

## Reliable Nonlinear Parameter Estimation in Predicting the Activity Coefficients for Complex Hydrocarbon Mixtures

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### Abstract

In conventional coke-oven gas scrubbing processes, the recovery of volatile organic compounds (VOC) is carried out in absorption units in which complex mixtures of high boiling polyaromatic components are used as absorbents (coal tar oils ~ washing oil). Due to the number of components (here 400 up to 500), which are similar in their molecular weight and structure, and the lack of data describing the interactions of VOCs in this mixture, the determination of activity coefficients at infinite dilution and Henry coefficients, respectively, is an essential basic for process calculations. To overcome this problem, in this work, a stochastic search method is combined with a Quasi-Newton approach in order to estimate the UNIFAC parameters which describe the interactions between the washing oil (regarded as one type of pseudo-component) and the light aromatic compounds. For this purpose, experimental studies were also carried out.

### Keywords

Activity coefficients, Pseudo-Components, Stochastic Search Approach, SQP

## 1. Introduction

The recovery of aromatic hydrocarbons from coke-oven gases (Fig. 1) is one of several process units which are located on the “White Side” of the coke oven plant in order to reduce the amount of harmful as well as toxic components and to recover valuable chemicals which can be sold to the chemical industry. For the regarded process a mixture of high boiling, polyaromatic hydrocarbons is used as washing oil which is specified at least of 400 to 500 different components.

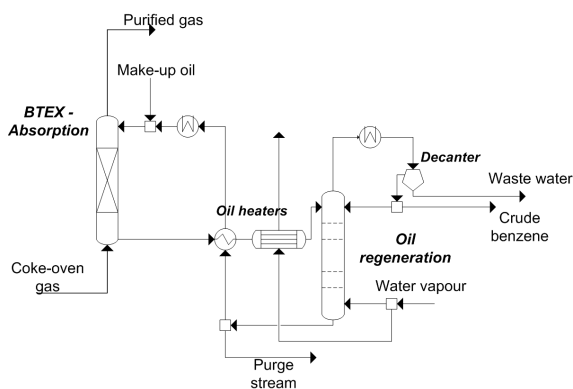


Fig. 1 General flow sheet of BTX recovery process.

Due to the fact that only a minimum of these components can be identified by gas chromatographic analysis and also because of the great number of different components the application of mixing rules in order to determine the thermodynamical behavior of this mixture fails completely. Therefore, experimental studies were conducted in

order to compare the results obtained with different predictive models based on mixing rules and the normalized known composition, which sums up to 55% of the whole mixture. The comparison has shown that great deviation between the measurements and the predictive results arise with regard to all investigated properties, namely, the mixture density, viscosity, heat capacity and especially the phase equilibrium behavior of the VOC components as well as the solubility of overcritical components in the washing oil. Furthermore, it can also be observed that calculations carried out by the commercial simulation software ChemCAD are too inaccurate for a general process description.

## 2. Problem statement

In process operation planning, it is necessary to match a set of target criteria performance, usually through process simulation. Thus, in many cases the process model has to be as accurate as possible. However, due to the fact that the thermo-dynamical calculations, which are one of the most important calculations in the case of mass transfer operations, are too inaccurate any model-based process optimization fails because of great deviations occurring by changes in the state variables. Previous investigations have shown that by the

use of internal units offered by e.g. ChemCAD, the calculations are not able to predict the process behavior accurately. Based on these studies the most essential thermo-dynamical properties were determined in conducted experiments and compared to those results obtained by the process simulation software.

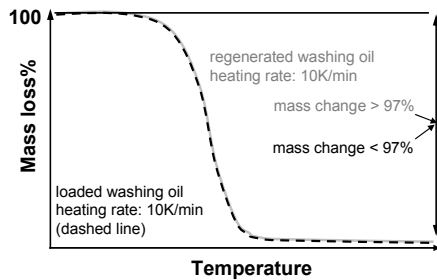


Fig. 2 Distillation curves regenerated and loaded washing oil.

These comparisons have clarified that the properties of the investigated mixture have to be adjusted, which can be realized for instance by the introduction of one or more pseudo components. In the case of the phase equilibrium behavior, the computational effort can be reduced significantly by the introduction of only one pseudo component which represents the whole composition justified by slightly changes in the composition and, therefore, in the thermo-dynamical properties. This issue can be seen, for example, in Fig. 2 which illustrates the distillation curves of the loaded and regenerated washing oil over a wide temperature range and based on the fact that during the stripping process, which is taking place at high temperatures, the greatest changes arise in the composition.

One of the main problems regarding the parameter estimation is caused by the deviation of the measurements, which is the result of the complexity of the mixture, the low vapor pressures and especially the low molar fractions that has to be investigated in order to determinate the activity coefficients at infinite dilution and the Henry coefficients, respectively.

### 3. Solution approach

The aim of this work is concerned with the parameter determination of the UNIFAC model for the calculation of the interaction parameters between the absorbed components and the washing oil components. In order to be able to find the global minimum for several pairs of parameters, a stochastic search approach, namely, the particle swarm optimization method PSO has been applied. It should be noted that a nonlinear expression with multiple local solutions [1] can be found in general (see Eqs. 1-3).

$$\gamma_i = \gamma_i^{comb} \cdot \gamma_i^{res} \quad (1)$$

where  $\gamma_i^{res}$  is the residual part which describes the interaction forces between the functional groups and the temperature dependency of the activity coefficients. It can be obtained by using Eqs. 2 and 3.

$$\gamma_i^{res} = f(x_k, Q_n, v_n, \psi_{nm}) \quad (2)$$

$$\psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm} \cdot T + c_{nm} \cdot T^2}{T}\right) \quad (3)$$

Furthermore, for the pseudo component only one functional group is used as reference. Because of the arbitrary choice of the molecular structure of the washing-oil-pseudo-component only four pairs of parameters are to be fitted concerning the interactions between the washing-oil-pseudo- component and the aromatic bounded C-H group, as well as the aromatic bounded methyl-group. The parameters to be fitted are the UNIFAC group interaction parameters ( $a_{nm}$ ,  $b_{nm}$  and  $c_{nm}$ ) in Eq. 3, which are then used to obtain the temperature dependent residual part  $\gamma_i^{res}$  of the activity coefficient. For functional groups of the aromatic hydrocarbons ACH and ACCH3, several works has been published in the open literature [1], however, the pseudo component group of parameters are fitted in this work. Thus, the choice of the combinatorial parameters, used for solving Eq. (1), is assumed arbitrarily since all deviations are covered by the residual part.

### 3.1. Particle swarm optimization

The particle swarm optimization has many advantages over other stochastic techniques such as it can be easily implemented and has a great capability of escaping local optimal solution [2,4]. The PSO algorithm works with a population formed by a certain number of particles (i), which search for a global minimum through the desired space of n dimensions. The motion of each particle is ruled by his vector. The size and direction of this vector depend on three facts, the previous velocity, the best position that the particle has found and the best position that the complete population has found following the function

$$v_i(t+1) = v_i(t) \cdot w + c_1(x_i(best) - x_i(t)) + c_2(x_{globbest} - x_i(t)) \quad (4)$$

Where  $v_i$  is the velocity vector, t the number of iteration, w the weight of the particles velocity,  $x_i(best)$  is the best position of each particle and  $x_{globbest}$  is the best position of the hole population. The new position  $x_i(t+1)$  is determined by adding the former position with the actual vector. Parameter  $c_1$  and  $c_2$  change the influence of the particle's best position and the population's best position respectively. An optimization with a big  $x_i(best)$ -influence will take a big number

of iterations to convert. On the other hand, if  $c_2$  is much greater than  $c_1$  the population will easily be trapped in a local minimum. The position of each particle in the next iteration is obtained with a simple equation.

$$x_i(t+1) = x_i(t) + v_i(t+1) \quad (5)$$

Each particle is again evaluated to compare them with the previous  $x_i(\text{best})$  and  $x_{\text{globest}}$  and a new velocity vector is calculated so the particle can continue its search (Fig. 3). These steps are followed until all particles reach the best minimum that the population has found or until a goal value is reached.

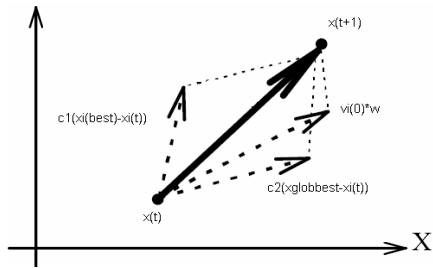


Figure 3. Calculation of  $v_i(t+1)$  and  $x(t+1)$ .

#### 4. Numerical results

The result of the optimization is a new estimated residual part of the activity coefficient which permits the pseudo molecule to feature the equivalent interaction with Benzene, Toluene (which depends on the pseudo component-ACH and the pseudo component-ACCH3 interactions) in the same way the washing oil does. Furthermore, the calculations have shown that the fitted parameters match also the measurements concerning m-Xylene, which is slightly different in its structure than toluene because of one additional methyl-group, thus, validating the results obtained by the optimization approach. Another advantage of the parameter estimation is that the dependence of the activity coefficient with respect to the temperature is also considered by fitting these in a temperature range between 300 and 340K. The results for the measurements of the activity coefficients at infinite dilution of benzene, toluene and meta-xylene can be found in [3]. Fig. 4 and Fig. 5 illustrates the comparison between the measured and predicted activity coefficients at low molar fractions between 0.3 and 2.0 mole-% of the BTX species depending on the temperature after parameter fitting. The optimized parameters a, b and c are also listed in table 1. The combinatorial parameters are chosen as:  $Q = 2.4561$  and  $R = 1.7334$ . In Fig. 5 the deviation caused by the measurements is shown. This deviation becomes even higher for lower vapor pressures.

Table 1. Interaction parameters of functional groups of BTX with pseudo component group (j)

Functional group (i)	a(ij)	a(ji)	b(ij)	b(ji)	c(ij)	c(ji)
ACH	25.2984	73.7451	-0.3132	0.1122	0.0	0.0
AC-CH3	67.227	217.5	-0.55337	0.10786	0.0	0.0

The comparison between the measured and the calculated activity coefficients is showing a good agreement regarding the average values of the measurements. In total a number of 56 measurements for the determination of ACH as well as 62 measurements for the ACCH3 group interactions are used for the determination of the parameters. For this purpose, seven different temperature levels are taken as basis.

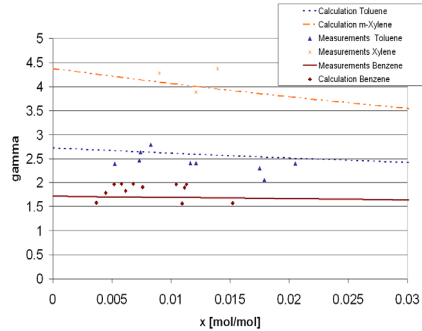


Fig. 4 Comparison between measured and predicted activity coefficients at T = 303.15K.

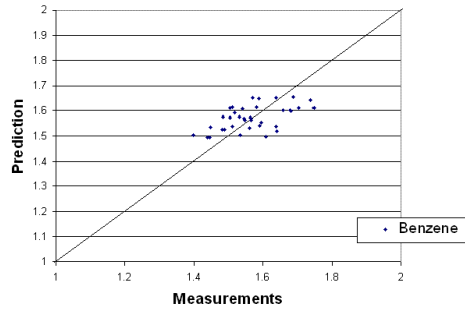


Fig. 5 Deviation of measurements for benzene.

## 5. Conclusions

In this work, essential parameters for the calculation of the phase equilibrium behavior of certain BTX components in a complex hydrocarbon mixture were determined. Based on these results the Henry coefficients as well as the modified activity coefficients are calculated depending on the concentration of the BTX fractions as well as on the temperature. By the application of the determined parameters more accurate mass transfer and equilibrium calculations can be achieved and thus also the whole process can be calculated accurately. Further investigations are carried out with regard to the entire process towards process modeling and optimization.

## References

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