The influence of non-ideal vapor-liquid-equilibrium on vaporization of multicomponent hydrocarbon fuels

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Abstract

In this work the differences between ideal and non-ideal vapor-liquid-equilibrium (VLE) and the effect on vaporization for multicomponent hydrocarbon fuels, which are representative for engines or gasifiers, are investigated. Based on these deviations, a parametric study of non-ideal VLE-behavior for a pressure range of 0.5-20.0 bar and a temperature range till 600 °C, which are typical vaporization conditions in technical systems, is performed. The VLE results are then applied for a 0D single droplet vaporization model, which can be considered as a base model for most CFD applications. The droplet life time and the vaporization rates of the single components are compared between ideal and non-ideal behavior varying the pressure, the temperature and the particle Reynolds number. The observed differences suggest that non-ideal VLE have a significant impact on the droplet vaporization characteristics for complex hydrocarbon mixtures.

Introduction

The vaporization of fuels is a relevant process in many practical devices like engines, furnaces and gasifiers which effects mixture formation and further steps like burning, gasification or pollutant formation. The accuracy of the droplet vaporization affects all the further steps significantly. Since real fuels consist of a large number of species, it is important to model the fuels with a multicomponent approach. Fuels are usually depicted with continuous thermodynamics, where all the single components are lumped together. The description of the real vapor pressure for mixtures has the main impact on the vaporization. Hence, the vapor-liquid-equilibrium (VLE) will be determined with suitable real approaches in contrast to the ideal approach of Raoult. The non-ideal VLE for mixtures is a classical topic of the multicomponent thermodynamics which is essential in all fluid separation technologies like in petrol chemistry or in gas treatment processes. In praxis there are significant differences in non-ideal behavior compared to the ideal assumptions. A very popular example is the mixture of ethanol and water which form an azeotrope. Several studies in the literature looked at non-ideal mixtures and their VLE. As an example Neroorkar et al. [1] analyzed already non-ideal vapor-liquid equilibrium properties of gasoline-ethanol fuel blends with an empirical Gasoline-Ethanol Flash model and Aspen Plus up to high temperatures but below its vapor pressure. Zhang et al. studied in [2] the vaporization of 100 μm oil droplets in pure nitrogen with continuous thermodynamics and especially for bio-oil droplets in [3].

Within the scope of this work the fuel vaporization is investigated with a single droplet of discrete components whereby ideal and non-ideal VLE approaches are compared. The hydrocarbon fuel vaporization is considered for single component fluids and binary mixtures. The fuel is assumed to be a mixture of iso-octane (2,2,4 trimethylpentane) and ethanol, which results in a ternary vapor-liquid equilibrium (VLE) with the surrounding nitrogen atmosphere. Iso-octane was chosen in order to model gasoline and was mixed with ethanol in all mixture ratios, for instance to model E10 (10 vol.-% ethanol in gasoline). The droplet vaporization is discussed in a pressure range from 0.5 bar till 20.0 bar and in a nitrogen atmosphere with temperatures between 0 °C and 600 °C.

The paper starts with a description of the chosen non-ideal VLE model and follows with an explanation of the 0D single droplet model for multicomponents. After that, the dependency of the ambient gas temperature, relative droplet velocity and the pressure impact on the droplet vaporization are discussed in the following section. Thereby, the differences between ideal and non-ideal VLE droplet vaporization are compared with each other.

Numerical Model

The numerical modeling can be divided into two parts. The first part deals with the description of the non-ideal VLE where the correction factors to account for the non-ideal thermo-chemical equilibrium of liquid and

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gas mixtures are determined. In addition, the iteration process will be introduced to determine the new boiling temperature of the mixture. The second part concerns the zero-dimensional description of the vaporization of a single droplet combined with the first part. Here, a multicomponent vaporization model is presented as given by Law in [4] and extended by improvements due to convection and non-ideal behavior.

Vapor-liquid equilibrium

The Gibbs' phase rule says that vapor and liquid are at the equilibrium-state 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 one of the liquid phase f_i^l for all single components, see eq. (1).

$$f_i^l = f_i^v \tag{1}$$

In general, the two ways beside the ideal approach of Raoult to determine the fugacity are the equations-of-states (EoS) models and excess Gibbs energy (G^E) models. A typical EoS model is the Redlich-Kwong-Soave-Wong-Sandler (RKSWS) model. Commonly used G^E models are the non-random-two-liquids-model (NRTL) and the Universal Quasichemical Functional Group Activity Coefficients model (UNIFAC). The VLE of the ternary mixture consisting of iso-octane, ethanol and nitrogen and it's binary mixture combinations is illustrated in Fig. 1. The VLE determination was done using mass fractions and transformed with a linear mixing rule into volume

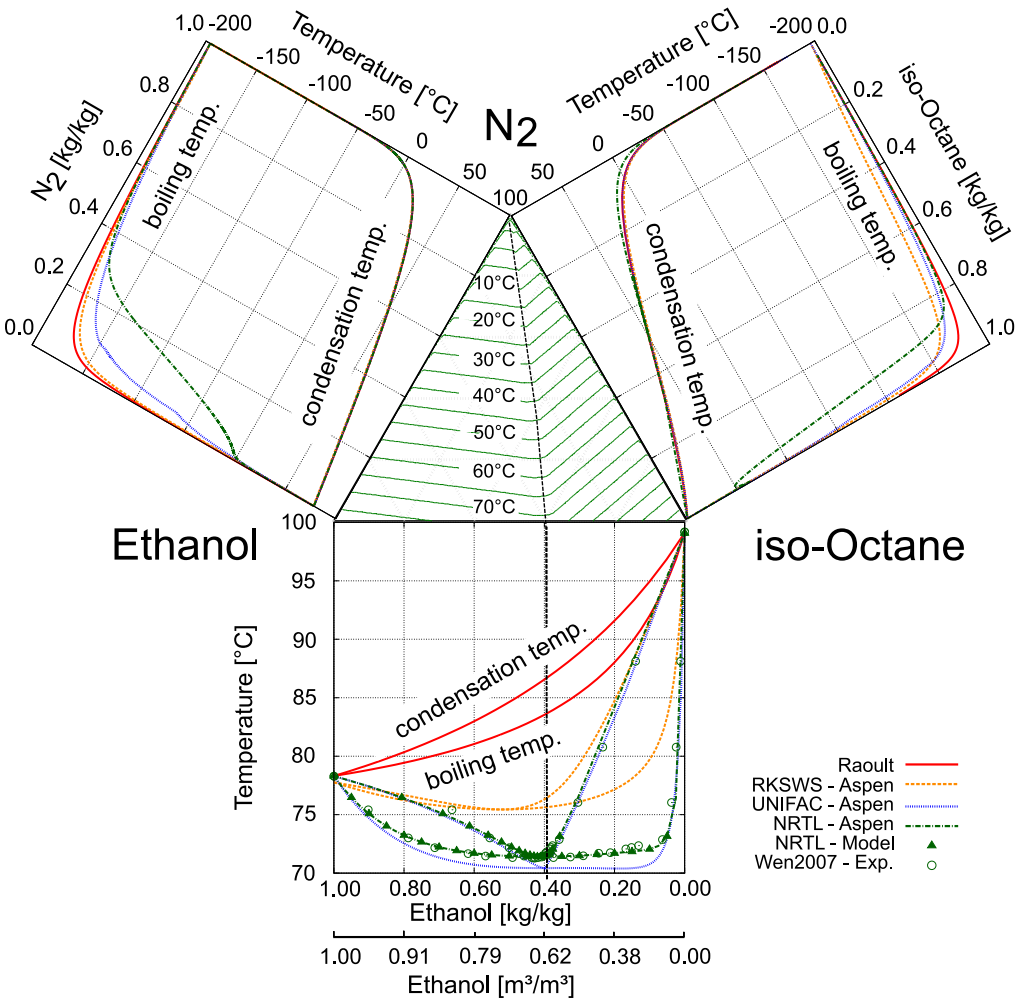

Figure 1. VLE of the ternary mixture consisting of iso-octane, ethanol and nitrogen and it's binary mixture combinations at 1.0 bar.

fractions. The volume fraction is used to describe common liquid mixing ratios in the droplet on volume base, like 10 vol.-% ethanol in gasoline, called E10. The VLE models are determined with Aspen Plus for Raoult's law and for the non-ideal methods NRTL, RKSWS and UNIFAC. Furthermore the results of an own implemented NRTL-model and the experimental data from Wen [5] for the binary mixture of iso-octane and ethanol are given in Fig. 1. The binary mixture of iso-octane and ethanol shows an azeotrope point at around 0.40 kg/kg ethanol and lower boiling and condensation temperatures for the non-ideal approaches as in Raoult's law, which is typically used in CFD calculations. The binary mixture of iso-octane with nitrogen and the mixture of ethanol with nitrogen are almost equal for the condensation temperatures of all of the four methods for both mixtures. In contrast to that the boiling temperature deviates. As a consequence the solubility for nitrogen in iso-octane and ethanol is set to zero in the single drop model, which will be discussed in the next section. The reason to use the NRTL-model in this work for the iso-octane/ethanol/nitrogen mixture is that the results from the NRTL-model match the measurement data from Wen [5] in good agreement. Furthermore, it is much easier implementable than the other models, RKSWS and UNIFAC.
The fugacity of the vapor phase is defined by eq. (2), where $\widetilde{y}_i$ is the molar fraction of the vapor of component i, φ_i^v are the fugacity coefficients of the vapor species and p the system pressure.

$$f_i^v = \varphi_i^v p_i = \widetilde{y}_i \varphi_i^v p \tag{2}$$

The fugacity of the liquid phase is formed by the activation a and a standard fugacity f^+ which has a freely selectable reference state, eq. (3). The activation of the liquid phase is determined by the molar fractions $\widetilde{x}_i$ of the liquid components and the activation coefficients γ_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 κ_i which describes the pressure dependency of the fugacity.

$$f_i^l = a_i f_i^+ = \gamma_i \widetilde{x}_i f_i^+ = \gamma_i \widetilde{x}_i f_i^0 = \gamma_i \widetilde{x}_i \varphi_i^0 p_i^0 \underbrace{exp\left(\int_{p_i^0}^{p} \frac{V_i^0}{RT} dp\right)}_{\kappa_i^0} \tag{3}$$

In order to determine the vapor fraction in the vapor liquid equilibrium, equations (2) and (3) are inserted in eq. (1) and result in (4).

$$\widetilde{y}_i = \frac{\gamma_i \widetilde{x}_i f_i^0}{\varphi_i^v p} = \frac{\gamma_i \widetilde{x}_i p_i^0 \varphi_i^0 \exp\left(\int_{p_i^0}^{p} \frac{V_i^0}{RT} dp\right)}{\varphi_i^v p} = \frac{\gamma_i \widetilde{x}_i p_i^0}{p} \cdot \frac{\varphi_i^0 \exp\left(\int_{p_i^0}^{p} \frac{V_i^0}{RT} dp\right)}{\varphi_i^v} = \frac{\gamma_i \widetilde{x}_i p_i^0}{p} \cdot \frac{\varphi_i^0}{\varphi_i^v} \kappa_i^0(T,p) \tag{4}$$

The Poynting correction can be determined by eq. (5), where $\widetilde{v}_{0,i}^l$ are the molar volumes of the liquid components, T the temperature and R the universal gas constant.

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

The fugacity coefficients of the vapor at system pressure and saturation state are calculated using eq. (6) and (7), respectively.

$$\varphi_i^v = exp\left\{\frac{\widetilde{B}_{ii}(T)}{RT} p\right\} \tag{6}$$

$$\varphi_i^0 = exp\left\{\frac{\widetilde{B}_{ii}(T)}{RT} p_{0,i}(T)\right\} \tag{7}$$

The second Virial coefficients $\widetilde{B}_{ii}$ are determined by the method of Tsonopoulos [6], and are in the form of eq. (8) which use the critical pressure p_c, the critical temperature T_c, the current drop temperature T and the reduced temperature $Tr = T/T_c$. This method is based on the correspondence principle of Pitzer and Curl [7].

$$\frac{\widetilde{B}_{ii} p_c}{RT_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + f^{(2)}(T_r) \tag{8}$$

The activation coefficients γ_i are determined applying the NRTL (non random two liquids) model, which was developed by Renon et. al [8], and can be calculated using equation (9). The NRTL model base on mass fraction x_i and on the temperature dependent NRTL parameters τ_{ij} and G_{ij}, which can be determined with eq. (10) till (12). The coefficients A_{ij}, B_{ij}, C_{ij}, D_{ij} come from the Aspen database.

$$\ln \gamma_i = \frac{\sum\limits_{j=1}^{K} x_j G_{ji} \tau_{ji}}{\sum\limits_{k=1}^{K} x_k G_{ki}} + \sum_{j=1}^{K} \frac{x_j G_{ji}}{\sum\limits_{k=1}^{K} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum\limits_{l=1}^{K} x_l G_{li} \tau_{li}}{\sum\limits_{k=1}^{K} x_k G_{kj}} \right) \tag{9}$$

$$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} \tag{10}$$

$$G_{ij} = exp\left\{-\alpha_{ij} \cdot \tau_{ij}\right\} \tag{11}$$

$$\alpha_{ij} = C_{ij} + D_{ij} \tag{12}$$

In contrast to the non-ideal VLE, in ideal approaches the activation and fugacity coefficients are equal to one in eq. (4) which is well known as Raoult's law. The results from the NRTL-model correspond with the measurement data from Wen [5] and are equal to the results obtained from the software ASPEN Plus. The VLE of the ternary mixture consisting of iso-octane, ethanol and nitrogen and its binary mixture combinations is calculated with eq. (4). The non-ideal vapor-liquid-equilibrium is calculated iteratively with eq. (4) by adjusting the temperature at a given system pressure, as $\gamma_i = f(x_i, T)$, is temperature dependent. Higher pressures lead to higher boiling and condensation temperatures. The azeotrope points change from 0.37 kg/kg at 1 atm at higher pressures to higher ethanol concentrations (0.57 kg/kg at 10 bar and 0.63 kg/kg at 20 bar). The differences between the non-ideal NRTL model compared with Raoult's law increase with pressure, especially at iso-octane contents lower than the azeotrope. Finally, it is demonstrated that the NRTL-model gives the same results as the ASPEN-NRTL-model even at high pressures and hence can be used in the single droplet model up to 20 bar.

Single Droplet Vaporization

The vaporization rate and change of composition, radius and temperature are calculated using the method of Law [4]. Assuming a unbounded atmosphere, the quasi-steady, isobaric and spherically symmetric vaporization of a single multicomponent droplet is described. The equations to calculate the mole fractions of the liquid components, the radius and the surface temperature of the droplet are written for a zero-dimensional droplet (discretized in time) and read

$$\widetilde{x}_i^{(n)} = \frac{\widetilde{x}_i^{(n-1)} (r^{(n-1)})^3 - \Omega_i \dot{m}_F \delta t \frac{3}{4\pi M_i} \sum_i \frac{\widetilde{x}_i^{(n-1)} M_i}{\rho_{i,l}^{(n-1)}}}{(r^{(n-1)})^3 - \sum_i \frac{\widetilde{x}_i^{(n-1)} M_i}{\rho_{i,l}^{(n-1)}} \cdot \sum_i \Omega_i \dot{m}_F \delta t \frac{3}{4\pi M_i}} \tag{13}$$

$$r^{(n)} = \sqrt[3]{\left((r^{(n-1)})^3 - \frac{3}{4\pi} \delta t \sum_i \frac{\Omega_i \dot{m}_F}{\rho_{i,l}^{(n-1)}} \right) \frac{\sum_i \frac{\widetilde{x}_i^{(n)} M_i}{\rho_{i,l}^{(n)}}}{\sum_i \frac{\widetilde{x}_i^{(n)} M_i}{\rho_{i,l}^{(n-1)}}}} \tag{14}$$

$$T_s^{(n)} = T_s^{(n-1)} + \frac{\dot{m}_F \delta t H}{c_{p,g} \frac{4}{3}\pi (r^{(n-1)})^3 \rho_{m,l}^{(n-1)}} \tag{15}$$

with total vaporization rate $\dot{m}_F$, fractional vaporization rates Ω_i, heat input function H, molar masses M_i, densities of liquid components $\rho_{i,l}$ and liquid mixture $\rho_{m,l}$, time step size δt, heat capacity of gas mixture $c_{p,g}$, radius r and surface temperature T_s. The superscripts $(n-1)$ and (n) denote the old and new state, respectively. All of the specie properties are calculated temperature dependent with the equations and coefficients from Yaws [9]. The original equation was formulated by Law [4] for stagnant environments only. As the drop has a motion relative to the ambient atmosphere, the heat and mass transfer across the drop surface are increased. Hence, the Nusselt number requires a convection correction as proposed by Turns [10]. The total vaporization rate then reads

$$\dot{m}_F = 2Nu \frac{\pi \lambda_g r}{c_{p,g}} \ln\left(1 + \frac{y_{F,s}}{1 - y_{F,s}}\right) \tag{16}$$

with

$$Nu = 2.0 + \frac{0.555 Re^{1/2} Pr^{1/3}}{\left(1.0 + \frac{1.232}{RePr^{4/3}}\right)^{1/2}}, \tag{17}$$

thermal conductivity of the gas mixture λ_g and total surface mass fraction of vapor $y_{F,s}$. This surface mass fraction is determined using the VLE-model mentioned previously and hence includes non-ideal behavior of liquids and gases, too. The Reynolds number Re represents the relative motion between droplet and the ambient medium. The single droplet model is solved by integrating the eq. (13) till (15) with fixed time steps of order $\delta t \approx 10^{-5}$ s.

Results and Discussion

In this section the temperature, relative droplet velocity and the pressure dependency applying the single droplet model is discussed. The impacts are described for different initial compositions, first for the single components iso-octane and ethanol and second for the mixtures. For instance, E90 represents a mixture of 90 vol.-% ethanol and 10 vol.-% iso-octane. For all cases, the single droplet model is initialized with a diameter of $D_d = 100\,\mu$m and at liquid temperature of $T_{\text{liquid}} = 25°$C. The solution of single droplet model is obtained by integrating the equations of the previous section and ended because of numerical reasons at a final droplet size with $r = 5\,\mu$m.

Temperature dependency

The temperature dependency is discussed at a system pressure of 10 bar. The results are illustrated in Fig. 2 whereas an ambient gas temperature of 25 °C is represented in the left column and 600 °C at the right column. Various initial compositions are used for both ambient gas temperatures. All these cases are calculated with Raoult's law as well as the NRTL-model. Figure 2 shows the transient normalized squared diameter in the first row. The time scale is normalized with the droplet life time (DLT). This time scale is applied for all the pictures in Fig. 2. For pure iso-octane (E00) at 25 °C gas temperature the DLT is $1.0444\ s$ in the ideal case and $0.6885\ s$ in the NRTL-model case, which results in an error of 51.7%. The error decreases with a higher ethanol content. For instance to 34.7% at 0.60 mol/mol ethanol, whereas the DLT increase to $1.6448\ s$ in the ideal case and $1.2214\ s$ in the NRTL-model case. The minimal error is at 0.92 mol/mol ethanol with 19.5% and increases at 1.00 mol/mol ethanol to 20.4%. At 600 °C gas temperature the droplet vaporize 40 till 60 times faster than at 25 °C gas temperature both with the NRTL as well with the Raoult approach. In the case of 600 °C gas temperature the DLT is longer in the NRTL-model case compared to the ideal DLTs at 25 °C gas temperature. The error is always lower then 12.0%. The transient surface temperatures of the droplet are illustrated in the second row of Fig. 2. Figure 3 gives the transient equilibrium molar fractions in the gas phase of iso-octane and ethanol for the initial compositions E10 and E90. The remain to 100 % is nitrogen.

In Figure 2 at 25 °C gas temperature, both pure ethanol and pure iso-octane show a linear D^2-law behavior for the Raoult approach as well as for the NRTL-model. Even for mixtures with less ethanol like E10, the droplet diameter decreases with an almost linear D^2-law behavior, as the vapor pressures are close to each other. Only for higher ethanol contents with a non-ideal NRTL approach, the droplet shrinking velocity shows a characteristic turning point after ethanol left the droplet completely. At the same time the droplet surface temperature increases because the enthalpy of vaporization of iso-octane is lower than the one of ethanol. For the ideal approach the droplet

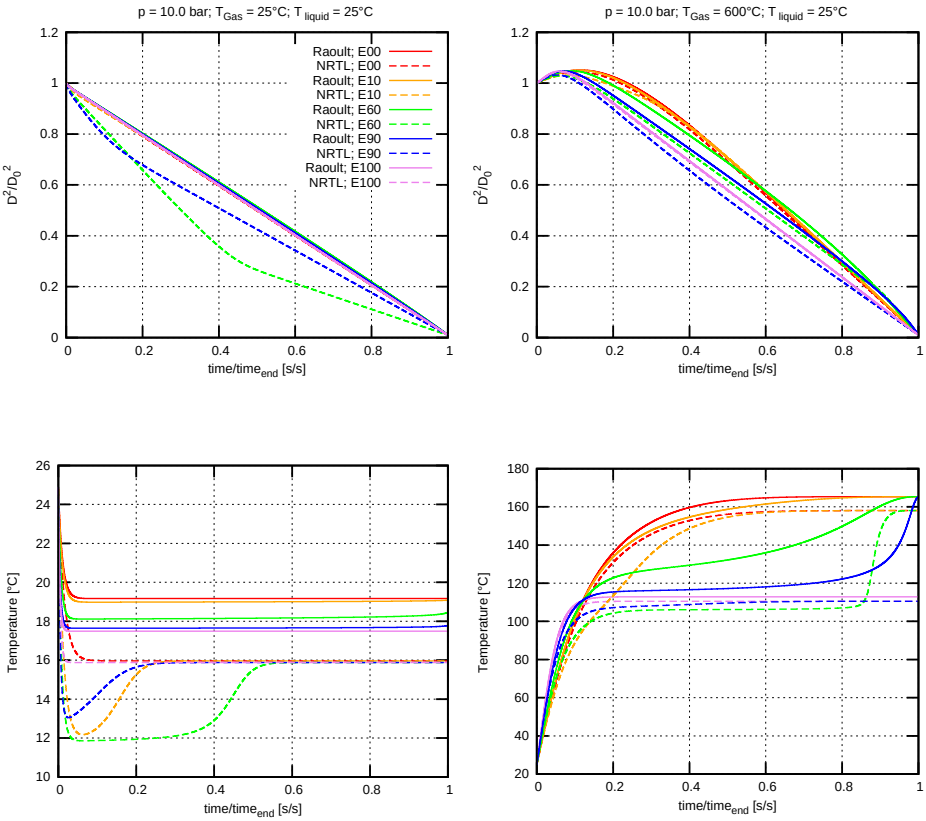

Figure 2. Normalized droplet square diameter and surface temperature at $T_{gas} = 25$ °C (left) and $T_{gas} = 600$ °C (right) at 10 bar, $T_{liquid} = 25$ °C, Re = 10

vaporization rate and the temperature are constant for the most of the time as the differences between condensation and the boiling curve are almost equal, see Fig. 1.

The conclusions derived from the 25 °C gas temperature case can be adapted to the 600 °C case. But the droplet expands at the beginning of the vaporization because of thermal expansion and has a higher vaporization rate in the case of gas temperature 600 °C compared to 25 °C in the ambient atmosphere. The droplet expands, as the density reduces at higher temperatures by the equations of Yaws [9], whereby no correction for the property mixing is implemented as the error is assumed to be small. The error occurs as well in the ideal and in the non-ideal case. Consequently, the assumption has no impact on the difference between ideal and non-ideal droplet vaporization, which is the focus in this work. The transient droplet surface temperature converges to iso-octane boiling temperature ($T_{\text{boil}} = 252.6$ °C at 10 bar) when ethanol left the droplet completely. Figure 3 shows the ethanol and the iso-octane content in the vapor phase at the droplet surface. If the vapor phase content of a specie is zero, the specie does not exist in the droplet anymore, too. Ethanol leaves the droplet completely in the ideal and the NRTL approach if only less ethanol, like E10, is in the initial composition of the droplet. At higher initial ethanol content, like E90, ethanol leaves the droplet completely only for the ideal approach. For the NRTL approach the droplet surface temperature is close to the mixture boiling point temperature at 10 bar, and the droplet consists of both ethanol and iso-octane till the end of the droplet life time, see Fig. 3.

Finally, it can be concluded that the vaporization takes longer the higher the initial content of ethanol is and that at higher temperatures, the difference in the DLT between the ideal and the non-ideal behavior is reduced. But for initial compositions with a high ethanol content the error increases again after a decrease, see Fig. 4. At 25 °C gas temperature, the maximum error is at $+82\%$ related to an initial composition of 40 vol.-% ethanol. Whereas at 600 °C gas temperature the maximum error is at -12% related to an initial composition of 70 vol.-% ethanol. The regions of error maxima can be better derived from Fig. 4 which will be discussed in a later section.

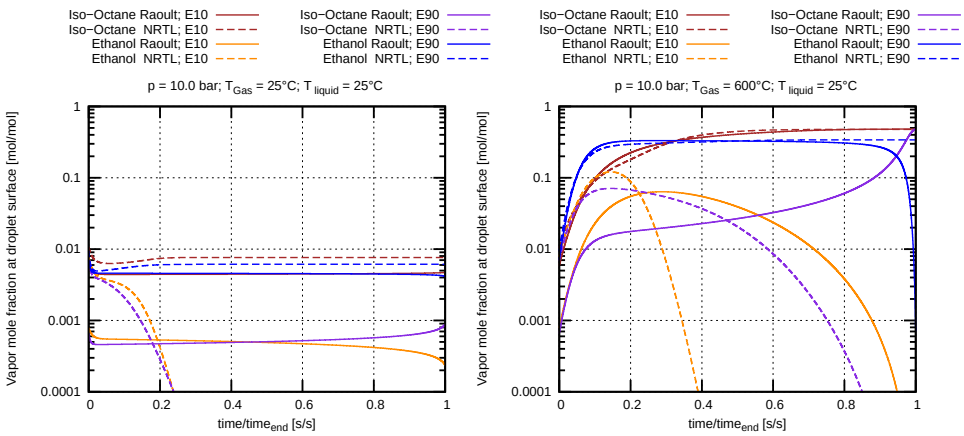

Figure 3. Equilibrium vapor mole fraction for E10 and E90 at $T_{gas} = 25$ °C (left) and $T_{gas} = 600$ °C (right) at 10 bar, $T_{liquid} = 25$ °C, Re = 10

Relative droplet velocity dependency

The vaporization rate of the droplet is affected by the gas flow around the droplet. Increasing relative velocities between gas and droplet are represented by an increasing Reynolds number Re. The Reynolds number can only be increased to a maximum value of $Re = 100$ in order to avoid droplet break-up. Because of integration into the vaporization rate, the DLT of course decreases with increasing Re. The relative error of the vaporization rate between the ideal and the non-ideal approach can be calculated with the help of eq. (16) in eq. (18). As eq. (18) can be reduced by the $Nu(Re, Pr)$, the relative motion has no impact on the error. The error has the maximum at initial composition around the azeotrope concentration.

$$\frac{\dot{m}_{\text{F,ideal}} - \dot{m}_{\text{F,non-ideal}}}{\dot{m}_{\text{F,non-ideal}}} = \frac{2Nu(Re,Pr)\frac{\pi\lambda_g}{c_{p,g}r}\ln\frac{1+y_{\text{F,s,ideal}}}{1-y_{\text{F,s,ideal}}} - 2Nu(Re,Pr)\frac{\pi\lambda_g}{c_{p,g}r}\ln\frac{1+y_{\text{F,s,non-ideal}}}{1-y_{\text{F,s,non-ideal}}}}{2Nu(Re,Pr)\frac{\pi\lambda_g}{c_{p,g}r}\ln\frac{1+y_{\text{F,s,non-ideal}}}{1-y_{\text{F,s,non-ideal}}}} \tag{18}$$

Pressure dependency

The vaporization of the fuel droplet is analyzed with the single droplet model with pressures at 0.5 bar, 5 bar, 10 bar and 20 bar. Furthermore, the ambient gas temperature is variated in a range from $T = 0$ °C to $T = 600$ °C and the initial mixture is changed from 0 vol.-% to 100 vol.-% ethanol for a parameter study. The difference in the DLT between the ideal and the non-ideal approach f_{rel} is calculated wit eq. (19) and is represented in Fig. 4.

$$f_{\text{rel}} = \frac{\text{DLT}_{\text{ideal}} - \text{DLT}_{\text{real}}}{\text{DLT}_{\text{real}}} \tag{19}$$

The DLT with the Raoult approach is longer than with the NRTL approach at low temperatures. This is because the vapor pressure is increased using the NRTL approach for the ethanol/iso-octane mixture. Thereby, the differences increase with higher pressures. Whereas high temperatures reduce the differences between the vapor pressure. Hence, the DLT error between ideal and non-ideal decreases. Except for high ethanol contents in the initial composition at high temperatures the DLT is longer with the NRTL approach than with ideal approach as the vaporization of iso-octane is preferred at the beginning in the non-ideal approach in contrast to the ideal approach. This behavior can be derived from Fig. 1.

In general, the DLT increases with the pressure increase. The positive maximum of the DLT error is always at 0 °C. Only the initial ethanol content varies which results in a maximum shift from 37 vol.-% to 23 vol.-% at a pressure change from 0.5 bar to 20 bar. The maximum of the negative error is at the limit of the discussed region at 600 °C and at 74 vol.-% ethanol for 5, 10 and 20 bar. Only at 0.5 bar, the maximum of the negative error is at a gas temperature of 270 °C and at 68 vol.-%.

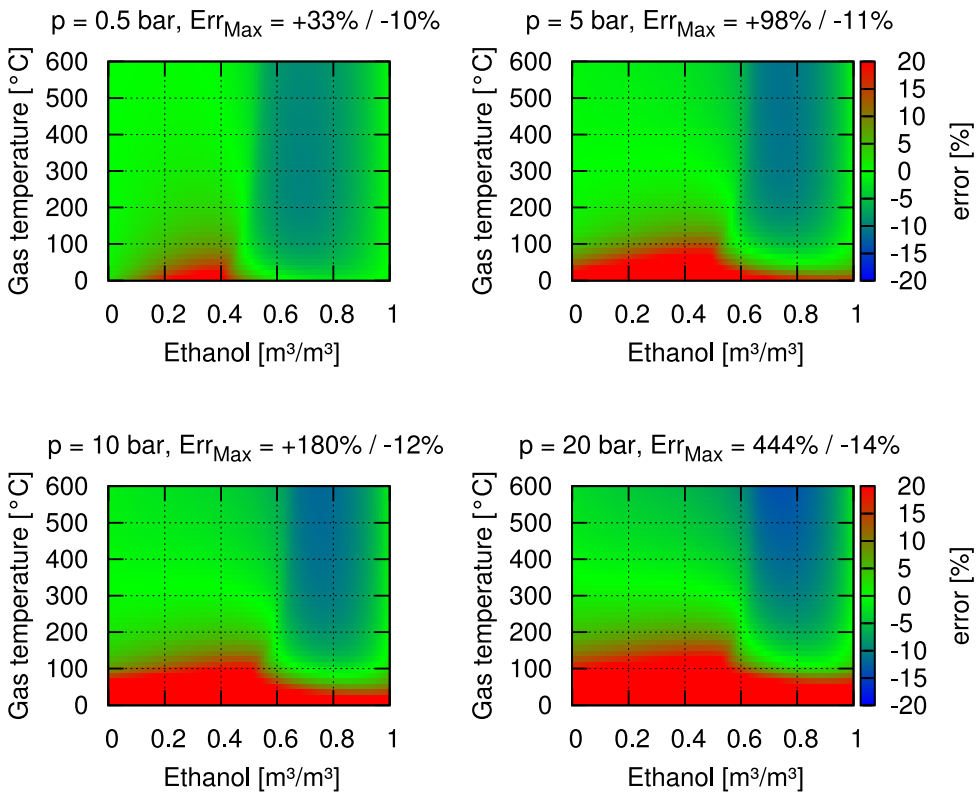

Figure 4. Error of droplet-life-time between Raoult and NRTL approach at 0.5, 1.0, 10 and 20 bar for initial mixtures of ethanol an iso-octane between 0% - 100% ("+"/"red" $\triangleq$ non-ideal is faster than ideal) and ("-"/"blue" $\triangleq$ ideal is faster than non-ideal) by $T_{liquid} = 25$ °C and independent of Re. Colorbar is scaled to +20% and -20%.

Summary and Conclusions

The use of Raoult's law instead of a non-ideal approach like NRTL can lead to an error in the droplet life time up to more than 400%. Critical regions are at ambient gas temperatures lower than around 100 °C especially at initial compositions with lower ethanol content than at the azeotrope point. The error increases with higher pressures and lower temperatures. For the current formulation, the Reynolds number has no impact in a 0D single droplet model on the error between ideal and non-ideal approaches. Finally, it can be concluded that non-ideal descriptions of vapor-liquid-equilibriums should be included in CFD solvers, as significant differences between ideal and non-ideal approaches can be noticed even in simple single droplet models.

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