures.

As shown in Figure 5, when the pressure approaches 50 bar, a large amount of CO_2 has been injected into the vessel for a small increase of pressure. We have a Liquid-Vapor (L-V) system at pressures below 50 bar consisting of a CO_2 rich vapor phase and an oil rich liquid phase. Although the saturation point of pure CO_2 at 25 °C is 64 bar, when the pressure approaches 50 bar, a second liquid phase is generated. In this system three phases occur − an oil rich liquid, a CO_2 rich liquid mixed with light hydrocarbons extracted from the crude oil, and a CO_2 rich vapor – a Liquid-Liquid-Vapor (L-L-V) system. The CO_2 - rich liquid phase requires a large amount of CO_2 and causes the jump in Figure 5 when the pressure is close to 50 bar. When the pressure is beyond the saturation point of CO_2, 64 bar, the CO_2 is in the liquid phase and we have a Liquid-Liquid (L-L)

system. The phase change phenomena mentioned above have also been reported by Orr et al. in their study of the phase behavior of CO_2 with crude oil and with alkanes [13].

As mentioned in the literature, in the L-L-V phase, the extracted light hydrocarbons significantly increase the viscosity of the CO_2 - rich liquid phase, while the CO_2 dissolved reduces the viscosity of the oil rich phase [13]. Therefore, at 60 bar the viscosity of the resulting mixture of these two liquid phases no longer follows the exponential decrease of the mixture viscosity with pressure increase, but decreases only slightly compared to the previous point which is for a mixture with a L-V phase. When the pressure is above the saturation point of CO_2, the viscosity measured is for a L-L system, and increases at higher pressure.

Correlations

As discussed above, in the L-V region where the pressure is less than 50 bar, the viscosity of the CO_2 and diluted crude oil mixture reduces exponentially with pressure increase, because of CO_2 dissolution. The pressure dependence can be described by

$$\ln\left(\eta_{\mathrm{m}}\right) = a_1 P + b_1 \quad @ \ \ P \leq 50 \text{ bar} \tag{1}$$

When the pressure is above 50 bar, giving rise to the L-L-V or L-L region, the viscosity of the mixture increases linearly with pressure:

$$\eta_{\mathrm{m}} = a_2 P + b_2 \quad @ \ \ P > 50 \text{ bar} \tag{2}$$

The values of the fitting parameters a_1, b_1, a_2, and b_2 are summarized in Table 3.

Additionally, in the L-V region, the amount of CO_2 injected into the mixer corresponds to the amount of CO_2 dissolved in the diluted crude oil, since it is only way the CO_2 can be consumed.

Given that the amount of diluted crude oil loaded in the mixer is known, one can calculate the mass fraction of CO_2 in the mixture, which is in fact the solubility of CO_2 in the diluted crude oil. Therefore, the viscosity data and CO_2 solubility at pressures lower than 50 bar have been correlated using the equation reported by Shu [14], which is a modified version of the classic Arrhenius expression ,

$$\ln(\eta_m) = X_o \ln(\eta_o) + X_s \ln(\eta_s) \tag{3}$$

with

$$X_s = \frac{v_s}{\alpha v_o + v_s} \tag{4}$$

$$X_o = 1 - X_s \tag{5}$$

where v is volume fraction and the subscripts o, s, and m stand for diluted crude oil, CO_2 and CO_2/diluted crude oil mixture, respectively. The pressure dependence of the diluted crude oil viscosity was not significant and was ignored. The viscosity of pure CO_2 as a function of temperature and pressure was obtained from the NIST Chemistry WebBook [9].

The empirical parameter α in Equation (4) has to be determined by fitting data via a nonlinear optimization that minimizes the absolute average relative deviation, $\Delta_{AAD, X}$

$$\Delta_{AAD,X} = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{|X_i - X_{i,\text{fit}}|}{X_i} \right) \tag{6}$$

where X_i is the experimental data, $X_{i,\text{fit}}$ calculated from the correlation applied at the same conditions, and N the total number of points. The resulting values of the parameter α for the

diluted crude oils are given in Table 3. The correlation results are illustrated in Figure 6, and the $\Delta_{\text{AAD}, X}$ for both diluted crude oils is 1%.

Conclusions

According to our observations, for our particular diluted crude oil samples, CO_2 dissolution does not cause non-Newtonian behavior for CO_2 - diluted crude oil mixtures. In the L-V region the dissolved CO_2 causes an exponential decrease in the viscosity of the L phase with increasing pressure. When the system reaches the L-L-V region, increasing pressure further results in a slight linear increase in the viscosity of the densest phase. The system reaches the L-L region at a pressure lower than the pure CO_2 vapor-liquid saturation pressure. In addition, the modified Arrhenius equation developed by Lederer provides a good correlation between the viscosity data and the amount of dissolved CO_2 in the L-V region.

FIGURES
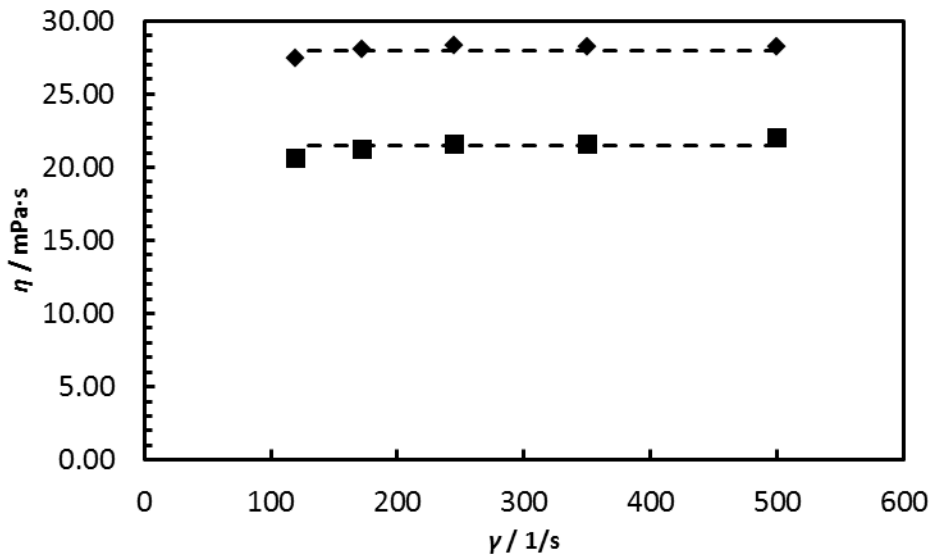
Figure 1. Comparison between the viscosity measurements by the circulation system and the literature values of squalane and its mixture with CO_2 at 25°C. ◆, 1 bar, pure squalane; ■, 4.3 bar, squalane saturated with CO_2; – –, reference value.
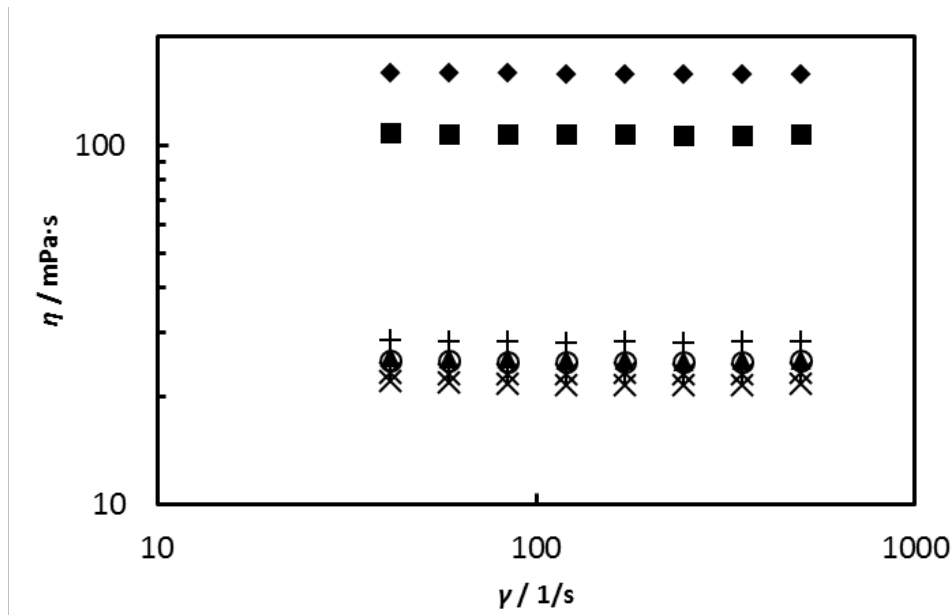
Figure 2. Viscosity measurement for diluted crude oil 1 with CO_2 at 25 °C and various shear rates. ◆, 1 bar; ■, 10 bar; ▲, 40 bar; ✕, 60 bar; ✳, 100 bar; ○, 140 bar; ✚, 220 bar.
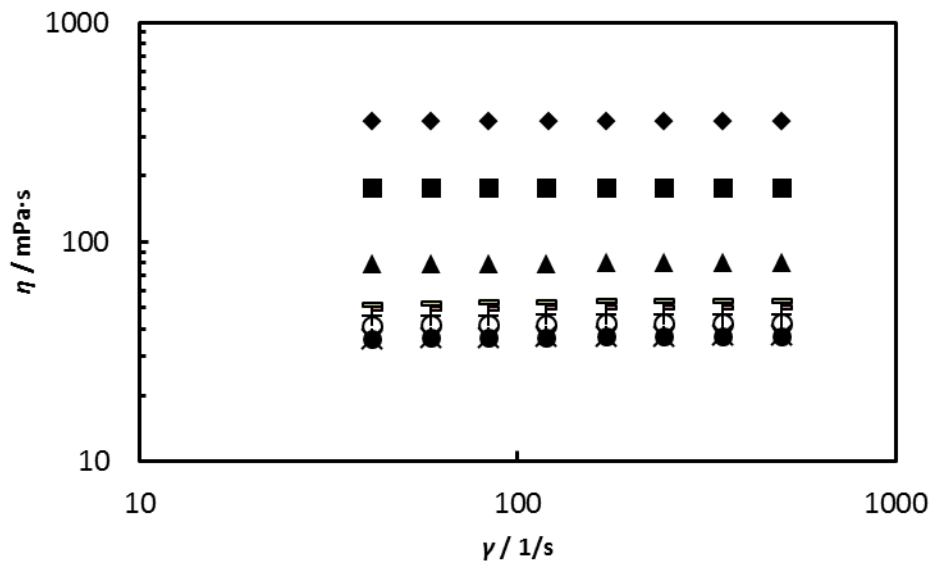

Figure 3. Viscosity measurement for diluted crude oil 2 with CO_2 at 25 °C and various shear rates. ◆, 1 bar; ■, 15 bar; ▲, 30 bar; ●, 45 bar; ✳, 60 bar; ○, 100 bar; ✚, 140 bar; △, 180 bar; ◇, 220 bar.
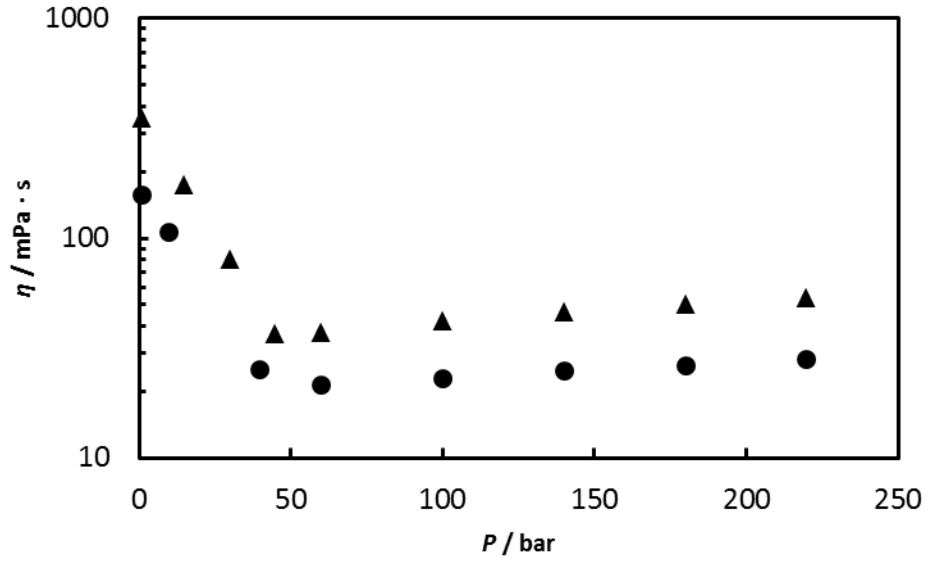
Figure 4. Viscosity measurement for diluted crude oil 1 and 2 with CO_2 at various pressures at 25 °C. ●, diluted crude oil 1; ▲, diluted crude oil 2.
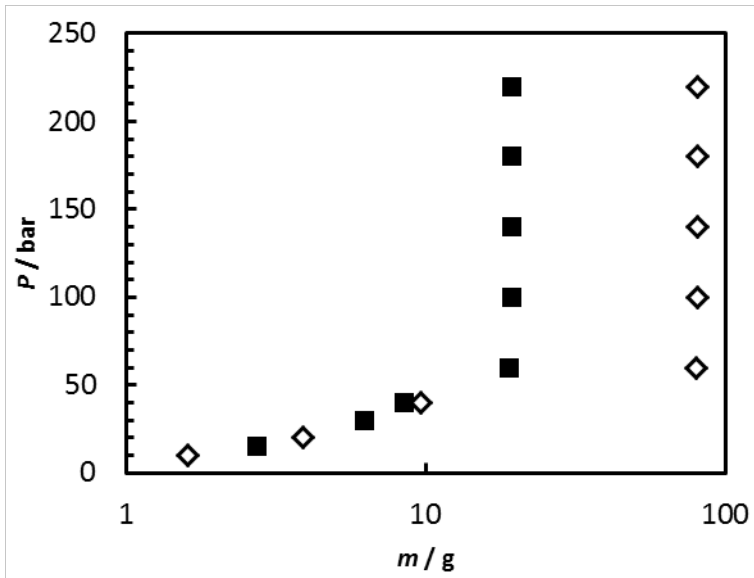

Figure 5. The mass of CO_2 injected into the mixer at difference pressure and 25 °C. ◇, diluted crude oil 1; ■, diluted crude oil 2
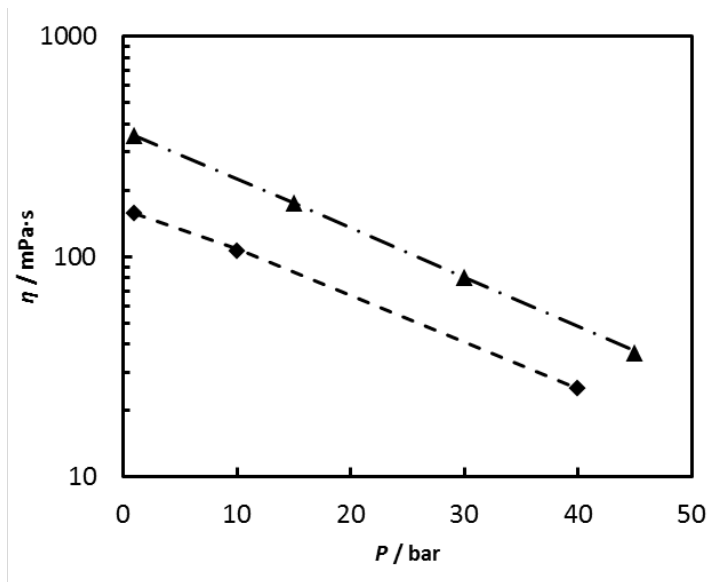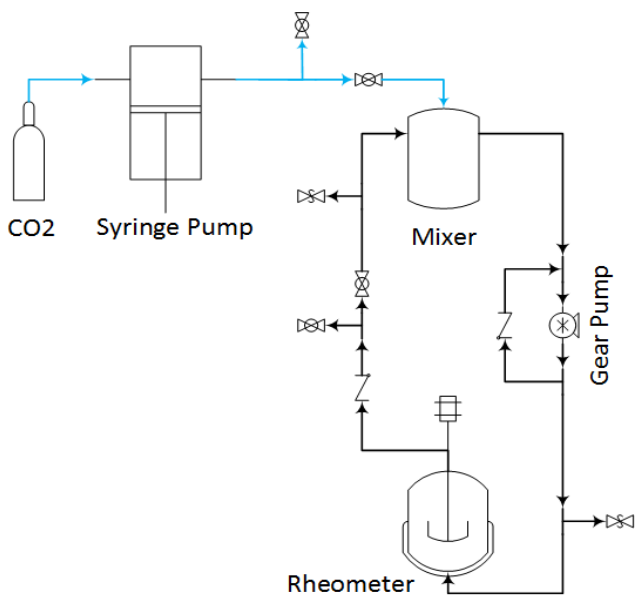
Figure 6. The comparison between the correlation results from Equation Error! Reference source not found. **and measurement. ◆, viscosity measurement for diluted crude oil 1; ▲, viscosity measurement for diluted crude oil 2; ‑ ‑, correlation for diluted crude oil 1; ▬ ·, correlation for diluted crude oil 2.**

SCHEMES

Scheme 1. The scheme of the circulation system to measure the viscosity of CO_2 saturated crude oils. The blue line in the scheme represents CO_2 flow, while black one the crude oil mixtures.
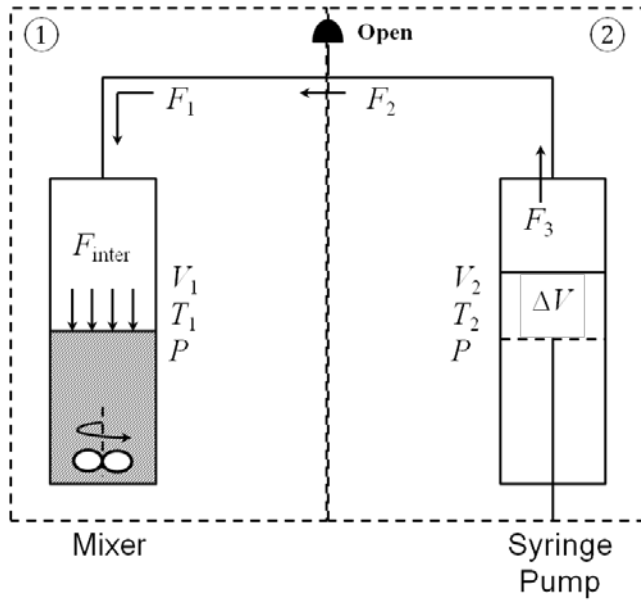
Scheme 2. The scheme showing the principle of measuring the amount of CO2 injected into the mixer. F_i **is the flowrate of CO$_2$ at position i, ΔV the volume change in the syringe pump. $F_1 = F_2 = F_3 = F_{inlet}$ when the syringe pump is set to operate at constant pressure mode.**

TABLES.

Table 1. The characteristics of the crude oil used in this study

Characteristics	Value
API Gravity	9.28
Barrel Factor (bbl/t)	6.27
Total Sulphur (% wt)	3.35
Reid Vapour Pressure (kPa)	1
Pour Point (°C)	24
Existing H$_2$S Content (ppm)	-
Potential H$_2$S Content (ppm)	115
Potential HCl Content (ppm)	-
Calc. Gross Cal. Value (kJ/kg)	41855

Table 2. The composition of the diluted crude oil studied.

Component	Composition
Diluted crude oil 1	80 w% Crude oil + 20 w% Toluene
Diluted crude oil 2	85 w% Crude oil + 15 w% Toluene

Table 3. The value of fitting parameters in Equation (1), (2) and (4)

Component	a_1	b_1	a_2	b_2	α
Diluted crude oil 1	-0.047	5.123	-0.052	5.930	188.648
Diluted crude oil 2	0.043	18.833	0.103	31.448	174.302

AUTHOR INFORMATION

Corresponding Author

* E-mail: e.boek@imperial.ac.uk.

Funding Sources

ACKNOWLEDGMENT

REFERENCES

1. NRC, *Advancing the Science of Climate Change*. 2010: The National Academies Press.
2. Srivastava, R.K., S.S. Huang, and M.Z. Dong, *Asphaltene deposition during CO2 flooding*. Spe Production & Facilities, 1999. **14**(4): p. 235-245.
3. Barnes, H.A.H.J.F.W.K., *An introduction to rheology*. 1989, Amsterdam; New York: Elsevier : Distributors for the U.S. and Canada, Elsevier Science Pub. Co.
4. Kariznovi, M., H. Nourozieh, and J. Abedi, *Experimental apparatus for phase behavior study of solvent–bitumen systems: A critical review and design of a new apparatus*. Fuel, 2011. **90**(2): p. 536-546.
5. Behzadfar, E. and S.G. Hatzikiriakos, *Rheology of bitumen: Effects of temperature, pressure, CO2 concentration and shear rate*. Fuel, 2014. **116**(0): p. 578-587.

6.   Seifried, C.M., J. Crawshaw, and E.S. Boek, *Kinetics of Asphaltene Aggregation in Crude Oil Studied by Confocal Laser-Scanning Microscopy.* Energy & Fuels, 2013. **27**(4): p. 1865-1872.

7.   Arnolds, O., *Rheology at high pressure setup and performance of the 1000 bar pressure cell.* 2013, Anton Paar.

8.   McManamey, W.J. and J.M. Woollen, *The diffusivity of carbon dioxide in some organic liquids at 25° and 50°C.* AIChE Journal, 1973. **19**(3): p. 667-669.

9.   Linstrom, P.J. and E. W.G. Mallard, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69.* 2014: National Institute of Standards and Technology.

10.   Ciotta, F., et al., *Viscosity and Density of Carbon Dioxide + 2,6,10,15,19,23-Hexamethyltetracosane (Squalane)†.* Journal of Chemical & Engineering Data, 2009. **54**(9): p. 2436-2443.

11.   Tomida, D., A. Kumagai, and C. Yokoyama, *Viscosity Measurements and Correlation of the Squalane + CO2 Mixture.* International Journal of Thermophysics, 2007. **28**(1): p. 133-145.

12.   Chai, C.-P. and M.E. Paulaitis, *Gas solubilities of carbon dioxide in heavy hydrocarbons.* Journal of Chemical & Engineering Data, 1981. **26**(3): p. 277-279.

13.   Orr, F.M., A.D. Yu, and C.L. Lien, *Phase-Behavior of Co2 and Crude-Oil in Low-Temperature Reservoirs.* Society of Petroleum Engineers Journal, 1981. **21**(4): p. 480-492.

14.   Shu, W.R., *A Viscosity Correlation for Mixtures of Heavy Oil, Bitumen, and Petroleum Fractions.* Society of Petroleum Engineers Journal, 1984. **24**(3): p. 277-282.