Use of real crude oil fractions to describe the high pressure phase behavior of crude oil in carbon dioxide

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ABSTRACT

The knowledge about crude oil phase behavior at high-pressures is a challenge for scientists due to inherent complexity to this systems. Some works employ model systems attempting to predict crude oil behavior, but the results are normally poor. In this sense, the use of real crude oil fractions can be an alternative to improve the accuracy of the models used in these simulations. In this work, a light oil sample has been fractionated to generate four representative fractions. An approach to estimate the critical properties of these distilled fractions using only density and vapor pressure experimental data is presented. In sequence, phase behavior of the pseudo binary (carbon dioxide (CO_2) + real crude oil fractions), multicomponent (mixture of fractions + CO_2) and original crude oil + CO_2 systems were determined using static synthetic method and static synthetic + NIR, with CO_2 molar fraction range of 0.367-0.986, temperature range of 20–80 °C and pressure up to 300 bar. Binary interaction parameters (BIP) were estimated for each pair (CO_2 + distilled fraction) and employed to describe the phase behavior of a CO_2 + crude oil systems with Peng-Robinson equation of state (PR-EOS) and quadratic mixing rule. The results suggest that the use of real fractions can be a safer strategy for predicting the phase behavior of petroleum in carbon dioxide. Besides, NIR spectroscopy showed to be a good alternative to study phase behavior of dark/opaque systems.

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1. Introduction

High-pressure phase equilibrium data is a key role for planning and evaluation of pressurized industrial processes. In the upstream petroleum industry, these data provide valuable information about the phenomena that can occur from natural reservoirs to production and processing facilities for several purposes, as enhanced oil recovery (EOR) projects [1]. Carbon dioxide flooding has been long recognized as an efficient method to be used in Enhanced Oil Recovery (EOR) projects, and it can be applied to a variety of oil reservoirs [2]. This method has been studied since the 1950's, and several commercial projects have been successfully started since the 1970's [3].

Although the majority of CO_2-EOR projects are still in the U.S., some pilots and commercial projects have been implanted or planned worldwide [4–7]. In these projects, the mixture of CO_2 and hydrocarbons (HC) usually exhibit complex phenomena, like liquid-liquid (LLE) and liquid-liquid-vapor (VLLE) equilibrium [8,9], and in some cases, miscibility cannot be achieved even with very high pressures [10].

For an accurate production forecast, investigating the complex phenomena present on these projects, phase behavior calculation based on a cubic equation of state, like Peng-Robinson (PR-EOS), is available in several commercial reservoir simulators. The usual approach employed in industry is to estimate critical and physical properties of components, as well as the binary interaction parameters, through some correlations. Additionally, if some laboratorial data are available, these estimated properties are fitted to match the experiments. Despite the available computational resources available nowadays, it's common to represent the hydrocarbon mixture by few representative components, usually called "pseudo components", aiming to reduce the simulation time [11]. Although it is a

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practical necessity, the properties of the new grouped components may impair the fluid behavior representation, making it necessary a new tune procedure. This approach can misrepresent the complex behavior of crude oil multicomponent mixtures.

The study of the interaction of a whole oil fraction with the solvent can be a useful methodology to achieve a better understanding of the phase behavior in complex systems, like CO_2-crude oil [12]. The use of direct fractions from crude oil for study the high-pressure phase behavior of crude oil in solvents can be a useful technique, as distinct fractions can be combined to model several crude oils.

In this direction, this work presents a study on the high-pressure phase equilibria of crude oil fractions with carbon dioxide. A Brazilian crude was fractionated, and the fractions were characterized in terms of vapor pressure, density, and chemical profile, from where critical properties of each fraction were estimated. The phase behavior of pseudo binary (crude oil fractions + CO_2), multicomponent (mixture of fractions + CO_2) and original crude oil + CO_2 systems were experimental determined and modeled with the Peng-Robinson EOS. The results indicated that a better representation of the phase behavior of the multicomponent mixture in carbon dioxide was achieved when using the individual fractions characteristics.

2. Material and methods

2.1. Crude oil fractionation and characterization

A sample of Brazilian dead light oil, with a density of 0.832 g.cm^{-3} at 25 °C and API of 36.9, was fractionated through a vacuum distillation process. The distillation was conducted in a vacuum column with independent temperature, pressure, and reflux systems control, in three 800 mL batches. The crude oil was fractionated into four fractions, named F1 to F4 (from the lighter to the heavier fraction).

Chromatographic analyses were performed by gas chromatography coupled to mass spectrometry (Shimadzu GCMS-QP 2010 Plus). Samples of 1.0 μL of fractions F1–F3 were injected (split mode 1:50), in a Rtx-5 column (5% diphenyl/95% dimethyl polysiloxane), with 0.25 mm of internal diameter and 30 m length, with injector and interface temperatures of 280.0 °C and 300.0 °C, respectively, using helium at 1.2 mL min^{-1} as carrier gas. The temperature program started at 40.0 °C (30 min), heated at 1.0 °C min^{-1} up to 60.0 °C (5 min) and at 2.0 °C min^{-1} up to 280.0 °C (10 min). The heavier fraction (F4) was not analyzed by GC/MS due to its high molecular weight.

Density, vapor pressure and true boiling point (TBP) of each fraction were experimentally measured and used for estimation of fractions' critical properties. Density values were measured in triplicate in a digital densitometer (Anton Paar, DMA 4500 M), which provides results with a standard deviation of 10^{-5} g cm^{-3}. The vapor pressure and TBP data of each fraction were measured using the distillation vacuum column in total reflux in a two-step process (decreasing and increasing of the pressure). The uncertainties calculated for the vapor pressure and TBP were 0.01 bar and 2.0 °C, respectively.

Pure hydrocarbon compounds, whose vapor pressure data and density were close to the fractions' data [13], where selected in order to provide initial estimates for critical properties of fractions. The selected compounds, corresponding to fractions F1 to F4, were n-octane (C_8H_{18}), n-undecane ($C_{11}H_{24}$), n-hexadecane ($C_{16}H_{34}$), and n-octacosane ($C_{28}H_{58}$), respectively.

Critical properties of fractions were calculated by regression using a Particle Swarm Optimization (PSO) algorithm [14] in order to match PR-EOS simulated results against experimental data, with critical pressure (Pc), critical temperature (Tc), and acentric factor

(ω) as regression variables. For fraction F4, as composition has not been analyzed, molecular weight was also included as a regression variable.

2.2. Phase equilibrium apparatus and procedure

Phase equilibrium experiments were carried out employing a static synthetic method with a high-pressure variable-volume view cell. The experimental unit and procedure is similar to those extensively used for high-pressure phase behavior studies [15–18]. Briefly, the experimental set-up consists of an equilibrium cell (maximum internal volume of 28.0 cm^3) equipped with two sapphire windows (one for visual observation and image recording and another for light inlet), an absolute pressure zero volume transducer (NOVUS, TP HUBA 691, with a precision better than 0.05 bar), and J type thermocouple (Salcas, with a precision better than 0.5 °C), both connected to universal process indicators (NOVUS, N1500) and, a syringe pump (ISCO, 260D). The equilibrium cell contains a movable piston, which permits the pressure control inside the cell (up to 300 bar) and a magnetic stirring system. Phase transitions in the clear systems formed by CO_2 and light crude oil fractions (F1, F2 and F3) were visually recorded through pressure control by the syringe pump using the CO_2 as the pneumatic fluid. For the dark system, formed by CO_2 and original crude oil, a near infrared (NIR) probe for transflectance measurements with 1.0 mm of optical pathlength (Solvias) was connected to the cell aiming to detect the phase transitions. In this case, the system pressure is limited up to 200 bar because the probe limitation, consequently it was applied for systems with low CO_2 content were the transitions pressures are below of 200 bar. A detailed description of the apparatus containing NIR probe connected to the high pressure cell and experimental procedures can be found in our previous work [19]. In addition, to improve the visualization of the phase transitions in the dark system, an infrared camera (Dino-Lite Pro) was positioned in the sapphire window (front of the cell) and the cell was slightly tilted, to induce the new phase nucleation in the front part of the cell (close to the sapphire window), facilitating the visualization. The pressures transitions detected with the infrared camera were compared with those captured by the NIR. A detailed comparison of the different methods is presented in our previous work [19].

In a typical run, a precise amount of the crude oil fraction or crude oil was weighed on a precision scale balance (Shimadzu, AX 200, with 0.0001 g of accuracy), and loaded into the equilibrium cell. The cell was then closed and a preselected amount of solvent (CO_2) was loaded into the equilibrium cell using the syringe pump. A continuous agitation was performed with a magnetic stirrer to improve the miscibility of the sample. Temperature control was performed by an aluminum block with internal channels for water circulation coupled to a thermostatic bath (Julabo, F32). After the desired temperature was reached (±0.5 °C), the system pressure was increased until the complete miscibility was observed. At this point, the cell was kept stirring for at least 20 min to allow stabilization. The pressure was then slowly decreased through a programmable controller of the syringe pump, typically at a rate of 1.0–3.0 bar min^{-1} until incipient formation of a new phase was detected. When NIR probe was connected to the cell to study the phase behavior of crude oil + carbon dioxide system, NIR spectra were collected each 1.0 bar during the depressurization. The spectra were stored for post-analysis following the procedure described elsewhere [19]. This procedure was repeated at least three times for each temperature experimentally measured. After conclusion of the measurement at a given temperature, the cell temperature was set at a new value and the experimental procedure described above was repeated.