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# Thermodynamic Modelling to Enhance Natural Gas Quality

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### Introduction

Natural gas is getting more and more attention in the market due to its increasing use for heating and transportation purposes. To ensure process and product quality, adequate design and control are of utmost importance both in surface and subsea processing and transportation. Despite the fact that natural gas consists mostly of hydrocarbon components which are generally easy to model, an appropriate thermodynamic framework should be developed since several impurities, such as water or hydrate inhibitors, may intensively affect the thermodynamic properties of the pure gas. What is of most importance in the industrial practice is the ability to import the aforementioned models in a process simulator, in order to be able to predict Natural Gas properties or to model process operations such as sweetening or dehydration of natural gas. In such processing, absorption using alcohols or glycols occurs, rendering important the miscibility of those components to hydrocarbons and vice versa. The water presence in natural gas can cause many problems both in processing and transportation. The most commonly occurring obstacle is the formation of gas hydrates in the presence of water and light hydrocarbons in high

pressure and low temperature conditions, such as the operating conditions of subsea transport pipelines which can cause problems to the flow and in some cases they can totally block the pipeline. To prevent



hydrate formation certain additives, such as alcohols and glycols, act as hydrate inhibitors by improving the HC and water miscibility to hydrocarbon rich and water rich phase respectively. The availability of a thermodynamic model able to accurately predict the multicomponent phase equilibria contributes significantly to produce reliable process simulations as to avoid hydrate formation.

## **Thermodynamic Modelling**

**PR**: the classic cubic EoS with the Mathias – Copeman expression to improve vapor pressure of pure components.

**UMR-PRU:** a model belonging to the EoS/G<sup>E</sup> class, combining

the PR EoS with the UNIFAC activity coefficient model, resulting in

**CPA:** combines the PR EoS with the Wertheim's association theory to explicitly account for associating effects exhibited in mixtures containing compounds able to hydrogen bond.

 $Z^{CPA} = Z^{PR} + Z^{Assoc.}$ 

**PC-SAFT:** one of the most successful SAFT type models proposed by Gross and Sadowski.

 $Z^{\text{PC-SAFT}} = 1 + Z^{\text{Hard Sphere}} + Z^{\text{Dispersion}} + Z^{\text{Assoc.}}$ 

### Results

advanced mixing rules.

#### Binary Systems (Correlation Results)

The binary interaction parameters of the models were estimated by fitting binary VLE data and then they have been used for the prediction of the equilibrium of multicomponent systems.

In the following figures representative results of binary systems comprised of natural gas components with water and associating compounds used either as hydrate inhibitor or as part of the refining process are shown.



left: methane/water at 298.15K with PR EoS (blue dashed line),UMR-PRU (red solid line) and CPA (green dotted line), right: CO<sub>2</sub>/water with the UMR-PRU (solid line).



left: methane/methanol at 298.15K, right: methane/ethylene glycol at 298.15 K with PR EoS (blue dashed line), UMR-PRU (red solid line) and CPA EoS (green dotted line). It is shown that all models are able to correlate satisfactorily the VLE of the binary systems, while UMR-PRU and CPA have advantage over PR in the description of the vapor phase.

## Multicomponent Systems (Prediction Results)

The challenge is to satisfactorily predict the phase equilibria of multicomponent systems for which few experimental data are available. The mutual solubility in vapor and liquid phase of mixtures comprised of methane, which is the main component of natural gas, hydrate inhibitors – such as alcohol, ethylene glycoland water, are of utmost importance, since it depicts the amount of impurities in the natural gas, as well as the amount of fuel loss in the aqueous phase.



left: methane/methanol/water at 298.15K (50% wt. methanol – methane free), right: methane/ethylene glycol/water (51% wt. MEG – methane free), with PR EoS (blue dashed line), UMR-PRU model (red solid line) and CPA EoS (green dotted line).

The same behavior is observed both for the system containing methanol and the system containing ethylene glycol as hydrate inhibitor. The Peng – Robinson EoS predicts higher solubility of the associating compound in the vapor phase, while with the use of advanced mixing rules (UMR) a substantial improvement is observed. Finally, CPA, which directly accounts for the hydrogen bonding interactions among the components, yield very satisfactory results, especially for the solubility of the inhibitor in the vapor phase.

### Natural Gas Mixtures Containing Water

Despite the fact that the phase envelope of dry gas is well studied and the behavior of the thermodynamic models is well known, the presence of traces of water may significantly affect the equilibrium. Two synthetic natural gases (SNG) of known composition have been selected, in order to avoid the uncertainty of characterization of the heavy end fraction of the real gases, and the phase envelope of their mixtures with water has been predicted with PR EoS, UMR-PRU model and PC-SAFT EoS. SNG 1 has higher carbon dioxide content (25%), while SNG 2 is closer to the usual natural gas.

	Composition
Mixture 1	SNG 1 + 0.035% water
Mixture 2	SNG 1 + 0.170% water
Mixture 3	SNG 2 + 0.040% water
Mixture 4	SNG 2 + 0.150% water

## Conclusions

#### **Binary Systems**

- All models correlated sufficiently the VLE of the binary systems containing natural gas components and an associating compound.
- ✓ Application of advanced mixing rules (UMR) improves the predictive performance of the PR EoS, as for the solubility of the associating component in the vapor phase. The addition of the Wertheim's associating term (CPA), also significantly improves PR.

#### **Multicomponent Systems**

- ✓ PR EoS fails to describe the VLE of the ternary systems, overpredicting the solubility of hydrate inhibitor and water in vapor phase. UMR-PRU and CPA yield superior prediction results.
- All models predict a more ideal behavior of the SNG mixtures with water. The model directly accounting for association (PC-SAFT) has no advantage over the UMR-PRU model.

#### Future work

The next step is the implementation of the aforementioned models in the simulation of a Natural Gas dehydration unit, using TEG as absorber.



left: **SNG 1** and its mixtures with water, right: **SNG 2** and its mixtures with water, with PR EoS (dashed line), UMR-PRU model (solid line) and original PC-SAFT EoS (dotted line). All models describe satisfactorily the phase envelope of the dry natural gas. However, - all models- yield a more ideal behavior for the mixtures with water. Although PC-SAFT includes an explicit associating term, has no advantage over the UMR-PRU model. The worst results are obtained again by PR EoS.

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