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TÍTULO DO TRABALHO:

CHALLENGES IN MODELING FLUID SYSTEMS WITH UNUSUAL CONTENTS OF DISSOLVED CO₂ IN HYDROCARBON SYSTEMS: COLOMBIA'S SEDIMENTARY BASINS CASE OF STUDY

AUTORES:

Nicolas Avendaño-Vasquez, Lizeth-Fernanda Gutierrez-Henao, Raul Osorio Gallego and Jaime Eduardo Arturo-Calvache

INSTITUIÇÃO:

Ecopetrol S.A. - Meridian Consulting Ltda. – Fundación Universidad de América

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Abstract

Several fields in the Caguán-Putumayo Basin of southern Colombia have produced oil with CO₂ dissolved in the crude oil at reservoir conditions above and below 50% mol over the last 5 decades. These fields are currently undergoing CO₂ EoR and CCUS studies, which require that historically used PVT models be re-evaluated using the state-of-the-art thermodynamics available for this purpose. The most appropriate model is presented for this Colombian basin where the hydrocarbon systems present are very different from each other, have unusual and variable contents of originally dissolved CO₂, and some of them correspond to fluid systems that are close to the critical point under reservoir conditions, increasing the difficulty of modeling, due to their supercritical fluid condition and their PVT properties at reservoir pressures and temperatures. The main objective of the study was to build a Peng-Robinson Cubic Equation of State (PREOS) so that a predictive model with minimal or no regression could be generated. Furthermore, this model allows us to determine the volumetric and phase properties of the different fluid systems and to evaluate the diffusion phenomena that dominate the gradients of compositional variation with depth. The proposed-fluid-model is currently being used in numerical reservoir simulation, improved recovery processes, and CCUS studies.

An integrated analysis of the basin was performed during its productive life, allowing a compositional analysis of the available fluids, considering crude with API gravity of 25° to 50° and dissolved CO₂ between 10% and 90% mol in the live fluid in the reservoir. Subsequently, with the application of the three-parameter gamma function, the modeling of the different compositional distributions typical of the different API gravities found in the basin was conducted, characterizing, and adjusting the three-parameter PREOS for the different fluid systems. PVT properties were calculated, obtaining a deviation of less than 10% concerning the experimental data, good enough for the basin scale. After adjusting the PREOS parameters, finally, the compositional variation with depth models was generated. The main finding of the predictive model developed was the generation of different scenarios where it was identified that the vertical distribution of the components is linked to pressure diffusion, especially for those that have a greater quantity of heavy components inside the fluid. In addition, it was found that CO₂ is significantly sensitive to thermal diffusion within the hydrocarbon reservoirs, so a direct relationship between the thermal effect and the acceleration of the compositional gradient was identified.

Key Words: Compositional Gradient, Equation of State, Fluids Model, Gradient PVT Properties, Caguán-Putumayo Basin, PVT Properties, CO₂.

Introduction

The Caguán-Putumayo Basin belongs to a geological region across three countries, Colombia, Ecuador, and Peru, and it has extensive oil production that began in 1963 with the discovery of the Orito field by the Texas Oil Company. Nowadays, more than ten oil fields have been drilled in the Colombian basin, which has more than fifty years of production, from the Caballos Formation, and are characterized by primary recovery, low recovery factors, and high and unusual contents of originally dissolved CO₂.

This article shows a rigorous analysis of the different and varied fluid systems present in the Caguán-Putumayo basin where fluids such as black oil/volatile oil up to high/low performance-gas condensate are found, with gas-liquid transitions of the system that may exhibit a behavior close to the critical point, emphasizing the contents unusually variable CO₂.

Carbon dioxide is a compound that exhibits supercritical fluid behavior under high temperature and pressure conditions. The CO₂ being inside a complex mixture, such as hydrocarbons, generates its thermodynamic modeling more difficult. The methodology implemented for the analysis of PVT data consistencies and their representativeness obtained from the first studies and the most recent analyses is presented. The modeling of PVT data is shown using an approach that corresponds to the calibration of a cubic equation of state after the rigorous handling of the characterization of the C₇₊ fraction using the best practices of the oil industry. Finally, an analysis of compositional variation in depth and the mechanisms of diffusion related to this variation is shown.

The proposed basin model functions as a main PVT model, from which fluid properties can be obtained for the different assets, focusing to optimize development plans, production strategies, and improved recovery plans. Additionally, the basin PVT model is being used for exploratory prospects.

Basin Description

The stratigraphic column found in the Caguán-Putumayo Basin (Figure 1) covers the countries of Colombia, Ecuador (Marañón Basin), and Peru (Orient Basin). In Colombia, this basin belongs to one of the thirteen sedimentary basins into which the territory is divided, which is in the southeast of the country. Geologically, the basin is located between the Guyana Shield and the Andes Mountain Range and is characterized by the presence of Cretaceous and Tertiary sediments, in a Sea-Littoral deposit environment.

The Caballos Formation, which is the formation of interest in the development of the project, lithological describes the beginning of the marine transgression in the Caguán-Putumayo basin which is constituted by four subunits with different petrophysical characteristics U1, U2, U3, and U4 in which there is a sequence of sandstones with varying thicknesses ranging from 10 to 32 feet, with thin intercalations of black lutites.

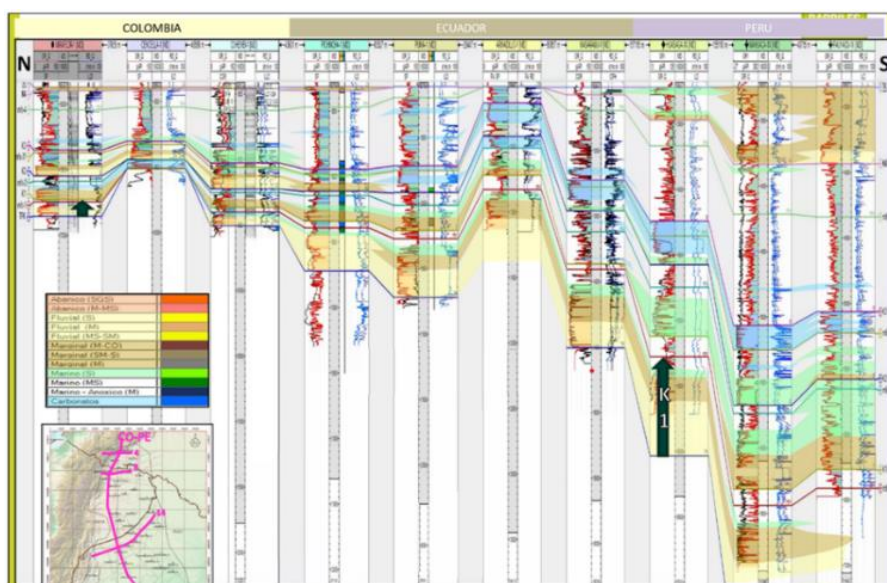


Figure 1 - Caguán-Putumayo-Marañón-Orient Basin

Methodology

The methodology proposed in the development of the study allows us to understand and gather each of the factors that influence the PVT behavior of fluids at initial conditions and throughout the productive life of the reservoir, as shown in Figure 2. The proposed method allows for a generation of a predictive fluid model with minimal or no regression which can be used in different fluid systems with variable and unusual CO₂ contents for a wide range of reservoir conditions.

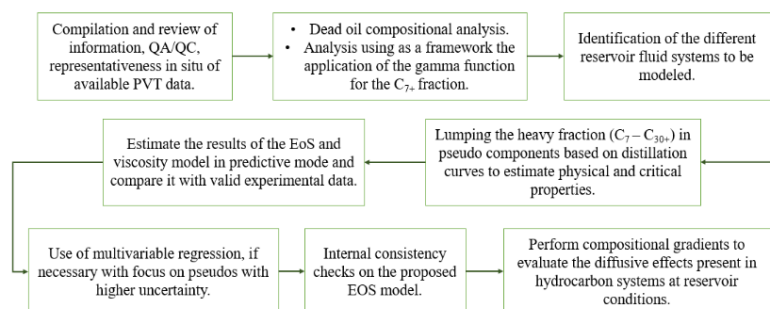


Figure 2 – Methodology used in the development of the project

Collection of PVT data, fluid characterizations, and basin information.

Hydrocarbon production in the Caguán-Putumayo basin is approximately sixty years old, where different PVT and fluid characterization information have been obtained that allows the identification and understanding of the different hydrocarbon systems in the area and their variable and unusual contents of originally dissolved CO₂. It should be emphasized that the data taken at initial conditions is key to know the behavior of the fluids at the beginning of the development of the asset.

Initially, PVT reports, crude distillations, and fluid basic characterizations were collected for diverse types of fluid (black oil, volatile oil, low to medium yield gas condensate, and hypercritical fluids).

Production data. Most of the development of the early stage of the Caguán-Putumayo basin is related to the Caballos formation, reaching the completion of wells in more than ten fields, which have a considerable number of production tests taken at initial conditions, allowing to observe the different and characteristic behavior of the fluids present in the basin. Figure 3, Figure 4, and Figure 5 show the PVT information from the different production tests of one of the fields present in the basin, which was called field O.

Within the basin, field O is the largest hydrocarbon reservoir discovered nowadays and has one of the most complex fluid systems in Colombia. In Figure 3 it is possible to observe that in the fluid system the API gravities range varies from 33° on the flank of the structure to more than 50° at the top of the structure, presenting a transition particularly accelerated in the reservoir near the critical point. In Figure 4 it is possible to identify that the gas-oil ratio, GOR, shows a characteristic behavior of hydrocarbon systems that are close to the critical point with accelerated variations in not very wide depth intervals and that for this field it ranges from 200 SCF/STB to more than 8000 SCF/STB. In other fields of the basin, as in field O, production tests were conducted in a thorough and orderly manner that allowed the identification of fluid systems of diverse types (black oil, low-performance gas condensate, and volatile oils close to saturation pressure at the initial conditions of the reservoir).

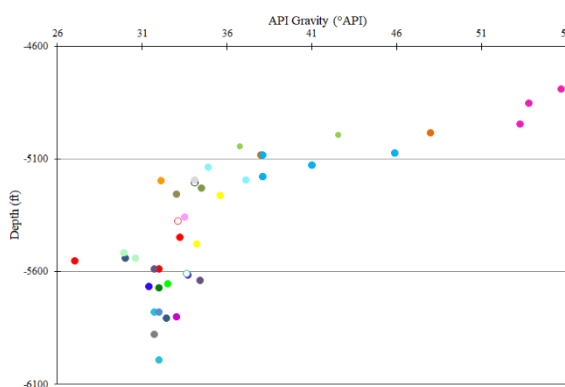


Figure 3 - API gravity variation vs depth field O

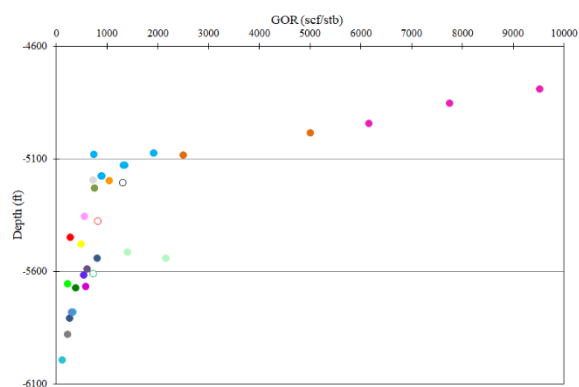


Figure 4 - GOR variation vs depth field O

Figure 5 shows the variation of CO₂ content with depth in the fluid system of field O. In the basin, there are other assets with fluids that even exhibit contents as low as 10% mol and as high as 90% mol, which do

not exist in the O field. In Figure 6 it is possible to identify the different hydrocarbon systems of the basin according to the API gravity and C_{7+} molecular weight.

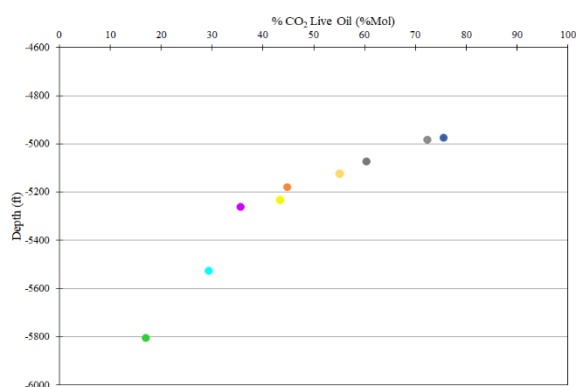


Figure 5 - % mol CO_2 variation vs depth field O

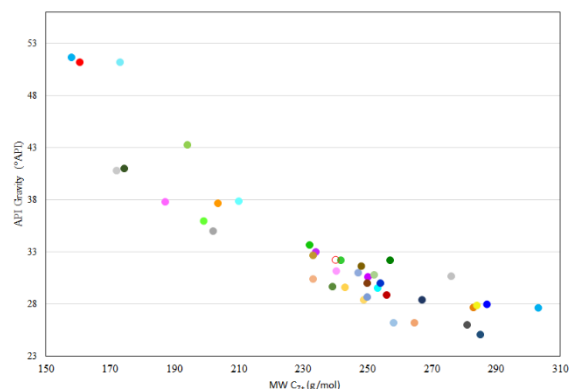


Figure 6 - MW C_{7+} vs °API

Pressure data. The initial pressure of the different reservoirs was rigorously monitored, with robust data that allows the identification of the clear trends present in the basin. Initial reservoir pressure ranges from -3090 psia for shallower reservoirs (-4900 ft TVDss) and may be as high as 4615 psia in the deeper parts of the area (-9590 ft TVDss).

Temperature data. Throughout the productive life of the basin, different temperature measurements are available, most of them taken with formation testers during pressure tests and with values ranging from 170°F to 230°F. Considering that temperature data play a crucial role in fluid systems close to the critical point or with a small degree of sub-saturation, a more exhaustive analysis is required. More information, looking for temperature measurements from other sources that are more accurate and that allow finding a reliable temperature data point.

Temperature data at the initial conditions of the reservoir have a higher degree of uncertainty compared to the behavior of the pressure. Temperature measurements within a reservoir require a longer contact time between the rock and the sensor, to achieve the thermal equilibrium required for accurate measurement (CUNDAR, et. al. 2017).

PVT data of live crude oil. The Caballos Formation has been extensively developed and during its productive life thirty PVT analyses of recombination and subsurface samples have been performed at various times and with different technologies, but always trying to reproduce the original conditions of the fluid. The oldest PVT dates to 1963 in wells O-1 and O-2, and with the information reported there, a recombination was generated in 2019 under the same conditions obtaining repeatability of PVTs from the 1960s. Within the PVT data collected, it is important to highlight the tests carried out on the 3 DSTs taken at well O-15, where it was possible to observe the behavior near the critical point of the fluid system, a change of more than 1000 SCF/STB and about 6°API at less than 100 ft and where the qualitative description of the laboratory reports mentions the red staining at pressures close to the reservoir pressure. By analyzing the live oil PVT, it was possible to identify the different fluid systems of the basin, and the amount of unusually dissolved and variable CO_2 was identified.

Results and discussion

A fluid model based theoretically on PREOS was developed, which allows a prediction of the volumetric properties with a reasonable degree of precision, without being subjected to any regression, a product of the rigorous compositional management, and the primary physical properties of dead oil. The proposed model

allows, using different compositional gradient algorithms, to evaluate the different effects produced by the diffusion mechanisms present in the hydrocarbon systems of the Caguán-Putumayo basin.

Compositional analysis. Rigorous compositional handling of the different phases of hydrocarbons is fundamental in the generation and development of fluid models. The components used in the characterization of gas and oil are divided into pure components, light fraction, and heavy fraction C_{7+} , as reported in most of the available PVT, however, current chromatographic techniques allow characterization up to C_{36+} .

The methodology used to perform the expansion of the C_{7+} heavy fraction and the compositional modeling is based on the application of the gamma probability function proposed by Whitson et. al. (WHITSON, 1984). This theoretical concept allows to perform a molar and molecular weight distribution using the gamma function of three parameters and allows to generate an expanded compositional profile up to a new heavy fraction, for this project C_{30+} .

For this project different compositional expansions were carried out with α form-factor values ranging from 0.65 to 0.8, where 0.65 models the behavior of gas condensate and the value of 0.8 models black oils, volatile oils, and fluids near the critical point.

As part of the compositional analysis, distillation curves and primary physical properties measured at each of the cuts were interpreted, to ensure that the properties assigned to the components of the PREOS, calculated in this case by correlations, are accurate values of the measured experimental data and that, because of this rigorous analysis, unnecessary regressions were not required which may lead to physically unrealistic results or scenarios of thermodynamic instability. Figure 7, Figure 8, and Figure 9 show the comparison of the primary physical properties with the values proposed for the cubic equation of state model.

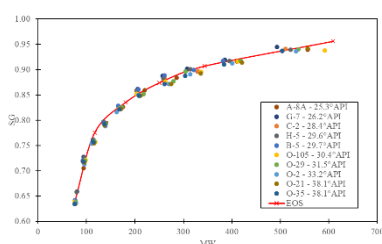


Figure 7 – Dead Oil MW vs Dead Oil SG

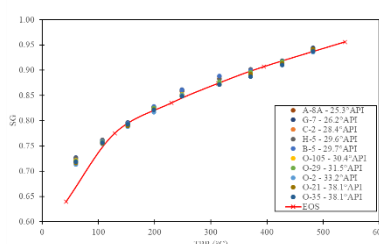


Figure 8 – Dead Oil TBP vs Dead Oil SG

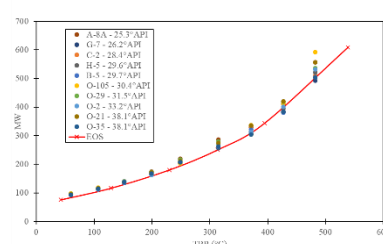


Figure 9 – Dead Oil TBP vs Dead Oil MW

Adjustment of the Equation of State. For the development of the fluid model, the three-parameter Peng-Robinson cubic equation of state was selected, which, according to the literature review, generates better predictions of the volumetric properties of liquids, especially density (WHITSON, 1995). The general form of the Peng-Robinson cubic equation of state is given by Equation 1.

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + c)(V + 2c + b) + (b + c)(V - b)} \quad (1)$$

Critical properties were obtained employing Kesler-Lee correlations and acentric factors using Edmister correlation from the rigorously assigned primary physical properties, as presented above.

It is necessary to verify the predictive capacity of the model, whereby a comparison between experimental and theoretical volumetric properties (API gravity, gas-oil ratio, saturation pressure, and specific gas gravity) was done, achieving predictions with error percentages of less than 10%. Figure 10 and Figure 11 show the results obtained from the comparison for two of the properties mentioned above, saturation pressure and gas-oil ratio, for the PVT data available in the Caguán-Putumayo basin.

Viscosity model. Viscosity is one of the most relevant properties in numerical reservoir simulation models and the generation of hydrocarbon reservoir development plans. As mentioned above, to adjust the viscosity model different thermodynamic principles were evaluated and the Lohrenz-Bray-Clark model was selected,

which is based on the concept of residual viscosity and the corresponding state theory (LOHRENTZ et. al. 1964).

For the fluid model developed, a single viscosity model was generated that can represent the wide variety of fluids in the basin, in which the model's prediction shows an error rate of less than 10% for all quality data comparisons.

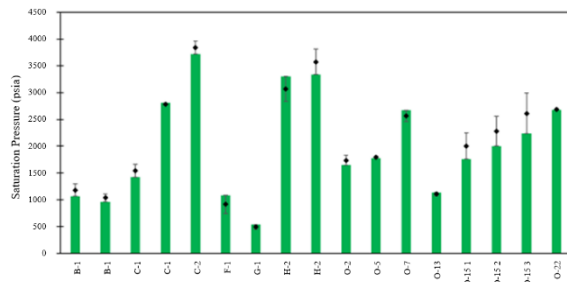


Figure 10 – Saturation Pressure EoS results

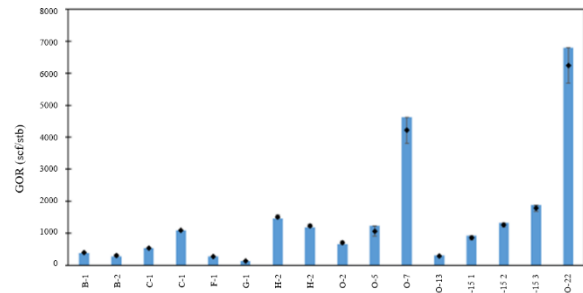


Figure 11 – GOR EoS results

Initialization of the fluid model. As a fundamental part of the project, once the parameters of the EoS and the viscosity model were adjusted, the fluid model was initialized within each reservoir located inside the Caguán-Putumayo basin and significant changes in the composition of the fluids, both areal and vertically produced by geological events or thermodynamic phenomena (diffusion and/or convection) were evaluated. To perform a proper initialization of the model, it is important to characterize the following aspects adequately and with the least degree of uncertainty (HØIER and WHITSON, 2000):

- Reservoir thickness, stratigraphic continuity of formations, WOC location, top, and base of each reservoir.
- Composition of the sample that will be used to initialize the fluid model.
- Reference depth from which the sample is to be used to initialize the reservoir.
- The temperature value at the reference depth will have a significant impact on fluid systems near saturation pressure.
- The reservoir pressure at the reference depth.
- Initial production tests in order to corroborate the results of the compositional gradients and identify significant variations both areal and vertically within each reservoir.

In the Caguán-Putumayo basin, convective phenomena were not identified, however, and according to the initial production tests, there is a variation of PVT properties within the vertical relief of the reservoirs. For this reason and to model this variation of PVT properties, different compositional gradients (Isothermal, passive thermal, Haase, Kempers, and Shukla-Firoozabadi-Ghorayeb) were generated using tools available in corporate proprietary and commercial PVT software. All these methods differ in the way they manage the term used to compute the flux due to thermal diffusion of component i in the following net flux general equation:

$$\sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial x_k} \right)_{p,T,x_{j \neq k}} \nabla x_k = F_{Gi} - F_{Ti} \frac{\nabla T}{T} \quad (2)$$

Applying the different methodologies mentioned above, the diffusive phenomena present in each of the reservoirs of the Caguán-Putumayo basin were evaluated using the different compositional gradient options and three different fluid systems were identified: sub-saturated fluids, saturated fluids, and hypercritical fluids.

Sub-saturated fluids: It was possible to find several systems of fluids with a high degree of sub-saturation within the Caguán-Putumayo basin, which it was possible to model using the compositional isothermal gradient, which is based on the effect of gravitational effect to explain the segregation of the

components in the reservoir. Figure 12 shows the compositional gradient (reservoir and saturation pressures) generated for a field with a high degree of sub-saturation.

Saturated Fluids: Within the analysis carried out, fluid systems consisting of two phases were identified inside the reservoir, a gas cap composed mostly of CO₂, and a black-oil zone. According to the different results generated by the different compositional gradients, it was identified that there are reservoirs that require thermal-diffusive effects to explain the variation of PVT properties within the vertical relief of the reservoir evidenced in historical production data. The transition zone of these fields is characterized by not being in phase equilibrium, there is an abrupt change in the volumetric properties between the gas and oil zone, specifically in the GOC. Figure 13 shows the compositional gradient (reservoir and dew/bubble pressures) generated for one of the fields with a saturated fluid system.

Hypercritical fluid: Inside the Caguán-Putumayo basin, there is one of the most complex and challenging fluid systems in terms of understanding and thermodynamic modeling discovered nowadays in Colombia. The hypercritical fluid system (defined as fluid systems close to their transition zone to the critical point of the mixture) of the O field, is dominated by equilibrium mechanisms such as gravitational effect (gas condensate zones on the top and oil on the flank), and given the presence of CO₂, there may be diffusion effects which more accurately represent the compositional behavior observed in the reservoir.

In this fluid system, the transition zone is determined to be sub-saturated with a continuous but accelerated behavior of the volumetric properties in the area closest to the critical point of the reservoir and which, according to the study performed, requires thermal and gravitational effects to model this acceleration of properties. Figure 14 shows the compositional gradient (reservoir and dew/bubble pressures) generated for a field with a hypercritical fluid.

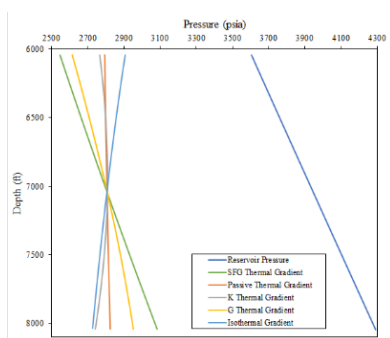


Figure 12 – CvsD sub-saturated fluid

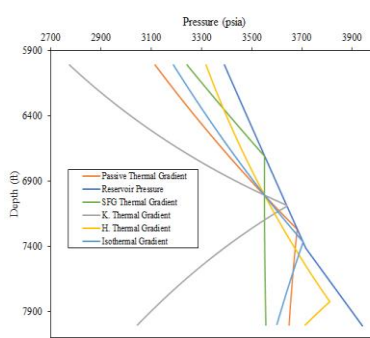


Figure 13 – CvsD saturated fluid

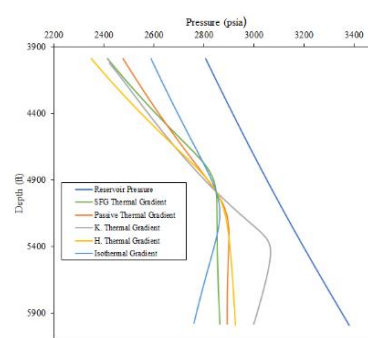


Figure 14 – CvsD hypercritical fluid

Conclusions

The hydrocarbon systems of the Caguán-Putumayo basin were identified and characterized, consisting of a wide variety of fluids and with an unusual characteristic, their variable, and unusual content of originally dissolved CO₂ (10-90% mol based on the composition of live oil or gas condensate).

A PVT property model based on a single set of parameters of the Peng-Robinson cubic equation of state was generated, with which it was possible to predict the volumetric behavior of the different fluid systems with a significantly reasonable degree of accuracy for a basin scale, error percentages less than 10% in all cases. More accurate sub-models can be obtained from this mother basin model, depending on the purpose.

Equilibrium and non-equilibrium mechanisms, such as saturated and unsaturated gas-oil transition zones, were found within hydrocarbon systems dominated by gravitational effects and by thermal and molecular diffusion phenomena, generating different scenarios in each of the reservoirs.

It is possible to conclude that CO₂ is one of the components that respond in a more significant way to the thermal-diffusion effects that occur inside the hydrocarbon reservoirs, the greater the amount of CO₂ and the greater the thermal contribution, the faster the compositional gradient within the reservoir.

The developed PVT property basin model is currently being used to recalculate initial hydrocarbon volumes in situ, optimize development plans and production systems, and design PVT tests for enhanced recovery plans with a special focus on gas injection. It is also being used for CCUS studies.

According to the authors' best understanding of the subject, this is the first time that both PVT data and real compositional gradients associated with such a wide variety of types of hydrocarbon reservoir systems with naturally occurring CO₂ content over such wide ranges of °API, GOR, and hypercritical or non-hypercritical nature of GOC transition zones, gas transitions saturated, or unsaturated liquid is published.

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