Multicomponent Vaporization Modeling of Petroleum-Biofuel Mixture at High-Pressure Conditions
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Abstract. Numerical simulation of the vaporization of multi-component liquid fuels under high-pressure conditions is conducted in this study. A high-pressure drop vaporization model is developed by considering the high-pressure phase equilibrium which equates the fugacity of each component in both liquid and vapor phases. Peng-Robinson equation of state is used for the calculation of fugacity. To model the vaporization of diesel fuel under high-pressure conditions, continuous thermodynamics based on a gamma distribution is coupled with phase equilibrium by correlating the parameters of the equation of state with the molecular weights of the continuous components. The high-pressure vaporization model is validated using the experimental data of n-heptane drops under different ambient pressures and temperatures. Good levels of agreement are obtained in drop size history. Predicted results of the vaporization of diesel fuel drops show that increasing ambient pressure leads to a shorter drop lifetime under high temperature conditions (e.g., 900 K). The model was further applied to biodiesel and its blends with diesel fuel. The fuel blend is modeled based on a method that continuous thermodynamics is used to model diesel fuel and biodiesel is modeled as a mixture of its five representative components. Results of single drop vaporization history show that drop lifetime increases as the volume fraction of biodiesel in the fuel blend increases. It is also observed that the volume fraction of biodiesel in the fuel blend increases during vaporization and its vapor concentrates near the tip of the liquid spray while diesel fuel vapor is around the entire liquid spray.

Introduction
Liquid drop vaporization modeling in multi-dimensional engine simulation is of great importance due to its impact on the accuracy of spray combustion prediction. Since the compositions of practical engine fuels are very complicated, an important means to improve vaporization modeling is to replace the single-component assumption with a multi-component approach. Multi-component approach based on continuous thermodynamics can be used to model complex fuels such as gasoline and diesel fuel, which are usually composed of hundreds of components [1]. Using this approach, fuel is assumed to be composed of an infinite number of continuously distributed components, and a probability distribution function (PDF) is used to model the distribution of the molecular weights of the components in the fuel.

In addition to the composition of multi-component fuels, vaporization modeling also needs to consider the effects of high pressure since liquid fuel drops frequently experience such conditions in practical combustion devices such as diesel engines and gas turbines. Traditionally, for computational efficiency, drop vaporization models are mostly based on the Raoult’s law which is a low-pressure simplification of the general vapor-liquid phase equilibrium. The phase equilibrium calculation based on the Raoult’s law involves the assumptions of ideal gas law and no gas dissolving in the liquid phase. Since such assumptions are not entirely true under high-pressure conditions, errors will be generated in the prediction of drop vaporization rate and vapor distribution at high-pressure conditions. To improve the accuracy of multi-dimensional computational fluid dynamics simulation, general phase equilibrium relations, which are characterized by the equality of fugacities of both phases, need to be used to replace the Raoult’s law in drop vaporization simulation.

Since petroleum fuels are questionable in availability in the future, biorenewable fuels are being used in many kinds of combustion devices. Especially in diesel engines, since biodiesel is close to diesel fuel in terms of physical and chemical properties, it can be used without significant modifications to the engine. Due to the high miscibility, biodiesel is usually blended with regular diesel fuel in practical applications. Successful applications of biodiesel in diesel engines rely on the detailed knowledge of its spray and combustion behaviors. Research has shown that most of biodiesel derived from vegetable oils are mainly composed of five C16 to C18 fatty acids [2, 3]. The vaporization of biodiesel and its blends with diesel fuel at various ambient temperatures was simulated under atmospheric pressure by Zhang and Kong [4], who assumed biodiesel as a mixture of five components and applied a mixing rule to obtain the properties of biodiesel.

The purpose of present study is to predict the vaporization behaviors of diesel fuel, biodiesel, and the blend of both fuels under engine operating conditions which are characterized by high pressures and temperatures. A multi-component drop vaporization model for...
high-pressure conditions based on continuous thermodynamics is developed. The model is first validated using the high-pressure vaporization experiments of single-component fuel (i.e. n-heptane). Both the drop vaporization history and the vapor distribution of liquid spray using biodiesels and its blends with diesel fuel under high-pressure conditions will also be shown.

MODEL FORMULATION

In this section, the phase equilibrium in a vapor-liquid system, which is composed of fuel components and the species of the surrounding gases at the surface of the liquid drop, will be discussed. Such an equilibrium provides boundary conditions for the governing equations of both phases. In solving the one-dimensional governing equations in the gas phase, the pseudo-steady assumption will be applied. The methods for calculating the physical properties of the fuels at high-pressure conditions will also be presented.

Gas and fuel species in both phases at the phase interface can be regarded as a system in thermodynamic equilibrium at a specific pressure and temperature. Such an equilibrium requires the minimum of the total Gibbs free energy, namely, \( \partial G = 0 \) [5]. It can be shown that this requirement will lead to the equality of fugacity

\[ \dot{f}_{i,l} = \dot{f}_{i,v}. \]  (1)

Subscripts \( l \) and \( v \) denote the liquid and vapor phases, respectively. \( \dot{f}_i \) indicates the fugacity of component \( i \), and \( ^\ast \) denotes the property of a component in a mixture. In practice, the fugacity coefficient is more frequently used in describing phase equilibrium replacing fugacity in the above equation and is defined by

\[ \dot{\phi}_i = \frac{\dot{f}_i}{y_i P}. \]  (2)

In the above equation, \( y_i \) is the mole fraction of component \( i \) at the phase interface, and \( P \) is the pressure of the mixture. By substituting Eq. (2) into Eq.(1), the mole fraction of component \( i \) of the fuel in the vapor phase \( (y_i) \) can be obtained as

\[ y_i = \frac{x_i \dot{\phi}_i}{\dot{\phi}_v}. \]  (3)

where \( x_i \) is the liquid phase mole fraction of component \( i \) at the phase interface.

In modeling the vaporization of petroleum fuels composed of hundreds of components, continuous thermodynamics is preferable because of its capability in depicting the complicated composition. By using continuous thermodynamics, the composition of the fuel is described by a distribution of component molecular weights with a probability density function (PDF). Therefore, the phase equilibrium in Eq. (3) can be further written as

\[ y_i f_i^\ast (I) \dot{\phi}_i (I) = x_i f_i (I) \dot{\phi}_v (I). \]  (4)

In the above equilibrium formula, subscript \( F \) denotes petroleum fuel, and fugacity coefficients are functions of molecular weight. \( f \) is the probability density function determining the shapes of the molecular weight \( f(l) \) distributions in both phases. In this paper, a gamma distribution defined by the following formula will be used as the PDF for petroleum fuel.

\[ f(l) = \frac{(l - \gamma)^{x-1}}{\beta^x \Gamma(x)} \exp \left(-\frac{l - \gamma}{\beta} \right). \]  (5)

In the above distribution, \( \alpha \) and \( \beta \) are the parameters determining the shape of the distribution originated from \( \gamma \), and \( \Gamma(x) \) is a gamma function. Eq. (4) describes the phase equilibrium of each component of the multi-component fuel. It can be seen that such phase equilibrium will lead to a different molecular weight distribution in the vapor phase. Rearranging Eq. (4) and integrating from \( \gamma \) to \( \infty \), the overall vapor mole fraction of the petroleum fuel at drop surface can be obtained as

\[ y_v = \int y_v f^\ast (I) dI = \int x_v \frac{\dot{\phi}_v^\ast (I)}{\dot{\phi}_v (I)} f^\ast (I) dI. \]  (6)

Multiplying the molecular weight \( I \) and \( f^2 \) on both sides of Eq. (4), the integration will lead to the expression of first moment (i.e., mean molecular weight) \( \theta_v \) and second moment \( \psi_v \) in the vapor phase as

\[ y_v \theta_v = \int y_v f^\ast (I) I dI = \int x_v \frac{\dot{\phi}_v^\ast (I)}{\dot{\phi}_v (I)} f^\ast (I) I dI \]  (7)

and

\[ y_v \psi_v = \int y_v f^\ast (I) I^2 dI = \int x_v \frac{\dot{\phi}_v^\ast (I)}{\dot{\phi}_v (I)} f^\ast (I) I^2 dI \]  (8)

Using the above two relations and assuming \( \gamma \) to be constant over the phase interface, the distribution parameters, i.e., \( \alpha \) and \( \beta \), in the vapor phase can be calculated.

As can be seen in the above equations, to calculate the mole fraction of the fuel in the vapor phase, the fugacity coefficients, which are functions of component
molecular weight, need to be determined. It can be shown that the fugacity coefficient of a component in a mixture can be calculated by considering the departure function of Helmholtz energy [6] as

$$RT \ln \hat{\phi} = \int \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n} - \frac{RT}{V} \right] dV - RT \ln Z .$$  \hspace{1cm} (9)

In the above equation, $Z$ is the compressibility factor of the mixture defined as $Z = PV/RT$, and $n_i$ is the number of moles for component $i$ in the mixture. To calculate the fugacity coefficient as described in Eq. (9), the pressure-volume-temperature ($P$-$V$-$T$) relation of the mixture must be known. In this paper, a two-parameter cubic equation of state, which is applicable for both liquid and vapor, is selected to provide the real fluid behavior, i.e., the $P$-$V$-$T$ relationship. Such an equation of state is applicable for both pure components and their mixtures and can be expressed in a general form as

$$P = \frac{NRT}{\bar{V} - Nb} - \frac{N^2a}{\bar{V}^2 + ubN\bar{V} + wN^2b^2} .$$  \hspace{1cm} (10)

Peng-Robinson, Redlich-Kwong, Redlich-Kwong-Soave, and van der Waals equations of state are most widely used two-parameter cubic equations of state. In the above equation, $N$ is the total number of moles of the fluid, $u$ and $w$ are the two parameters that determine the type of the cubic equations of state, and for Peng-Robinson equation of state, $u=2$ and $w=-1$. Previous research shows that it provides the best accuracy in predicting the compressibility factor compared to the other equations of state. Therefore, Peng-Robinson equation of state will be used in this study. $a$ and $b$ in Eq. (10) are functions of the critical temperatures and pressures of the components and the composition of the mixture. By using continuous thermodynamics to model the multi-component fuel, both parameters are correlated as functions of molecular weight, and the mean values of the fuel can be evaluated using the distribution function as

$$a = \left( \int a^{1/2}(I) f(I) dI \right)^2$$ \hspace{1cm} (11)

and

$$b = \int b(I) f(I) dI .$$ \hspace{1cm} (12)

Eqs. (11) and (12) serve as the mixing rule for applying the equation of state for a multi-component fuel using continuous thermodynamics.

Substituting the above mixing rule into Eq. (9), the fugacity coefficient of continuously distributed components as a function of molecular weight can be calculated as

$$\ln \hat{\phi}(I) = \ln \left( \frac{v}{v-b} \right) - \ln Z + \frac{b(I)}{b} (Z-1) + \frac{a}{RTb\sqrt{a^2 - 4w}} \left[ \frac{b(I) - 2a^{1/2}(I)}{a^{1/2}} \right].$$ \hspace{1cm} (13)

In the above equation, $v$ is the molar volume ($m^3/mol$) of the mixture. This equation provides a means to determine fugacity coefficient as a function of molecular weight based on continuous thermodynamics. It can be seen from the above equation that the correlations of $a$ and $b$ as functions of molecular weight $I$ must be obtained to calculate the fugacity coefficient. In this paper, based on the data for C1 to C20 alkanes, $a(I)$ for Peng-Robinson equation of state is correlated as

$$a^{1/2}(I) = (115.65559 - 2.54784 T^{1/2}) \times I - 363.60516 + 24.04255 T^{1/2} ,$$ \hspace{1cm} (14)

and, $b(I)$ is a linear function of the molecular weight described as

$$b(I) = 1.62213 \times I - 25.52276 .$$ \hspace{1cm} (15)

Substituting the above two correlations into Eq. (13), the logarithmic fugacity coefficient as a function of molecular weight and can be generalized as a linear function of molecular weight as

$$\ln \hat{\phi}(I) = AI + B .$$ \hspace{1cm} (16)

It can be seen that $A$ and $B$ are determined by pressure, temperature, and the compositions of the liquid or vapor phases. Substituting the above relation into Eqs. (6), (7), and (8), the mole fraction, mean molecular weight, and second moment can be calculated as

$$y_i = \frac{x_i \exp \left[ \gamma (A_i - A) + (B_i - B) \right]}{[1 - \beta_i (A_i - A)]^\gamma} ,$$ \hspace{1cm} (17)
Performing the iterative calculations described in Eqs. (13) to (19), the molecular weight distribution for the multi-component fuel vapor at the drop surface can be obtained. Due to the fact that the vapor mean molecular weight is smaller than that of liquid phase, the continuously distributed components will vaporize in an order according to their molecular weights. In general, lighter components tend to vaporize earlier than the heavier components. This phenomenon will cause the composition distribution in the liquid phase to shift to the high-molecular-weight end and cause the mean molecular weight of the fuel to increase.

Results and discussion

The high-pressure vaporization model described above is first applied to n-heptane drop vaporization at various ambient pressures and temperatures. The comparisons between numerical results and experimental data by Nomura et al. [9] are shown in Fig. 1. It can be seen that the numerical results in various ambient conditions agree well with the experimental data in both the shape of the drop size history and the total lifetime. The traditional low-pressure model based on the Raoult’s law is also applied to the same conditions and compared with the high-pressure model results and experimental data. It can be seen that the application of the Raoult’s law leads to longer drop lifetime and will subsequently affect the distribution of fuel vapor in practical combustion devices under high-pressures.

In this paper, the composition of diesel fuel is modeled using continuous thermodynamics based on a gamma function shown in Eq. (5). For diesel fuel, the distribution parameters are $\alpha=23$, $\beta=8.15$, and $\gamma=0$. The continuous thermodynamics model is coupled with high-pressure phase equilibrium as described by Eqs. (13), (14), and (15). The vaporization of diesel fuel drops at ambient temperature 900 K and various ambient pressures within the range of engine in-cylinder conditions is simulated. In these cases, diesel drops with initial diameter of 0.1 mm and initial temperature of 300 K is exposed to a pure nitrogen environment. Histories of the drop surface temperature and the square of the reduced drop diameter for different ambient pressures are shown in Fig. 2. It can be seen that as ambient pressure increases, the heating period, which is characterized by the increased drop size, is prolonged. On the other hand, if the pressure is higher, the vaporization rate (i.e., slope of the curve) following the heating period will increase, causing the overall drop lifetime to decrease. As can also be seen in Fig. 2, the drop surface temperature is significantly higher for high-pressure conditions. One reason leading to the difference in drop surface temperature is the relationship between pressure and enthalpy of vaporization. The enthalpy of vaporization of diesel fuel with the initial composition ($\alpha=23$, $\beta=8.15$, $\gamma=0$) as a function of temperature under different ambient pressures is shown in Fig. 3. It can be seen that the enthalpy of vaporization decreases steadily to zero as the temperature increases to the value at the critical mixing point of a particular pressure. At higher pressures, the enthalpy of vaporization is lower, leading to a higher drop vaporization rate.

**Figure 1.** Vaporization history of a single n-heptane drop at $P=2.0$ MPa, $T=656$ K.

**Figure 2.** Drop size and surface temperature histories for diesel fuel drop at different ambient pressures, $T_{\text{amb}}=900$ K.
Biodiesel is a feasible alternative fuel for compression-ignition engines due to its close physical and chemical characteristics to regular diesel fuel. The composition of biodiesel can be complicated due to the variation in the feedstock. However, the major components of biodiesel are five methyl esters, namely, palmitic (C_{16}H_{32}O_{2}), stearic (C_{18}H_{36}O_{2}), oleic (C_{18}H_{34}O_{2}), linoleic (C_{18}H_{32}O_{2}), and linolenic (C_{18}H_{30}O_{2}). Therefore, the present paper assumes that biodiesel is a mixture of the above five components. The present model was used to simulate the vaporization of biodiesel drops under high pressure and high temperature conditions similar to those in diesel fuel vaporization study. The drop size histories of biodiesel drops at 900 K and various pressures are shown in Fig. 4. It can be seen that biodiesel drops generally have longer lifetime than diesel drops in the same ambient condition. The lifetime of the biodiesel drop varies in the same way as the diesel fuel drop when pressure changes, i.e., higher pressure reduces drop lifetime.

On the other hand, in a diesel engine, considering engine performance and emissions, a practical way of using biodiesel is to blend it with diesel fuel in different volumetric ratios due to their high miscibility. In this study, the vaporization of B20 drops, which are blends of 20% biodiesel and 80% diesel on volume basis, under different ambient pressures are simulated. The histories of drop size under different ambient pressures are shown in Fig. 5. Results show that the vaporization histories of B20 drops are in between those of diesel fuel and biodiesel at the same ambient conditions.
Figure 6. Diesel fuel and biodiesel vapor distributions for B0, B20, and B100 sprays at t=1.4 ms, T_{amb}=900 K, P=38 bar.

Conclusion
Numerical modeling was performed to simulate the vaporization of multi-component fuel drops under engine operating conditions which are characterized by high pressures and high temperatures. The phase equilibrium calculation under high-pressure conditions is based on the equality of fugacity of each component in both phases. To couple continuous thermodynamics with high-pressure phase equilibrium, the parameters of Peng-Robinson equation of state are correlated with the continuously distributed molecular weights of the components based on a gamma distribution.

The present high-pressure vaporization model was validated using the experimental data of n-heptane drops. The predicted history of drop size during vaporization agrees well with the experimental data. The present model was further applied to predict the vaporization of diesel fuel drop under different ambient temperatures and pressures. Results of the 900 K ambient temperature case show that the drop lifetime decreases with increased ambient pressure. It is found that two competing factors, namely, reduced mass transfer number (decreasing vaporization rate) and reduced enthalpy of vaporization (increasing vaporization rate) for higher pressure conditions determine the way in which the drop lifetime changes with ambient pressure. In any case, model results show that the molecular weight of the vapor is smaller than that of the liquid and both molecular weights keep increasing during the process, indicating that lighter components vaporize earlier than heavier components.

The vaporization of biodiesel and its blend with diesel fuel was also simulated. Biodiesel is modeled as the mixture of five representative components with compositions determined by the feedstock. Results of biodiesel drops show a similar trend to diesel fuel in drop lifetime with respect to ambient pressure. In the vaporization modeling of the blend of diesel fuel and biodiesel, continuous thermodynamics is used to model diesel fuel and biodiesel is assumed to be a mixture of the five components. The predicted vaporization history of the fuel blend lies in between those of diesel fuel and biodiesel. Results of the sprays show that at a certain point in time, the vapor of biodiesel only concentrates in a small region near the tip of the spray, while diesel fuel vapor exists in a much wider region around the entire liquid spray.

References

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