# The influence of non-ideal vapor–liquid equilibrium on the evaporation of ethanol/iso-octane droplets

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ABSTRACT

The present work investigates the differences between ideal and non-ideal vapor–liquid equilibria (VLE) and their effect on vaporization for multicomponent hydrocarbon fuels, which are representative for combustion and gasification. For this purpose, a parametric study is performed for examining non-ideal VLE behavior within a pressure range from 0.5 to 20.0 bar and an ambient temperature range from 0 °C to 600 °C, which are typical vaporization conditions in technical systems. The VLE results are then applied in a 0D single-droplet evaporation model, which can be considered a base model for most CFD applications. The droplet life time and the evaporation rates of the individual liquid components are studied for ideal and non-ideal VLE by varying the pressure, the temperature and the particle Reynolds number. A detailed analysis of the transient processes is performed in binary and ternary diagrams and a separation factor is introduced as a quantitative means of measuring for the effective relative volatility of the species. The observed differences suggest that non-ideal VLE have a significant impact on the droplet evaporation characteristics for complex hydrocarbon mixtures.

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## 1. Introduction

The vaporization of fuels is an important process in many practical devices such as engines, furnaces and gasifiers, influencing the mixture formation and subsequent processes such as burning, gasification or pollutant formation. The accuracy of the droplet evaporation modeling effects all the subsequent steps significantly. In spray simulations the droplet evaporation model strongly influences the liquid and vapor penetration length and the species profile in the gas phase.

The fuel considered here is a mixture of iso-octane and ethanol. Iso-octane was chosen as a surrogate for gasoline and was mixed with ethanol with varying mixture ratios, in order to model common ethanol/gasoline mixtures. Abbreviations such as E85 refer to an ethanol fuel blend of 85 vol% ethanol and 15 vol% iso-octane. Iso-octane with 10 vol% ethanol would thus be called E10, which is a fairly common fuel nowadays. Recently, there has been increasing interest in the study of ethanol blends, as is indicated by the work of several authors [1–3].

The evaporation of a droplet is dominated by the phase change of the components at the surface of the droplet. The relation between the liquid droplet phase and the surrounding vapor phase is known as the vapor–liquid equilibrium (VLE). The VLE model has the main impact on the calculated evaporation rate. The present work focuses on a description of VLE modeling, especially on comparing an ideal and a non-ideal VLE model. Typical phenomena for multicomponent droplet evaporation are discussed in [4–6], which also discuss general conservation equations.

In general real fuels consist of a large number of species. In order to take into account the impact of the individual components on the VLE and hence on the evaporation, it is important to model the multicomponent thermodynamics accurately.

Therefore, in the present work ideal and non-ideal VLE models are compared. Non-ideal VLE for mixtures is a classical topic of multicomponent thermodynamics, and is essential in all fluid separation technologies, e.g. in petrol chemistry or gas treatment processes. In practice there are significant differences caused by non-ideal behavior compared to the ideal assumptions. An illustrative example is the mixture of ethanol and water that forms an azeotrope, which can not be depicted using ideal VLE approaches. A comparison between ideal and non-ideal model assumptions for the liquid phase during the droplet evaporation of ethanol and acetone mixtures is given in [1], where a simplified model for a bi-component mixture is used. The same non-ideal VLE model is applied in [2] for a droplet with an ethanol/acetone mixture in air. A multicomponent droplet evaporation model including non-ideal thermodynamics is investigated in [7]. A comparison of experimental and theoretical droplet evaporation with an ethanol/acetone mixture is given in [8] by applying the model from [7].

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The modeling approaches for the thermodynamics of multicomponent mixtures can be classified into two main categories. The first category uses continuous thermodynamics or distillation curve models, where individual components are lumped together. That model is suitable to describe a large number of components. The second category is the discrete component modeling approach, which is limited in the number of components due to computational aspects, but is in principle capable of modeling multicomponent thermodynamics more precisely.

A couple of relevant examples for the first group are discussed in the following. Burger et al. [9] described multicomponent fuel vaporization mixtures with a single progress variable, which is the molar weight. This approach can be used with non-ideal thermodynamics. Non-ideal vapor–liquid equilibrium properties of gasoline-ethanol fuel blends are analyzed with an empirical gasoline/ethanol flash model and with the software Aspen Plus up to high temperatures in [10]. The evaporation of 100 µm oil droplets is studied in pure nitrogen with continuous thermodynamics in [11] and specifically for bio-oil droplets in [3]. A multicomponent droplet model is developed for heating and evaporation applying pseudo-components with abstract properties for diesel fuels [12] and additionally for gasoline fuels [13].

For the second category with VLE considering discrete components, the models can be divided into the ideal approach, applying what is known as Raoult's Law, and non-ideal approaches. Saha et al. [14] studied a spherical bi-component droplet as a one-dimensional transient problem with an ideal VLE approach. Multicomponent droplet evaporation of n-decane/3-pentanone mixtures at atmospheric pressure is also studied by Sazhin et al. [15] with an ideal VLE approach. A comprehensive review of advanced models is given in [16], where both the droplet heating and the vaporization are described. In the present work the VLE is modeled with discrete components applying both ideal and non-ideal approaches and comparing them with one other. Brenn et al. [17] investigated multicomponent droplet evaporation considering non-ideal vapor–liquid equilibria, where the liquid activity coefficients are described by Wilson coefficients for binary mixtures and for more components (in their work up to five) the UNIFAC method is chosen. In this work, the analysis of multicomponent droplet evaporation is extended to strongly non-ideal mixtures forming azeotropes and wider ranges of temperatures, pressures and initial compositions are investigated. Furthermore, we specifically aim at defining measures such as the separation factor for such strongly non-ideal mixtures.

The thermodynamics at the surface must be coupled with the droplet model. In the present work a 0D droplet is applied as a base model using a similar approach as that reported in a number of studies in the literature for multicomponent mixtures [17–23].

In Section 2 the applied non-ideal VLE model is described and the separation factor is introduced. The connection to the single-droplet model with evaporation is illustrated in Fig. 1. The impact of the initial composition and the ambient properties (temperature, pressure and Reynolds number) are discussed in Section 3. Conclusions regarding the differences between ideal and non-ideal VLE assumptions in droplet evaporation models are given in Section 4.

## 2. Numerical model formulation

The numerical modeling can be divided into two parts. The first part deals with a description of the non-ideal VLE determining the correction factors that account for the non-ideal thermodynamic equilibrium of liquid and gas mixtures. The second part includes a the zero-dimensional description of evaporating droplets accounting for non-ideal VLE and convection.

### 2.1. Vapor–liquid equilibrium

The following describes how the VLE is defined and how it can be determined for multicomponent mixtures. Gibbs' phase rule states that the vapor and liquid are in a state of equilibrium if the pressures of both phases are equal. In order to describe the non-ideal behavior, the pressure of species or mixtures is replaced in the Gibbs–Duhem equation by a corrected pressure, the so-called fugacity $f$. The non-ideal VLE is achieved if the fugacity of the vapor $f_{i,v}$ is equal to the fugacity of the liquid phase $f_{i,l}$ for each component

$$f_{i,l} = f_{i,v}. \tag{1}$$

In general, the two approaches (in addition to the ideal approach) to determine the fugacities are equations-of-state (EoS) models and excess Gibbs energy ($G^E$) models [5]. A typical EoS model is the Redlich-Kwong-Soave–Wong-Sandler (RKSWS) model. Commonly used $G^E$ models are the non-random two liquids (NRTL) model and the universal quasi-chemical functional group activity coefficients (UNIFAC) model. In the present work, the NRTL model is used as a representative of the $G^E$ models, to describe the non-ideal VLE. Other VLE models are possible and an overview of the $G^E$ models is given in [24]. A comparison between different non-ideal VLE models is not attempted here, whereas the present work focuses on the different effects of ideal and non-ideal VLE on droplet evaporation. The fugacity of the vapor phase is defined in Eq. (2), where $x_{i,v}$ is the mole fraction of the vapor of component $i$, $\varphi_{i,v}$ is the fugacity coefficient of the vapor species, $p$ the system pressure and $p_i$ the partial pressure of component $i$, respectively.

$$f_{i,v} = \varphi_{i,v} p_i = x_{i,v} \varphi_{i,v} p. \tag{2}$$

The fugacity of the liquid phase is described by activity $a$ and a standard fugacity $f^+$, which has a freely selectable reference state (Eq. (3)). The activity of the liquid phase is determined by the mole fractions of the liquid components $x_{i,l}$ and the activity coefficients $\gamma_i$. Usually, the fugacity of the pure component at saturation state is selected. Therefore, the vapor pressures $p_i^0$ can be used together with the Poynting corrections $\kappa_i$, describing the pressure dependency of the fugacity.

$$f_{i,l} = a_i f_i^+ = \gamma_i x_{i,l} f_i^+ = \gamma_i x_{i,l} f_i^0 = \gamma_i x_{i,l} \varphi_i^0 p_i^0 \exp\left(\int_{p_i^0}^{p} \frac{v_i^0}{RT} dp\right)$$
$$= \gamma_i x_{i,l} \varphi_i^0 p_i^0 \kappa_i^0. \tag{3}$$

In order to determine the vapor fraction in the vapor–liquid equilibrium, Eqs. (2) and (3) are inserted into Eq. (1) and result in

$$x_{i,v} = \frac{\gamma_i x_{i,l} f_i^0}{\varphi_{i,v} p} = \frac{\gamma_i x_{i,l} p_i^0 \varphi_i^0 \exp\left(\int_{p_i^0}^{p} \frac{v_{i,l}^0}{RT} dp\right)}{\varphi_{i,v} p} = \frac{\gamma_i x_{i,l} p_i^0}{p} \frac{\varphi_i^0}{\varphi_{i,v}} \kappa_i^0. \tag{4}$$

This equation has the same structure as Raoult's Law but contains the correction coefficients $\gamma_i$, $\varphi_{i,v}$, $\varphi_i^0$ and $\kappa_i^0$, which are discussed in more detail below. The Poynting correction can be calculated by

$$\kappa_i^0 = \exp\left(\frac{\tilde{v}_{i,l}^0}{RT}(p - p_i^0)\right), \tag{5}$$

where $\tilde{v}_{i,l}^0$ is the molar volume of the liquid components, $T$ the temperature and $R$ the universal gas constant. The fugacity coefficients of the vapor at system pressure and saturation state are calculated using

$$\varphi_i^v = \exp\left(\frac{p}{RT}\left(2\sum_j B_{ij} x_{j,v} - \tilde{B}\right)\right) \quad \text{and} \tag{6}$$

$$\varphi_i^0 = \exp\left(\frac{B_{ii}}{RT} p_i^0\right). \tag{7}$$