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Calculation of saturation water content in natural gas with association models and implementation of a custom HYSYS module.

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Abstract
In the natural gas industry, moisture determination is essential to avoid problems related to corrosion and hydrate formation. Process simulation tools as HYSYS are widely used to model natural gas processing. For the accurate representation of saturation water content in natural gas, good thermodynamic models are required. HYSYS currently has a PC-SAFT and CPA implementations, but they are limited in flexibility as adding new physical contributions and tuning parameters. Therefore we have implemented PC-SAFT and CPA equations of state with parameters found adequate to natural gas containing water, CO2 and H2S and created an extension module for these calculations to be called from HYSYS. The method uses a water saturation algorithm based on stability analysis. An auxiliary dynamic link library was written in C#. This enables seamless data transfer and calculations between our thermodynamic kernel and the process simulation. In order to allow the user to change parameters or association models within HYSYS, a custom unit operation was designed inside HYSYS with graphical interface using the EDF native format. In conclusion, we have developed a flexible extension to the HYSYS software that significantly enhances its capabilities by incorporating calculations from an external custom library and a user-friendly unit operation interface, with benefit of industrial sectors utilization of EOS research.

Keywords
thermodynamics, natural gas, process simulators, phase equilibrium, water content

Introduction
The exploration of Brazilian oil and gas reserves, particularly in the pre-salt fields, has unveiled a myriad of technological hurdles, particularly in managing gas emissions. These challenges stem from the operational demands imposed by ultra-deep-water production, characterized by high pressure and low temperature conditions, coupled with prevalent CO2 presence and moisture. This combination often triggers flow assurance and corrosion issues. [1]
A critical concern in this context is the formation of gas hydrates—a phenomenon arising from the condensation of water in natural gas during production, transportation, and processing. Gas hydrates, notorious for their rapid formation rate compared to other solid deposits, pose significant risks of partial or total blockages in pipelines, necessitating meticulous flow assurance strategies.
Navigating these complexities requires a comprehensive understanding of the thermodynamic and operational aspects governing water interaction with natural gas components, underscored by ongoing research efforts aimed at refining measurement techniques and flow assurance methodologies, specially association interaction between water and acid gases.

Methodology
This works use association models for the self association of water and interactions with CO2 and H2S as cross association in natural gas.

$$\tilde{a}^{asc} = \sum_i x_i \sum_j \left(\ln X_{ij} - \frac{X_{ij}}{2} + \frac{1}{2} \right) \quad (1)$$

Where $\tilde{a}$ is the reduced Helmholtz energy, x_i is the molar fraction array, and X_{ij} is the array of the fraction of non-associated sites.
The fraction of non-associated sites is solved using a successive substitution algorithm.
We have implemented the PC-SAFT [2,3] and the CPA [4] equations of state using that contribution.

We calculate the saturation water content using an algorithm based on Michelsen [5] stability analysis.

$$\Delta\tilde{g} = \sum x_i(\mu_i^A - \mu_i^Z) \qquad (2)$$

Where $\Delta\tilde{g}$ is the reduced Gibbs energy of phase formation, x_i is the molar fraction array of the trial phase, μ_i^Z is the chemical potential array of the bulk phase and μ_i^A is the chemical potential array of the trial phase A.

The TPD algorithm consists of minimizing Eq. (2) with respect to trial phase composition, using near pure water as initial guess. The saturation calculations consist in determining the mole fraction of water in the bulk phase (z_w) for which the optimized Gibbs energy of phase formation is null, using Dalton law as initial guess.

Results and Discussion

We generated phase equilibrium diagrams showing saturation water content in several mixtures to validate the model and algorithm implementations.
Figure 1 shows saturation water content for a mixture of CO2 with H2S at two temperatures.

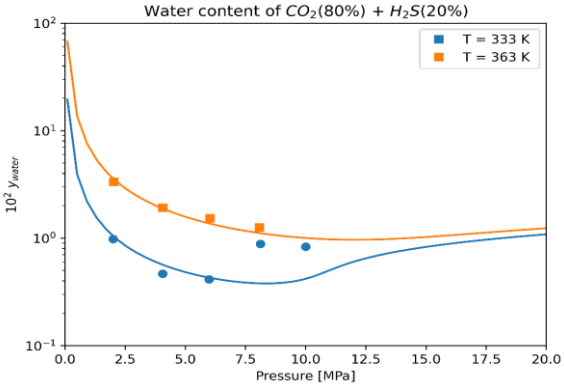

Figure 1. Saturation water content for a mixture of 80% CO2 with 20% H2S at two temperatures: 333K and 363K.

The calculations are consonant with experimental data at pressure up to 5MPa, between 5 and 10 MPa deviations are believed to be due to the compressibility of the gas, and proximity with condensation region for the nonpolar components. Parameters and data are taken from Fouad's thesis [6]

Figure 2 shows the resulting interface for the custom unit operation for the calculation of saturation water content of natural gas streams in the HYSYS environment [7].

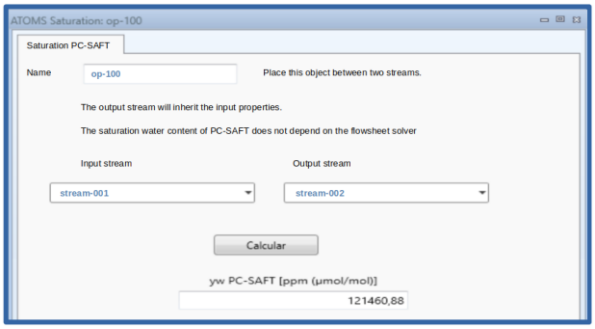

Figure 2. custom unit operation interface for the calculation of saturation water content in natural gas streams.

The custom operation module works as an analyzer in the sense that it does not modify the stream as regular unit operations involving heat, work, mixing or phase splits do, it only gathers information in order to perform some external calculations and print the results in a designated field. The analyzer operation works as follows: (i) it gets Temperature, Pressure, and dry basis composition of the input stream; (ii) it uses the external kernel to calculate saturation water mole fraction with our external thermodynamic model; (iii) it reports the calculated water content and warns if the stream is at risk of water condensation by comparison of the actual water content of the input stream and the calculation of saturation value made by the custom thermodynamic model.
The custom operation only executes the saturation calculations when the user explicitly requests via the “Calculate” button of its interface, therefore the process simulation is executed as usual with the chosen fluid properties package while the external thermodynamic model is used to validate the stability of selected streams with respect to its water content on a successfully converged simulation.
This extension should be useful for process engineers that run gas processing or gas injection simulations on hysys to assess the risk of water condensation in key streams of their processes using an external and customizable thermodynamic model that runs integrated to their simulation suite.

Conclusions

We have developed a flexible extension to the Hysys software that significantly enhances its capabilities by incorporating calculations from an external thermodynamic calculator with customizable parameters and association schemes with a user-friendly unit operation interface, pushing the boundaries of simulation for the benefit of industrial sectors.

The association models were implemented adequately and the parameters used were able to represent experimental data satisfactorily.
The simulator kernel was successfully used as a HYSYS module extension leveraging applied research of the laboratory to an engineering tool.

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Responsibility Notice

The authors are the only responsible for the paper content.

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