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Gas condensate characterization from chromatogram areas and retention times

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ABSTRACT

In a routine thermodynamic modeling performance test, mean values for pseudocomponents' critical temperatures and pressures up to C_{40} are re-estimated for Brazilian gas condensate fields based on Gas Chromatography (GC) areas and retention times. Once the fraction's n-paraffin is located by its retention time in the chromatogram, the areas of all other peaks after the previous n-paraffin are computed to make up a fake non-paraffinic compound of the fraction, whose mean boiling temperature is related to its area-weighted retention time. Using a traditional three-parameter relationship among density, molecular weight and boiling temperature, these parameters, together with the molecular weight and density of the non-paraffinic compound, are estimated for each fraction up to C_{40}, and used for the other samples to provide local Single Carbon Number (SCN) tables. The performance of such tables is compared with the original one proposed in the literature in predicting experimental PVT data using Peng-Robinson EOS in commercial simulators. Results were not improved as expected, suggesting that gas condensate thermodynamic properties are very sensitive to heavy ends mole fraction provided by GC. Rather than introducing new concepts on gas condensate thermodynamic modeling, this paper intends to provide new experimental data (and also some simple treatment on them), checking some day-by-day tools to confirm that EOS tuning strategies for gas condensate fluids remain unavoidable.

1. Introduction

Measured PVT properties are usually used as experimental data to fit parameters of a thermodynamic model and then improve its ability to represent reservoir fluids. The most widely used mathematical models are cubic Equations of State (EOS), which are implemented in equipment design software and reservoir simulators, among other applications. When dealing with black oils, for which one has methane and heavy fraction C_{20+} contents as high as 40 mol% in the reservoir fluid, its basic properties molecular weight and density are calculated to match respectively molecular weight and API of the crude oil, both measured in laboratory. Default values assigned for lighter Single Carbon Number (SCN) fractions do not show much influence in the heavy fraction basic properties. As for gas condensate fluids, for which one can have detailed compositions up to C_{40}, even extremely high values for density and molecular weight might be observed for the C_{20+} fraction, depending on the values assumed for lighter SCN fractions. Broad et al. [1] compared several methods of analytical characterization of gas condensate samples and showed that its PVT properties can be very sensitive to molar compositions provided by different techniques and basic properties of SCN fractions. These authors recommend Gas Chromatography (GC) + Mass Spectrometry (MS) as the most powerful characterization technique for the liquid phase, which coupled with a precise description of the gas-phase, may minimize EOS tuning afterwards. Regarding EOS modeling, critical properties and acentric factors for all fractions up to C_{19} can be calculated by many correlations using basic properties from the SCN table provided by Katz and Firoozabadi [2]. As for the heavy fraction EOS properties, correlations may also be used to provide good initial estimates for them. Al-Meshari and McCain [3] provide a good review of such correlations and suggest the one proposed by Cavett [4] to calculate Tc and Pc. Sancet [5] recently introduced a molecular weight-dependent correlation to calculate critical properties of C_{7+} fractions for Peng-Robinson EOS. In most common black oil cases, since one attributes all modeling uncertainties to the heavy fraction, it is still necessary to perform some regression on Tc, Pc, ω, together with its volume shift [6] and binary interaction parameter (BIP) of CH_4-C_{20+} pair in order to match PVT experimental data. There are many procedures proposed in the literature in order to perform such a regression. Pedersen and Christensen [7] propose their own set of correlations for critical properties as well as a splitting–lumping procedure for the plus fraction basic properties which fulfills mass balance restrictions. The most important

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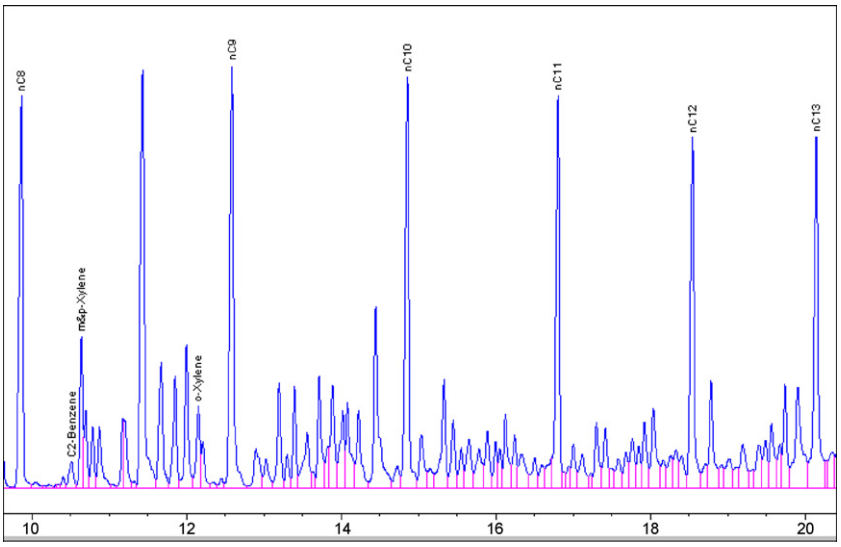

Fig. 1. Typical condensate chromatogram cut, from C8 to C13 (complete pictures run from C3 to C40). Peaks between two adjacent n-paraffins will make up a fake non-paraffinic component for its specific hydrocarbon fraction.

parameters are selected and optimized to match PVT data. Volume shift parameters are calculated as being the difference between the density obtained by the splitting–lumping procedure and that estimated by the EOS at 60 °F. Temperature dependence is also allowed while computing shift parameters. BIPs are assumed to be zero. Isehunwa and Falade [8] introduced a correction factor in Kay's mixing rule in order to obtain a better value for the molecular weight of the plus fraction. These authors state that a more accurate molecular weight of the plus fraction should make tuning of EOS parameters less necessary, but they do not provide any regression to experimental data to verify such a statement for their equation. Egwuenu et al. [9] showed that including miscibility data in the regression, a lumped fluid model with four or five components can represent flow and phase behavior in gas injection cases as well as an extended composition does. Regarding gas condensate reservoir fluids, however, the plus fractions respond for amounts lower than 1 mol% of the global composition, but thermodynamic properties like dew points, phase densities and compositions, as well as GOR and retrograde liquid dropout, are extremely sensitive to heavy ends content. However, regression on the properties of a lumped plus fraction (say C_{40+}, C_{30+} or C_{20+}) within a bracketed feasible interval, like in the case of black oils, might not be enough to match PVT data as well, since their very small amounts can limit the influence of such properties in the whole reservoir fluid global ones. On the other hand, small changes directly in such amounts can lead to significant changes in dew point values and CCE retrograde liquid dropout [1]. We will show later that small perturbations in C_{20+} mole fraction (say ±0.01 mol%) can change dew point pressure in ±5%. Lumping heavy components from C_7 in order to perform a regression in the same way as black oil cases may lead to lack of information about detailing on heavy components which cause dew point to be higher. Splitting C_{7+} fraction using distribution functions – see for example, Pedersen and Christensen [7] and Hosein and McCain [10] – has shown to be the best way of modeling gas condensate global compositions, but results regarding PVT data prediction are, of course, dependent of pseudocomponents properties.

2. Issues to be regarded and main goals

From the above background, one should expect that, when dealing with gas condensates, a reliable extended composition till C_{40} obtained by Gas Chromatography – or even GC + MS, as recommended by Broad et al. [1] – should not be enough to provide the best modeling for reservoir fluid to match PVT data with no regression at all. This may be mainly due to three issues that introduce considerable complications in this quite detailed characterization: inaccuracy involved in the applied GC method; reliability of pseudocomponents basic properties from Katz and Firoozabadi's table, and finally, not only the ability of the chosen correlations to provide good values for Tc, Pc and ω but the performance of the EOS itself in modeling thermodynamic behavior in near critical regions. The objective of this work, rather than introducing new concepts on thermodynamic modeling, is to use some new experimental data to get through the second issue. We propose to update Katz and Firoozabadi's table in such a way that we can build a particular one for each gas condensate reservoir fluid, based on chromatogram information data bank, i.e., peaks areas and retention times of a collection of Brazilian gas condensate samples. Knowing that the n-paraffin is the last component of the fraction to leave the column, we have defined a fake non-paraffinic component, made up of all the other peaks after the previous n-alkane. Basic properties molecular weight and density of all fake non-paraffinic components were determined statistically up to C_{40}, using 10 gas condensate chromatograms recently analyzed in Petrobras Research Center. Assuming that the average boiling temperature is proportional to retention time, being also related to molecular weight and density through a traditional functional relation, the parameters of such correlation were re-estimated, which allowed us to build a particular characterization table for any further sample, once we are given its chromatogram. It was observed that the new tables do not differ too much from the original Katz and Firoozabadi's one. We tested this procedure in four samples analyzed in 2008, comparing calculated GOR, API, dew point and CCE liquid dropouts using Peng-Robinson EOS [11] with experimental data. Results were not as good as expected, confirming that the main error sources to modeling shall be the inaccuracy in GC compositions as well as the performance limitations of cubic EOS, for which some fitting effort by regression to experimental PVT data remains unavoidable. Therefore, lumping the original chromatographic heavy mole fractions in C_{7+} and splitting it using a distribution function with further regression still seems to be the best way to model the reservoir fluid.