Calculation of Vapor-Liquid-Liquid Equilibria for the Fischer-Tropsch Reactor Effluents using Modified Peng-Robinson Equation of State

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Abstract

A modified Peng–Robinson equation of state is used to develop the methods for calculating the thermodynamic equilibrium in Fischer–Tropsch synthesis products. A group contribution method allowing the estimation of the temperature dependent binary interaction parameters (kij(T)) for the widely used Peng-Robinson equation of state (EOS) [1] has been extended to include additional groups relevant to GTL products. A key point in this approach is that the k_{ij} between two components i and j is a function of temperature (T) and of the pure components critical temperatures and pressures and acentric factors. This means that no additional properties besides those required by the EOS itself (T_C, P_C, ω) are required. By using a single binary interaction factor, it is sufficient for this correlation to represent a binary system over a wide range of temperatures and pressures. The added groups which are defined in this paper are: H2O, Ethylene, CH=, CH2=, CO and H2 which are added to CH_3, CH_2, CH, C, CH_4 (methane), C2H6, CO2 which means that it is possible to estimate the k_{ij} for any mixture of saturated hydrocarbons (n-alkanes and branched alkanes), olefins, water, hydrogen whatever the temperature. The results obtained in this study are in many cases very accurate.

Introduction

One of the possible methods for processing oil-well gases is based on the process in which the Fischer–Tropsch method is used to produce high-molecular-weight hydrocarbons from synthesis gas (syngas) [2]. In this reaction, the total number of components is as large as several hundreds, the vapor phase contains a considerable proportion of water, and there are both hydrophobic and hydrophilic compounds among the resulting hydrocarbons [3]. Obviously, this mixture should be treated as nonideal in phase-equilibrium calculations.

Different approaches have been presented in the literature to calculate the vapor-liquid equilibriums [4-11]. The empirical methods for estimating the liquid–vapor equilibrium characteristics in multi-component synthesis products, such as the Henry constants, cannot be applied because of the complex composition of the products. These works used a simplified thermodynamic model for the VLE, in which the liquid is assumed to be an ideal solution, the hydrocarbon products are assumed to be linear paraffins and the inorganic gases are considered insoluble in the liquid phase. In other words, these models ignored the non-ideal phase equilibrium problem of a FT reactor.

The rigorous calculation method is based on the use of state equations with appropriate mixing rules [12]. It could be used if the critical thermodynamic constants for pure substances and the Pitzer acentric factor are known. For simple gases and hydrocarbons with a number of carbon atoms less than 20, these constants can be found in the reference literature [3, 4]. For heavier hydrocarbons, the data on the critical thermodynamic properties are fragmentary or not available at all. In this situation, the critical thermodynamic properties and acentric factors of heavy hydrocarbons should be estimated by calculation.

Huang et al. [13] showed that the solubility of gas solutes in heavy paraffins can be described with an extended form of Soave equation of state which was coupled with the Huron–Vidal type mixing rule. This model is so extensive attaining relatively high accuracy. However, the introduction of many new parameters for each binary system restricts its application to the engineering calculation and the possibility of extending to other systems. Some researchers even presented several semi-empirical correlations such as solubility enthalpy model [14].

Cubic equations of state have probably been the most widely used methods in the petroleum-refining process industries for the calculation of vapor-liquid equilibrium because they allow accurate prediction of phase equilibrium for mixtures containing non-polar components and industrial-important gases. However, to apply cubic equations of state to model petroleum processes, binary interaction parameters are required because phase equilibrium prediction is sensitive to the parameters in the mixing rules.

The Peng-Robinson equation of state slightly improves the prediction of liquid volumes. It performed as well as or better than the Soave-Redlich-Kwong equation. Han et al. [15] reported that the Peng-Robinson equation was superior for predicting vapor-liquid equilibrium in hydrogen and nitrogen containing mixtures. The advantages of these equations are that they can accurately and easily represent the relation among temperature, pressure, and phase compositions in binary and multi-component systems. They only require the critical properties and acentric factor for the generalized parameters. Little computer time is required and good phase equilibrium correlations can be obtained.

Jaubert et al. [16] have shown that the binary interaction coefficient value has a huge influence on a calculated phase diagram. They have extended the PR EOS to contain temperature-dependant binary coefficients. Their approach is used in this project and extended to include the components which are present as GTL products.

The general approach of this work is as follows (as it is shown in Figure 1): First, we calculate the number of phases using the approach in [6]. Since convergence of these algorithms depend on the initial estimates of equilibrium distribution of components between different phases (K values) and each methodology may fail given poor initiation values, in each step and for each 2-component pair different initial points are used to solve the problem and the best result is saved. In the next step, after doing the flash calculations, the temperature-dependant interaction factors are calculated by optimization and the parameters A and B are obtained for each pair of components. Besides, since the number of phases which has been possibly formed in a specified condition is not clear, the phase stability analysis should be used. The phase stability analysis problems are complex in nature and are used to check the optimization methods [17-22].

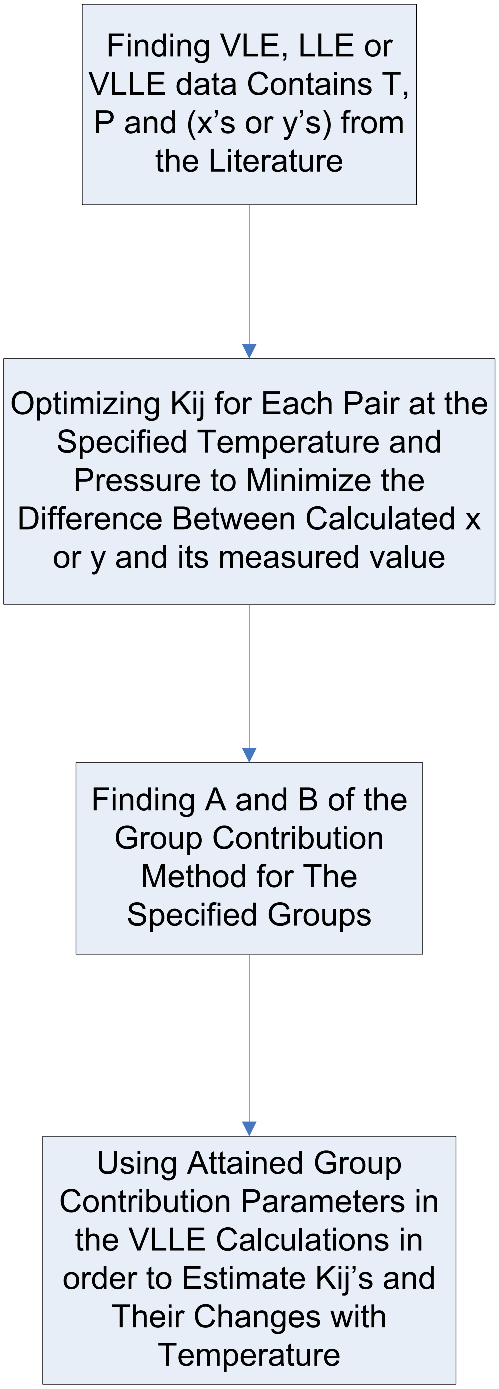

Figure 1. General procedure for extending the group contribution method

The modified Peng-Robinson Model

In 1978, Peng and Robinson [23] published an improved version of their original well-known equation of state [24] .

For a pure component, the PR78 EOS is:

$$P = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} \tag{1}$$

$$R = 8.314472 \, J \, mol^{-1} K^{-1}$$
$$b_i = 0.0777960739 \frac{RT_{ci}}{P_{ci}}$$
$$a_i = 0.457235529 \frac{R^2 T_{ci}^2}{P_{ci}} \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^2$$
$$\text{if } \omega_i \le 0.491, \quad m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$
$$\text{if } \omega_i > 0.491, \quad m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3$$

where P is the pressure, R the ideal gas constant, T the temperature, v the molar volume, T_c the critical temperature, P_c the critical pressure and ω the acentric factor, a denotes the attractive term and b is the covolume (if the molecules are represented by hard-spheres of diameter σ, then $b = 2\pi N\sigma^3/3$). The corrective terms a and b are expressed as functions of the critical coordinates of both the solvent and the solute.

The difference between the original and modified EOS is in the definition of m_i (equation (2)). The later work was modified to cover the components heavier than heptanes.

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (PR76) \tag{2}$$

To apply such an EOS to mixtures, mixing rules are used to calculate the values of a and b of the mixtures. Classical mixing rules are used in this study:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i z_j \sqrt{a_i a_j} \left(1 - k_{ij}\left(T\right)\right) \qquad (3)$$

$$b = \sum_{i=1}^{N} z_i b_i$$

where z_k represents the mole fraction of component "*k*" in a mixture and *N* is the number of components in the mixture. In Eq. (03), the summations are over all chemical species. *kij*(*T*) is the so-called binary interaction parameter characterizing molecular interactions between molecules "*i*" and "*j*". When *i* equals *j*, *kij* is zero. *kij*, which depends on temperature, is calculated by a group contribution method [1] through the following expression:

$$k_{ij}\left(T\right) = \frac{-\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} \left(\alpha_{ik} - \alpha_{jk}\right)\left(\alpha_{il} - \alpha_{jl}\right) A_{kl} \left(\frac{298.15}{T}\right)^{\left(\frac{B_{kl}}{A_{kl}} - 1\right)} - \left(\frac{\sqrt{a_i\left(T\right)}}{b_i} - \frac{\sqrt{a_j\left(T\right)}}{b_j}\right)^2}{2 \frac{\sqrt{a_i\left(T\right) a_j\left(T\right)}}{b_i b_j}} \qquad (4)$$

In which, *T* is the temperature. a_i and b_i are calculated by Eq. (1). N_g is the number of different groups defined by the method. α_{ik} is the fraction of molecule *i* occupied by group *k*. $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where *k* and *l* are two different groups) are constant parameters determined after calculating the binary interaction coefficients ($A_{kk} = B_{kk} = 0$).

$$\alpha_{ij} = \frac{occurence\ of\ \ group\ k\ in\ molecule\ i}{total\ number\ of\ \ groups\ \ present\ in\ molecule\ i} \qquad (5)$$

Fugacity coefficient is derived from the following equation:

$$\ln\frac{f_i}{y_iP}=\frac{b_i}{b}(Z-1)-\ln(Z-B)-\frac{A}{2\sqrt{2}B}\left[\frac{2\sum_{j=1}^{c}y_ia_{ij}}{a}-\frac{b_i}{b}\right]\ln\frac{Z+2.414B}{Z-0.414B} \tag{6}$$

where Z is the compressibility factor. A and B are defined as below

$$A=\frac{aP}{R^2T^2} \tag{7}$$

$$B=\frac{bP}{RT}$$

It is clear that the equivalence of fugacity coefficients in two phases is the criteria which should be reached when the phases are in equilibrium.

Because this model relies on the Peng–Robinson EOS as published by Peng and Robinson in 1978 and because the addition of a group contribution method to estimate the *kij* makes it predictive, the model was called predictive 1978, Peng–Robinson (PPR78)[1]. Major components in GTL products are listed in Table 1. Table 2 contains the sources of binary experimental data used for the calculations.

Table 1. List of components used for the study and their thermodynamic properties

Component	$T_c\left(K\right)$	$P_c\left(MPa\right)$	ω
Methane	190.6	4.6	0.008
H2O	647.3	22.048	0.3442
H2	33.4397	1.3155	-0.12009
CO2	304.21	7.383	0.223621
CO	132.9490	3.498750	.09300
Ethane	305.32	4.808	0.0995
Propane	369.82	4.2496	0.15176
nC4	425.199	3.79662	0.201
iC4	408.096	3.64762	0.18479
n-Pentane	469.6	3.37512	0.25389

i-Pentane	460.398	3.33359	0.22224
n-Hexane	507.898	3.03162	0.3007
n-Heptane	540.158	2.73678	0.34979
n-Octane	568.598	2.49662	0.40180
n-Nonane	594.598	2.30007	0.44549
n-Decane	617.598	2.107550	0.488480
2-methylbutane	460.398	3.33359	0.22224
2,2,4-Trimethylpentane	543.96	2.56757	0.31
Ethylene	282.34	5.041	0.087
Propene	365.57	4.665	0.1408
1-Butene	419.5	4.02	0.192225
1-Pentene	464.699	3.5287	0.23296

Table 2. Experimental data used for the calculations

Component	**T range (K)**	**P range(MPa)**	Data Type	No. of Points	**Ref**.
CO2 – H2O	274.14 – 353.1	0.190 - 9.333	T-P-x	74	[25-28]
CH4 – H2O	274.19 - 318.12	0.491 - 9.082	T-P-y & T-P-x	46	[29-32]
C2H6 – H2O	274.26-343.06	0.373 – 4.952	T-P-y & T-P-x	50	[32-35]
nC4H10 – H2O	298.15 - 423.15	0.1043 - 4.13	T-P-x	32	[36, 37]
C3H8 – H2O	277.62-368.16	0.357-3.915	T-P-y & T-P-x	67	[37-39]
iC4H10 – H2O	298.23- 363.19	0.354 – 1.712	T-P-x	8	[37]
nC5H12 – H2O	298.28 - 343.15	0.498 - 0.508	T-P-x	10	[37, 40]
nC6H14 – H2O	298.09 - 477.59	0.207 - 3.241	T-P-x	32	[41-43]
2MButane – H2O	279.15- 294.95	0.101	T-P-x	10	[40]
2-MPentane – H2O	573.15 - 628.15	14.18 - 70.91	T-P-x	38	[44]
nC7H16 – H2O	295 - 355	17.22 - 70.91	T-P-x	25	[44]
nC8H18 – H2O	298- 473	6.5	T-P-x	5	[45]
2,2,4-tmPentane– H2O	298.15 - 473	0.5-6.5	T-P-x	9	[41, 45]
nC10H22 – H2O	423.15- 583.15	0.52- 9.36	T-P-x	15	[46]
Propylene – H2O	310-410	0.2-8	T-P-y & T-P-x	52	[47, 48]
Ethylene – H2O	310-410	1.37-10.3	T-P-y & T-P-x	47	[49, 50]
CO2 – 1-hexene	313 - 393	1.74 – 12.06	BP	59	[51]
CO2 – 2-ethyl-1-butene	313 - 373	2.43 – 11.55	BP	27	[51]
CO2- 1-Hexene					[52, 53]
CO2- 1-Heptene					[52]
Propylene-CO2	283-298	0.97-6.02	T-P-x T-P-y	58	[54]
Propylene-Ethylene	283-298	1.03-5.38	T-P-x T-P-y	86	[54, 55]
Ethylene - 4-Methyl-1-pentene	293 - 373	0.79 – 8.51	T-P-x T-P-y	46	[19]
Ethylene - 2,2,4-Trimethylpentane	323 - 423	0.44 – 2.32	T-P-x T-P-y	30	[56]
Ethylene + Hexane	391-495	1.5-9.09	BP	106	[57]
Ethylene -1-Butene	293 - 374	0.6 – 6.6	T-P-x T-P-y	48	[58]

Ethylene – 1-Octene	303 - 342	1 – 8.9	T-P-x T-P-y	20	[58]
Ethylene – n-Eicosane	290 - 323	1 – 15	T-P-x	33	[59]
Ethylene – 2,2,4-Trimethylpentane	323 – 423	0.44 – 2.42	T-P-x T-P-y	20	[60]
Ethylene – Hexane	390 - 450	1.5 – 8.5	BP	130	[61]
Butane – 1-Butene	310 - 338	0.35 – 0.86	T-P-x T-P-y	60	[62]
Ethylene – 1-Butene	293 - 375	0.6 – 6.06	T-P-x T-P-y	25	[63]
Propylene-Ethane	283-298	0.89-4-07	T-P-x T-P-y	50	[54]
Propylene-Propane	273-350	0.47-3.51	T-P-x T-P-y	350	[14, 64, 65]
1-Butene – 1-Hexene	373	0.4 – 1.4	T-P-x T-P-y	11	[19]
1-Butene – H2O	293 - 323	0.101	T-P-x	13	[66]
H2 – nHexane	377.6-477.6	6.9-34-48	T-P-x T-P-y	60	[67, 68]
H2 – nHexadecane	524-664	2.01-25	T-P-x T-P-y	20	[67]
H2 – 2,3-dimethylbutane	423-453	4.3-8.9	T-P-x	8	[67]
H2 – n-Eicosane	373 - 573	1 – 5.07	T-P-x T-P-y	15	[69]
H2 – H2O	273 - 300	.101	T-P-x	38	[70, 71]
CO – Hexane	293 - 473	1.26 – 10.5	T-P-x T-P-y	49	[72]
CO – Eicosane	373 - 573	1.02 – 5.03	T-P-x	15	[69]
CO – n-decane	310 - 377	2.84 – 10.2	T-P-x	18	[73]
CO – C8H18	463 - 533	0.67 – 3.9	T-P-x T-P-y	41	[73]

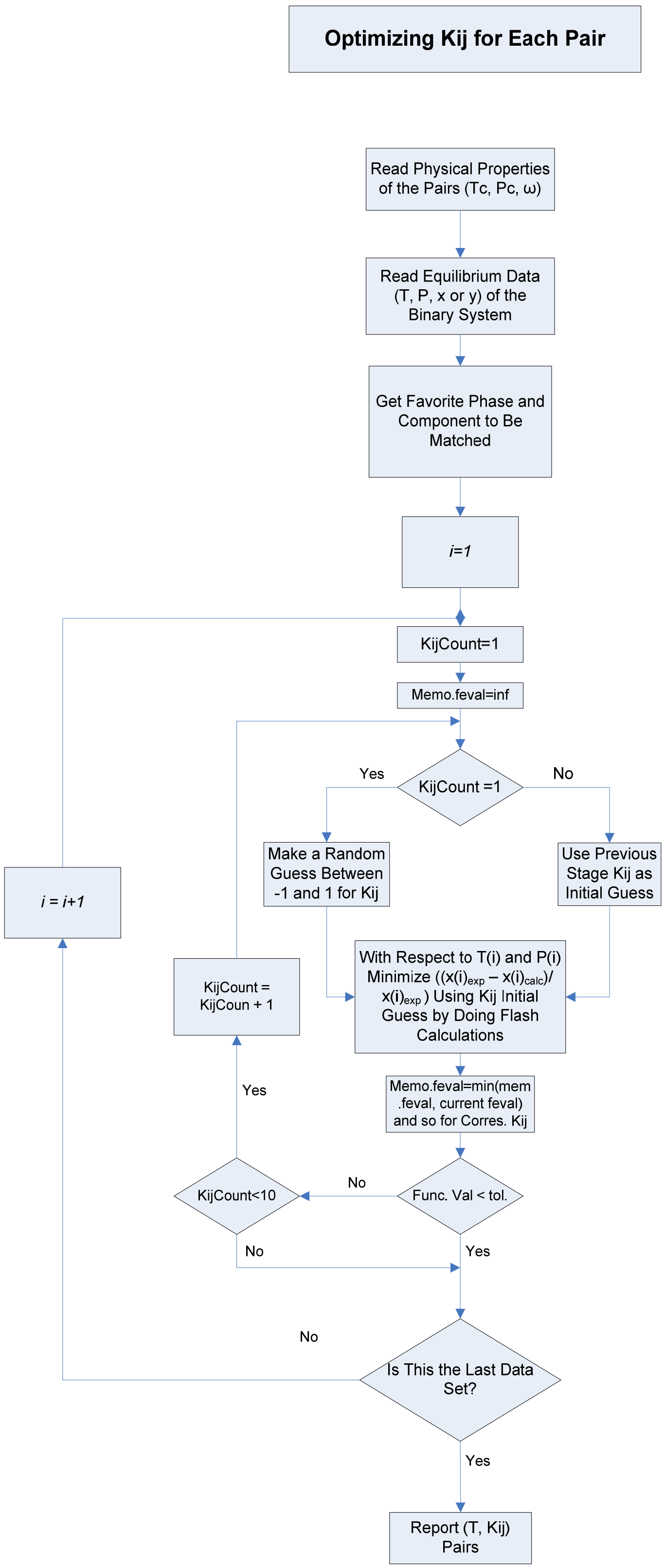

Figure 2. Calculation of binary interaction coefficient parameters for each pair

Figure 2 shows the procedure of calculating the binary interaction coefficient variables. The inner loop in the diagram shows the trials to calculate the optimum K_{ij} for each data set and the outer loop is the iteration on data set for a binary pair. As it was mentioned before, since the calculations are sensitive to the initialization, different points were chosen as the initial value and the best result was reported. In addition, Wilson equation (the equation below) was used for the initial guess of distribution factor in flash calculations:

$$K_i = \frac{P_c}{P} \times \exp\left(5.37 \times \left(1+\omega\right)\right) \times \left(1 - \frac{T_c}{T}\right) \tag{8}$$

The groups which are defined in this work are: group 1=CH3; group 2 =CH2; group 3 = CH; group 4 =C; group 5=CH4, i.e. methane; group 6 =C2H6, i.e. ethane; group 7: H2O, group 8: CO2, group 9: CO, group 10: H2, group 11: Ethylene, group 12: CH=, group 13: CH2=. These groups are chosen as representatives of the components which are present in the GTL process. Figure 3 shows the procedure of calculating A and B parameters from the set of temperatures and K_{ij} values. The error which should be minimized in this phase is the difference between calculated K_{ij} from eq. 4 and the calculated one from previous step. For clarification, we will explain more on an example. Suppose, we want to calculate the interaction parameters (A and B) between hydrocarbons and H2. The data for calculation of these parameters come from H2-Hexane, Hydrogen/n-hexadecane, and Hydrogen/23-dimethylbutane pairs. So, the groups matrix shows the share of each group in each component. The symbol ✓ in matrices A and B means that these elements are calculated previously. There remain 6 unknowns which are obtained by optimization targeting the minimum difference in the calculated K_{ij} from these parameters and the ones which were calculated from before.

$$groups=\begin{array}{cc} \begin{matrix} H_2 & CH_3 & CH_2 & CH \end{matrix} & \\ \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 4 & 0 \\ 0 & 2 & 14 & 0 \\ 0 & 4 & 0 & 2 \end{bmatrix} & \begin{matrix} H_2 \\ \text{Hexane} \\ n-\text{Hexadecane} \\ \text{23-dimethylbutane} \end{matrix} \end{array}$$

$$A=\begin{array}{cc} \begin{matrix} H_2 & CH_3 & CH_2 & CH \end{matrix} & \\ \begin{bmatrix} 0 & x(1) & x(2) & x(3) \\ x(1) & 0 & \checkmark & \checkmark \\ x(2) & \checkmark & 0 & \checkmark \\ x(3) & \checkmark & \checkmark & 0 \end{bmatrix} & \begin{matrix} H_2 \\ CH_3 \\ CH_2 \\ CH \end{matrix} \end{array}, \quad B=\begin{array}{cc} \begin{matrix} H_2 & CH_3 & CH_2 & CH \end{matrix} & \\ \begin{bmatrix} 0 & x(4) & x(5) & x(6) \\ x(4) & 0 & \checkmark & \checkmark \\ x(5) & \checkmark & 0 & \checkmark \\ x(6) & \checkmark & \checkmark & 0 \end{bmatrix} & \begin{matrix} H_2 \\ CH_3 \\ CH_2 \\ CH \end{matrix} \end{array}$$

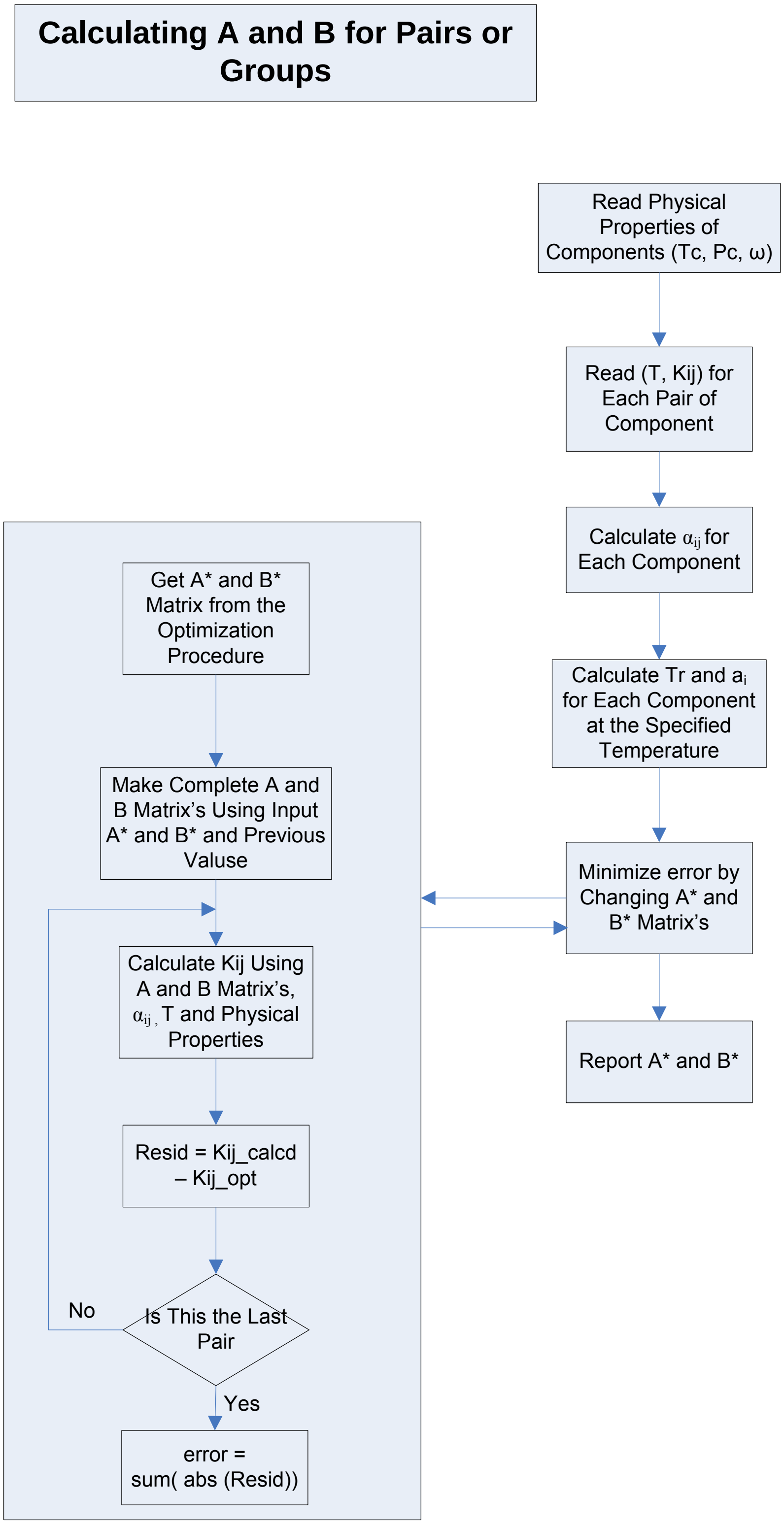

Figure 3. Calculation of A and B parameters for each pair of components

Stability Analysis

The stability analysis test is possible through two approaches: solving the nonlinear system of equations and minimization. We have used the second approach for our work. The function to be minimized is as below

$$\min F(\tilde{x}) = \sum_i x_i \bigl(\ln x_i + \ln \phi_i(\tilde{x}) - \ln z_i - \ln \phi_i(\tilde{z}) \qquad (9)$$

$$\textit{subject to}: \sum_i x_i = 1 \quad 0 \le x_i \le 1$$

In fact, a mixture with the mole fraction *z* is in equilibrium when for every value for *x*, the above expression results in a positive value. By performing an optimization we can get the minimum value which results in positive value of *F*. If the obtained minimum value is negative, this means the system is unstable. So, in order to get the number of phases which are in equilibrium in a specified operating point, it is sufficient to do the flash calculations for two phases and if the criterion is not satisfied, the number of phases will be increased.

Results and Discussions

As summarized in the flowcharts (Figures 1-3), the approach of this work consists of two stages: First, the binary interaction for each pair of components is optimized so that the difference between the resulting compositions from flash calculations and the experimental ones will be minimum. Second, A and B parameters are optimized in order to minimize the difference between the calculated binary interaction from the previous step and the one which is derived from equation (4).

There isn't any clue about the initial guesses for the binary coefficient factor. So, we start with different random initial points. Then, successive substitution method is used to do the flash calculation. The initial guess for this stage is derived from Wilson equation for the distribution factor and the experimental data for compositions of the phases. In this manner, we can have a good guess for the amount of vapor. After reaching to the point which we don't see any improvement (the change in the distribution coefficient value in two subsequent iterations is less than some specified tolerance) or when the maximum number of iteration is reached, we switch to the other approach of flash calculations, which is solving a system of equations (1 total mol balance, n-1 component balance, two equations for summation of mole fractions in two phases and n equi-fugacity of components in two phases). We use the solution from the previous approach as an initial point in this step.

Figures 4-13 show some of the cases the P-x-y diagrams in different temperatures. It was observed that for a few cases the error tolerance for higher pressures were more, especially in higher temperatures. However, in our case the points near the operational conditions in GTL process are of more importance. There are also a few graphs (Figures 15, 16) which shows the functionality of the binary interaction coefficient of some pairs as a function of temperature.

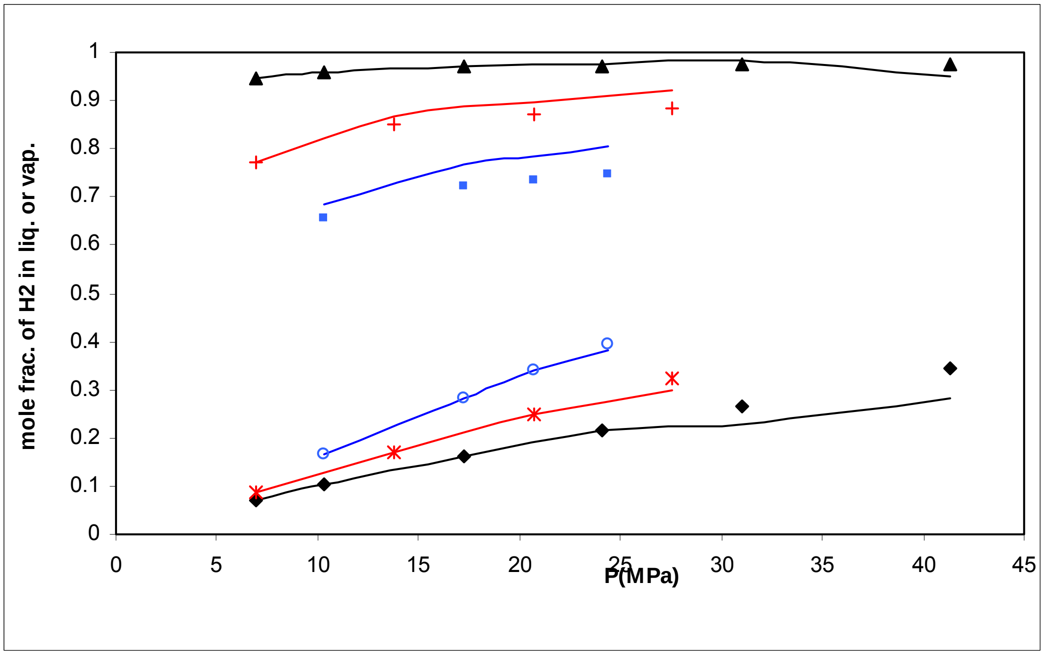

Figure 4. $H_2/n\text{-}C_6H_{14}$: black: experimental (◆ and ▲) and calculated data @ 377.6, red: experimental (∗ and +) and calculated data @ 444.3, blue: experimental (○ and ▪) and calculated data @ 477.6

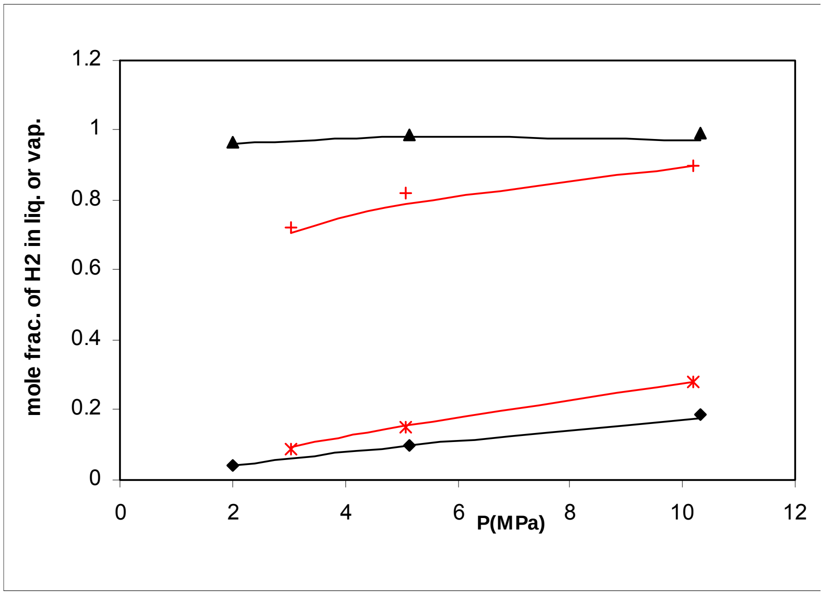

Figure 5. $H_2/n\text{-}C_{16}H_{34}$: black: experimental (◆ and ▲) and calculated data @ 542.3K, red: experimental (∗ and +) and calculated data @ 664.1K

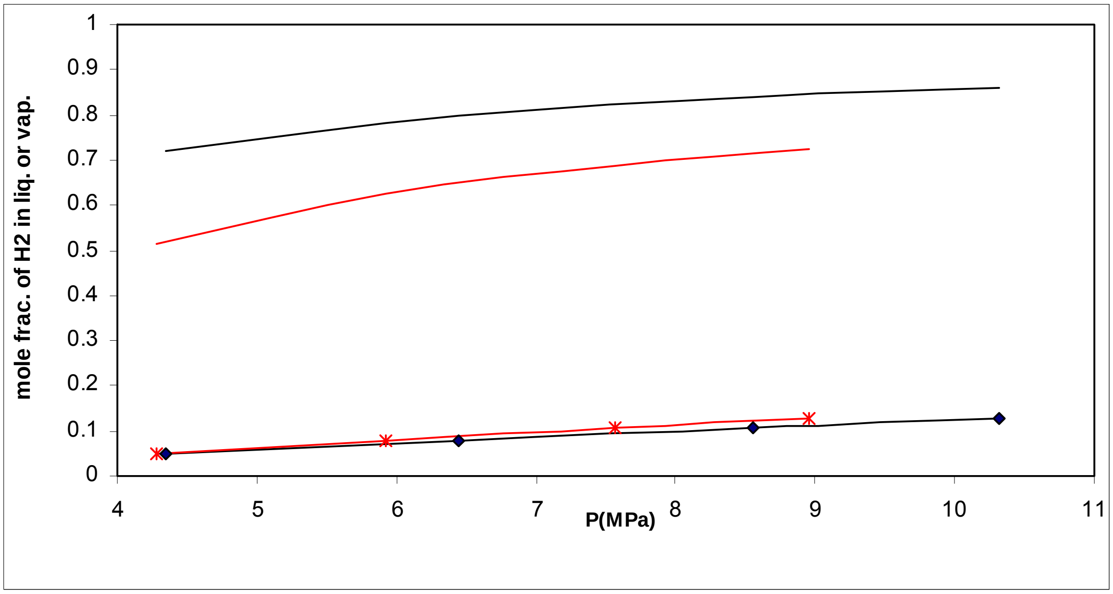

Figure 6. H_2/ 2,3-dimethylbutane: black: experimental (◆) and calculated data @ 423.2K, red: experimental (∗) and calculated data @ 453.2K

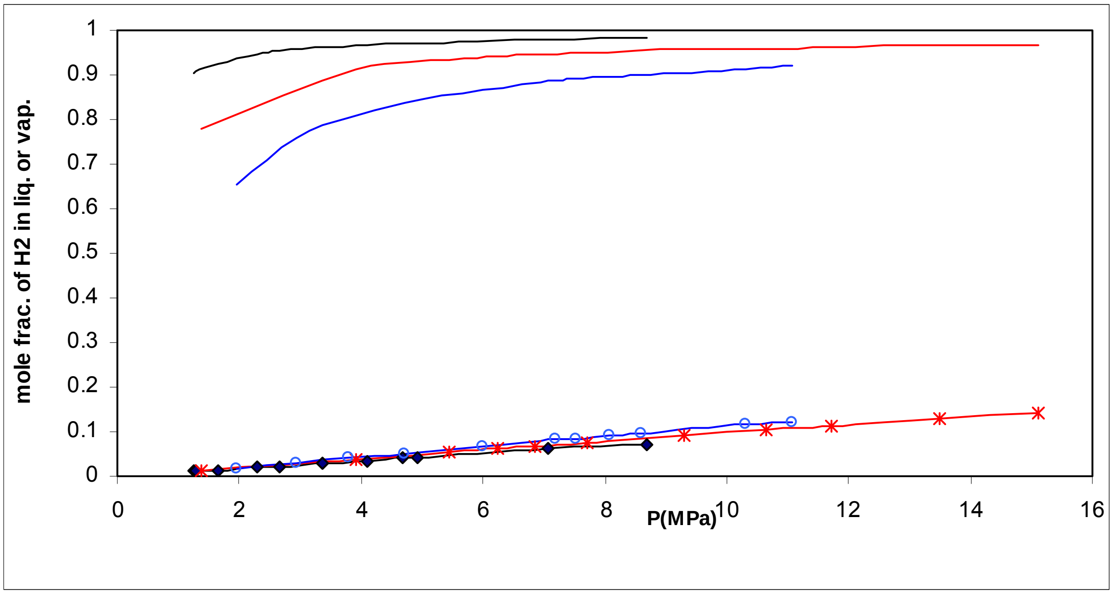

Figure 7. H_2/n-C_6H_{14} : black: experimental (◆ and ▲) and calculated data @ 344.3K, red: experimental (∗ and +) and calculated data @ 377.6K, blue: experimental (○ and ▪) and calculated data @ 410.9K

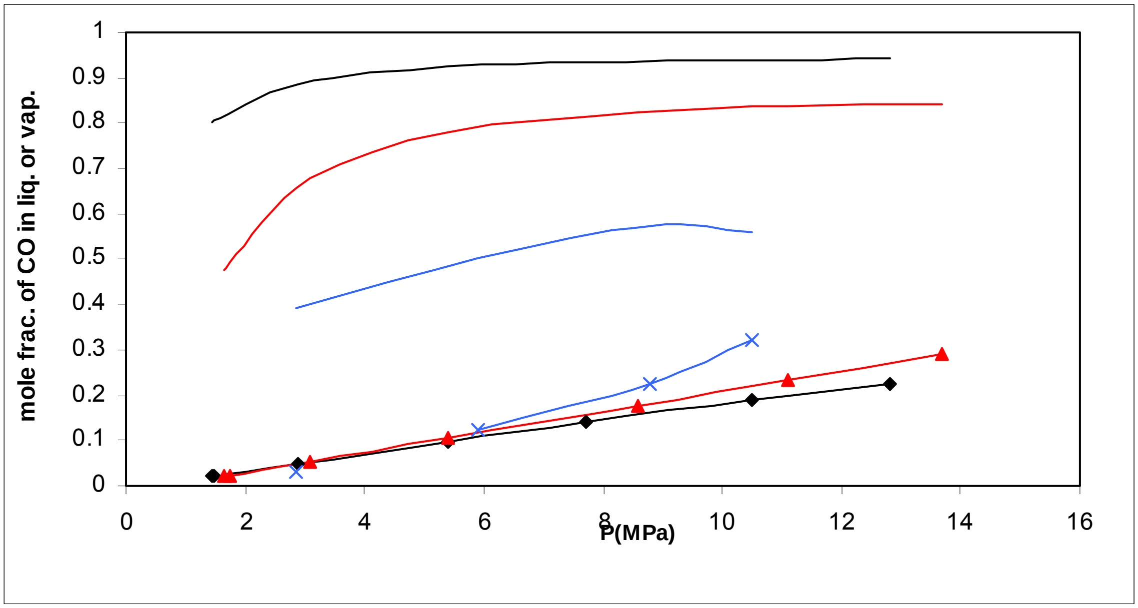

Figure 8. CO/n-C_6H_{14} : black: experimental (◆) and calculated data @ 373K, red: experimental (▲) and calculated data @ 423K, blue: experimental (×) and calculated data @ 473K

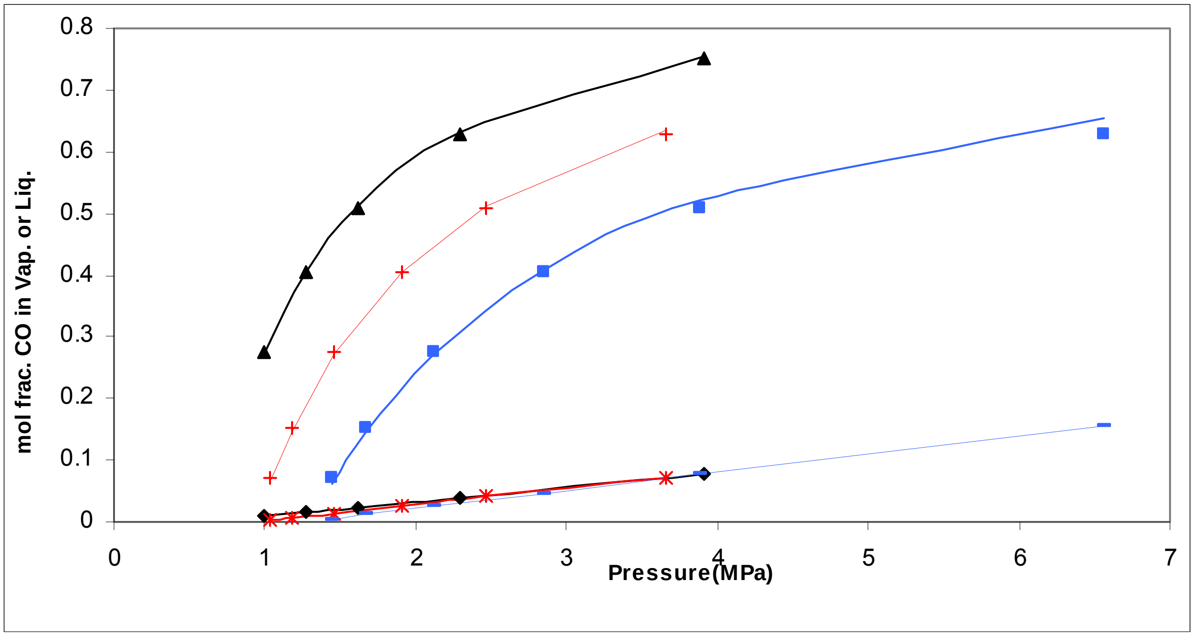

Figure 9. CO/n-C_6H_{14} : black: experimental (◆ and ▲) and calculated data @ 483K, red: experimental (∗ and +) and calculated data @ 503K, blue: experimental (- and ▪) and calculated data @ 523K

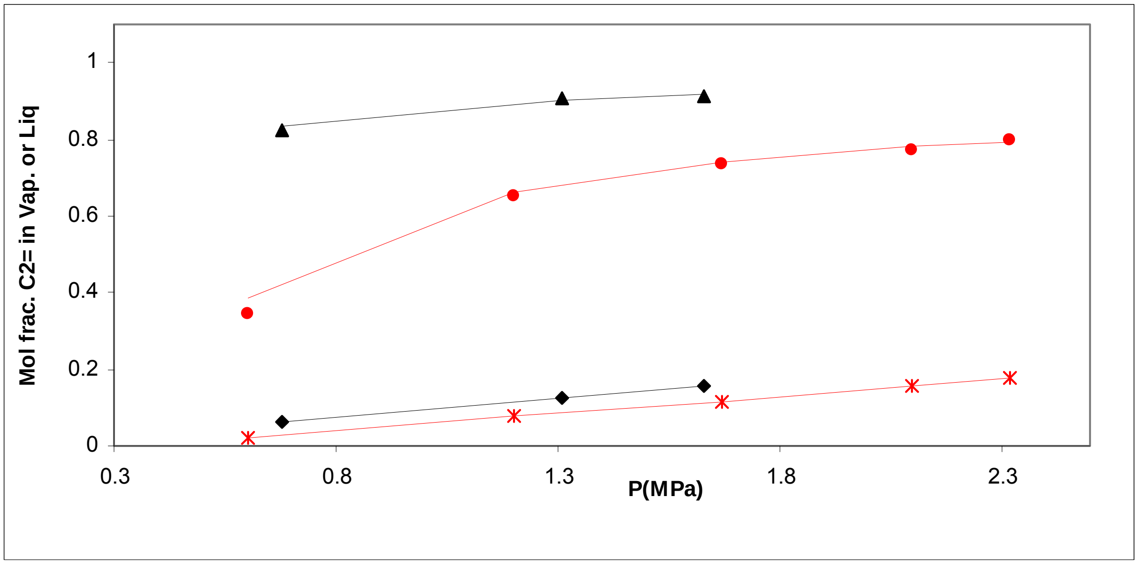

Figure 10. C_2H_4/2,2,4-Trimethylpentane: black: experimental (◆ and ▲) and calculated data @ 373K, red: experimental (✶ and ●) and calculated data @ 423K

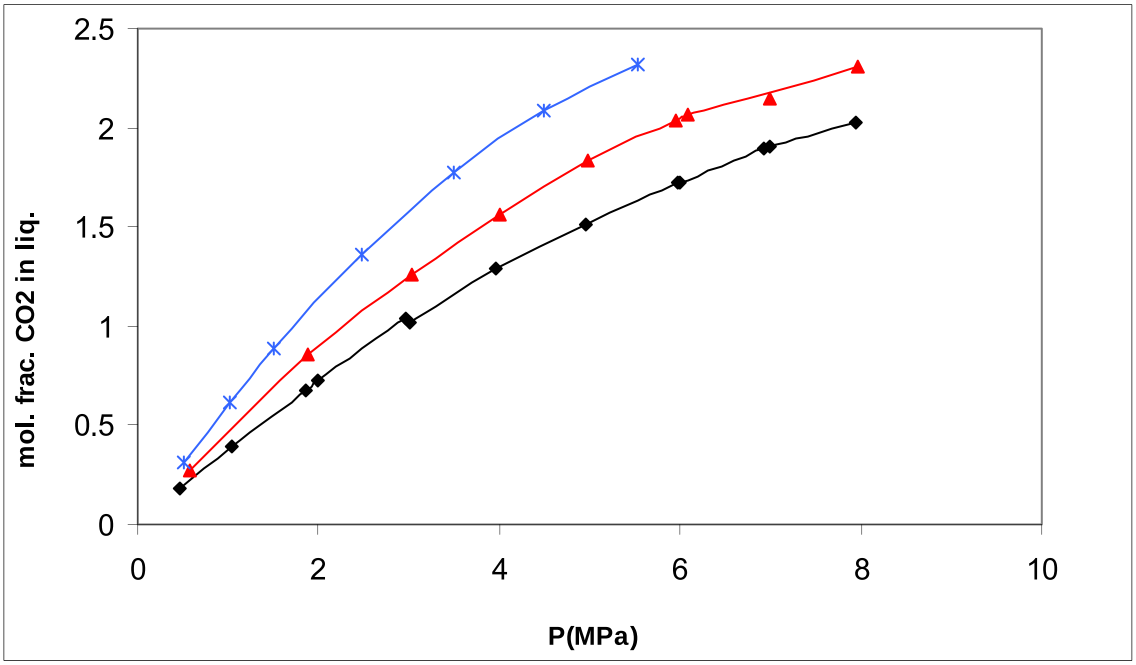

Figure 11. CO_2/H_2O: black: experimental (◆) and calculated data @ 318K, red: experimental (▲) and calculated data @ 308K, blue: experimental (✶) and calculated data @ 298K

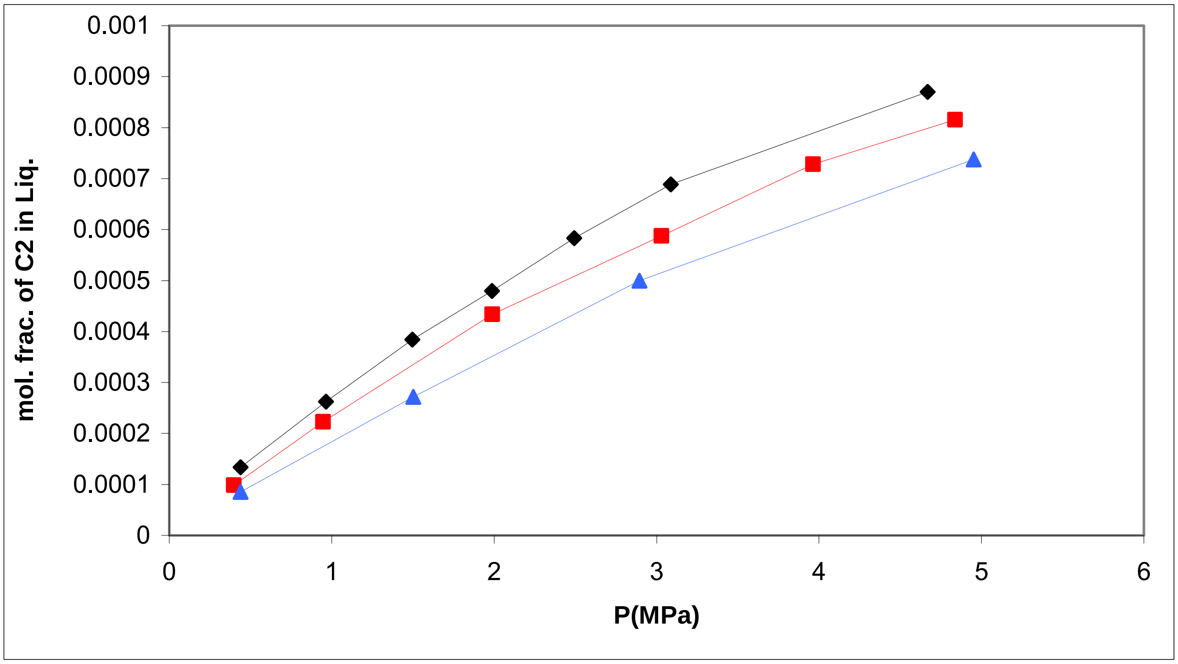

Figure 12. C_2H_6/H_2O: black: experimental (◆) and calculated data @ 313K, red: experimental (■) and calculated data @ 323K, blue: experimental (▲) and calculated data @ 343K

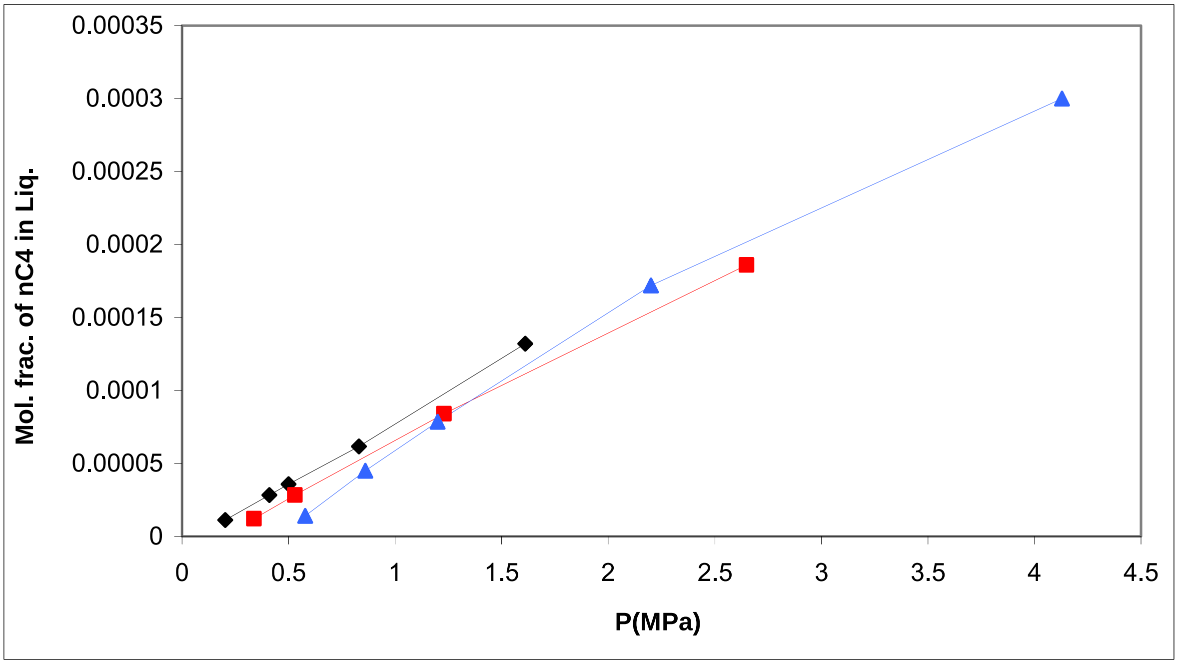

Figure 13. nC_4H_{10}/H_2O: black: experimental (◆) and calculated data @ 373K, red: experimental (■) and calculated data @ 398K, blue: experimental (▲) and calculated data @ 423K

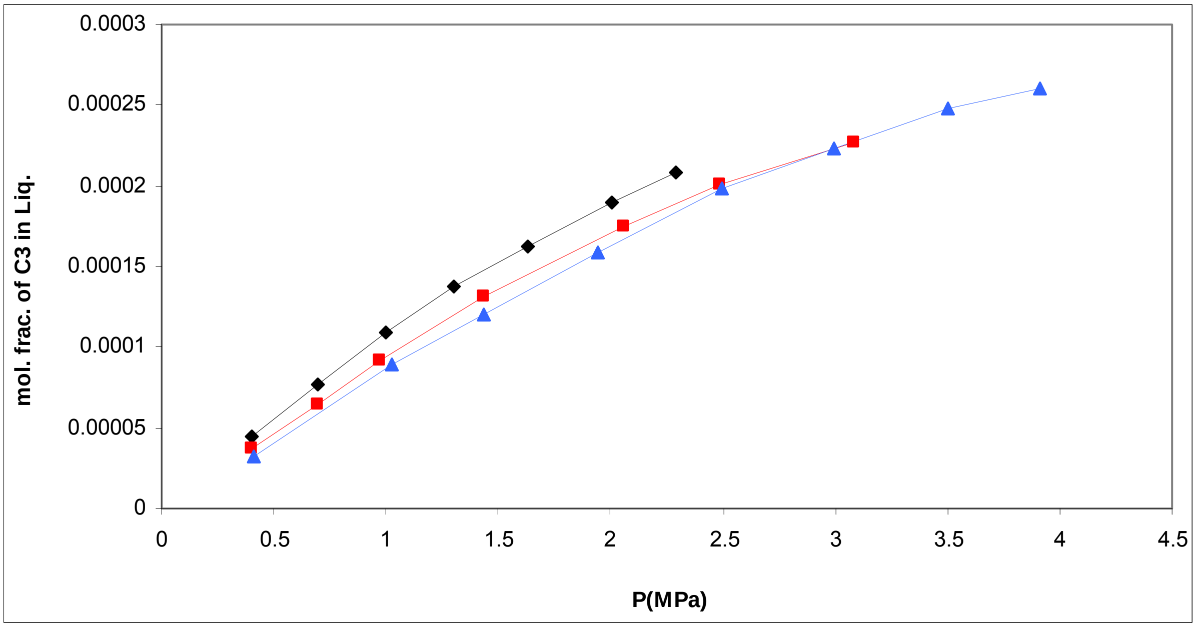

Figure 14. C_3H_8/H_2O: black: experimental (◆) and calculated data @ 338K, red: experimental (■) and calculated data @ 353K, blue: experimental (▲) and calculated data @ 368K

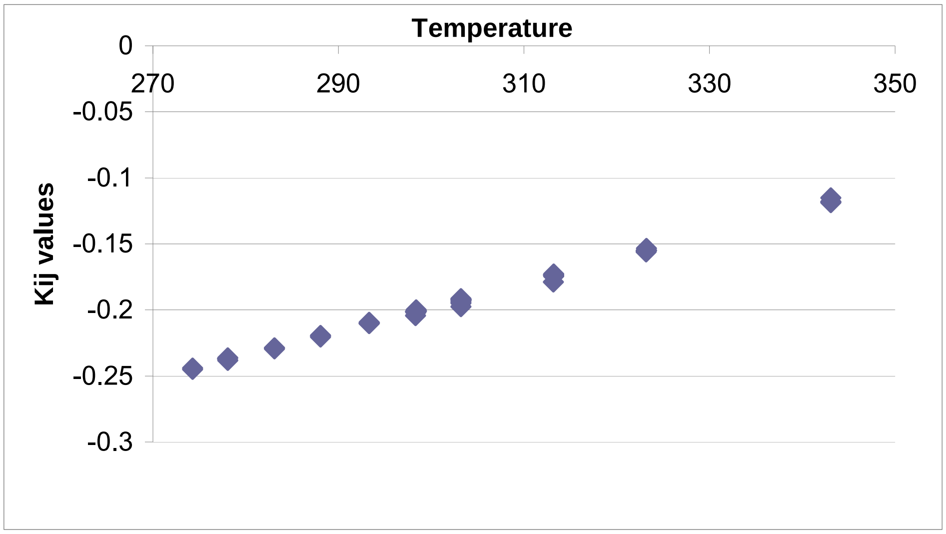

Figure 15. Kij values of H2O-Ethane

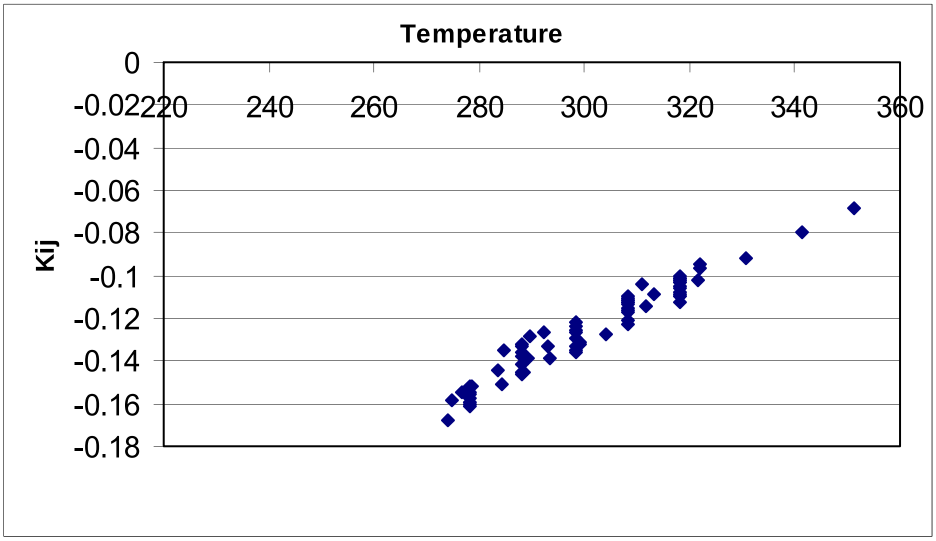

Figure 16. Kij values for H2O-CO2

As mentioned previously, this work is a development of previous works done by Jaubert et. al [1, 74] to make it applicable to GTL process. The binary interaction coefficients between CO2 and Hydrocarbons which is presented in Table 3 is from their work. Addition of water, CO, CO2, H2, Ethylene and other olefins is our contribution in order to provide a tool for thermodynamic studies of GTL process. Table 3 presents the parameter values which are the result of this work. There are some missing data in the table due to different reasons which is described below:

- The vapor-liquid equilibriums of some groups are not in the range of temperatures and pressures which are applicable to our case. For example, the equilibrium data which were found for H2-CH4 are in the range of 103.15-173.65 K and 10-110 MPa for temperature and pressure respectively. In the operational condition under study, these components will be in the supercritical state. CH4-Ethylene, CO-H2, H2-Ethylene and carbon monoxide–methane are other examples.
- It is said that the values of the Kij parameters for the CH4–C2H6, CH4–C2H4, and C2H6–C2H4 are close to zero, which indicates the near athermal character of these mixtures [75]. We have used this assumption to calculate the parameters for the last two pairs due to lack of data.
- Groups C and C= should also be present as two of the groups in the study. However, due to the lack of experimental data, the group contribution is not calculated in some cases. There are very few works which have dealt with the equilibrium of different components with branched hydrocarbons (especially alkenes).

- One other point is that performing the experiments in order to get the VLE data is costly and there is always a reason to do it. So, it’s maybe natural that finding the data is so difficult for every pair of components of interest in different ranges of temperatures and pressures.

Table 3. A and B parameters which are needed to calculate Kij as a function of temperature

	CH3		CH2		CH		C		CH4		C2H6		CO2		H2O	
CH3	0	0														
CH2	74.81	165.7	0	0												
CH	261.5	388.8	51.47	79.61	0	0										
C	396.7	804.3	88.53	315	-305.7	-250.8	0	0								
CH4	33.94	-35	36.72	108.4	145.2	301.6	263.9	531.5	0	0						
C2H6	8.579	-29.51	31.23	84.76	174.3	352.1	333.2	203.8	13.04	6.863	0	0				
CO2	164	269	136.9	254.6	184.3	762.1	287.9	346.2	137.3	194.2	135.5	239.5	0	0		
H2O	559.4083	-204.813	0.0288	-0.8781	0.0114	-0.4669	-915.918	-438.848	124.1	2484	691.2692	-109.009	489.797	-399.749	0	0
H2	317.5348	-67.478	51.18	297.4748	-186.083	72.1725	-	-	-	-			-	-	123.2	60.1
CO	98.0672	-137.8	52.929	398.8686	-	-	-	-	-	-			-	-	241	152.32
Ethylene	0.0476	-0.7808	75.2236	313.1654	186.7467	339.2428	171.5267	313.959	5.8826	9.357	0.0052	0.041	-	-	638.3672	138.8688
CH=	88.5	51.7943	-0.5604	13.8159	348.8818	-7.7501							263.8316	345.7421	322.24	-145.23
CH2=	102.4364	60.9804	0.6879	29.2979	351.8326	-21.2664							-90.845	564.2252	100.32	54.75

			CO		Ethylene		CH=		CH2=	
CH3										
CH2										
CH										
C										
CH4										
C2H6										
CO2										
H2O										
H2	0	0								
CO	-	-	0	0						
Ethylene	-	-	-	-	0	0				
CH=					0.001	0.5949	0	0		
CH2=					66.7801	73.9685	91.6826	7.8722	0	0

Conclusion

In this work the dependency of Kij on temperature has been derived for the pairs of component which are included in the GTL reactor effluents. The calculation of Kij was done was done with the criteria of maximum 1% difference between the experimental and calculated mole fractions, while in the next step the error (the difference between the calculated Kij from the previous step and the current one) is so low.

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