



Barotropic Inversion in Brazilian Pre-Salt Carbon-Dioxide-Rich Gas Condensate

Emerson Lourenço^{1*}, Alexandre J. M. Vieira¹

¹Fluid Technologies/CENPES, PETROBRAS, Brasil, *emerson.lourenco@petrobras.com.br

Abstract

Different accumulations found in Brazil present high API gravity, increased Gas-Oil Ratio (GOR), and carbon dioxide content up to 90 mol%. The phase behavior during reservoir flow, treatment, and reinjection operations gets more complex for such fluids. Understanding this complex system at different pressures and temperatures through accurate experimental data is relevant to minimizing flow assurance problems. Carbon dioxide could induce corrosion, scaling, wax and asphaltene precipitation, and compatibility issues. This work reports the Liquid-Liquid-Vapor phase equilibrium (LLVE) and barotropic inversion observation for the first time in real Brazilian reservoir fluids.

Keywords

barotropic inversion, carbon dioxide-rich gas condensate, phase behavior

Introduction

Pre-salt reserves have been one of the most relevant discoveries for the oil industry in the last decades, leading Brazil to a worldwide position in ultra-deepwater production (depth > 1500 m). These areas often present complex fluids with a high GOR and carbon dioxide (CO₂) content. The presence of CO₂ is a significant challenge due to the production of a considerable amount of greenhouse-effect gas that must be processed, separated, and adequately addressed, considering the climate change protocol recommendations. [1,2,3,4].

Understanding the phase behavior is critical to properly designing the production system setup. The changes in the thermodynamic conditions and the complex fluid composition are the leading causes of multiphasic equilibria during production [5,6,7]. The primary data related to phase behavior are obtained through routine experimental PVT analyses, which allow reserve volume prediction and support exploitation strategy decisions and production system design. [7].

CO₂ reinjection has been a well-established EOR method since the 1970s in the USA, spreading its economic use worldwide [8]. From the beginning, CO₂-rich gas alternating with water injection (WAG) was chosen as a preferential EOR method in Pre-salt reservoirs [2].

The CO₂-rich gas injection can be miscible or immiscible depending on the injection conditions and the compatibility between reservoir oil and gas compositions. The oil recovery due to CO₂ injection is higher when the process is miscible and governed by interactions between CO₂, oil, and formation rock [9].

The increase in carbon dioxide concentration at the reservoir results in a fluid with complex phase behavior presenting Liquid-Liquid Equilibrium (LLE), Liquid-Liquid-Vapor Equilibrium (LLVE), in some cases Liquid-Solid Equilibrium (LSE), and even barotropic phenomena (density inversions) due to the immiscibility of CO₂ and the reservoir fluid at high pressures [2,6,7,8,10,11].

Barotropic inversion, also known as mass density inversion, corresponds to a particular case when densities of – at least – two phases coexisting in a heterogeneous mixture change positions in a gravitational field. The literature reports that mass density inversions depend on the mixture components' molecular size and molar mass [12]. The understanding of barotropic inversion is crucial in the design and operation of separation processes, particularly when considering the use of subsea CO₂ separation facilities to alleviate bottlenecks in conventional production topside arrangements. The coexistence of two liquid phases in equilibrium, an oil-rich phase and a CO₂-rich phase, may occur in Pre-Salt reservoir conditions and allows the employment of high-pressure gravity separators [1,2,11,12,13]. However, a barotropic inversion event can disturb the process and eventually make it unfeasible.

In this work, the Liquid-Liquid-Vapor phase equilibrium (LLVE) and barotropic inversion are reported for the first time in a real Pre-Salt fluid, employing a single-phase sample collected downhole during a typical reservoir formation test, investigating temperatures varying from 50.0 °C to 90.0°C and pressures from 2000 to 5000 psig.

Methodology

Experimental Procedure

The phase behavior of the CO₂-rich gas condensate sample with approximately 90.0% mol CO₂ was monitored during Constant Composition Expansion (CCE) tests run in a PVT visual cell (Figure 1) at 50, 70, 60, and 91 °C.

Thermodynamic Equilibrium Visual Cell

This equipment is typically used to evaluate the dew point and density of hydrocarbon gas condensate samples as a function of pressure and temperature. The PVT cell is installed inside a temperature-controlled oven (Figure 1a). The visual cell is a cylindrical-shaped glass protected by a steel jacket, with two glass windows on opposite sides (Figure 1b). The space between the glass cylinder and the steel jacket is filled with mineral oil that acts as an overburden fluid, transmitting the same confining pressure to the sample through a floating piston. A magnetic mixer is coupled to the upper part of the cell, promoting intense stirring. The conical floating piston sits in the lower part of the cell, controlling the sample pressure through mineral oil displaced with a computer-controlled automatic pump.

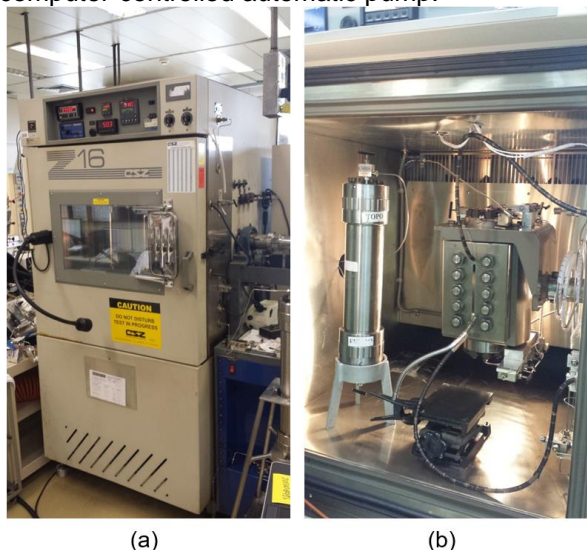


Figure 1. PVT visual cell: (a) external and (b) internal view of the oven.

Constant Composition Expansion (CCE)

The reservoir fluid (a CO₂-rich gas condensate), at a fixed temperature and initially above the reservoir pressure, is slowly depressurized by expansion in constant pressure steps searching for the dew point. For gaseous samples, the appearance of the first liquid drops can be inferred by the mist, which condenses later in the cell wall and accumulates in the annular space between the glass cylinder and the conical piston. Below the retrograde dew point pressure, the liquid phase volume is accounted for by the height of the Liquid-Vapor interface.

Phase inversion measurement procedure

Liquid-Liquid-Vapor Equilibrium (LLVE) was observed below the dew point at a given pressure and test temperature in the CCE tests run on the CO₂-rich gas condensate sample, measuring the phase volumes. A single yellow liquid phase exists below the dew point in the early depressurization stages. The appearance of a secondary, pale white liquid atop the yellow phase was observed at pressures between 1500 to 2500 psig, at different temperatures below the dew points. The second liquid phase volume is nearly constant with the pressure decrease. The barotropic inversion occurs at pressures between 1100 psig to 1500 psig below the secondary liquid appearance, when the pale white liquid exchange places with the yellow liquid phase and moves towards the bottom of the cell. Furthermore, decreasing the pressure even more, the second liquid phase disappears at pressures from 300 psig to 600 psig below the barotropic inversion point.

Thermodynamic simulation

The simulated and experimental Liquid-Liquid-Vapor Equilibrium (LLVE) phase envelopes were compared using the commercial PVTsim Nova 5.0 thermodynamic simulator. The simulations employed three equations of state without any previous adjustments: Soave-Redlich-Kwong [14] and Peng-Robinson 78 [15] (both with temperature-dependent Peneloux correction term) and PC-SAFT. [16]

For comparison, the SRK EOS was tuned to reproduce GOR and API values, saturation pressures, and constant composition expansion properties (relative volume, liquid dropout, and density) at 50, 60, 70, and 91 °C.

Results and Discussion

The single-phase, bottom-hole, CO₂-rich gas condensate was supplied by Petrobras and sampled during a reservoir well test. The average reservoir temperature is 91.0 °C. Table 1 highlights the main fluid properties and components.

The dew point pressure at 91.0°C is 6500 psig, while the second liquid phase appears at 5000 psig and vanishes at 3000 psig. The barotropic inversion takes place at 3600 psig. The liquid dropout amount of the pale white phase varies from 0.17 to 0.47% before the phase inversion without any noticeable increasing or decreasing trend. In contrast, below the barotropic inversion pressure, the second phase liquid dropout decreases until it completely disappears.

Several pictures were captured during the CCE test run at 91.0 °C, illustrating the unusual behavior. The presence of the second, pale-white liquid phase is clearly seen atop the yellow liquid phase at 5000 and 4500 psig (Figures 2a and 2b). At 3500 psig they have already exchanged places, and now the pale-white phase rests below the yellow liquid phase (Figure 2c). A single liquid phase remains at 3000 psig (Figure 2d).

Table 1. Reservoir fluid characterization

Properties	
Carbon dioxide (mol%)	90.04
Methane (mol%)	6.66
Hydrogen sulfide (ppm)	7.00
GOR (STD m ³ / STD m ³)	3828
API gravity	40.75

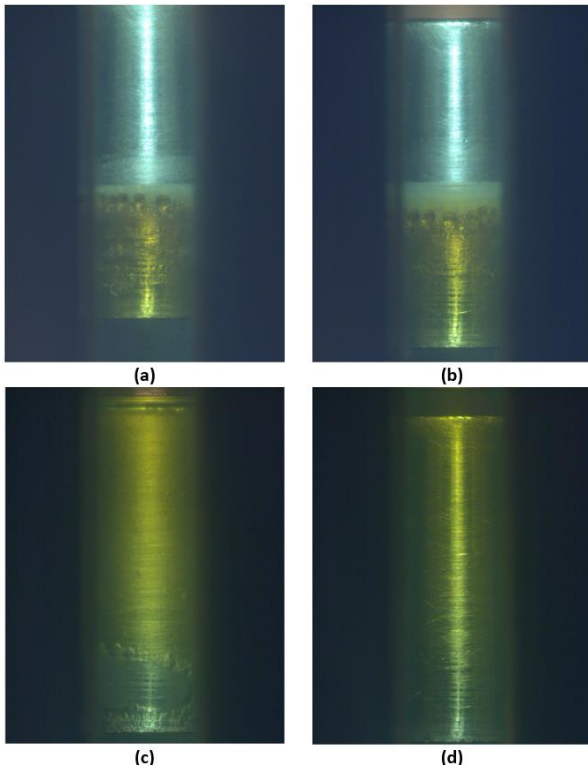


Figure 2. Phase behavior of carbon-dioxide-rich gas condensate at 91.0 °C: the second liquid phase is present at (a) 5000 psig and (b) 4500 psig, (c) just after barotropic inversion at 3500 psig and (d) single liquid phase remains at 3000 psig.

The CCE test run at 50.0 °C presents the same behavior as the ones at 70.0 and 91.0 °C. The dew point pressure drops to 6500 psig, and the appearance of the second liquid phase takes place at 4000 psig (Figure 3a). The phase inversion pressure occurs at 2500 psig (Figure 3b). With the subsequent pressure reductions (Figures 3c and 3d), the second phase vanishes at 2100 psig. The liquid dropout of the pale white phase varies from 0.20 to 0.39 before the phase inversion, without any apparent trend. In contrast, below the barotropic point pressure, the second phase dropout ratio decreases until its disappearance. The same behaviors are observed at 70.0 and 60.0°C.

Table 2 summarizes the events observed during the CCE test set. The appearance pressure of the second liquid phase decreases with temperature, from 5000 psig (91.0 °C) to 4000 psig (50.0 °C). The barotropic pressure has a similar trend, varying from 3600 psig (91.0 °C) to 2500 psig (50.0 °C), as well as the second phase vanishing pressure, decreasing from 3000 psig (91.0 °C) to 2100 psig (50.0 °C).

Table 2. Events in CCE tests at different temperatures.

CCE temperatures ^(a)	Pressure ^(b)		
	91.0	70.0	50.0
dew point	6500	7000	6500
second liquid phase appearance	5000	4500	4000
barotropic inversion	3600	3100	2500
second liquid phase vanishing	3000	2800	2100

(a) temperature (°C), (b) pressure (psig).

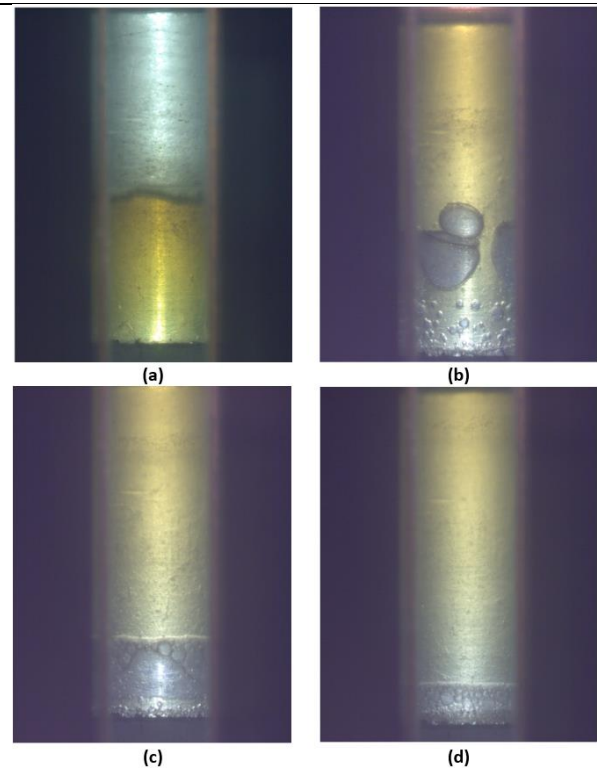


Figure 3. Phase behavior of carbon-dioxide-rich gas condensate at 50.0 °C: (a) presence of two liquid phases at 4000 psig, (b) phase inversion takes place due to isodensity effect at 2500 psig and the second fluid phase in the bottom of CO₂-rich liquid phase at 2300 (c) and at 2200 psig (d).

Figure 4 compares simulated and experimental LLVE phase envelopes. Four simulation scenarios were run with the PVTsim Nova 5.0 thermodynamic simulator and compared to the experimental values collected during the CCE tests. The simulations were run with three typical equations of state that were not tuned previously with any experimental data (Soave-Redlich-Kwong and Peng-Robinson, both corrected with temperature-dependent Peneloux term, and PC-SAFT). Moreover, a fluid model was developed with SRK Peneloux EOS by tuning to experimental PVT data (GOR, API gravity, and relative volumes). These models were not capable of representing the experimental three-phase events.

Conclusions

A barotropic behavior was observed for an authentic Brazilian Pre-Salt reservoir live fluid. The phase behavior observed for this CO₂-rich gas condensate is both complex and fascinating. In the early stages of depressurization below the dew point, a Liquid-Vapor Equilibrium (LVE) is observed

until a second liquid phase appears, establishing a Liquid-Liquid-Vapor equilibrium (LLVE). Then, the barotropic inversion phenomenon takes place at pressures from 1100 psig to 1500 psig below the appearance of the second liquid phase. Further decreasing in the pressure promotes the disappearance of the second liquid phase, returning to an ordinary Liquid-Vapor equilibrium (LVE). This unique behavior was observed at four different temperatures, covering a wide pressure range. The simulations run with commercial EOS software could not reproduce the experimental data.

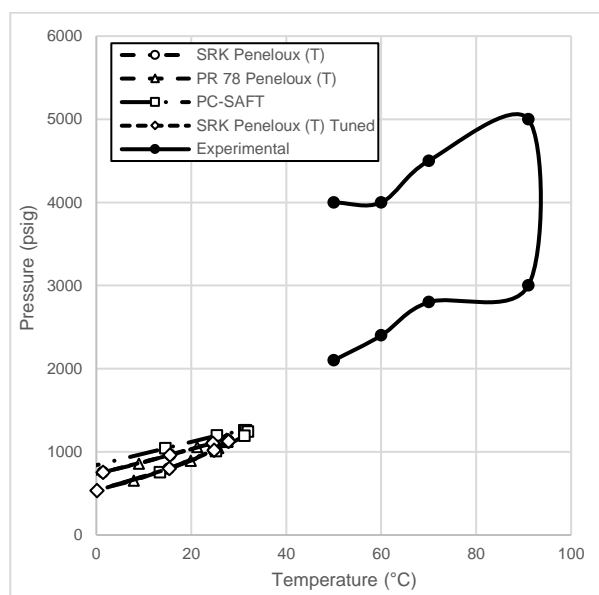


Figure 4. Comparison of simulated and experimental three-phase area (LLVE) for the CO₂-rich gas condensate

Acknowledgments

The authors would like to thank Petrobras for allowing this work to be published.

Responsibility Notice

The authors are the only ones responsible for the paper's content.

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