

Prediction of Solid Paraffin Precipitation Using Solid Phase Equation of State

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Abstract

In the traditional methods for wax precipitation prediction, the fugacity of solid is calculated using a hypothetical thermodynamic cycle. In this study, a new method based on TST solid equation of state is proposed to calculate the fugacities of solid phases. The multi-solid approach is used for description of solid phases. Obtained parameters for this equation of state is useful for future works.

Keywords: wax precipitation, solid equation of state, multi-solid

1. Introduction

Wax deposition from gas and oil production facilities and pipelines is undesirable. The flow-lines and process equipments may be plugged by wax deposition. Different physical and chemical methods have been proposed to remove deposited solids, which increases operating costs. A reliable model for wax precipitation calculations is highly valued for design and operation of flowlines.

Since 1990s, so many efforts have been done to predict conditions under which the waxes can precipitate and the amount of precipitated wax in functions of pressure, temperature and composition. At first, the calculations were based on the solid-liquid equilibrium assumption. Later on, the gas phase was included in the calculations [1, 2]. There are two clearly defined assumptions for the determination of the thermodynamic equilibrium wax-liquid in established multi-component hydrocarbons systems: solid solution, and the formation of multiple solid phases. In the former case, different methods were proposed based on the activity coefficient model assuming the non-ideality of liquid and solid phases [3, 4]. Solid phase transition and vapor phase were then considered in other works [5-7]. The non-ideality was defined using Wilson or UNIQUAC equations. Lira-Galeana et al. [8] developed the multi-solid approach in 1996. In this model, it is assumed that the solid wax consists of several pure solid phases, in which the number and nature of them will be obtained from phase stability analysis. Coutinho showed that the solid phase is a multi-solid solution in nature and supported by experimental data [9].

In this work, the wax-precipitation model based on solid phase equation of state will be presented. The multi-solid approach is used because of its wide acceptability and limitation of using solid phase equation of state. The parameters of the equation of state are obtained in the case that vapor, liquid and solid phases are included in the system.

2. Solid Phase Equation of State

The equations of state that can be applied to a system containing solid, liquid and vapor phases simultaneously are scarce[10,11]. In this project, TST¹ equation of state is used [11]. The general form of the equation is as below

$$P = \frac{RT}{v-b} - \frac{a}{(v+ub)(v+wb)} \quad (1)$$

In this equation, u and w are 3 and -0.5 respectively. Also,

$$a_c = 0.470507R^2T_c^2 / P_c \quad (2)$$

$$b_c = 0.0740740RT_c / P_c \quad (3)$$

$$Z_c = 0.296296 \quad (4)$$

$$a = \alpha a_c \quad (5)$$

Alpha function for liquid and vapor phases could be used in conventional polynomial form or in exponential form. In this equation, a new alpha function is introduced for the solid phase, which will be discussed later.

In order to calculate fugacity of each component in pure solid state, the following equation is used [12].

$$d \ln f = -\frac{\Delta H}{RT^2}dT + \frac{v}{RT}dP \quad (6)$$

Where,

f : fugacity

ΔH : enthalpy change in result of change in system temperature

v : partial molar volume

By integrating the above equation from the triple point pressure to the system pressure for liquid and solid phases and dividing the two equations, the following relation will be obtained. In this equation, ΔH^f and Δv are supposed to be independent of pressure and temperature.

$$\ln \frac{f^S}{f^L} = -\frac{\Delta H^f}{RT} \left(1 - \frac{T}{T_r} \right) - \frac{\Delta v P}{RT} \quad (7)$$

¹ Twu-Sim-Tassone

Suppose that the pressure system is equal to zero, we will have

$$\ln \frac{f^S}{f^L} = -\frac{\Delta H^f}{RT} \left(1 - \frac{T}{T_r}\right) \quad (8)$$

This equation is similar to the equation that was proposed by Prausnitz et al. [13] for the calculation of solid phase fugacity. If the fugacity is calculated at zero pressure,

$$\ln \left(\frac{f^S}{P} \right) = -1 - \ln b^* - \ln(v^{*S} - 1) - \frac{1}{(w-u)} \frac{a^{*S}}{b^*} \ln \left(\frac{v^{*S} + w}{v^{*S} + u} \right) \quad (9)$$

Where,

$$v^{*S} = \frac{1}{2} \left\{ \left(\frac{a^{*S}}{b^*} - u - w \right) - \left[\left(u + w - \frac{a^{*S}}{b^*} \right)^2 - 4 \left(uw + \frac{a^{*S}}{b^*} \right) \right]^{1/2} \right\} \quad (10)$$

$$a^* = \frac{Pa}{R^2 T^2} \quad (11)$$

$$b^* = \frac{Pb}{RT} \quad (12)$$

And,

u and w are the parameters of the equation of state. By equalizing the two equations, we will get

$$-1 - \ln b^* - \ln(v^{*S} - 1) - \frac{1}{(w-u)} \frac{a^{*S}}{b^*} \ln \left(\frac{v^{*S} + w}{v^{*S} + u} \right) = \ln \left(\frac{f^L}{P} \right) - \frac{\Delta H^f}{RT} \left(1 - \frac{T}{T_r}\right) \quad (13)$$

The only unknown variable in the above equation is a^{*S} . Therefore, the equation is solved to obtain a^{*S} for different temperatures. The parameters of predefined solid alpha function are calculated by correlating the data to the following equation

$$\alpha^S(T) = 1 + l_s(1 - T_r^{0.5}) + m_s(1 - T_r)^{n_s}(0.7 - T_r) \quad (14)$$

In which α^S can be calculated using

$$\alpha^S = a^S / a_c \quad (15)$$

$$a^S = \frac{a^{*S} R^2 T^2}{P} \quad (16)$$

In order to calculate the optimum parameters, the following goal function was used to minimize the difference between the presented data and the calculated data from eq. 9.

$$f(x) = \sum \left(1 + l_s(1 - T_{r,i}^{0.5}) + m_s(1 - T_{r,i})^{n_s}(0.7 - T_{r,i}) - \alpha_i^S \right)^2 \quad (17)$$

The simplex-Nelder-Mead algorithm was utilized to obtain the optimum parameters, which minimizes the goal function. Due to the nonlinearity of the function, the results

will drastically depend on the initial guess for the optimal parameters. To avoid this problem, the optimization problem is run for different starting points.

3. Wax Precipitating Model

The following expressions are used to describe the system in which vapor, liquid and pure solids are in equilibrium state.

Mass balance for precipitating components:

$$y_i^v n^v + x_i^L n^L + n^{S_i} - z_i^f n^F = 0 \quad (18)$$

Where

$$i = 1, \dots, N_c \quad , \quad j = 1, \dots, N_p$$

N_p : Number of precipitated solids

N_c : Number of components

Mass balance for non-precipitating components:

$$y_i^v n^v + x_i^L n^L - z_i^f n^F = 0 \quad (19)$$

Equality of fugacities in the liquid and gas phases for each component:

$$f_i^v - f_i^L = 0 \quad (20)$$

Equality of fugacities in the liquid and solid phases for precipitating components:

$$f_i^L - f^{S_i} = 0 \quad (21)$$

Summation of mole fractions in liquid and gas phases are equal to unity

$$\sum_{i=1}^{N_c} x_i - 1 = 0 \quad (22)$$

$$\sum_{i=1}^{N_c} y_i - 1 = 0 \quad (23)$$

All the equations above constitute a system of equations, which should be solved in order to define the equilibrium system completely. An error function is introduced to check the convergence of the system of equations.

$$f(\delta) = \sum_{i=1}^{2N_c + N_p + 2} |\delta_i| \quad (24)$$

Where δ_i 's are the right hand expressions in equations 13-17.

4. Results and Discussions

The composition of oil samples and some synthetic mixtures, which were used in this project are shown in tables 1-4. Since the references are different, the components considered for each sample are not the same.

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Table 1. Mole fractions for two synthetic mixtures [7]

Component	Mixture C	Mixture B
<i>n</i> -C ₁₀	0.5876	0.5101
<i>n</i> -C ₁₈	0.0513	0.0819
<i>n</i> -C ₁₉	0.0486	0.0694
<i>n</i> -C ₂₀	0.0463	0.0590
<i>n</i> -C ₂₁	0.0440	0.0506
<i>n</i> -C ₂₂	0.0418	0.0433
<i>n</i> -C ₂₃	0.0397	0.0373
<i>n</i> -C ₂₄	0.0378	0.0319
<i>n</i> -C ₂₅	0.0359	0.0274
<i>n</i> -C ₂₆	0.0342	0.0236
<i>n</i> -C ₂₇	0.0327	0.0202
<i>n</i> -C ₂₈	0	0.0176
<i>n</i> -C ₂₉	0	0.0148
<i>n</i> -C ₃₀	0	0.0127

Table 2. Mole fractions for a synthetic mixture [14]

Component	Bim 13	Component	Bim 13
C ₁₀	80.01	C ₃₄	0.61
C ₁₈	7.09	C ₃₅	0.53
C ₁₉	6.09	C ₃₆	0.45
C ₂₀	5.220		

Table 3. Mole fractions of heavy oil fractions [5]

Oil 5		
Peusocomponent	Mole percent	MW
<i>P</i> -C ₁₀₊	4.4627	167.0
<i>N</i> -C ₁₀₊	6.4827	160.0
<i>A</i> -C ₁₀₊	15.126	160.0
<i>P</i> -C ₁₅₊	2.9096	237.0
<i>N</i> -C ₁₅₊	3.8627	233.0
<i>A</i> -C ₁₅₊	8.9664	233.0
<i>P</i> -C ₂₀₊	1.5426	307.0
<i>N</i> -C ₂₀₊	2.1514	302.0
<i>A</i> -C ₂₀₊	5.0199	302.0
<i>P</i> -C ₂₅₊	0.7856	375.0
<i>N</i> -C ₂₅₊	1.389	372.0
<i>A</i> -C ₂₅₊	3.2409	372.0
<i>P</i> -C ₃₀₊	0.3528	449.0
<i>N</i> -C ₃₀₊	1.4348	440.0
<i>A</i> -C ₃₀₊	1.4348	440.0
<i>P</i> -C ₃₅₊	0.1377	511.0
<i>N</i> -C ₃₅₊	1.5694	512.0
<i>A</i> -C ₃₅₊	0.0174	512.0
<i>P</i> -C ₄₀₊	0.0648	590.0
<i>N</i> -C ₄₀₊	1.1964	587.0
<i>A</i> -C ₄₀₊	0.0491	587.0
<i>P</i> -C ₄₆₊	0.0259	713.0
<i>N</i> -C _{PI+}	0.3143	724.0
<i>A</i> -C _{PI+}	1.8285	724.0
<i>N</i> -C _{CP2+}	0.2257	901.0
<i>A</i> -C _{CP2+}	1.3396	901.0

Table 4. Mole fractions of heavy oil fractions [5]

<i>Oil 6</i>		
Pseudocomponent	Mole percent	MW
<i>P-CP1</i>	3.5922	157.0
<i>N-CP1</i>	4.7712	157.0
<i>A-CP1</i>	4.7712	157.0
<i>P-CP2</i>	2.7858	201.0
<i>N-CP2</i>	4.5495	201.0
<i>A-CP2</i>	4.5495	201.0
<i>P-CP3</i>	1.8055	252.0
<i>N-CP3</i>	2.9829	252.0
<i>A-CP3</i>	4.4744	252.0
<i>P-CP4</i>	1.2238	300.0
<i>N-CP4</i>	2.9018	300.0
<i>A-CP4</i>	4.3527	300.0
<i>P-CP5</i>	0.3674	563.0
<i>N-CP5</i>	2.5116	563.0
<i>A-CP5</i>	5.1937	563.0
<i>P-CP6</i>	0.0581	654.0
<i>N-CP6</i>	1.0319	654.0
<i>A-CP6</i>	1.6277	654.0
<i>P-CP7</i>	0.0736	666.0
<i>N-CP7</i>	1.0099	666.0
<i>A-CP7</i>	2.8634	666.0
<i>N-CP8</i>	0.8611	744.0
<i>A-CP8</i>	2.1707	744.0

The parameters of the equation of state (l_s , m_s , n_s) are calculated as discussed in the previous section. The optimal values for the mentioned parameters for the oil samples are in tables 5-9. The initial guess for the system of equilibrium equations is given from the results of a two-phase flash calculation. Then, the dogleg method [15] is applied to check the convergence criteria, i.e. the right-hand side expression in equation 19 should be less than $1e-7$. If the criterion is not met, the program will shift to simplex algorithm that uses the results of the previous step as the initial points. There is a normalizing step, which filters the incoming physically unacceptable data. The physical properties data are derived from databooks or are estimated from proposed methods in the literature.

Table 5. Parameters of EOS for *mixture B*

Component	l_s	m_s	n_s
<i>n-C₁₀</i>	-9.4224	13.239	-0.18762
<i>n-C₁₈</i>	7.1395	-0.44956	-4.3144
<i>n-C₁₉</i>	-8.9293	15.535	-0.035543
<i>n-C₂₀</i>	7.9884	-0.52493	-4.2596
<i>n-C₂₁</i>	-9.2735	16.518	-0.016801
<i>n-C₂₂</i>	8.6106	-0.57798	-4.2509
<i>n-C₂₃</i>	-9.5182	17.335	-0.0037988
<i>n-C₂₄</i>	9.4021	-0.64356	-4.223
<i>n-C₂₅</i>	-9.7652	18.107	0.006465
<i>n-C₂₆</i>	10.112	-0.70408	-4.209
<i>n-C₂₇</i>	-9.7534	18.749	0.019831
<i>n-C₂₈</i>	10.816	-0.76167	-4.198

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Table 5. Parameters of EOS for mixture B (contd.)

<i>n</i> -C ₂₉	-9.9905	19.304	0.020441
<i>n</i> -C ₃₀	11.444	-0.81451	-4.1968

Table 6. Parameters of EOS for mixture C

Component	l_s	m_s	n_s
<i>n</i> -C ₁₀	-9.4224	13.239	-0.18762
<i>n</i> -C ₁₈	7.1395	-0.44956	-4.3144
<i>n</i> -C ₁₉	-8.9293	15.535	-0.035543
<i>n</i> -C ₂₀	7.9884	-0.52493	-4.2596
<i>n</i> -C ₂₁	-9.2735	16.518	-0.016801
<i>n</i> -C ₂₂	8.6106	-0.57798	-4.2509
<i>n</i> -C ₂₃	-9.5182	17.335	-0.003799
<i>n</i> -C ₂₄	9.4021	-0.64356	-4.223
<i>n</i> -C ₂₅	-9.7652	18.107	0.006465
<i>n</i> -C ₂₆	10.112	-0.70408	-4.209
<i>n</i> -C ₂₇	-9.7534	18.749	0.019831

Table 7. Parameters of EOS for bim13

Component	l_s	m_s	n_s
C ₁₀	-10.833	14.648	-0.20581
C ₁₈	7.3255	-0.47341	-4.2847
C ₁₉	6.4639	-0.29946	-4.5263
C ₂₀	8.0223	-0.53895	-4.2522
C ₃₄	12.906	-1.0438	-4.151
C ₃₅	-16.406	28.979	0.10221
C ₃₆	13.603	-1.1167	-4.1423

Table 8. Parameters of EOS for Oil 5

Pseudocomponent	l_s	m_s	n_s
<i>P</i> -C ₁₀₊	-8.6201	12.786	-0.17239
<i>N</i> -C ₁₀₊	3.2125	-0.08398	-5.1386
<i>A</i> -C ₁₀₊	3.2267	-0.12094	-4.9696
<i>P</i> -C ₁₅₊	5.9567	-0.27612	-4.5308
<i>N</i> -C ₁₅₊	-5.7139	9.9654	-0.17938
<i>A</i> -C ₁₅₊	-6.0577	9.9896	-0.1857
<i>P</i> -C ₂₀₊	7.492	-0.3908	-4.4207
<i>N</i> -C ₂₀₊	-6.3593	11.679	-0.15433
<i>A</i> -C ₂₀₊	-5.8307	10.416	-0.21188
<i>P</i> -C ₂₅₊	8.9575	-0.50176	-4.3724
<i>N</i> -C ₂₅₊	-7.4047	13.844	-0.12532
<i>A</i> -C ₂₅₊	-6.0942	11.417	-0.22147
<i>P</i> -C ₃₀₊	10.561	-0.6278	-4.3345
<i>N</i> -C ₃₀₊	-8.6504	16.201	-0.098267
<i>A</i> -C ₃₀₊	-6.588	12.693	-0.21949
<i>P</i> -C ₃₅₊	11.921	-0.73866	-4.3053
<i>N</i> -C ₃₅₊	-10.129	18.873	-0.072922
<i>A</i> -C ₃₅₊	-7.2483	14.239	-0.21087
<i>P</i> -C ₄₀₊	13.681	-0.88703	-4.2681
<i>N</i> -C ₄₀₊	-11.777	21.772	-0.050509
<i>A</i> -C ₄₀₊	-8.0138	15.977	-0.19855
<i>P</i> -C ₄₆₊	16.492	-1.1337	-4.209
<i>N</i> -C _{P1+}	-14.927	27.217	-0.01868
<i>A</i> -C _{P1+}	-9.4777	19.316	-0.1736
<i>N</i> -C _{CP2+}	-19.061	34.309	0.0097925
<i>A</i> -C _{CP2+}	-13.495	23.969	-0.20113

Table 9. Parameters of EOS for Oil 6

Pseudocomponent	l_s	m_s	n_s
P-CP1	-7.6701	11.668	-0.1522
N-CP1	-4.7492	7.8714	-0.16432
A-CP1	3.1885	-0.13346	-4.7521
P-CP2	-7.9844	13.428	-0.047253
N-CP2	3.8369	-0.10604	-4.8242
A-CP2	3.6483	-0.11553	-4.8232
P-CP3	6.4993	-0.37657	-4.2186
N-CP3	-4.3969	9.1252	-0.094925
A-CP3	-4.3753	8.6468	-0.11886
P-CP4	7.6419	-0.49264	-4.1055
N-CP4	-4.6555	10.188	-0.064131
A-CP4	-4.0311	8.8143	-0.12237
P-CP5	13.934	-1.2069	-3.8195
N-CP5	-7.8951	17.942	0.063654
A-CP5	-4.135	12.168	-0.078385
P-CP6	16.199	-1.4885	-3.754
N-CP6	-9.3345	20.954	0.090889
A-CP6	-4.4112	13.697	-0.055752
P-CP7	16.502	-1.5269	-3.7459
N-CP7	-9.5289	21.355	0.094017
A-CP7	-4.4491	13.904	-0.052763
N-CP8	-10.807	23.979	0.1122
A-CP8	-4.6938	15.265	-0.033513

α^s is independent of pressure and it can be used for the solid volume prediction [11]. The error function for lighter components, like C_{10} , are greater than heavy fractions. The reason is that the calculations are done in a temperature far from the melting point.

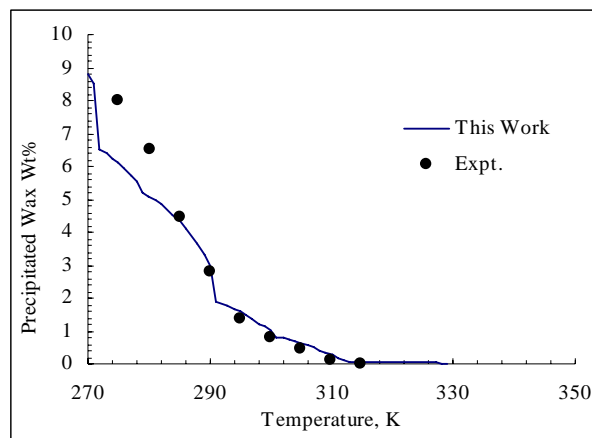


Figure 1. Experimental and calculated amount of precipitated wax for Oil 5

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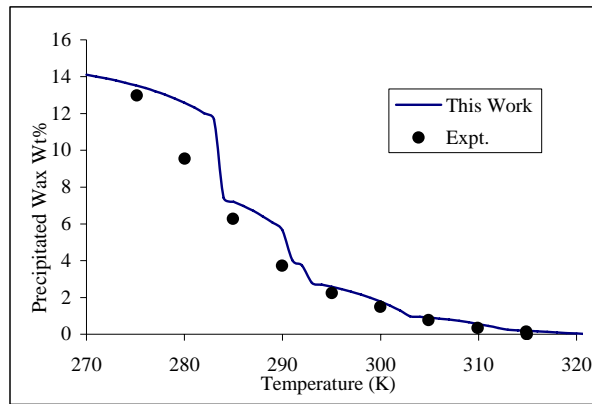


Figure 2. Experimental and calculated amount of precipitated wax for *Oil 6*

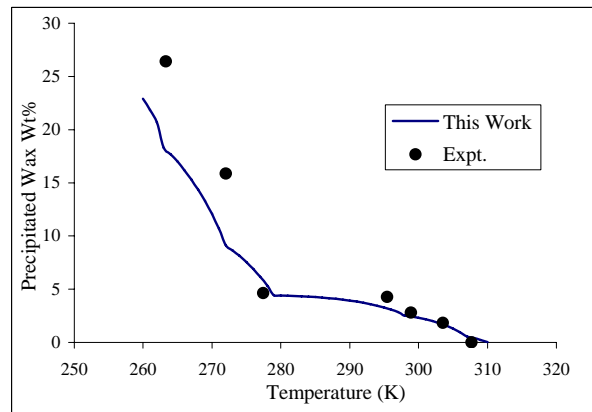


Figure 3. Experimental and calculated amount of precipitated wax for *bim13*

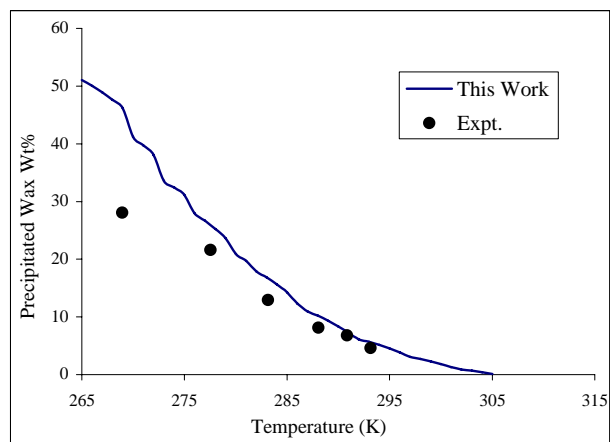


Figure 4. Experimental and calculated amount of precipitated wax for *mixture B*

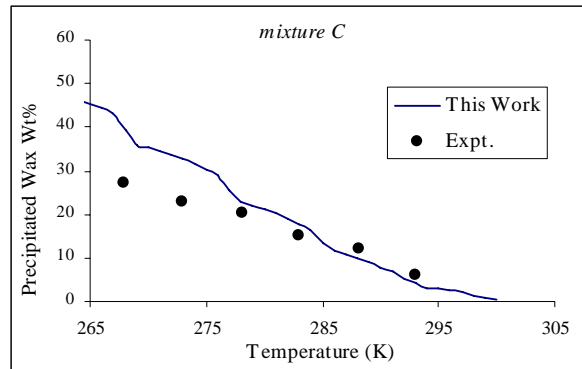


Figure 5. Experimental and calculated amount of precipitated wax for *mixture C*

5. Conclusion

Complex behavior of solid phase in oil mixture and wide range of its application in solid precipitation and deposition petroleum fluids (wax, asphaltene, ...) need to be modeled via applicable and efficient methods. Here application of a solid EOS for description of solid phase was tested for wax precipitation in petroleum mixtures. In this work, TST solid equation of state is used for describing wax precipitation phenomena in some synthetic and real oil mixtures. This solid equation of state is based on an alpha function. Using thermodynamic cycle for pure solid fugacity from pure liquid fugacity, the TST parameters were tuned before its application for wax precipitation prediction. The multisolid phase approach is used for determination of the nature and number of solid phases. As it can be seen in the previous sections, the obtained results in this work are in good agreements with the experimental data.

References

- [1] Won K. V., *Fluid Phase Equilibria*, 53, 377 (1989).
- [2] Won K. V., *Fluid Phase Equilibria*, 30, 265 (1986).
- [3] Daridon J.-L., Pauly J., Coutinho J. A. P., and Montel F., *Energy and Fuels*, 15, 730-735 (2001).
- [4] Coutinho J. A. P. and Daridon J.-L., *Energy and Fuels*, 15, 1454 (2001).
- [5] Vafaie-Sefti M., Mousavi-Dehghani S. A., and Mohammad-Zadeh Bahar M., *Fluid Phase Equilibria*, 173, 65 (2000).
- [6] Nichita D. V., Goual L., and Firoozabadi A., *SPE 74686* (2001).
- [7] Feyzi F. and Dalirsefat R., *Fuel* (2007), doi:10.1016/j.fuel.2006.11.034, Article in Press.
- [8] Lira-Galeana C., Firoozabadi A., and Prausnitz J. M., *AIChE*, 42, 239 (1996).

- [9] Coutinho J. A. P., Edmonds B., Moorwood T., Szczepanski R., and Zhang X., *SPE* 78324 (2002).
- [10] Yokozeki A., *International Journal of Thermophysics*, 24, 589 (2003).
- [11] Twu C. H., Tassone V., and Sim W. D., *AIChEJ*, 49, 2957 (2003).
- [12] Ness H. C. V. and Abbott M. H., *Classical Thermodynamics of Non-Electrolyte Solutions with Application to Phase Equilibria*. New York: Mc-Graw Hill (1982).
- [13] Prausnitz J., Lichtenthaler M., R. N., and de Azevedo E. G., *Molecular Thermodynamics of Fluid-Phase Equilibria*. Upper Saddle River, New Jersey: Prentice Hall (1999).
- [14] Escobar-Remolina J. C. M., *Fluid Phase Equilibria*, 240, 197 (2006).
- [15] Powell, M. J. D., *Numerical Methods for Nonlinear Algebraic Equations*, P. Rabinowitz (1970)