Velocity and density of CO_2-oil miscible mixtures

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Summary

Different structure of CO_2 from hydrocarbon gases and oils has a significant impact on properties of CO_2-oil miscible mixtures in comparison with "live" oil with dissolved hydrocarbon gases. We have systematically investigated velocity and density of CO_2 with different oil (API) mixtures above their bubble point. The measurement condition is ranged with CO_2 GOR up to 310L/L, temperature from 40°C to 100°C, and pressure from 20MPa to 100MPa. Based on our updated database we have developed preliminary models for the velocity and density of the CO_2-oil miscible mixtures.

Introduction

Due to different molecular structures, carbon dioxide (CO_2) has different properties from organic hydrocarbon (HC) gas and liquid. Therefore, we cannot treat CO_2 similarly as hydrocarbon gases, especially when dealing with CO_2 mixtures with oil. The FLAG program of the oil calculator (the Fluid Application Geophysics program developed by the Fluids/DHI consortium) cannot be used directly to calculate properties of CO_2-oil mixtures when CO_2 as a major gas component is dissolved into hydrocarbon oil. There are three phases of CO_2 separated by phase boundaries between solid, liquid, and gas, and supercritical fluid in conjunction with the triple point (0.518 MPa and -56.6 ºC) and critical point (7.38 MPa and 31.1 ºC). In general, at in situ temperature and pressure condition, which is higher than the critical point, CO_2 is in supercritical fluid phase. In this phrase, there is no phase boundary to separate liquid and gas clearly. With higher temperature and lower pressure, its property is more like gas; with lower temperature and higher pressure, its property is more like liquid (Han et al., 2010). In comparison of hydrocarbon gases, CH_4 as a major component of hydrocarbon gases is always in gas phase at in situ condition because of its super low critical temperature in comparison with in situ temperature. As CO_2 becomes a focal target for sequestration, it also becomes a focal agent to be used to enhance hydrocarbon recovery (Lazaratos and Marion, 1997; Majer et al., 2006).
We have launched a new effort to investigate CO_2 effects on properties of CO_2-oil mixtures. At the first step, we investigate properties of CO_2 mixtures with gas-free oil above their bubble point, in which CO_2 is fully dissolved into oil and they become single phase miscible mixtures. Here the phase boundary (bubble pressure line) is the low bound for under-saturated CO_2 to oil. But CO_2 phase can be either gas or liquid phase depending on pressure and temperature conditions. We realize that CO_2-oil mixtures may be also influenced with different hydrocarbon gas saturation, but we start from a simple condition first. Also, we assume that effects of hydrocarbon gas saturation can be treated as linear superposition effect to the CO_2 saturation effect if both hydrocarbon gas and CO_2 are not dominated in the composition of mixtures.

In this paper, we present our measured velocity and density of CO_2-oil mixtures at the conditions of temperature from 40°C to 100°C, pressure from 20MPa to 100MPa, and GOR up to 310L/L. Based on measured data we have developed preliminary velocity and density models for CO_2-oil mixtures.

Experiments

Sample preparation

In order to investigate CO_2 effect on oil we made "live" oil with different GORs (CO_2 gas - oil volume ratio at the standard condition) and prepared three groups of the "live" oil samples.

Group 1 is for studying different effects of CO_2 and hydrocarbon gas on velocity and density as they are dissolved into the same oil. The oil with API 32.84 is used to compose two "live" oil samples with GOR=200L/L. CO_2 with gas gravity of 1.5281 is used in Sample A, and hydrocarbon gas with gas gravity of 0.91118 is used in Sample B.

Group 2 is for investigating effects of CO_2 on velocity and density as it is dissolved into oils with different APIs. Three oils are selected to make CO_2-oil mixtures with GOR=100L/L. APIs of oils are 23.00, 32.84 and 39.81, respectively.

Group 3 is for examining effects of CO_2 on velocity and density as it is dissolved into same oil but different GORs. The oil with API 32.84 is selected to make CO_2-oil mixtures with various GORs up to 310L/L.

The key to making proper "live" oil is to put pressure vessel into an oven with temperature controlled at 50 °C. We find that CO_2 has limited solubility at room temperature, even with sufficient high pressure.

DOI http://dx.doi.org/10.1190/segam2012-1242.1

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Experiment setup and procedure

Instruments used for investigating CO_2 effect on oil are the same as those used for light oil measurements (Han et al., 2010). Except for routine calibrations to warrant data quality, there are special procedures required and performed for CO_2-oil measurements.

Since the critical point of CO_2 is at 7.38 MPa and 31.1 ºC, CO_2 exists as supercritical fluid at most in-situ condition. Any phase variation caused by temperature and/or pressure change will dramatically modify its properties of velocity and density. In order to measure the velocity and density of the "live" oil at the interested range of temperature and pressure, from 40°C to 100°C and 20MPa to 100MPa, we must always keep the sample above CO_2's critical point. From making the "live" oil samples in the storage vessel, transferring the "live" oil sample from the storage vessel to the measurement vessel, to measuring the oil under different temperature and pressure conditions, we have been keeping the whole system above the minimum condition, 40°C and 20MPa.

Measured data and discussions

Velocity

Like the velocity of "live" oil composed mainly of hydrocarbon gas, the velocity of "live" oil composed of CO_2 increases with increasing pressure and decreases with increasing temperature. The nearly parallel lines with temperature increasing also show almost independent effects of temperature and pressure at the research range (Figure 1).

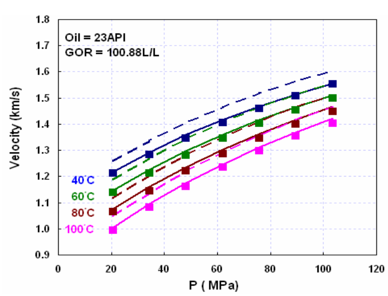

Figure 1: The measured velocity of the sample (symbol) with calculated values via FLAG (dashed line) and the model (solid line).

But there are two apparent differences comparing the effect of CO_2 with the effect of hydrocarbon gas. One is the effect of pressure. Due to different physical properties of CH_4 and CO_2, with pressure going up, the velocity of Sample A (CO_2-oil) increases slowly compared to that of Sample B (hydrocarbon -oil). That means to keep other conditions the same, CO_2 will decrease the velocity of "live" oil more than hydrocarbon gas does with pressure increases (Figure 2.A).

The other is the effects of CO_2 with different APIs. Since the FLAG can estimate the velocity of "live" oil with hydrocarbon gas very well, we are able to use it to calculate the velocities of "live" oil with GOR is equal to 100L/L and gas gravity 1.5281, which is the gas gravity of CO_2. Comparing the calculated values with the measured data, a correlation of CO_2 and API of host oil is clearly shown in Figure 2.B. Obviously, the hydrocarbon velocity model used in FLAG overestimates the velocities of CO_2-oil mixtures for low-API oil. And in contrast, it underestimates them for high-API oil. If we consider the calculated values as the velocity of "live" oil with heavier hydrocarbon gas, CO_2 will decrease velocity more than hydrocarbon gas does in low-API oil.

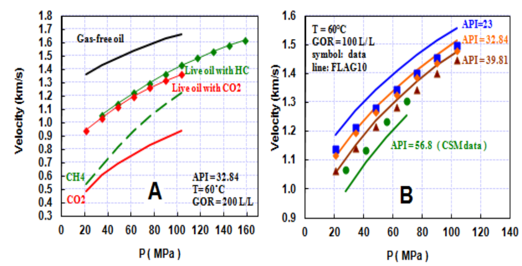

Figure 2: A. Velocities of the CO_2-oil and hydrocarbon-oil; B. Velocity differences with API variation.

Density

The density of samples shows a typical property of "live" oil density: it increases with increasing pressure and decreases with increasing temperature (Figure 3). But the CO_2 effect is markedly different from that of hydrocarbon gas. Since the density of hydrocarbon gas is always lower than that of the gas-free oil, dissolved hydrocarbon gas always decreases the "live" oil density. The more hydrocarbon gas is dissolved (i.e. higher GOR), the more the density decreases. In contrast, CO_2 at its supercritical fluid state may have higher density than the gas-free oil depending on temperature and pressure variation. At a certain in-situ condition, the heavier CO_2 will increase the density of "live" oil to more than the density of the gas-free oil.

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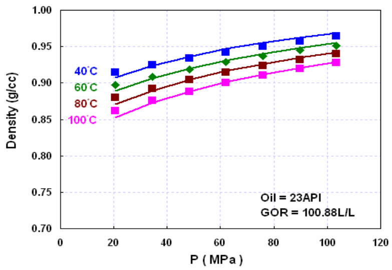

Figure 3: The density of the sample (symbol: measured data; line: calculated values by the model).

Modeling

Based on our measured data, preliminary models are developed within data limitation, where $40^\circ C \le T \le 100^\circ C$, $20MPa \le P \le 100MPa$, and $GOR < 310L/L$. In the following calculation, the gas gravity of CO_2 equals 1.5281.

Velocity model

The velocity equation of CO_2-oil miscible mixtures can be expressed as,

$$V = A - BT + C(\frac{1-D^p}{1-D}) + FTP. \quad (1)$$

Where V is the velocity in unit of m/s, P is the pressure in MPa, and T is the temperature in °C. A, B, C, D and F are coefficients, which are functions of velocity pseudo density and defined as,

$$A_i = a_{i1}\rho_{v\_seu}{}^{a_{i2}} + a_{i3} \quad (2)$$
$$B_i = b_{i1} + b_{i2}API_{v\_seu}$$
$$C_i = c_{i1}\ln(API_{v\_seu} + c_{i2}) + c_{i3}$$
$$D_i = d_{i1} + d_{i2}API_{v\_seu}$$
$$F_i = f_{i1} + f_{i2}\rho_{v\_seu} + f_{i3}e^{f_{i4}\rho_{v\_seu}}.$$

The velocity pseudo density can be obtained as the following by refitting the new model of apparent liquid density (Liu, J., and D. Han, 2010, New Model of Apparent Liquid Density, Fluids / DHI Consortium).

A hypothetical density of dissolved CO_2 as a function of oil API without effects of GOR, is modeled as,

$$\rho_{a1} = M_s + N_s\ln(G)$$
$$M_s = 0.564125 + 6.79\times10^{-6}API \quad (3)$$
$$N_s = 0.132216 + 0.000199874API.$$

To include GOR effect, it becomes,

$$\rho_{a2} = [M_g + N_g(\frac{\rho_{p1}}{\rho_0})]\rho_{a1}. \quad (4)$$

Where

$$\rho_{p1} = \frac{\rho_0 + M_{co2}}{1 + M_{co2}/\rho_{a1}}, \quad (5)$$

$M_g = -0.53253$, and $N_g = 1.583188$.

So, the velocity pseudo density is

$$\rho_{v\_seu} = \frac{\rho_0 + \varepsilon M_{co2}}{1 + M_{co2}/\rho_{a2}} \quad (6)$$

and its API is

$$API_{v\_seu} = \frac{141.5}{\rho_{v\_seu}} - 131.5. \quad (7)$$

Where ρ_0 is the density of gas-free oil in g/cc and M_{co2} is the mass of CO_2, which can be calculated by gas and oil ratio GOR in L/L, $M_{co2} = 0.001868866GOR$. An effective gas parameter, ε = 0.113, which represents the effectiveness of the gas portion (weight fraction) contributed to pseudo-liquid velocity.

Their sub coefficients in the coefficient group (2) are listed in the following tables for different ranges of the velocity pseudo density.

For $API_{v\_seu} \le 100$, i=1

j	1	2	3	4
a_{1j}	3940.7	0.32162	-2289.41	
b_{1j}	3.26313	0.00879		
c_{1j}	19.6028	307.7138	- 109.694	
d_{1j}	0.99221	-4.71742×10^{-5}		
f_{1j}	0	0	0.050622	-1.60696

If $API_{v\_seu} \ge 200$, i=2

j	1	2	3	4
a_{2j}	3940.70	0.32162	-2289.41	
b_{2j}	4.0525	- 0.0025		
c_{2j}	9.880896	0	- 36.322	
d_{2j}	0.985352	-1.482×10^{-5}		
f_{2j}	0.000881	0.011597	0	0

During $100 < API_{v\_seu} < 200$, then

$$A = A_1 = A_2$$
$$B = 0.01[(200 - API_{v\_seu})B_1 + (API_{v\_seu} - 100)B_2]$$
$$C = 0.01[(200 - API_{v\_seu})C_1 + (API_{v\_seu} - 100)C_2]$$
$$D = 0.01[(200 - API_{v\_seu})D_1 + (API_{v\_seu} - 100)D_2]$$
$$F = 0.01[(200 - API_{v\_seu})F_1 + (API_{v\_seu} - 100)F_2].$$

Good matches are shown in Figure 1 and Figure 4. With GOR increases, the velocity of the "live" oil will decrease toward the velocity of pure CO_2. This velocity trend can be simulated by the model as displayed in Figure 4, where the top line is the velocity of dead oil and the bottom line is the velocity of the pure CO_2. Between them the velocity of "live" oil decreases with GOR increases.

DOI http://dx.doi.org/10.1190/segam2012-1242.1

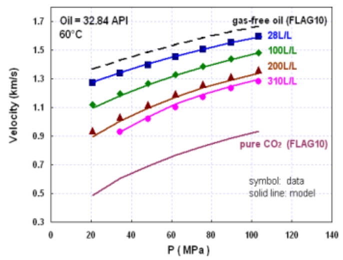

Figure 4: The measured velocity (symbols) and the prediction by the model (lines) for deferent GORs.

Density model

We know that the density is correlated with API, GOR, and gas gravity, as well as with temperature and pressure. Preliminarily, an empirical model is created by assuming that the mass and volumes of CO_2 and dead oil are additive and then the density of mixtures can be described as,

$$\rho = f_{v\_co2}\rho_{e\_co2} + f_{v\_oil}\rho_{oil.} \qquad (8)$$

Where f_{v_co2} and f_{v_oil} are volume fractions of CO_2 and gas-free oil, respectively, and $f_{v\_co2} + f_{v\_oil} = 1$;

ρ is the density of CO_2-oil mixtures;

ρ_{oil} is the density of gas-free oil, which can be expressed as, $\rho_{oil} = \rho_0 + \Delta\rho_p - \Delta\rho_T$, and calculated via FLAG;

And ρ_{e_co2} can be called as an effective density of CO_2 with a formula

$$\rho_{e\_co2} = c_1 + c_2 T + c_3(\frac{1-c_4^{\,P}}{1-c_4}) + c_5 TP \qquad (9)$$

where T is temperature in degree C, P is pressure in MPa, and the coefficients $c_1 = 0.86476$, $c_2 = -0.001982$, $c_3 = 0.0074$, $c_4 = 0.9794$, and $c_5 = 7.4\times10^{-8}$.

For 1 cc of oil, the mass of CO_2 can be obtained from its gas gravity and GOR as $M_{co2} = 0.001868866GOR$,

and then the effective volume of the CO_2 is

$$V_{co2} = \frac{M_{co2}}{\rho_{e\_co2}} \qquad (10)$$

The volume fractions are

$$f_{v\_co2} = \frac{M_{co2}/\rho_{e\_co2}}{1+M_{co2}/\rho_{e\_co2}} \qquad (11)$$

and
$$f_{v\_oil} = \frac{1}{1+M_{co2}/\rho_{e\_co2}} \qquad (12)$$

By rearranging the equation (8), the density of CO_2-oil mixtures can be calculated by the formula,

$$\rho = \frac{\rho_{oil} + M_{co2}}{1+M_{co2}/\rho_{e\_co2}} \qquad (13)$$

The calculated values are shown as the solid lines in Figure 3 and Figure 5 for various conditions and they match the measured data pretty well within the limitation of the measurement condition.

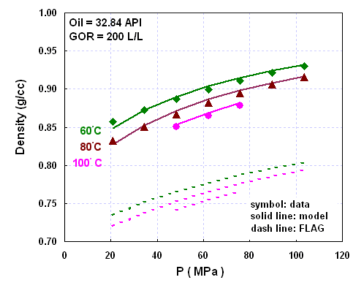

Figure 5: Density comparison of data with the models for CO_2-oil mixtures with GOR 200L/L.

Conclusion

We have measured the velocity and density to examine CO_2 effect as it is dissolved into oil with different API gravity in comparison with that of hydrocarbon gas.

We have observed that when CO_2 is dissolved in low-API oil, CO_2 will cause a more decrease of velocity than hydrocarbon gas does. In addition, since the density of hydrocarbon gas is always lower than that of oil, dissolved hydrocarbon gas always decreases the "live"-oil density. However, CO_2 can be heavier than oil at a certain condition, and the dissolved CO_2 increases the density of CO_2-oil mixtures to more than the gas-free oil density.

Based on measured data, preliminary velocity and density models are developed within measured conditions of $40^\circ C \le T \le 100^\circ C$, $20MPa \le P \le 100MPa$, and $GOR < 310L/L$. The calculated values fit the measured data well.

Acknowledgments

This research has been supported by the Fluids/DHI consortium, which is sponsored by industry in collaboration with the University of Houston and the Colorado School of Mines.

DOI http://dx.doi.org/10.1190/segam2012-1242.1

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EDITED REFERENCES

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