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COMPARISON OF CUBIC-PLUS-ASSOCIATION AND SOAVE-REDLICH-KWONG EQUATIONS OF STATE FOR PREDICTION OF VAPOR-LIQUID EQUILIBRIUM OF FISCHER-TROPSCH REACTION MIXTURE

Article Highlights

- Prediction of vapor-liquid equilibrium (VLE) for Fischer-Tropsch systems was examined
- Soave-Redlich-Kwong (SRK) and Cubic-Plus-Association (CPA) equations of state were used
- CPA was better for prediction of VLE for inorganic components
- Computational time for CPA was significantly longer

Abstract

Predictions of vapor liquid equilibrium for Fischer-Tropsch mixtures were compared using the classical Soave-Redlich-Kwong (SRK) and cubic-plus-association (CPA) equations of state. The performance of the two equations of state was evaluated based on comparison with results from eight sets of experimental runs in which different process conditions (pressure, reactants feed ratio, space velocity) were used. Flash calculations were used to determine the phase split at defined process conditions, whereas the phase equilibrium was defined utilizing the concept of equal fugacities in the vapor and the liquid phase for all components. A total of 75 components were considered in the reaction mixture: CO, H₂, H₂O, CO₂, C₁-C₅₇ paraffins and C₂-C₁₅ olefins. All calculations were performed in MATLAB. The results showed that both equations of state had similar performance regarding the hydrocarbons, whereas CPA gave better results with inorganic components and SRK with prediction of the composition of the liquid phase. Computational time for CPA was substantially (100 times with the CPU used) higher than that for SRK. Overall, the use of CPA did not improve VLE prediction for FTS systems significantly enough to be recommended for use in FTS reactor models.

Keywords: Fischer-Tropsch synthesis, VLE, equation of state, cubic-plus-association, Soave-Redlich-Kwong.

Fischer-Tropsch synthesis (FTS) is a catalytic, exothermal process of converting syngas, a mixture of carbon-monoxide (CO) and hydrogen (H₂), into a range of hydrocarbons (HCs) which can be utilized as clean synthetic fuels or feedstock for the chemical

industry. Several types of reactors, such as multitubular fixed-bed reactors (MTFBR), slurry reactors, fluidized bed reactors, etc., with cobalt (Co) or iron (Fe) based catalysts are employed in industrial facilities for FTS. Typical process conditions for FTS can roughly be defined as high temperature (HTFTS) and low temperature (LTFTS), the former resulting in mostly gaseous products, and the latter in a gas-liquid mixture of HCs. Additionally, inorganic components, such as unreacted CO and H₂, water and carbon dioxide (CO₂), can be present in substantial quantities in the product slate [1,2].

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The presence of a liquid phase can considerably influence performance of an FTS reactor. For example, in slurry reactors the hydrodynamics are influenced by the composition of the liquid phase, while in MTFBRs the liquid mostly influences the diffusion rate inside the catalyst particles (catalyst effectiveness) and heat removal (essential for MTFBR operation) [3]. Therefore, for reactor design and optimization of an FTS reactor performance it is very important to be able to accurately predict the amounts of liquid and gas formed during the process, as well as its composition. Additionally, these predictions depend not only on the description of the vapor-liquid equilibrium (VLE), but also on the prediction of the FTS reaction rates, *i.e.*, product formation rates, as well as other physical phenomena, such as fluid flow and heat and mass transfer. This is well elaborated in the work of Visconti [4], who showed that the selection of the kinetics model and the number of components considered in the FTS mixture can significantly influence the overall prediction of the amounts of gas and liquid formed in an FTS reactor.

Recently, our group has published several papers, dealing with modeling FTS in an MTFBR, in which various aspects of reactor performance were analyzed [5-8]. The results from these investigations, performed with the same type of catalyst used in this study, showed that the formation and presence of liquid inside the reactor can severely influence several factors: diffusion limitations, which can critically influence the catalyst effectiveness and product slate [5]; heat management [6], in which the liquid phase can improve heat transfer characteristics; the overall performance of an MTFBR, which is essential for optimization of the reactor performance [7,8].

The challenges one has to handle within the prediction of VLE for an FTS mixture, are associated with a large number of components (a typical FTS product comprises HCs, paraffins and olefins, with carbon number from 1 to over 100) and the fact that some of the components, mainly H₂O, are capable of forming hydrogen bonds which influence the overall thermodynamic behavior of the reaction mixture. Detailed description of the VLE is generally omitted in the reactor models for FTS reported in the literature, and the reaction mixture is represented usually as a single (gas or pseudo) phase. Depending on the level of details used in the reactor model (1D or 2D, homogeneous or heterogeneous), the existence of the liquid phase is accounted for in heat and/or mass transfer coefficients calculations, *i.e.*, the effective radial heat conduction and effective diffusion through the catalyst pores [9-13].

In the general description of the VLE in the FTS system, cubic equations of state (EOS) were mainly used where some authors opted for Peng-Robinson (PR) [13-17] and others for Soave-Redlich-Kwong (SRK) EOS [18-23]. Additionally, modifications of the two EOSs by using molecular weight of a component, instead of its acentric factor have been proposed, with modified SRK EOS showing better results compared to others, as shown in the study of Karimi *et al.* [22]. However, all of the above-mentioned models can be considered as traditional, not taking into account the potential associative interactions between molecules, *i.e.*, hydrogen bonds.

With the development of numerical tools (software) capable of solving complicated mathematical formulations, the application of more sophisticated ways of representing the VLE in an FTS system is enabled, whereas computational time (the time software needs to complete the task) becomes a potentially important parameter in the overall analysis.

In the presented work, we applied the cubic-plus-association (CPA) EOS, which was specifically developed for systems containing associating compounds in hydrocarbon mixtures, typically found in the oil and gas industry [24-26]. This approach expands on an older SRK method by adding an additional associative term, derived from the statistical associating fluid theory (SAFT), to account for the contribution of hydrogen bonding compounds present in the mixture. Predictions of the CPA method will be compared with those of the classical SRK method, as well as with experimental data obtained in a stirred tank slurry reactor [27].

EXPERIMENTAL

In order to evaluate the possibility of using the CPA EOS for calculations regarding VLE of an FTS system, experiments were performed in the stirred tank slurry reactor with Co-based catalyst at various process conditions shown in Table 1. Detailed description of the apparatus and experimental procedures can be found elsewhere [27]. In short, the liquid phase is pulled from the reactor, collected in the hot trap as liquid wax and subsequently analyzed for composition. The vapor phase mixture is taken from the top of the reactor and passed through the so-called warm and cold traps outside the reactor. The gas from the cold trap was analyzed for composition of the C₁-C₇ paraffins and olefins, while the product from the warm trap consisted of the so-called light wax (C₇₊ paraffins and olefins) and water mixture. The combined results from this analysis represent the

Table 1. Conditions for the eight sets of experimental data [27]

No. Exp.	T , K	P , MPa	FR	SV , NI/(g _{cat} /h)	X_{CO} , %
1	493	1.5	2.10	8.00	45.58
2				6.30	54.63
3				14.00	24.39
4			1.40	5.60	34.17
5			2.10	8.00	41.36
6			1.40	3.60	42.32
7		2.5	2.10	15.00	26.08
8				6.10	56.73

composition of the vapor phase used for subsequent analysis.

A total of 8 sets of process conditions, in which pressure, H₂/CO feed mole ratio (FR) and space velocity (SV) were varied, was analyzed. Different conditions resulted in different CO conversion for each set, thus covering a wide range of possible composition of the reaction mixture. Ranges of values for operating parameters were chosen to match those usually applied in industrial facilities for cobalt based FTS [1,2].

The results from experiments were analyzed to obtain information regarding the phase split of the reaction mixture and composition (components' molar fraction) of both phases. A total of 75 components were identified: inorganic compounds (H₂, H₂O, CO and CO₂), paraffins from C₁ to C₅₇ and olefins from C₂ to C₁₅.

Flash calculation

Determining the composition of the gas and liquid phase of an FTS reaction mixture has been performed using isothermal flash calculation. The objective of this procedure was to obtain information about the total amounts of liquid (L) and vapor (V) in the reaction mixture and components' mole fractions (x_i for liquid and y_i for vapor). For this purpose, the following relations have been used: overall material balance (Eq. (1)), material balance for each component (Eq. (2)), equilibrium constant (Eq. (3)) and fraction of liquid phase (Eq. (4)):

$$F = V + L \quad (1)$$

$$Fz_i = Vy_i + Lx_i \quad (2)$$

$$K_i = y_i / x_i \quad (3)$$

$$x^T = L/F \quad (4)$$

where F is the total amount of the reaction mixture, z_i is the total molar fraction of component i in the mix-

ture, x^T is the fraction of the liquid phase, and K_i is the equilibrium constant for component i .

Combining Eqs. (1)-(4) it is possible to relate mole fraction of a component in the liquid (Eq. (5)) and the vapor (Eq. (6)) phase to the total amount of reaction mixture and the total molar fraction of the respective component:

$$x_i = \frac{z_i}{x^T + K_i(1 - x^T)} \quad (5)$$

$$y_i = \frac{K_i z_i}{x^T + K_i(1 - x^T)} \quad (6)$$

Additional condition used for solving Eqs. (5) and (6) is given by Eq. (7):

$$\sum_{i=1}^n x_i - \sum_{i=1}^n y_i = 0 \quad (7)$$

If the values for total molar fractions, z_i , and equilibrium constants, K_i , are known for all components, the procedure for determining x_i and y_i is:

- assume a value for x^T ,
- calculate x_i and y_i using Eqs. (5) and (6),
- if the condition given by Eq. (7) is not satisfied, assume a new value for x^T .

Thus, for a flash calculation it is necessary to accurately predict/calculate the value of the equilibrium constant, K_i , for each component in the system. Vapor and liquid are in equilibrium if a fugacity of a component in the vapor phase is equal to the fugacity of the same component in the liquid phase (Eq. (8)):

$$f_i^V = f_i^L \quad (8)$$

Additionally, fugacity can be related to the fugacity coefficient (ϕ), according to Eqs. (9) and (10):

$$f_i^V = \phi_i^V y_i P \quad (9)$$

$$f_i^L = \phi_i^L x_i P \quad (10)$$

Combining Eqs. (3) and (8)-(10) results in Eq. (11):

$$K_i = \phi_i^L / \phi_i^V \quad (11)$$

Thus, for calculating the equilibrium constant it is necessary to determine the fugacity coefficient for every component in the mixture, in the vapor and the liquid phase. One way to do this is to use an appropriate EOS. As stated in the *Introduction* section, in this work we will use the SRK and CPA EOSs and compare their capability to predict VLE of the FTS system.

Equations of state

As our work considers VLE for a multicomponent FTS system, parameters of EOSs presented here correspond to a mixture, if not stated otherwise. The classical SRK EOS is given by Eq. (12):

$$Z^{SRK} = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT(V_m + b)} \quad (12)$$

where Z , P , V_m and T are the compressibility factor, pressure, molar volume and temperature of a mixture, and R is the universal gas constant. Parameters a and b are calculated using the classical mixing rules [24]:

$$a = \sum_i \sum_j u_i u_j a_{ij} \quad (13)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (14)$$

$$b = \sum_i u_i b_i \quad (15)$$

where u_i is the molar fraction of the component in the mixture (x_i for liquid and y_i for vapor), k_{ij} is the binary interaction parameter between components i and j , and a_i and b_i parameters are calculated based on critical properties of the components:

$$a_i = (1 + (0.48 + 1.574\omega - 0.176\omega^2(1 - T_{r,i}^{0.5}))^2) \frac{0.42747R^2T_{c,i}^2}{P_{c,i}} \quad (16)$$

$$b_i = \frac{0.08664RT_{c,i}}{P_{c,i}} \quad (17)$$

where ω is the acentric factor, T_c and P_c are the critical temperature and pressure, respectively, and T_r is the reduced temperature ($T_r = T/T_c$).

CPA EOS expands the SRK EOS by introducing a so-called association term, as shown in Eq. (18):

$$Z^{CPA} = Z^{SRK} + Z^{assoc} = \frac{V_m}{V_m - b} - \frac{a}{RT(V_m + b)} - \frac{1}{2} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (18)$$

where ρ is the molar density, g is the radial distribution function, x_i is the mole fraction of the component i in the mixture, and X_{A_i} represents the fraction of sites A on molecule i that do not form bonds with other active sites. Thus, if a mixture does not contain any associating molecules, the CPA EOS is reduced to SRK EOS, as X_{A_i} equals 1 for those species.

The fugacity coefficient of a component in a mixture can be calculated using Eq. (19):

$$\ln \phi_i = \frac{1}{RT} \left(\frac{\partial A^r}{\partial n_i} \right)_{T,V,n_j} - \ln Z \quad (19)$$

where A^r is the residual Helmholtz energy for the mixture. In the case of using the SRK EOS, Eq. (20) is reduced to an explicit form:

$$\ln \phi_i^{SRK} = \frac{b_i}{b} (Z^{SRK} - 1) - \ln(Z^{SRK} - B) + \frac{a}{bRT} \left[\frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}} \right] \ln \frac{Z^{SRK} + B}{Z^{SRK}} \quad (20)$$

This transformation is not possible with CPA EOS, where the residual Helmholtz energy consists of two terms, one of which corresponds to associating molecules:

$$A^r = A_{SRK}^r + A_{assoc}^r \quad (21)$$

A description of all parameters and their calculation, for both EOSs, has been described in details in the literature [24]. It is important to note, that in order to calculate the fugacity coefficient using the CPA EOS, it is necessary to determine the volume of the FT mixture, which, in turn, requires another objective function to be minimized [24]:

$$F(V) = P - \left[\frac{nRT}{V} - \left(\frac{\partial A_{assoc}^r}{\partial V} \right)_{T,n} - \left(\frac{\partial A_{SRK}^r}{\partial V} \right)_{T,n} \right] \quad (22)$$

Therefore, the use of CPA EOS requires additional effort in numerical procedures, compared to the SRK EOS.

Numerical procedure

Flash calculations were performed in MATLAB software using command "fmincon", a function which finds a minimum of a constrained nonlinear multivariable function. This was used to minimize the objective function which combines the mass balance equations

for all the species in the mixture and the difference between fugacities of components in the vapor and in the liquid phase (Eq. (23)):

$$F \left[f_i^V - f_i^L; x_i \cdot x^T + y_i (1 - x^T) - z_i \right] = 0 \quad (23)$$

The algorithm for the CPA EOS calculation is shown in Figure 1.

In general, based on input data, parameters of the SRK EOS are calculated. Then, the association term for the CPA EOS can be calculated by minimizing the so-called volume objective function (Eq. (22), see Figure 1). Finally, the fugacity coefficients are determined by minimizing the overall objective function (CPA_obj_fcn field in Figure 1, *i.e.*, Eq. (23)) and the mole fractions for all components in both phases and the fraction of total liquid are obtained. Calculations for the SRK EOS application are substantially simpler, as there is no additional minimizing function.

The *fmincon* command in MATLAB requires initial guesses for all the optimization parameters. As initial guesses for optimization variables in this problem (mole fraction of all components in the liquid and vapor phase and mole fraction of total liquid phase) we used values from the experimental results, for the conditions depicted in the section Experimental; namely, we used experimental values for total molar fraction for each component and assumed (as initial guesses) a distribution of the total flow rate between the vapor and liquid phase. This procedure was performed for various assumed fractions in order to obtain a global solution. Minimum and maximum constraints set are 0 and 1, respectively.

RESULTS AND DISCUSSION

In this section we will present the results of SRK and CPA EOSs calculations for the prediction of the VLE in the FTS system. Based on the performed calculations, for each set of process conditions, results were analyzed in terms of the fraction of the liquid phase in the reaction mixture, molar fractions for 4 inorganic components in gas and liquid phases, as well as the distribution of different chain length *n*-paraffins and 1-olefins between the phases. Due to practical reasons, we will show results for one set of process conditions, with one graph showing the comparison of selected results for all experiments. However, it is worth noting that the trends are very similar for all experimental and VLE prediction results. Therefore, the presented analysis of the results for the chosen set of process conditions is representative for all other sets as well.

Results of applying the SRK and CPA EOSs for the VLE description of the FTS reaction mixture are shown in Figures 2-8. Figures 2 and 3 show the mole fractions of inorganic components in the vapor phase, obtained using the two EOSs and the corresponding experimental values for all eight sets of experiments. It reveals that inorganic components make up for about 90% of the total molar amount of the vapor phase, for all process conditions considered. Therefore, the prediction of VLE for these components could have a significant influence on the analysis of the FTS reactor performance. Results for CO₂ are not shown for all eight sets of experiments because in all experiments the CO₂ was detected in quantities substantially smaller compared to the other components

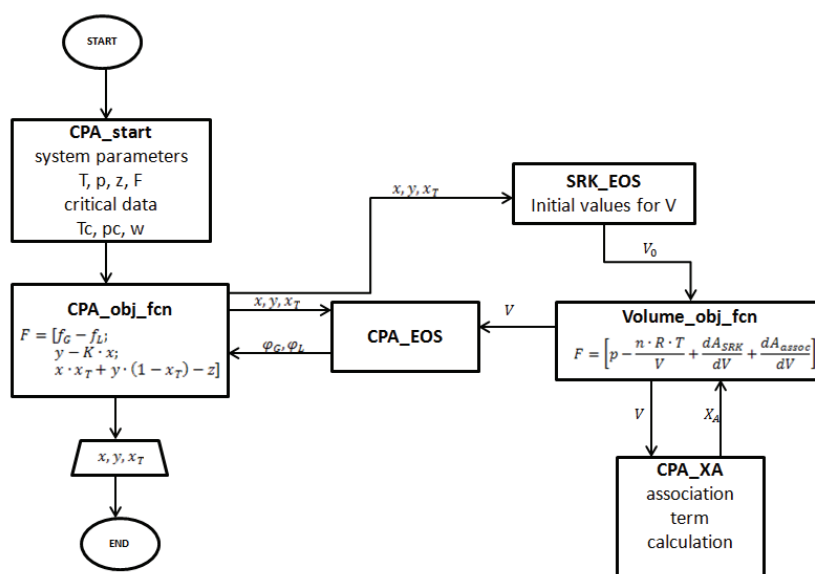


Figure 1. Algorithm for the CPA calculation.

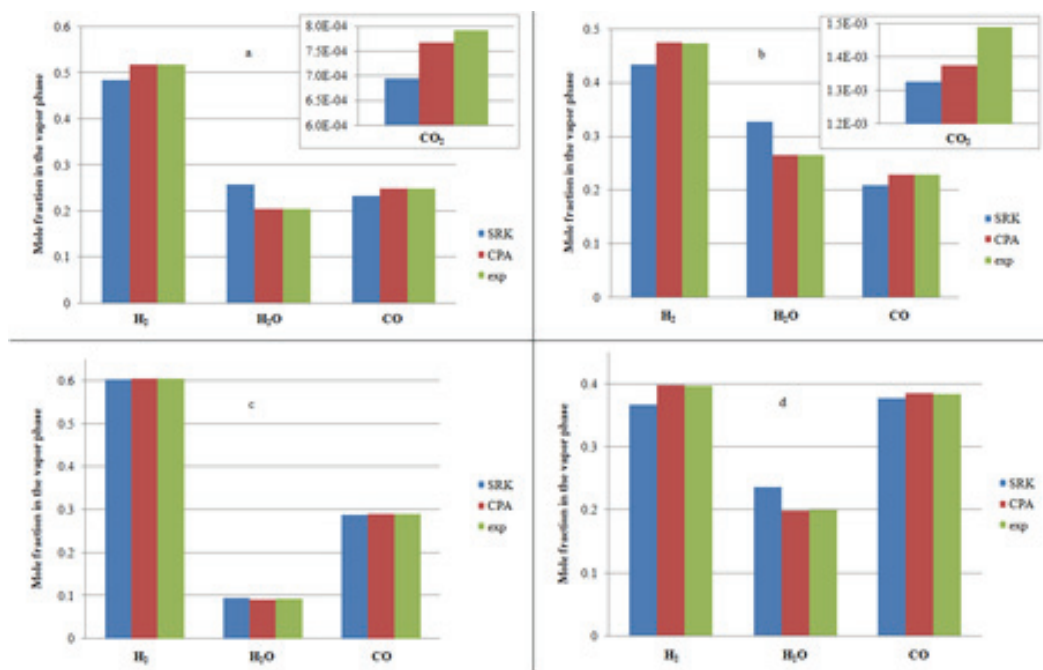


Figure 2. Mole fractions of inorganic components in the vapor phase (a - exp1, b - exp2, c - exp3, d - exp4).

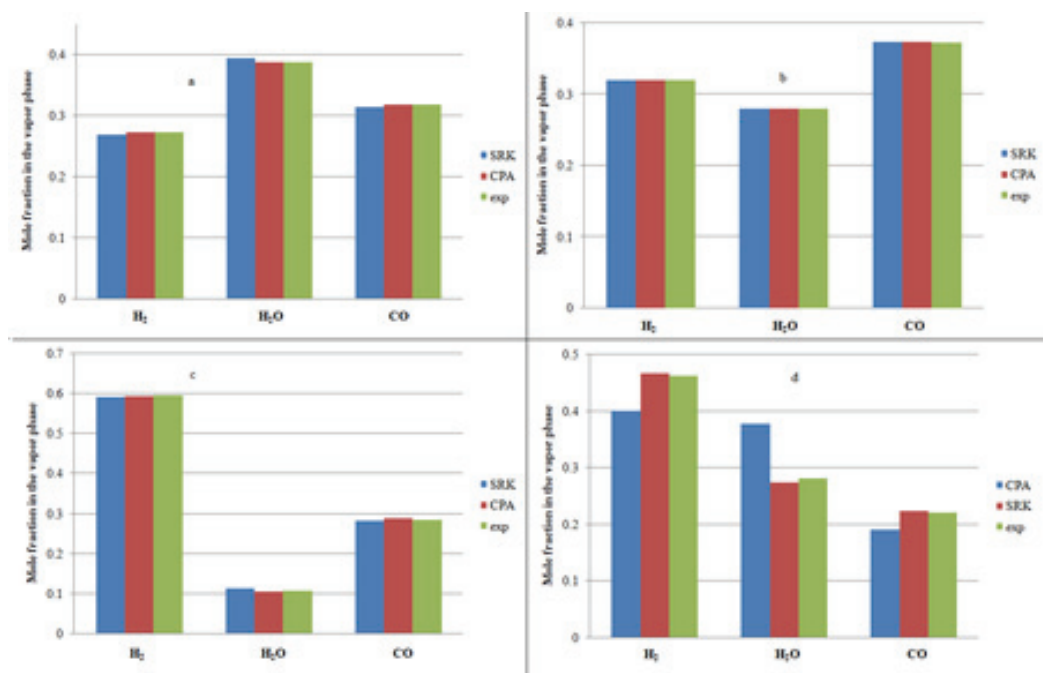


Figure 3. Mole fractions of inorganic components in the vapor phase (a - exp5, b - exp6, c - exp7, d - exp8).

(this is generally the case with Co-based catalysts, because the water-gas shift reaction is suppressed [1,2]). For the purpose of comparison, results obtained for CO₂ for the two sets of process conditions are included in Figure 2.

From the results shown in Figures 2 and 3 it can be deduced that the CPA EOS generally outperforms the SRK, for all inorganic components. These findings are in agreement with previous investigations in which

it was established that the CPA was better than the SRK EOS in prediction of VLE for systems containing water and hydrocarbons [24]. In our case, the standard deviation from experimental points was 0.0288 for SRK and 0.0016 for CPA, for all experimental results.

Figures 4-8 show comparison of simulation results with experimental results obtained at the following process conditions: temperature of 493 K, total

pressure of 1.5 MPa, H₂/CO feed mole ratio of 2.10 and space velocity of 6.30 NI/g_{cat}/h. The CO conversion under these conditions was 54.63%.

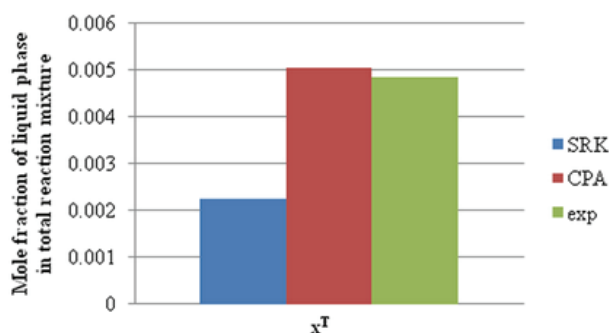


Figure 4. Mole fraction of the liquid phase in the reaction mixture for the selected set of process conditions ($T = 493$ K, $P = 1.5$ MPa, $FR = 2.10$, $SV = 6.30$ NI/g_{cat}/h).

In Figure 4, the results for mole fraction of the liquid phase in the reaction mixture are presented. The total amount of the liquid phase in an FTS system, at process conditions typical for FTS, is much smaller than the total amount of the gas phase (usually, the liquid phase amount is less than 1 mol% of the reaction mixture). On the other hand, the weight fraction of the liquid phase is considerably higher, due to the fact that liquid is consisted of HCs with high molecular weight, which, in turn, can influence the hydrodynamics inside the reactor (through mass flow rate and velocity of the liquid phase). Results presented in Figure 4 reveal that the CPA outperforms the SRK EOS for prediction of the fraction of liquid phase.

Figure 5 shows the results for mole fractions of inorganic components in the liquid phase of the reaction mixture. It should be noted that inorganic compounds were not detected experimentally in the liquid phase, and thus, experimental values in Figure 5 are not present.

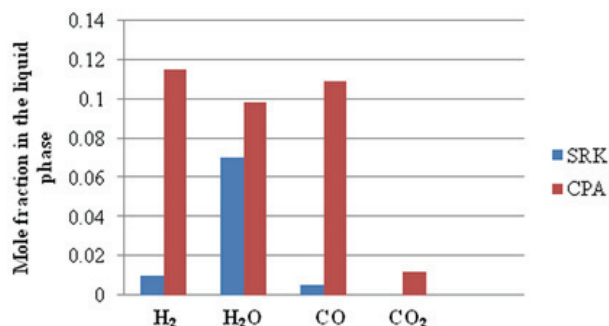


Figure 5. Mole fractions of inorganic components in the liquid phase for the selected set of process conditions ($T = 493$ K, $P = 1.5$ MPa, $FR = 2.10$, $SV = 6.30$ NI/g_{cat}/h).

Calculated values of molar fractions of inorganic compounds in the liquid phase are not equal to zero for both EOSs used, whereas the CPA predicts considerably higher values of inorganic components fractions, compared to the SRK. Nevertheless, the total amount of liquid phase is less than 1 mol%, so the calculated values, even if not accurately predicted, have a small influence on the overall modeling of FTS reactors.

In Figures 6 and 7 the results for *n*-paraffins, *i.e.*, their fractions in the liquid and vapor phase are shown, respectively. Results show that lighter paraffins (with less than 16 carbon atoms) in the liquid phase (Figure 6) and higher paraffins (with more than 25 carbon atoms) in the vapor phase (Figure 7) were experimentally not detected. According to the experimental results, mole fractions of paraffins in the liquid phase are increasing from C₁₆ to about C₂₀ (Figure 6), after which they decrease due to the characteristics of the FTS product distribution (*i.e.*, logarithmically decreasing total mole fraction with increasing chain length) [1]. This trend is also observed for the SRK calculations.

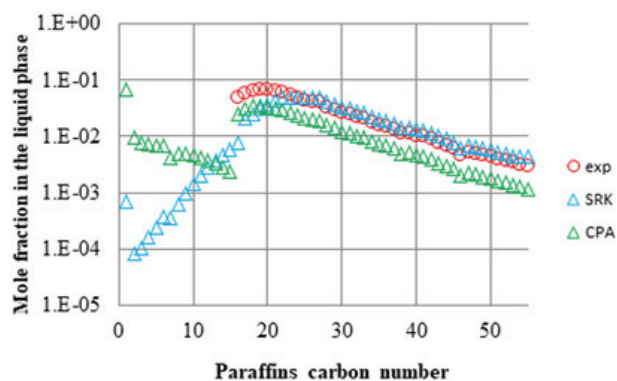


Figure 6. Mole fractions of paraffins in the liquid phase for the selected set of process conditions ($T = 493$ K, $P = 1.5$ MPa, $FR = 2.10$, $SV = 6.30$ NI/g_{cat}/h).

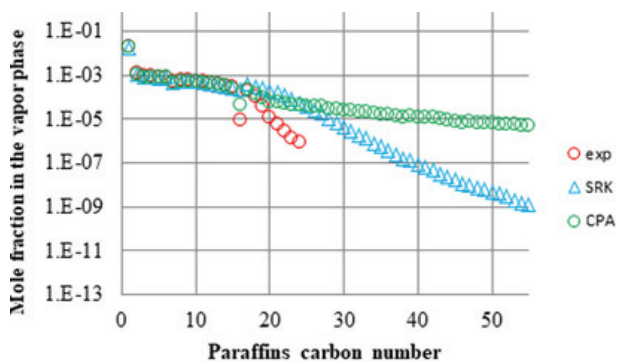


Figure 7. Mole fractions of paraffins in the vapor phase for the selected set of process conditions ($T = 493$ K, $P = 1.5$ MPa, $FR = 2.10$, $SV = 6.30$ NI/g_{cat}/h).

Agreement between experimental data and calculated values of mole fractions in the liquid phase (Figure 6) is better for the paraffin components with more than 20 carbon atoms. Furthermore, Figure 6 shows that SRK predicts the fraction of C_{20+} paraffins in the liquid phase slightly better than CPA EOS, when compared to the experimental results. CPA slightly underestimates the fraction of paraffins, although the position of maximum, around C_{19} is more accurately predicted than by SRK. Moreover, CPA predicts an unusual discontinuity in prediction of paraffins fractions, around C_{15} (see Figure 6). However, these fractions (C_1 - C_{17}) are very small and, as presented in the section Experimental, unaccounted for experimentally. Overall, the standard deviation from experimental points was 0.0118 for SRK and 0.0141 for CPA, regarding composition of the liquid phase for all experiments.

In the vapor phase (Figure 7), experimental results show a sharp decline in molar fractions for paraffins with more than 20 carbon atoms. For the prediction of paraffins' fractions in the vapor phase, the match between both EOSs and experiments are very good for HCs with up to 17 carbon atoms. However, both calculation methods fail to predict a steeper decline in mole fractions in the vapor phase for C_{20+} fraction of HCs, which is observed experimentally. Again, these fractions are very small and the discrepancy can be attributed to the accuracy of numerical methods. Regarding all experimentally detected components in the vapor phase, the standard deviation was $2.2e-4$ and $8.14e-6$ for SRK and CPA EOS, respectively.

Prediction of olefins' fractions in the vapor phase is presented in Figure 8. Olefins in the liquid phase were not analyzed because the typical FTS product slate is such that the amount of olefins decreases rapidly with chain length. Therefore, under typical FTS conditions for Co-based catalysts, they are present only in the gas phase. Thus, all of the olefins considered in this study were experimentally determined in the vapor phase, as can be seen in Figure 8. The agreement between calculated and experimental results for olefins in the vapor phase is good for both EOS (SRK and CPA), with somewhat better agreement achieved with CPA (standard deviation was $6.56e-6$ compared to $3.85e-5$ for SRK EOS).

From the results depicted in Figures 6 and 7 it can be deduced that for both SRK and CPA EOS methods predictions of mole fractions for paraffins are fair, although not reliable for those HCs that were not experimentally measured. Additionally, Figures 6 and 7 demonstrate that the CPA EOS gave somewhat

worse predictions than the SRK EOS. On the other hand, for olefins in the gas phase, the predictions are in a very good agreement with experiments, for both VLE methods (Figure 8).

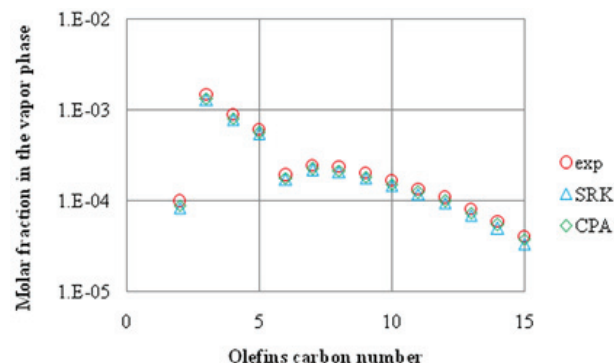


Figure 8. Mole fractions of olefins in the vapor phase for the selected set of process conditions ($T = 493$ K, $P = 1.5$ MPa, $FR = 2.10$, $SV = 6.30$ $Nl/g_{cat}/h$).

The result of predictions for components that were not experimentally measured is not directly related to the EOSs used but is a consequence of the conditions that need to be mathematically fulfilled in order for the software to be able to find a solution. As we stated in the section Experimental, the objective function that needs to be minimized comprises the difference between the fugacities in the vapor and liquid phase, for all components (Eq. (23)). Most of the components considered in this study were experimentally determined in only one phase, either vapor (lower molecular weight HCs and inorganic components) or liquid (higher molecular weight HCs). Since MATLAB uses experimentally determined values as initial guesses in its calculations, this leads to a situation in which the starting difference between the fugacities in both phases is for some components significantly larger than for others. For a highly nonlinear system with 75 components, this results in the software having a number of difficulties in minimizing the objective function, which results in physically unsound results in some cases, *i.e.*, the trends for low molecular weight HCs in the liquid (Figure 6) and for high molecular weight HCs in the vapor phase (Figure 7) compared to experimental results.

Finally, the last aspect we considered in this analysis is the computational time for both calculation methods, *i.e.*, the time needed to solve the problem defined by the objective function. This aspect is important as it directly affects the time necessary to obtain results in a simulation of a whole reactor. The computational time for CPA was significantly higher than for the SRK EOS. With i7-4790 CPU @3.60

GHZ, the computational time is around 100 times longer for the CPA method (0.600 s for SRK compared to 60.742 for CPA). An additional (internal) objective function for volume calculation, as well as additional calculations (associative term) within the CPA EOS (see algorithm in Figure 1) result in significantly longer computational time compared to the SRK method.

CONCLUSIONS

We compared the performances of SRK and CPA EOS for the prediction of VLE of an FTS reaction mixture. CPA provided better results regarding inorganic components in the vapor phase, while both EOSs provided qualitatively similar trends for HCs that were determined experimentally. Fairly good results were obtained for HCs present in larger quantities in one of the phases of the reaction mixture, while the results related to HCs that were not experimentally detected were relatively poor for both EOSs. The reason for this was related to minimization of the defined objective function for a system of 75 components with very different values of molar fractions in two phases which were used as initial guesses in the procedure. The prediction of the molar fractions of olefins was satisfactory for both of the EOSs used, while SRK predictions of paraffins' fraction in the liquid phase were in better agreement with experiments, than those obtained using the CPA EOS.

Although CPA gave better results for inorganic components, it did not improve the VLE prediction of the entire product spectrum. Additionally, computational time for CPA was about 100 times longer than that for SRK, which represents a significant drawback for modeling and simulation of an FTS reactor.

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NAUČNI RAD

POREĐENJE CPA (CUBIC-PLUS-ASSOCIATION) I SRK (SOAVE-REDLICH-KWONG) JEDNAČINA STANJA ZA PREDVIĐANJE RAVNOTEŽE GAS-TEČNO REAKCIONE SMEŠE U FISCHER-TROPSCH SINTEZI

Predviđanje ravnoteže gas-tečno za reakcionu smešu u Fischer-Tropsch sintezi izvršeno je korišćenjem klasične SRK (Soave-Redlich-Kwong) i CPA (Cubic-Plus-Association) jednačine stanja. Rezultati predviđanja analizirani su na osnovu poređenja sa rezultatima eksperimenata u kojima su varirani (kao procesni parametri) pritisak, molski odnos reaktanata i protok. Proračun jednostepenog (flash) razdvajanja je korišćen za određivanje sastava faza, dok je ravnoteža faza definisana pomoću koncepta jednakih fugaciteta u obe faze, za svaku komponentu. Razmatrano je ukupno 75 komponenti sistema: CO, H₂, H₂O, CO₂, C₁-C₅₇ parafini i C₂-C₁₅ olefini. Svi proračuni su urađeni u MATLAB programu. Rezultati su pokazali da dve jednačine stanja daju slična predviđanja raspodele između faza za ugljovodonike, dok se CPA pokazala kao bolja za neorganske komponente, a SRK za predviđanje sastava tečne faze. Proračun u MATLAB je u slučaju CPA jednačine stanje trajao znatno duže (oko 100 puta) u odnosu na proračun sa SRK jednačinom stanja. Zaključak ispitivanja je da korišćenje CPA jednačine stanja kvalitativno ne doprinosi poboljšanju predviđanja ravnoteže gas-tečno u smešama Fischer-Tropsch sinteze u meri koja bi je preporučila za korišćenje u modelima reaktora.

Ključne reči: Fisher-Tropsch sinteza, ravnoteža gas-tečno, jednačine stanja, CPA, SRK.