



The barotropicity of Brazilian stabilized condensate with high CO₂ content

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Abstract

The current Brazilian frontiers in the oil production from the challenging recently discovered reserves have led the country to a leadership position in technological development. High gas-oil ratio and elevated CO₂ content have been verified in areas like the pre-salt province and the Sergipe Águas Profundas. Thus, harsh production conditions have demanded disruptive solutions. The development of subsea systems to separate carbon dioxide from the reservoir stream and reinject it is one of the challenges to be overcome. In this scenario, this work has as its main goal the supplying of phase behavior data and the study of the mass barotropic effect in mixtures of stabilized liquid condensate and CO₂. A full visibility PVT cell was used to carry out Constant Composition Expansion essays of recombined samples at a carbon dioxide molar composition of 80%. The results showed the formation of a solid-like phase under reservoir conditions. It disappears during the sample depletion. Also, the occurrence of density inversion of the CO₂-rich phase was observed. The phase behavior diagram is reported with liquid-liquid and vapor-liquid-liquid equilibrium. Overall, the obtained results may be useful as a guideline for the development of flow assurance strategies.

Keywords

barotropicity; phase behavior; pre-salt

Introduction

The huge oil reservoir discoveries in the Brazilian areas of Pre-salt and Sergipe Águas Profundas led the country to a prominent position in the energy ecosystem. Also, it has pushed technological development to the next level facing the operational challenges originated from the current scenario. The reservoir's low temperature and the fluid composition with high GOR and elevated CO₂ content demand solutions for sustainable gas/oil separation and reinjection [1-3].

The current strategy employs the membrane permeation process at the topside of the platforms to separate the CO₂ and reinject it into the reservoir after its compression [4]. However, the complex phase behavior of the mixture oil-carbon dioxide concerns the production flow assurance. It promotes the asphaltene precipitation, wax, and hydrates formation, mainly during its decompression [5-7]. Once it might reduce the projects' economic attractiveness, as related by Passarelli (2017) [8], the subsea separation process has arisen as an alternative. Among its advantages, it is worth mentioning the lower risk of critic solids formation in the risers and flowlines between the seabed and the platform; the use of the reservoir energy thus reducing the demand of the compressors; and the reduction of real-state

area demand at the platform topside [9-10]. Also, the occurrence of two liquid phases at some thermodynamic conditions verified in the pre-salt fields favors the carbon dioxide separation by gravity difference [11].

However, what at first seems a benefit may also become an operational challenge. The density inversion of the CO₂-rich phase makes the operation of gravity vessels unfeasible. Thus, the main goal of this work is to study the occurrence of mass barotropicity under pre-salt thermodynamic conditions.

Methodology

Mixtures of carbon dioxide and the stabilized liquid condensate oil BR from the Brazilian pre-salt area were recombined at reservoir conditions of 650 bar and 64 °C. A recombination system equipped with an infrared probe to detect the proper recombination was used. It was supplied by Sanchez Technologies. In summary, known amounts of carbon dioxide and the stabilized liquid condensate were added into the recombination cell with the aid of a Stigma pump. The mixture was kept under agitation until a monophasic stable mixture was observed. Then, the samples were transferred into the PVT cell.

The so-far studied mixtures had a CO₂ molar composition of 80, 60, and 40%. The carbon

dioxide 5.0 was supplied by White Martins[®]. The stabilized liquid condensate was firstly characterized regarding its asphaltene content (ASTM D2007)[12], salt content (ASTM D3230)[13], water content (ASTM D4377)[14], SARA, and specific gravity (ASTM D5002)[15], and wax appearance temperature [16].

Thus, Constant Composition Expansion – CCE essays were performed by using a Sánchez's full visibility 400/1000 PVT Cell. Its characteristics are described elsewhere (Regueira et al., 2017)[17]. The phase transitions were visually identified with the aid of a CCD camera and the software Euclide[®].

The interface level variation was monitored to detect the formation of a new phase.

Results and Discussion

The oil characterization is described in Tab (1). As one may see, the oil is free of detectable water which is imperative for PVT analysis. Also, the studied oil had no asphaltenes insoluble in n-heptane in its composition. Further, the temperature at which wax crystallization was detected through differential scanning calorimetry was 19 °C. Thus, the mixture phase behavior for the current work was studied in temperatures above the WAT.

Table 1. Properties of the stabilized liquid condensate.

Property	Condensate BR
Water content (%)	< 0.5
API gravity (°)	34.7
Salt content (g/m ³)	26.6
n-Heptane insoluble (%)	0
WAT*	19 °C

*Wax appearance temperature

The first interesting finding during the CMD essays is shown in Fig (1). The samples recombined at temperatures higher than the critical temperature of pure CO₂ are translucent, thus allowing the visualization of the back section of the PVT cell. On the other hand, there is an increasing opacity as the temperature is reduced.

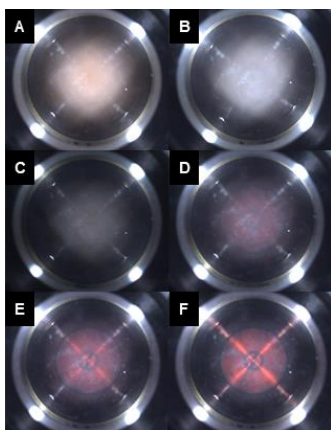


Figure 1: Opacity variation of the recombined condensate-CO₂ mixture at the carbon dioxide

molar concentration of 80%, pressure of 650 bar, and several temperatures. A: 20 °C; B: 25 °C; C: 27,5 °C; D: 30 °C; E: 40 °C; F: 64 °C.

The opacity variation might be the result of solidification and agglomeration of long-chain paraffin that got out of the solution by the carbon dioxide antisolvent action. Otherwise, it may also be caused by the miscibility reduction of the CO₂-rich phase at the studied temperature and carbon dioxide concentration, as suggested by Ahmed (2007)[18]. Although the exact cause is still not well defined, it is certain that the observed opaque phase has its intensity reduced as depressurization occurs until the liquid-liquid point is detected, then a new translucent phase is detected as shown in Fig (2).

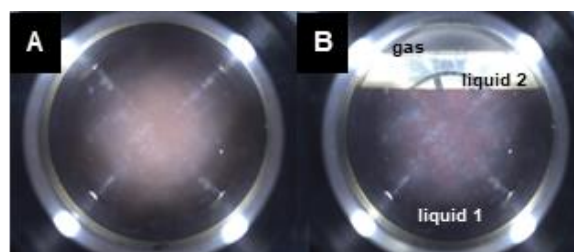


Figure 2: Opacity variation of the recombined condensate-CO₂ mixture at the carbon dioxide molar concentration of 80%, the temperature of 20 °C, and varied pressures: A: 600 bar; B: 70 bar.

Further, the phase behavior of the mixtures was studied at temperature ranges varying from the reservoir temperature of 64 °C to 20 °C, which is lower than the oil WAT. Also, the pressure variation was from 600 to 50 bar. As already mentioned, the phase evolution in the full visibility PVT cells is monitored through the height variation of the formed interface between 2 or more phases. Thus, based on a previous volume calibration, Fig. (3) shows that the emergency of a second liquid phase (liquid 2) from a liquid monophasic one (liquid 1) is measured by the relative volume variation of each phase. Furthermore, phase liquid 2 disappears and liquid 1 has its volume gradually reduced at the same volume variation verified for the increase of the gas phase volume.

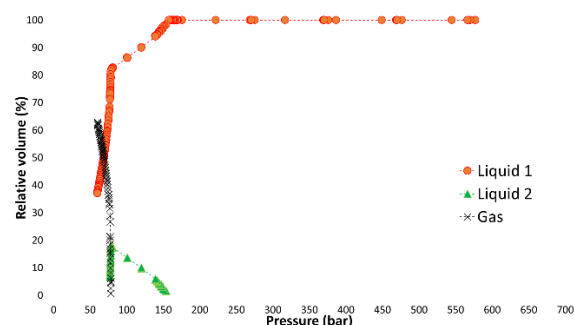


Figure 3: Diagram of relative volume variation for the observed phases in the function of pressure.

The CO₂-rich phase accumulated at the bottom in temperatures lower than 30 °C while it appeared at the top part of the cell in higher temperatures. However, a very interesting phenomenon was observed. As one may see in Fig. (4), this phase migrated from the bottom to the top once a specific pressure was reached. It denotes the occurrence of the phase's mass density inversion, which is commonly called as the mass barotropic effect. It is worth highlighting strongly that reports of such phenomena in complex mixtures of carbon dioxide and hydrocarbons have been made only for model systems. Thus, it may be the first time that mass barotropicity is presented for a real crude oil-CO₂ system.

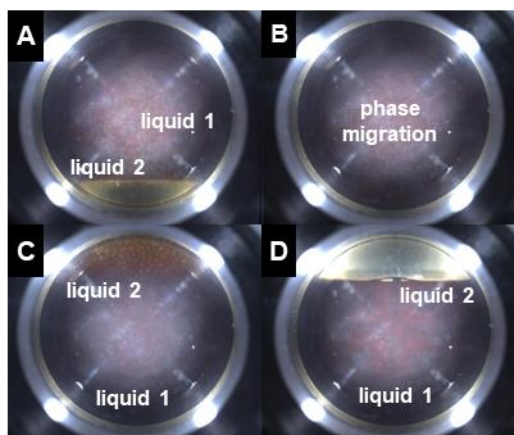


Figure 4: Density inversion of the CO₂-rich phase for the condensate-CO₂ mixture at the carbon dioxide molar composition of 80%. A: denser CO₂-rich phase; B: migration of the CO₂-rich phase from cell bottom to the top; C: phases stabilization; D: denser condensate-rich phase.

In simple words, a barotropic fluid is the one that undergoes density inversion according to pressure variation. The determination of the thermodynamic conditions in which it occurs is indispensable. According to de Souza et al. (2019) [19], the viability of the CO₂ subsea separation process is depended on the existence of a highly dense CO₂-rich phase in a large range of pressure and temperature conditions.

Also, the density inversion points are presented in Fig. (5), although it is not a common component of typical phase diagrams. One may see that it occurred only at temperatures below 27,5 °C for the recombined fluid composition with carbon dioxide molar content of 80%. The barotropic pressure as well as the total relative volume of the CO₂-rich phase decreases conform to temperature reduction. It stands as a piece of relevant guideline information for the operational optimization of technologies such as the HISEP®, as demanded by de Souza et al. (2019)[19].

Figure 5 also shows the PT diagram for the system containing 80% of CO₂ molar composition. It shows that the liquid-liquid equilibrium (ELL) pressure was kept at around 160 bar for temperatures between 30 °C and the reservoir one, which is 64 °C. There

was an increase in ELL pressure for lower temperatures according to temperature reduction. This behavior was observed by Daridon et al. (2021) [20] in CO₂-hydrocarbon model systems.

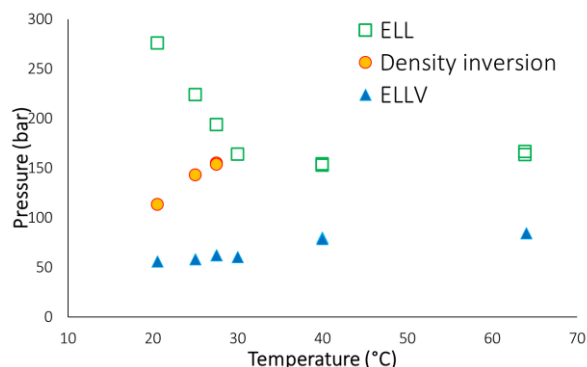


Figure 5: PT phase diagram for the mixture composed of condensate oil and carbon dioxide at a CO₂ molar concentration of 80%.

Further, the liquid-liquid-vapor equilibria (LLVE) points are shown in Fig.3. They were identified through the appearance of the first gas bubble, which promoted a change in the light refraction. As already expected, the LLVE average pressure increased at temperatures above the CO₂ critical temperature.

Conclusions

The complex phase behavior of a recombined mixture composed of carbon dioxide and stabilized liquid condensate is described at the CO₂ molar composition of 80%. The occurrence of mass barotropicity in a real stabilized condensate recombined with carbon dioxide at thermodynamic conditions of the Brazilian pre-salt reservoirs is reported for the very first time. Although further analyses are still being performed, the preliminary results meet the demand for phase behavior data requested by the developers of technological solutions for reservoir production.

Acknowledgments

The authors thank to Petrogal Brasil S/A, CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil) - Finance Code 001, CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), FAPITEC/SE (Fundação de Apoio à Pesquisa e à Inovação Tecnológica do Estado de Sergipe) and ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) for financial support and scholarships.

Responsibility Notice

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

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