HIGH PRESSURE PHASE EQUILIBRIA OF GUAIACOL SYSTEMS: MEASUREMENTS AND PREDICTIONS USING THERMODYNAMIC MODELS

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ABSTRACT

The present work presents the experimental equilibrium data of pure guaiacol and its mixture with methane at pressure from 5 to 35 MPa. Two molecular models were used to predict the phase equilibrium of the systems involving guaiacol: GC-PP-SAFT (Group Contribution-Polar Perturbed Chain- Statistical Associating Fluid Theory) equation of state and Molecular Simulation using the AUA4 force field were performed. In GC-PPC-SAFT, three association schemes for guaiacol were considered. Predictive phase behavior of its mixtures with associative, non-associative, polar, apolar compounds was evaluated. The new experimental data showed to be consistent with predicted values, provided that guaiacol is considered self-associating. The agreement of predicted values with literature data was related to the kind of association scheme considered for guaiacol. GC-PPC-SAFT EOS and molecular simulation were able to represent satisfactorily phase equilibria of all systems studied.

INTRODUCTION

The decrease of fossil fuels and the increased energy expenditure have forced the industry to search for new sustainable energy sources. In order to achieve its sustainable development aim, new products and new technologies have been considered as alternative. Recently, the biomass conversion into hydrocarbon fuels has drawn special attention due to its attractive characteristics as a source of renewable energy.

The liquid biomass product is a complex mixture rich in oxygenated organic compounds, such as aromatics, carboxylic acids, ethers, ketones, phenolic or furan derivatives. The most important compounds found in hydrotreating product oil are the guaiacols which can represent up 34% of the bio-oil [1].

Guaiacol is an organic compound biosynthesized by a variety of organisms [2], and obtained in the chemical industry from the pyrolysis of lignin. Due to it yellowish aromatic characteristic, this compound has several applications in the industry such as: antioxidant [3], precursor of various essential oils [4]-[5], presents in the flavor of many compounds [6]. However, in fact, its action is most significant as a constituent of bio-oil [7]-[9].

On this scenery, the chemical industry has focused its research on new technologies for the obtaining compounds with higher aggregated value. For that the knowledge of the phase equilibria is essential to evaluate systems in real processing conditions. In the technical and economic evaluations of new processes, the availability of appropriate thermodynamic models as predictive as possible is required.

Thus, the objective of this study was to evaluate the GC-PPC-SAFT model and molecular simulations using the AUA4 force field, to predict the phase equilibria of systems with guaiacol. The behavior of its mixtures with associative, non- associative, polar, apolar compounds was evaluated. Methane, carbon dioxide, ethanol, octanol, water and other components as H_2, CO, H_2S and NH_3 were evaluated in the binary systems. In order to evaluate the complexity of guaiacol, an analysis of the structure of guaiacol was also done.

MATERIAL AND METHODS

The experiments of phase equilibrium of the system methane + guaiacol were done at 443.15 K in an equilibrium cell with a variable volume at constant pressure. The procedure and details of the equipment are detailed in in Pereira et al [10]. For that, methane and carbon dioxide from Air Liquide (purity $\geq$ 99.998%), and guaiacol from SAFC (purity $\geq$ 98%) were used.

PREDICTION OF PHASE EQUILIBRIUM

In order to predict the phase equilibrium of the systems involving guaiacol, two molecular models were used: i) GC-PPC-SAFT EOS; and ii) Monte Carlo Molecular Simulation with the AUA4 force field.

a) GC-PPC-SAFT EOS

The GC-PPC-SAFT (Group Contribution- Polar Perturbed- Chain Statistical Associating Fluid Theory) Equation of State, originally proposed by Tamouza et al [11] and later extended by Nguyen Huynh et al [12], is a predictive model developed from the polar PC-SAFT equation coupled to a group contribution method (CG). It is expressed as a sum of Helmholtz energy contribution:

$$A^{res} = (mA^{hs} + A^{chain}) + A^{disp} + A^{assoc} + A^{multi-polar} \tag{1}$$

where the first four terms relate to the non-polar interactions and the last incorporate the contribution of polar interactions. The details for the description of these terms can be found in the original papers [13]-[16].

In order to calculate the equilibrium, the segment parameters (ε and σ) and the chain parameter *m* of the molecule are also required. These parameters are calculated from group contribution parameters ε_k, σ_k and R_k using the following relations inspired by the Lorentz-Berthelot combining rule:

$$\varepsilon = \sqrt[\sum_{k=1}^{n_{groups}} n_i]{\left(\prod_{k=1}^{n_{groups}} \varepsilon_k^{n_k} \right)} \tag{2}$$

$$\sigma = \sum_{k=1}^{n_{groups}} n_k \sigma_k \Bigg/ \sum_{i=1}^{n_{groups}} n_k \tag{3}$$

$$m = \sum_{k=1}^{n_{groups}} n_k R_k \tag{4}$$

where n_k is the number of groups k in the molecule made of n_{groups} different groups.

Other parameters such as the dipole moment μ and dipole fraction $\left(x_p^{\mu}.m\right)$, and for quadrupolar compounds (aromatic hydrocarbons), the quadrupole moment Q and the quadrupolar fraction $\left(x_p^{Q}.m\right)$ are also considered when polar compounds are evaluated.

In this study, different systems involving guaiacol were considered. All the pure compounds parameters were already determined in previous works [17]-[21]. For guaiacol, due to it multifunctional structure (phenol molecule linked to a methyl group), three schemes of association were considered:
i) Scheme 1: with 3 associative sites one positive and one negative in the group (OH) and one negative on the (O) of the ether function;
ii) Scheme 2: with 6 associative sites which one positive and two negative in the group (OH), the two negative of the group (O) of the ether function and a negative on the aromatic ring,
iii) Scheme 3: with no associative sites.

b) Molecular Simulation

The simulations of binary mixtures gas + guaiacol were carried out in the NPT Gibbs Ensemble [22]. A total number of 700 molecules was used. To simulate the pure compounds, the molecular models used were bases on different references [23]-[28].

The simulations were carried out using the GIBBS software (46) jointly developed by IFP Energies nouvelles and the Laboratoire de Chimie Physique (CNRS-Université Paris-Sud). The vapor pressure was calculated using the Virial equation in the vapor phase, and the molar vaporization enthalpy h^{vap} with the following relationship:

$$h^{vap} = N_a\left(\frac{\langle U^{vap}\rangle}{\langle N^{vap}\rangle} - \frac{\langle U^{liq}\rangle}{\langle N^{liq}\rangle} + P^{vap}\left(\frac{\langle V^{vap}\rangle}{\langle N^{vap}\rangle} - \frac{\langle V^{liq}\rangle}{\langle N^{liq}\rangle}\right)\right) \tag{5}$$

where N_a is the Avogadro number, P^{vap} the pressure calculated in the vapor phase, and $<U^i>$, $<N^i>$ and $<V^i>$ the average potential energy, total number of molecules and volume of phase i, respectively.

RESULTS AND DISCUSSION

Figure 1 presents the phase equilibrium of the system methane + guaiacol. For this system, no experimental data is available from literature. On the other hand, previous works with methane systems presented the good agreement of the experimental data with GC-PPC-SAFT and molecular simutation [17], [18]. Considering these facts, GC-PPC-SAFT and Molecular simulation were used as a reference to evaluate precision of the experimental data. This procedure to evaluate experimental data when no data from literature is available was also done by Rozmus et al [29]. It is possible to observe the experimental data of the methane + guaiacol system was coherent and consistent with the predicted values.

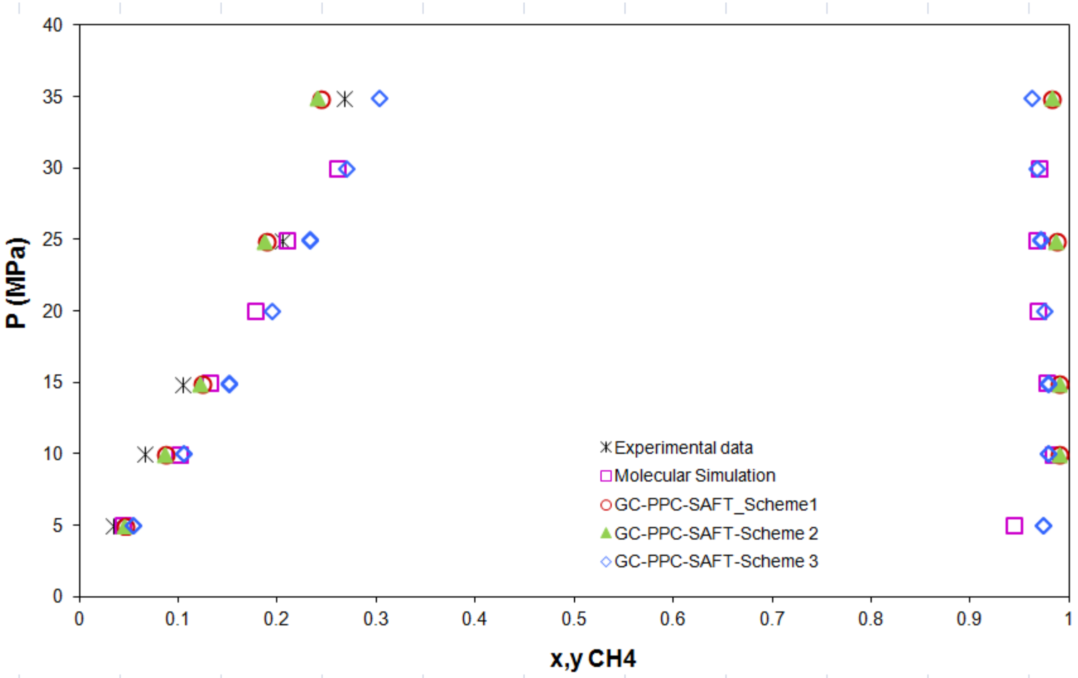

Figure 1: Phase diagram of the system methane + guaiacol 443.15 K.

The phase envelopes for the systems CO_2 + guaiacol determined by GC-PPC-SAFT and molecular simulations is presented in Figures 2 and 3. According to Figures 1 and 2, the Scheme 3 presented higher deviation compared with Schemes 1 and 2, thus, for the other systems, this scheme was not considered.

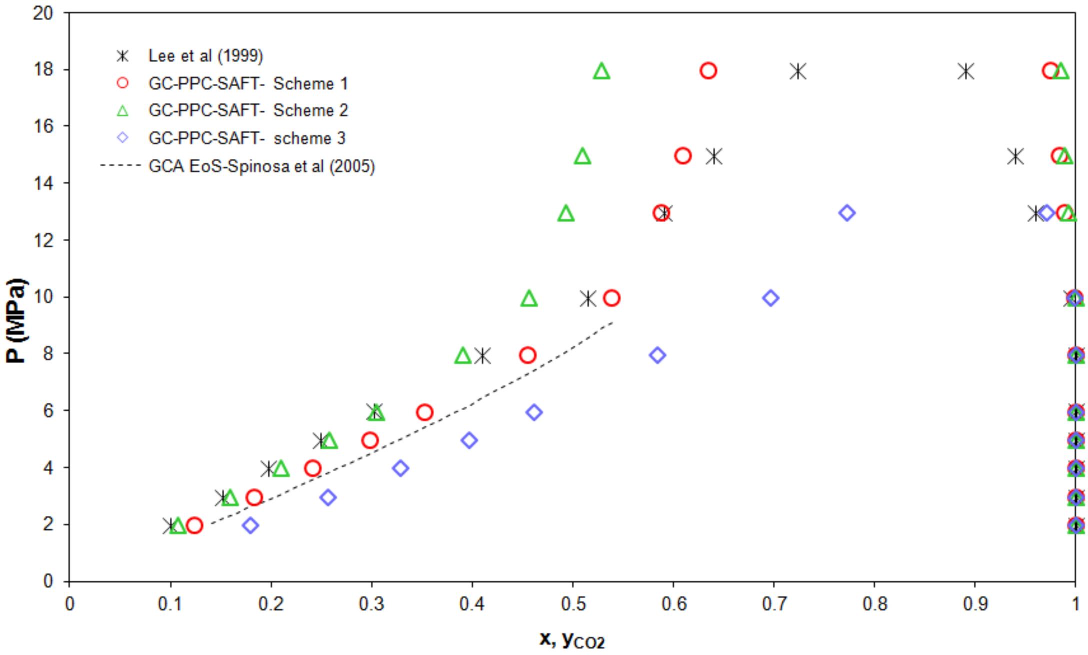

Figure 2: Phase diagram of the system CO_2+ guaiacol at 323.15 K.

According to Figure 2 and Table 1, the predictions made with GC-PPC-SAFT showed good agreement with experimental data [30], and better results than molecular simulation predictions. Espinosa et al [31] also evaluated the CO_2 + guaiacol system at the same conditions of temperature. The difference between the group contribution used by Espinosa et al [31] and that used by us is in the additional terms for the formation of chain and multipolar characteristic presented in this last model.

Studies with phase equilibria of CO_2 + guaiacol system [30] have demonstrated the cross-over occurrence. This behavior was also predicted by GC-PPC-SAFT EOS (Figure 3).

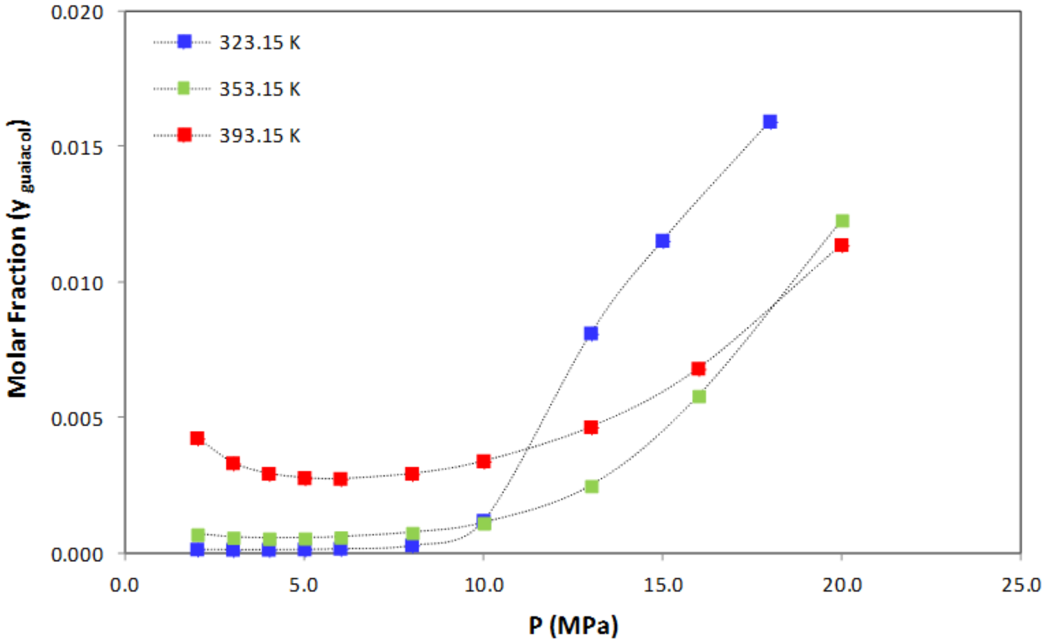

Figure 3: Cross-over behavior for CO_2 + guaiacol using predicted values from GC-PPC-SAFT.

Table 1 presents the standard deviations observed between experimental data and the predictions for different systems with guaiacol. For the systems with toxic gases, up to now there is no experimental data from literature, thus only predictions were done (Figures 4 and 5).

Table 1: Relative deviations of predictions of the phase equilibria of systems with guaiacol.

System	Temperature (K)	Relative Deviation (%)		
		GC-PPC-SAFT		Molecular
		Scheme 1	*Scheme 2*	Simulation
CO_2+ guaiacol*	323.15 - 393.15	11.6	8.2	56.4
Ethanol + guaiacol	290.15	6.2	9.1	n.d
Octanol + guaiacol*	433.15 - 488.15	1.2	3.1	n.d.
Water + guaiacol*	313.6- 372.0	13.9	>100	n.d.

* average value between the data from different temperatures; n.d= not done.

The predictions of phase equilibria for the systems ethanol + guaiacol, octanol + guaiacol and water + guaiacol also showed good agreement of the GC-PPC-SAFT EOS, with deviations < 14%.

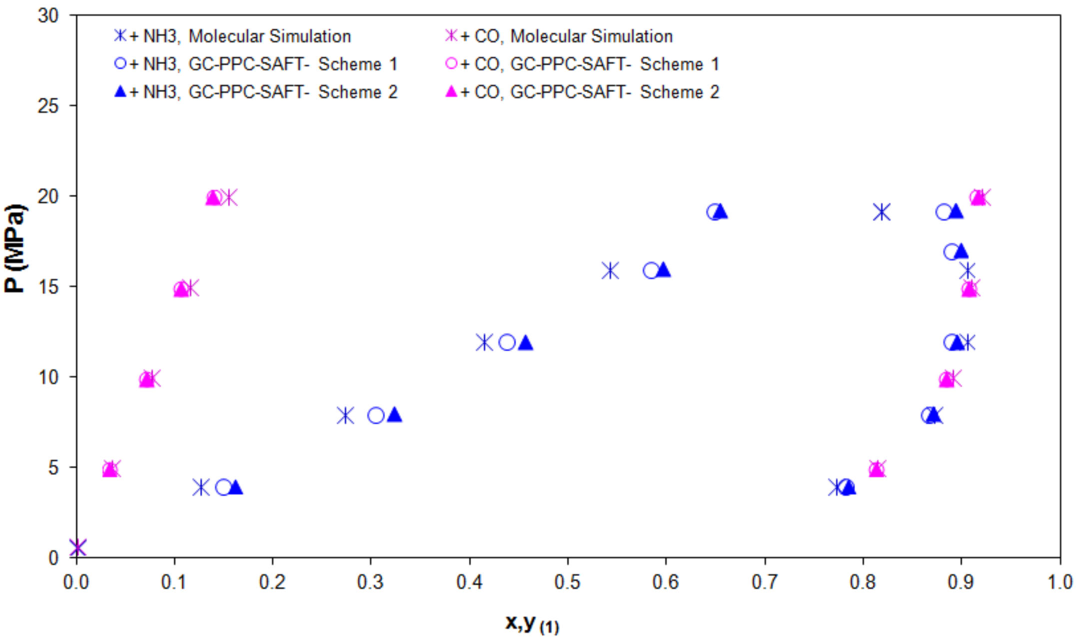

Figure 4: Phase diagram of the systems NH_3+ guaiacol and CO + guaiacol at 573.15 K.

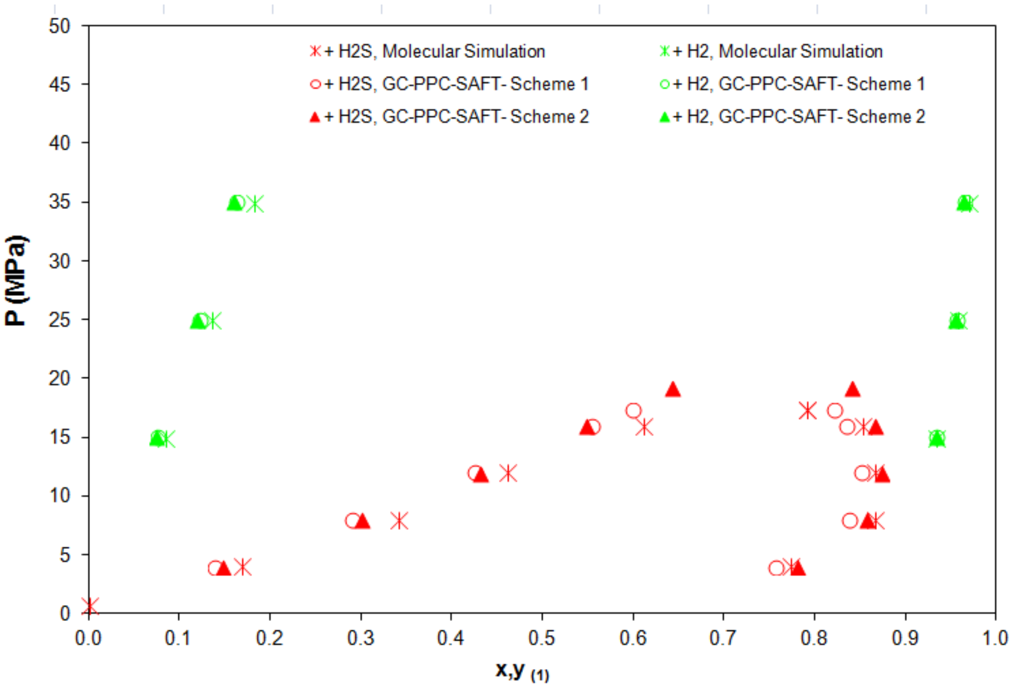

Figure 5: Phase diagram of the system H_2S+ guaiacol and H_2 + guaiacol at 573.15 K.

CONCLUSION

In this work, experimental data of phase equilibrium for the guaiacol + methane system was determined and compared with predictive models (GC-PPC-SAFT and Molecular Simulation). The experimental results showed to be consistent with predicted values. For the system CO_2+guaiacol, predictions indicated GC-PPC-SAFT can describe the cross over effect. These results are very interesting, considering that this effect is common in systems involving CO_2 at high pressure conditions Predictions of phase equilibria of other systems with guaiacol (+ethanol, +octanol, +water) were also done, showing good agreement with literature. In the predictions, it was also observed that guaiacol can be considered a self-associating compound.

5. REFERENCES

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