12º CONGRESSO BRASILEIRO DE PESQUISA E DESENVOLVIMENTO EM PETRÓLEO E GÁS

TÍTULO DO TRABALHO:

STUDY OF THERMOPHYSICAL PROPERTIES OF CO2/RESERVOIR OIL SYSTEMS

AUTORES:

Emaline C. Ferrari1, Sofia P. Bittencourt1, Arthur B. Soprano2, Gustavo G. Ribeiro, Antonio M. Barbosa Neto1,*

INSTITUIÇÃO:

1 ThermoPhase – FCSRG, Department of Petroleum Engineering, Santa Catarina State University

2 Computer Modelling Group Ltd.

STUDY OF THERMOPHYSICAL PROPERTIES OF CO2/RESERVOIR OIL SYSTEMS

Abstract

Oil and gas pre-salt systems development challenges require a deep study of complex fluid flow, especially CO_2-rich mixtures. The presence of carbon dioxide influences the thermophysical properties phase behavior and might yield problems in multiphase flow and flow assurance. Understanding thermodynamic properties for phase behavior prediction of CO_2-rich hydrocarbon mixtures is key to better evolving these fields. This work aims to investigate the influence of the CO_2 content on the phase properties of hydrocarbons, such as density, viscosity, surface tension, and Joule-Thomson coefficient. A compositional approach is considered to better predict the situations where two fluids with different percentages of CO_2 (5.5% and 76.4%) were investigated. This investigation used the Peng-Robinson 78 Equation of State (EoS) to determine the properties and phase behavior. Viscosity estimation involved the application of the Lorentz-Bray-Clark model (LBC), surface tension employed the Weinraub & Katz model, while the density and the Joule-Thomson coefficient were determined through the results obtained by the given EoS. The emergent region phases are displayed with a higher percentage of CO_2, giving rise to regions characterized by liquid-liquid (LLE) and vapor-liquid-liquid equilibria (VLLE). Identifying a three-phase region occurred exclusively when the CO_2 content surpassed the 60% threshold. Surface tension presented minor interfacial tension values than low CO_2 content hydrocarbon mixtures. The Joule-Thomson coefficient presents much higher gas values than for liquids in the mixtures investigated. Other properties diagrams generated in this study exhibit substantial variations when compared to the mixtures with low and high CO_2 percentages present in the composition.

Keywords: CO2, Brazilian pre-salt, PR78 EoS, phase equilibria, thermophysical properties.

Introduction

In the Brazilian pre-salt, it was revealed the production of oil fluids with high CO_2 percentage as Jupiter (up to 79%) (GAFFNEY *et al*., 2010), what considerably increased the studies about this component. Brazilian offshore fields present several challenges such as deep reservoirs, low temperatures and high pressures, high Gas-Oil Ratio (GOR), high CO_2 content, among others (CARNEIRO *et al*., 2015).

The higher concentrations of CO_2 percentage influence thermophysical properties (e.g density and Joule-Thomson coefficient) that will strongly influence the multiphase flow dynamics of the oil. These effects lead to uncertain prediction of pressure drop, holdups, flow rates and temperatures in production, injection, and transportation lines (CARNEIRO *et al*., 2015; PASQUALETTE *et al*., 2017) as well as hydrate formation, justifying the sought to understand thermophysical properties alteration with CO_2 rise. This work aims to analyze the concentration effects of CO_2 for each property of petroleum fluids for a given range of pressure and temperature in the case studies.

The impact of carbon dioxide in CO_2-rich hydrocarbon mixtures is a consequence of its own properties. Its critical temperature ($30.97\ °C$) and pressure ($73.77\ bar$) are inside production ranges that oil and gas operate (CARNEIRO *et al*., 2015; PASQUALETTE *et al*., 2017), and in the supercritical

range phase behavior of the system becomes more complex. The properties that will most impact flow dynamics with increasing CO_2 concentration are density, viscosity, superficial tension, and Joule-Thompson coefficient.

According to Sayegh *et al.* (1990), the variation of density values with CO_2 dissolution into the oil phase were relatively small. Two authors tested models for predicting the viscosity of CO2 with impurities and found that the Lohrenz-Bray-Clark (LBC) correlation might provide results with a large disagreement with the measurements for pure CO_2 and with impurities Nazeri *et al*. (2018) and cannot predict viscosity values for CO_2/heavy crude oil systems with good accuracy Lansangan *et al.* (1993).

For interfacial forces (ITF), Gasem *et al*. (1993) measured phase densities and ITF for a CO2/synthetic-oil system and a CO2/reservoir-oil system these mixtures tend to have lower ITF values when compared with others hydrocarbon mixtures, especially at high pressures. Carneiro *et al*. (2015) compared Joule-Thomson coefficient variation with pressure for different temperatures and for CO_2 and CH_4. At high pressures, the substances are either liquid or supercritical and at low pressures they are both gases. It is concluded that there is a potential impact of this coefficient for the gas phase and the relevance of investigating the variation of the total cooling of the fluids when the CO2 content is increased. Novosel *et al.* (2009) published field data of injecting CO2 into the reservoir. He selected two points of injection, at surface and at bottom of the injection well the surface line and the wellhead of the injection well were frozen by the effects of Joule-Thomson coefficient.

Methodology

A numeric implementation and thermophysical properties analysis is made in each present phase of the two compositional petroleum fluids with increasing CO_2 percentage. The implemented and evaluated properties presented above receive pressure, temperature, and phase composition as inputs of the model. The EoS and flash calculation provide fugacity coefficient and compressibility factor. The properties were plotted and calculated in a range of 200 steps from 20 to 200 bar, for pressure, and 95 steps from 100 to 500 K for temperature. The code used in this work is part of ESSS intellectual property.

For the thermodynamic modelling, the compositional approach was used to predict oil fluid properties. To the execution of flash calculation, the evaluation of phase equilibria of the mixture was made with Peng Robson (PR). This EoS is broadly used in Oil and Gas field and better performs in the prediction of vapor-liquid phase properties over other cubic EoS (QIU *et al*, 2014) (ROBINSON; PENG, 1978). The mixing rule chosen to be evaluated with the EoS is Whitson *et al* (2000).

Thermophysical properties calculated were density Wilkes (2017) and viscosity Lohrenz *et al*., (1964). In case the composition is defined in characterized form and densities are not available, the critical molar volume in $\left[\frac{m^3}{mol}\right]$ is given by the Riedel correlation (RIEDEL, 1954), in this equation, the critical molar volume in $\left[\frac{m^3}{mol}\right]$ is computed from Reid *et al* correlation (POLING *et al*.., 2001b). As for subsequent properties, surface tension it was calculated using the Weinaug; Katz (1943) method which is based in terms of the Parachor [P] of the pure components. The Joule-Thomson coefficient defined as the temperature variation caused by an isenthalpic pressure change is defined by Gustafsson (1970).

The fluids used to analyze the phase properties present increasing content of CO_2 and its compositions are based on petroleum mixtures found in the literature (CREEK; SHEFFIELD *et al*.,

1993; TUREK *et al*., 1988). Moreover, the fluid with higher CO2 concentration has its content based in a fluid from Brazilian pre-salt field and was manipulated in order to CO2 content becomes more relevant and remarkable for the analyzes that will be made (GAFFNEY *et al*., 2010). Fluid A presents 5.5% of CO_2 in composition, its effects are not predicted. With a sum of 93% of (C1-C4), characterizes a volatile fluid, and presents H_2S and N_2 impurities, Table *1*. Furthermore, fluid C presents a higher percentage of CO_2, 76%, then a strong effect is expected, it also presents impurities, and the light components represent lower percentage of total composition, 19%, representing a less volatile mixture, Table *2* .

Table 1 - Composition of Fluid A.

Component	Mol [%]
N2	0.5628872
CO2	5.4815520
H2S	0.0072165
C1	73.3132715
C2	10.5688769
C3	6.3420684
iC4	0.9288669
C4	1.7960843
iC5	0.3180416
C5	0.3839179
C6	0.1797940
C7	0.0678351
C8	0.0338145
C9	0.0338145
C10	0.0035051
C11	0.0011340
C12	0.0004124
C13	0.0001031

Source: Elaborated by the author, 2024.

Table 2 - Composition of Fluid C.

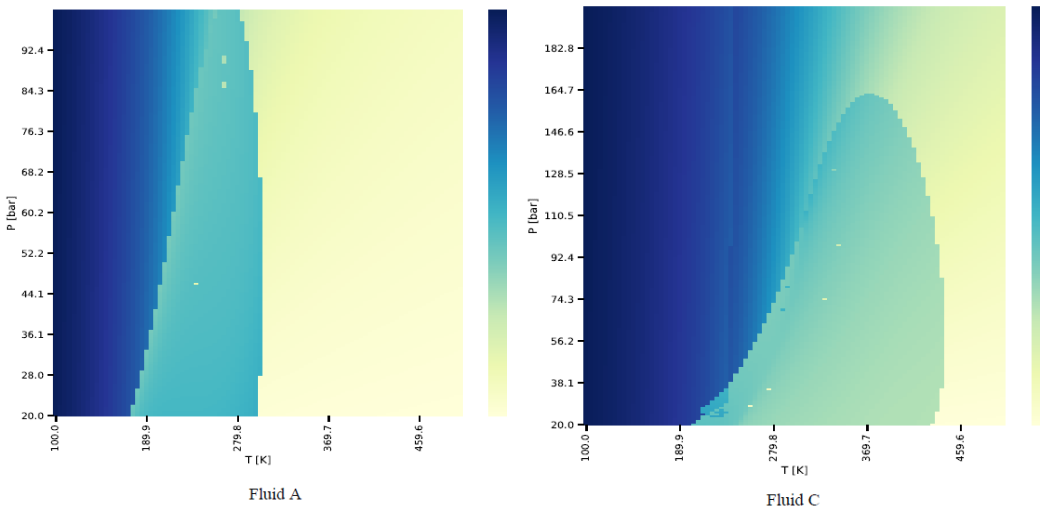
Component	Mol [%]
N2	0.1684391
CO2	76.4493743
H2S	0.0035461
C1	16.0499431
C2	1.3170166
C3	0.8705643
iC4	0.1567370
C4	0.3578001
iC5	0.1290776
C5	0.1765951
C6	0.2241127
C7	0.3074457
C8	0.3351052
C9	3.4542431

Source: Elaborated by the author, 2024.

Results and Discussions

Considering the compositional fluids A and C presented earlier, the density, viscosity, surface tension and Joule-Thomson coefficient are plotted and investigated. In Figure 1 density values found for fluid A, in the left and C, in the right are presented.

Figure 1 - Density values for each existing phase of fluids A and C.



Source: Bittencourt (2019)

The density diagram presents expected behavior for Fluid A with higher values for liquid, lower for gas regions and constant values for VLE. Fluid C presents a similar behavior, but VLE varies given VLLE and LLE regions, where these values become higher. Both liquid-liquid phases present similar densities, what can influence flow patterns and the validity of standard two-fluid closure models existing in the open literature. As brought by SAYEGH *et al*. 1990, the variation of density with CO_2 dissolution in oil phase is small, also, the influence of the pressure presented itself to be smaller than temperature for density variation.

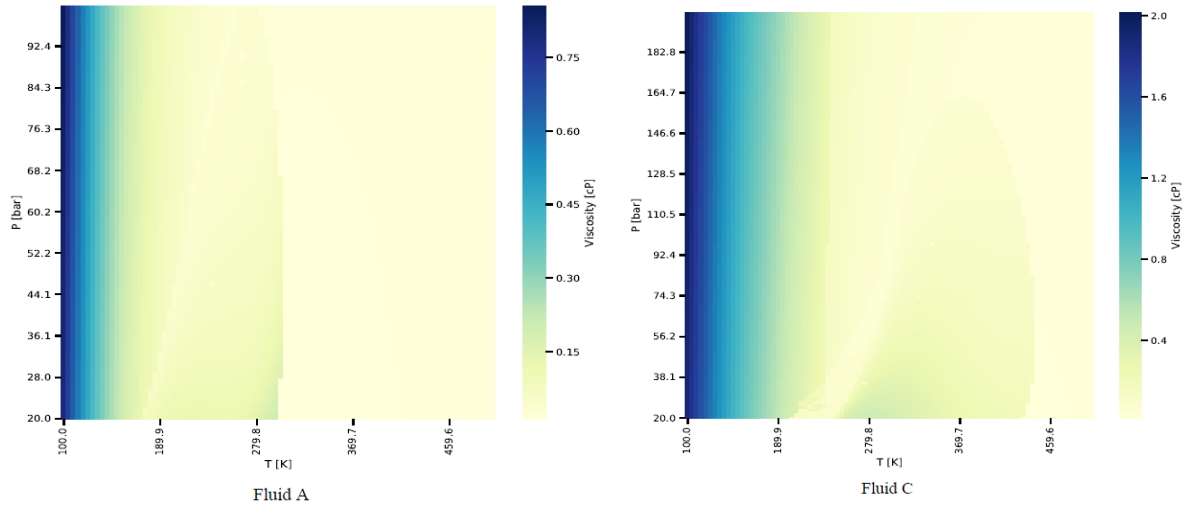
Figure 2 presents viscosity values found for fluid A, and C. Both fluids present a considerable variation for viscosity with temperature, but not for pressure. As expected, viscosity is greater for liquid than gas, although, for the closed envelope region, they vary due to the VLE and VLLE region. For fluid A, VLE region presents an increase in density with temperature in the gas region direction.

Besides similar behavior, in Fluid C, it can be seen an abrupt change in viscosity for the liquid-liquid region when LLE disappears, which might have been influenced by the loss of validation of the PR EoS at lower temperatures. The overall middle region envelope presents higher values than Fluid A, that also decrease in the direction of the bubble point but increase in the direction of VLLE with liquid phase delimitation due to the three-phase region. As it was reported by Nazeri *et al*. (2018) and Lansangan *et al*. (1993) the values obtained by the LBC model are probably over/sub-estimated and present poor precision.

For the surface tension values Figure 3 present values found for fluid A and C. The white parts plotted represent single-phase regions where the surface tension cannot be calculated. For fluid A, as expected, the region with higher surface tension is on the VLE in the two-phase middle region. For

higher pressures, the surface tension is lower because it moves in the direction of the LLE region. Fluid C presents a similar behavior in the LLE region for lower temperatures. In the middle part of the graph, values change steeply when approaching the VLLE region, probably due to the contact between gas and the behavior of gas for CO_2-rich liquid fluid. Other variations account for surface tension values between two liquids and gas and the liquid rich in hydrocarbons.

Figure 2 - Viscosity values for each existing phase of fluids A and C.



Source: Bittencourt (2019)

As seen, Gasem *et al.* (1993), CO_2-rich fluids tend to have lower interfacial force values when compared to hydrocarbon mixtures, where surface tension assumes lower values in the LLE regions. This behavior can impact the prediction of pressure drop and friction factors, probably causing a loss of validation of closure relations used in one-dimensional multiphase flow simulators once they are tuned against experimental data.

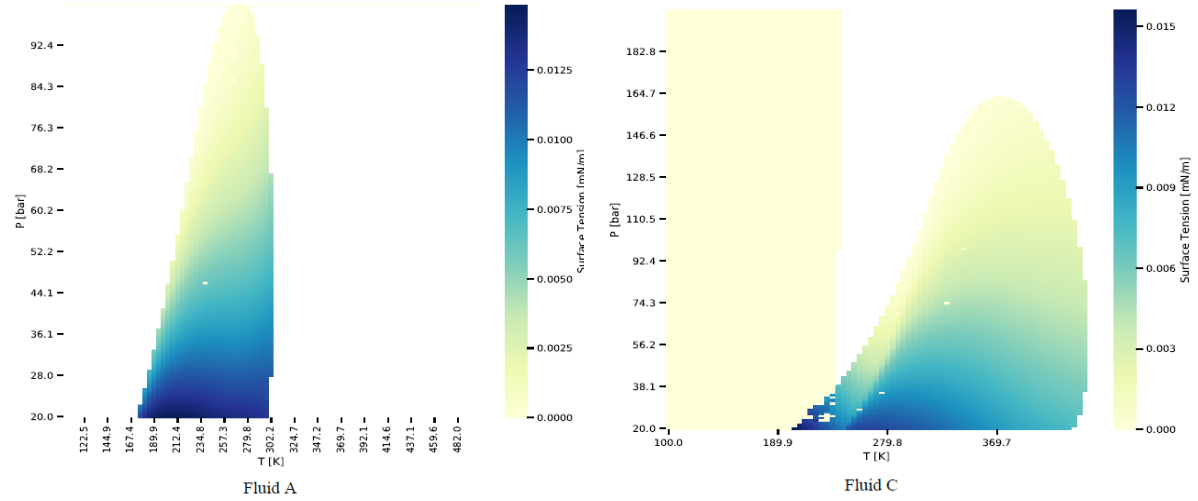
Figure 4 presents Joule-Thomson coefficient values found for fluid A in the left and C in the right. For fluid A, the Joule-Thomson coefficient values are higher in the gas region, as expected. There is a behavior close to dew and bubble points where the variations are intensified, and the influence of pressure and temperature are visible.

The graph presents a different aspect for fluid C, given the behavior of CO_2-rich hydrocarbon fluids. The tendency discussed for fluid A is reproduced in external zones of the middle area but with lower values. In the three-phase region, the values presented are higher and then highlighted from the rest of the VLLE. The Joule-Thomson Coefficient presents much higher values for gases than for liquids, which means that the cooling caused by this effect is more significant than the heating. As CO_2 presence inputs great values, larger effects are expected on the flow of CO_2-rich fluids, such as freezing equipment and lines (CARNEIRO *et al.*, 2015; NOVOSEL *et al.*, 2009). Given considerations can be seen in the graphs, also, values slightly increased with the CO_2 concentration rise. The variation of temperature in the pipeline can cause wax and hydrates as well as freezing equipment and flowlines.

Conclusions

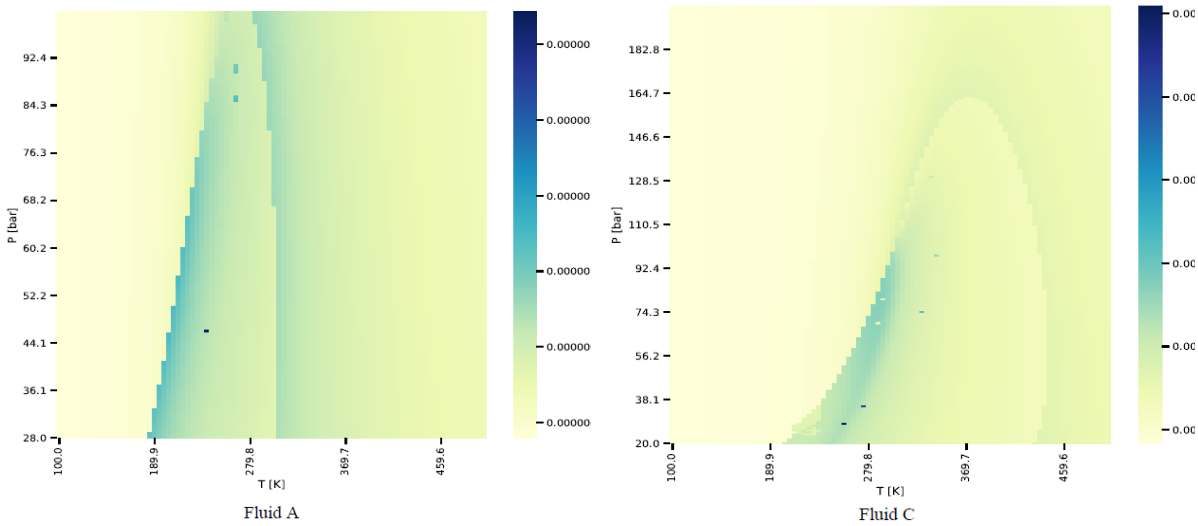
Understanding thermophysical properties of CO_2-rich fluids have a fundamental role in the

Figure 3 - Surface tension values for each existing phase of fluids A and C.



Source: Bittencourt (2019)

Figure 4 - Joule-Thomson coefficient values for each existing phase of fluid A and C



Source: Bittencourt (2019)

prevision of multiphase flows and several effects. The compositional approach used enabled to observe transitions in the results as composition changes justifying the computational cost. Density and surface tension showed a strong agreement with the literature. For fluid C the VLE varies more, given CO2 presence, and VLLE/LLE regions, what can influence flow patterns the validity of standard two-fluid closure models existing in the open literature. The results obtained to equilibrium calculations, using PR EoS, presented agreement with the literature but could be improved to obtain more accurate results by applying a volume correction proposed by Péneloux. Both fluids present a considerable variation for viscosity with temperature, but not for pressure.The steeply change in surface tension for fluid C, when approaching the VLLE region, can directly impact flow dynamics of the fluid. The Joule Thompson Effect results show that it is expected to have wax and hydrates, as well as, freezing equipment and flowlines. Considering the impact in oil and gas production effects, it is also suggested to study the impacts of these properties in multiphase flows dynamics predictions and, consequently, simulations.

Acknowledgment

We sincerely thank ESSS for their generosity in providing the software used to develop this work.

References

BELTRAO, R. L. C. *et al*. Ss: Pre-salt santos basin-challenges and new technologies for the development of the pre-salt cluster, santos basin, brazil. In: OFFSHORE TECHNOLOGY CONFERENCE. **Offshore Technology Conference**. [S.l.], 2009.

GAFFNEY, C. *et al*. **Review and Evaluation of Ten Selected Discoveries and Prospects in the Pre-Salt Play of the Deepwater Santos Basin, Brazil**. [S.l.]: Rio de Janeiro: Agencia Nacional de Petroleo, Gas Natural e Biocombustiveis-ANP, 2010.

CARNEIRO, J. *et al*. Numerical simulations of high co 2 content flows in production wells, flowlines and risers. In: OFFSHORE TECHNOLOGY CONFERENCE. **OTC Brasil**. [S.l.], 2015.

PASQUALETTE, M. *et al*. Parametric study of the influence of gor and co 2 content on the simulation of a pre-salt field configuration. In: OFFSHORE TECHNOLOGY CONFERENCE. **OTC Brasil**. [S.l.], 2017.

SAYEGH, S. *et al*. Phase behaviour and physical properties of lindbergh heavy oil/co2 mixtures. **Journal of Canadian Petroleum Technology**, Petroleum Society of Canada, v. 29, n. 06, 1990.

NAZERI, M. *et al*. Viscosity of co2-rich mixtures from 243 k to 423 k at pressures up to 155 mpa: New experimental viscosity data and modelling. **The Journal of Chemical Thermodynamics**, Elsevier, v. 118, p. 100–114, 2018.

LOHRENZ, J. *et al*. Calculating viscosities of reservoir fluids from their compositions. **Journal of Petroleum Technology**, Society of Petroleum Engineers, v. 16, n. 10, p. 1–171, 1964.

LANSANGAN, R.; SMITH, J. *et al*. Viscosity, density, and composition measurements of co2/west texas oil systems. **SPE reservoir engineering**, Society of Petroleum Engineers, v. 8, n. 03, p. 175–182, 1993.

GASEM, K. A. *et al*. Experimental phase densities and interfacial tensions for a co2/synthetic-oil and a co2/reservoir-oil system. **SPE reservoir engineering**, Society of Petroleum Engineers, v. 8, n. 03, p. 170–174, 1993.

NOVOSEL, D. et al. Thermodynamic criteria and final results of wag co2 injection in a pilot project in croatia. In: SOCIETY OF PETROLEUM ENGINEERS. **SPE Middle East Oil and Gas Show and Conference**. [S.l.], 2009.

WILKES, J. O. **Fluid mechanics for chemical engineers: with microfluids, CFD, and COMSOL multiphysics 5**. [S.l.]: Prentice Hall, 2017.

WEINAUG, C. F.; KATZ, D. L. Surface tensions of methane-propane mixtures. **Industrial & Engineering Chemistry**, ACS Publications, v. 35, n. 2, p. 239–246, 1943.

CREEK, J.; SHEFFIELD, J. et al. Phase behavior, fluid properties, and displacement characteristics of permian basin reservoir fluid/co2 systems. **SPE reservoir engineering**, Society of Petroleum Engineers, v. 8, n. 01, p. 34–42, 1993.

TUREK, E. A. et al. Phase behavior of several co2/west texas-reservoir-oil systems. **SPE reservoir engineering**, Society of Petroleum Engineers, v. 3, n. 02, p. 505–516, 1988.

GUSTAFSSON, O. On the joule-thomson effect for gas mixtures. **Physica Scripta**, IOP Publishing, v. 2, n. 1-2, p. 7, 1970.

POLING, B. E. et al. **The properties of gases and liquids**. [S.l.]: Mcgraw-hill New York, 2001. v. 5.

BITTENCOURT, Sofia Pamplona. **STUDY OF THERMOPHYSICAL PROPERTIES OF CO2/RESERVOIR OIL SYSTEMS**. 2019. 77 f. TCC (Graduação) - Curso de Eng. de Petróleo, Universidade do Estado de Santa Catarina, Baln. Camboriú, 2019.