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Thermodynamic modelling of CatLiq® biomass conversion process

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Introduction

Process:
A second generation catalytic liquefaction process for the production of bio-oil.

Raw Material:
DDGS (Dried Distilled Grain with Solubles), a byproduct in first generation ethanol production.

Process conditions:
280-350 °C and 225-250 bar, in the presence of homogeneous (K_2CO_3) and a heterogeneous (Zirconia) catalyst.

Products:
Main components are bio-oil, H_2O, CO_2, and water-soluble organic compounds.

Capacity:
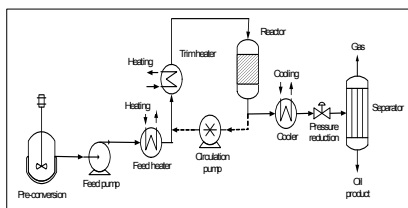10-20 L/h of wet biomass pilot plant with fixed-bed reactor.

Figure 1. CatLiq® process scheme

DDGS *Oil + water soluble organic compounds* *CatLiq® bio-oil*

Aim

Measurement and Prediction of bubble point pressures of selected model system to investigate phase boundaries of the CatLiq® process.

Experiment

The experimental study was carried out in a mercury free JEFRI-DBR high pressure PVT phase behavior system using composition of (7.0% CO_2+ 84.8% H_2O + 0.1% Ethanol + 0.1% Acetic acid + 8.0% Octanoic acid) as a model system for CatLiq® process.

Figure 2. JEFRI-DBR mercury free PVT system

Thermodynamic model

The results were correlated with PSRK model proposed by Holderbaum and Gmehling, which is predictive Soave-Redlich-Kwong EOS with the modified Huron-Vidal first-order (MHV1) mixing rule of Michelsen coupled with the UNIFAC model.
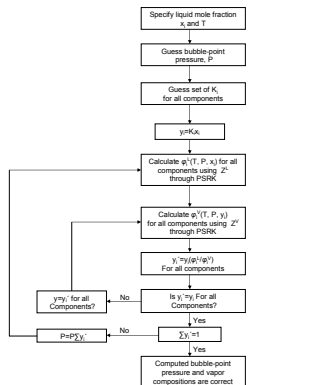

Figure 3. The proposed algorithm for bubble pressure calculation

Results

Bubble point Pressure at 40°C

Bubble point Pressure at 50°C

Bubble point Pressure at 60°C

Bubble point Pressure at 75°C

T/°C	Pexp/bar	Pcal/bar	Rel. Dev. (%)[a]
40	156.73	138.53	11.6123
50	190.88	169.22	11.3474
60	224.48	202.08	9.9786
75	258.97	253.85	1.9770
		AAD %[b]	8.728863

Table 1. Experimental and PSRK-estimated bubble point pressures for model system

[a]Relative Deviation (%) = (Pexp – Pcal)/Pexp×100

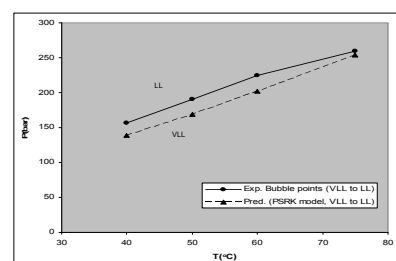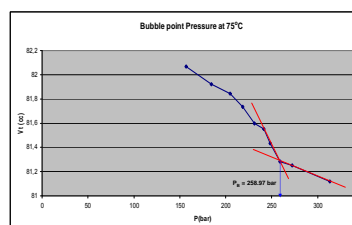*[b]Average Absolute Deviation (%) = ($\sum$ |error %|) /number of data points*

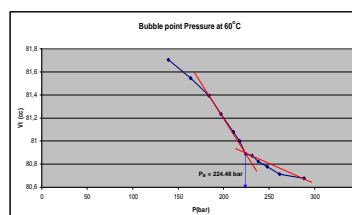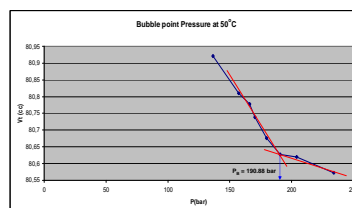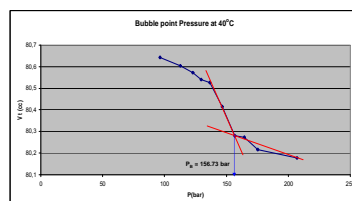*Figure 4. Measured and predicted phase boundaries for the model system*

Conclusion

Experimental and predicted data shows that the capability of the PSRK model is reasonably good in predicting the phase behaviour of such a model system for CatLiq® process.

This modelling work is useful for the CatLiq® process design, development and optimization, which provides a general thermodynamic approach on how to model biomass conversion processes.

References

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Sandler, S. I., Orbey, H., 1998. Modeling Vapor-Liquid Equilibria- Cubic Equations of State and Their Mixing rules. Cambridge University Press ISBN: 0-521-62027-9 (hb).

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