

Distillation-based Droplet Modeling of Non-Ideal Oxygenated Gasoline Blends: Investigating the Role of Droplet Evaporation on PM Emissions

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ABSTRACT

In some studies, a relationship has been observed between increasing ethanol content in gasoline and increased particulate matter (PM) emissions from vehicles equipped with spark ignition engines. The fundamental cause of the PM increase seen for moderate ethanol concentrations is not well understood. Ethanol features a greater heat of vaporization (HOV) than gasoline and also influences vaporization by altering the liquid and vapor composition throughout the distillation process. A droplet vaporization model was developed to explore ethanol's effect on the evaporation of aromatic compounds known to be PM precursors. The evolving droplet composition is modeled as a distillation process, with non-ideal interactions between oxygenates and hydrocarbons accounted for using UNIFAC group contribution theory. Predicted composition and distillation curves were validated by experiments. Detailed hydrocarbon analysis was applied to fuel samples and to distillate fractions, and used as input for the initial droplet composition. With composition calculated throughout the distillation, the changing HOV and other physical properties can be found using reference data. The droplet can thus be modeled in terms of energy transfer, which in turn provides the transient mass transfer, droplet temperature, and droplet diameter. Model predictions suggest that non-ideal vapor-liquid equilibrium along with an increase in HOV can alter the droplet composition evolution. Results predict that the presence of ethanol causes enrichment of the higher boiling fractions (T90+) in the aromatic components as well as lengthens the droplet lifetime. A simulation of the evaporation process in a transient environment as experienced within an engine cylinder predicts a decrease in mixing time of the heaviest fractions of the fuel prior to spark initiation, possibly explaining observations linking ethanol to PM.

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INTRODUCTION

The combustion of fossil fuel used for transportation of people and goods in the United States is the second largest contributor to CO₂ emissions (31%) and contributes to 25% of the total greenhouse gas emissions [1]. Demand for liquid fossil fuels is continuously increasing, [2] motivating the need for vehicles that run on low-net-carbon biofuels (or biofuel blends) with high efficiencies. One such biofuel is ethanol that has been shown to reduce life-cycle greenhouse gas emissions [3]. Pump gasoline can contain up to 15% ethanol per volume in the US – although 10% blends are most common. In addition to reducing fossil fuel consumption, ethanol has the potential to enable improved spark ignition engine performance through higher compression ratio, higher boost pressure and/or optimizing spark

timing (i.e. combustion phasing) [4, 5, 6, 7]. These benefits are partly a result of ethanol's comparatively high octane ratings, but also stem from ethanol's high heat of vaporization (HOV), which is a fluid property that describes the necessary energy to evaporate a prescribed amount of liquid. Direct Injection Spark Ignition (DISI) engines utilize the fuel's evaporative cooling potential to lower combustion chamber temperatures allowing higher loads to be achieved without knock, [8, 9, 10, 11] which in turn allows for higher compression ratios or increased pressure from forced induction. Due to higher HOV, increased ethanol content should lead to greater evaporative cooling allowing engine designers to further leverage these effects which in turn can increase efficiency and ultimately reduce greenhouse gas emissions.

Particulate matter (PM) is a combustion product that can present serious health and environmental risks, is formed in fuel-rich zones when fuel and air are not fully premixed, and in particular in a DISI engine when the fuel spray impinges on the cylinder wall or piston [12, 13, 14]. Research has shown that increasing the ethanol percentage in gasoline produces in most cases a reduction in PM [9, 13, 15] but in other cases elevated PM levels [16, 17]. General observations suggest that for fuels containing low ethanol concentrations (e.g. E0 – E15) PM emissions are insensitive to ethanol content [14]. For moderate ethanol concentrations (e.g. E20– E40), increased PM emissions relative to E0 have been observed [9, 17]. PM is reduced at high ethanol concentrations, such as E85, because it is likely that blending with ethanol dilutes PM precursors such as aromatic compounds in the gasoline [13].

The fundamental cause of the PM increase seen for moderate ethanol concentrations is not well understood. Current theories suggest that the high HOV of ethanol can cool the cylinder environment slowing the evaporation rate and preventing the highest boiling compounds in gasoline from fully vaporizing and mixing with air in the combustion chamber. The formation of this non-homogenous mixture would be even more likely if there was impingement of the fuel spray on the cylinder wall or piston. The pool or film of fuel can burn in a diffusion flame where these high boiling species are more concentrated in the rich zone leading to hydrocarbon molecular weight growth and increased PM production [16, 17]. Additionally, ethanol as well as other potential biofuels can form azeotropes when blended with gasoline. These non-ideal interactions can alter the boiling temperatures (i.e. the distillation curve) of the fluid as well as the time dependent vapor and liquid composition that can dictate the in-cylinder reactant composition distribution. For example, these interactions can enrich the heavy fractions of the liquid droplet with certain species such as aromatics which have shorter kinetic pathways and greater potential to form PM [9, 18].

A numerical model was created to simulate the droplet evaporation dynamics of ethanol/gasoline fuel blends to explore the role of these unique behaviors and properties (*i.e.* azeotropes and increased HOV) on recent observations linking ethanol content to PM emissions. Validation of the model's ability to predict the fuel's vapor liquid equilibrium and evolving thermophysical properties is carried out through comparisons with data gathered from experiments with the Advanced Distillation Curve [19]. Following validation, an isentropic single cylinder engine model was developed to evaluate droplet evaporation under dynamic temperature and pressure conditions for a set of ethanol-gasoline blends. Results from these simulations, including the net droplet evaporation times, are then compared and used to explain the link between the HOV of ethanol and reported PM emissions.

METHOD

Gasoline/Ethanol Blends

The base gasoline used in this work was the Fuels for Advanced Combustion Engines reference gasoline B (FACE B) [20]. FACE B was chosen because of its relative simplicity as compared to a

commercially available gasoline. This simplified composition reduced model run times, yet still provided enough complexity to capture the physics experienced in a real life pump fuel.

A detailed hydrocarbon analysis (DHA) of the neat FACE B revealed that 29 compounds were required to describe 99.9% of the fuel's mass. DHA was performed using ASTM Method D6729 [21] and Hydrocarbon Expert 5. [22] The result of the DHA for the neat FACE B is provided in Table 2 in Appendix A.

Distillation experiments were carried out to provide comparison data for model development using the well documented Advanced Distillation Curve (ADC) approach. [19] ADC experiments were performed on three FACE B/ethanol blends containing 0% (E0), 15% (E15), and 30% (E30) ethanol by volume. Distillation curves were measured for the three fuel blends and the evolving composition of the distilling fuels was quantified by sampling and performing a DHA on the condensate during the distillation. This condensate composition data was then used to determine the changing mixture averaged properties of the fuel to compare with model predictions. The distillations and corresponding simulations were performed at an average ambient pressure of 81.2 kPa (1760 m elevation).

In the case of some models, a wider gamut of gasoline ethanol blends was used. These represent E0 to E85 in 5 percent increments by volume. The volume fraction of gasoline was multiplied by a normalized composition of FACE B as measured by DHA, so that the volume fractions of the components in the model summed to unity. Differences in composition between FACE B samples and errors due to mixing were thus controlled in order to directly quantify the effect of increasing ethanol content.

Ideal Distillation Model

Ideally, vapor-liquid equilibrium (VLE) can be determined from Raoult's Law and Dalton's Law, as in Eq. (1). The mole fraction of each component in the liquid is defined as x_i and the mole fraction within the vapor as y_i . The ratio of these values defines the equilibrium constant (K_i) which can be found knowing the ratio of the species' vapor pressure (P_i^0) to the total pressure of the system (P_{tot}), multiplied by an interaction term (γ_i) to account for non-ideal vaporization behaviors (typical of biofuels). If molecular interactions are neglected, the interaction term γ can be ideally assumed to be unity.

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^0}{P_{tot}} \quad (1)$$

To predict the distillation curve of a complex fuel, one needs to be able to predict the change of composition of the fluid as it evaporates. This change in the liquid composition can be described as a function of the instantaneous vapor composition [23], and simplified using the equilibrium ratio to the ordinary differential equation provided in Eq. (2), where L is the fraction of total moles in the system that are in the liquid state.

$$\frac{dx_i}{dL} = \frac{(K_i - 1)x_i}{L}$$



The set of differential equations describing the change of the liquid mole fraction of each species, Eq. (2), are then solved for set increments of L with the convergence criteria described by the equilibrium condition that all the species' vapor pressures sum to the system's total pressure as described in Eq. (3).

$$p_{tot} = \sum \gamma_i x_i p_i^0 \quad (3)$$

Assuming the total pressure remains constant, a Newton-Raphson Method is used to find the liquid temperature which dictates each species' vapor pressure to satisfy the equilibrium condition described in Eq. (3) [23]. Vapor pressure is calculated using coefficient lookup tables based on DIPPR empirical relationships, [24] which are shown in Appendix C. This application of the Newton-Raphson Method is summarized by Eq. (4).

$$f(T) = p_{tot} - p_{\infty} = 0 \quad \& \quad T_{i+1} = T_i - \frac{f(T_i)}{f'(T_i)} \quad (4)$$

For both the modeling and the experiments, the HOV of the mixture is calculated as a composite sum weighted by the mole fraction of each component as described by Eq. (5) [8]. The HOV of each component is calculated with the empirical relationship provided by DIPPR [24]. Other mixture properties, such as thermal conductivity and specific heat capacity, were also calculated as a composite based on mole fraction.

$$\bar{H}_{fg,mix} = \sum_i y_i \bar{H}_{fg,i} \quad (5)$$

UNIFAC

In the ideal case, the gamma term in the set of differential equations previously defined can be assumed to be equal to unity. This is acceptable for gasolines and other hydrocarbons, but is inaccurate when ethanol is present in the mixture. The UNIFAC group contribution theory is one of several methods that are used to quantify the correct gamma values to model realistic vapor liquid equilibrium for chemically dissimilar compounds. It consists of geometric and polarity-driven pieces, referred to as combinatorial and residual, which both contribute to the total non-ideal coefficient, Eq. (6) [23, 25].

$$\ln \gamma = \ln \gamma_r + \ln \gamma_c \quad (6)$$

The combinatorial component of the UNIFAC group contribution theory, γ_c , deals with geometric interaction between molecules, and is applicable even in the absence of non-ideal interactions. The residual UNIFAC term, γ_r , is a function of polarity and temperature. Unlike the combinatorial portion, the main interaction parameters, a_{mn} , are purely empirical in nature. These terms describe the effect that the polarity of one structure has on another. Because this term is a function of polarity, and there is zero residual interaction between

structures of the same category, alkane blends have no residual term γ_r . This term is thus only needed when oxygenates and, to a far lesser extent, aromatics are present in the mixture. It can otherwise be omitted for the sake of performance, as in the case of pure FACE B. The residual parameter ψ_{mn} , as defined in Appendix B Eq. (12), is a function of droplet temperature and a_{mn} , and must be determined at every step of the solver.

Droplet

In order to model the distillation process as a droplet, energy transfer must be taken into account. A zero-dimensional form is used that includes heat conduction, sensible heat of the droplet, and latent heat of vaporization. As this is zero-dimensional, composition and temperature within the droplet are assumed to be uniform. This assumption has been shown to accurately predict the droplet evaporation dynamics for fuels and conditions similar to those reported here [26].

When modelling distillation, the system of differential equations depended on the changing composition. (Eq. 2) When modeling a droplet, the Newton-Raphson Method is no longer needed to solve for saturation temperature, but vapor pressure must still be calculated as shown in Eq. (3). It is also necessary to include a term for the change in volume fraction, which allows radius to be calculated, and the change in mass fraction, which allows the elapsed time to be determined based on the diffusion equation. Equations 7 and 8 show the change in volume fraction distilled and mass fraction distilled, respectively. These are negative, as they describe, in nondimensional form, the volume and mass leaving the droplet. The term c is the molar concentration of each component [24].

$$\frac{dv^*}{dL} = - \frac{\sum_i \frac{y_i}{c_i}}{\left[\sum_i \frac{x_i}{c_i} \right]_{initial}} \quad (7)$$

$$\frac{dm^*}{dL} = - \frac{\sum_i y_i MW_i}{\left[\sum_i x_i MW_i \right]_{initial}} \quad (8)$$

The time rate of mass change, Eq. (9), is found using diffusion. In this expression, Y_F represents the vapor mass fraction of the fuel at the droplet surface. An approximation was used to solve for the diffusivity term as a function of molecular weight of the fuel air mixture surrounding the droplet, which is shown in Eq. (10) [27]. The change in mass with respect to L , Eq. (8), and the change in mass with respect to time, Eq. (9), can be combined to find the change in time with respect to L . This allows for time to be calculated as an independent variable. Conservation of energy is used with latent heat, sensible heat, and conduction terms. The sensible heat term is used to find transient temperature change, Eq. (11). Change in time with respect to L was calculated as shown in Eq. (12), so Eq. (11) can be redefined with respect to L to add a dT/dL term to the system of equations. Heat conduction, as shown in Equations 13 and 14, is the only form of heat transferring to the droplet from the environment, with radiation and convection neglected.

$$\frac{dm}{dt} = \dot{m} = 4\pi r_s \rho_{vap} D_{FA} \ln \left(\frac{1}{1-Y_F} \right) \quad (9)$$

$$D_{FA} = \frac{0.0266 T^{\frac{3}{2}}}{p_{tot} \Omega_D \sigma_{AF}^2 \sqrt{MW_{mix}}} \quad (10)$$

$$\frac{dT}{dt} = \frac{-\dot{Q}_{cond} - \dot{m} h_{fg}}{m_{drop} c_{p,liq}} \quad (11)$$

$$\frac{dt}{dL} = \frac{dm}{dL} \left(\frac{dt}{dm} \right) = m_{init} \frac{dm^*}{dL} (\dot{m})^{-1} \quad (12)$$

$$\dot{Q}_{cond} = -\frac{k A_s Z \dot{m}}{r_s^2} \left[\frac{(T_{\infty} - T_s) \exp\left(-\frac{Z \dot{m}}{r_s}\right)}{1 - \exp\left(-\frac{Z \dot{m}}{r_s}\right)} \right] \quad (13)$$

$$Z = \frac{c_{p,gas}}{4\pi k} \quad (14)$$

The system of ordinary differential equations used to model an evaporating droplet defines changes of the liquid molar concentrations for each species, time, temperature, mass fraction distilled, and volume fraction distilled with respect to changes in L . The resulting ODE is shown below, Eq. (15). A stiff ODE solver was utilized in MATLAB to integrate this system.

$$\bar{f} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \\ t \\ T \\ m^* \\ V^* \end{bmatrix} \quad \& \quad \frac{d\bar{f}}{dL} = \begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \vdots \\ \dot{x}_n \\ \dot{t} \\ \dot{T} \\ \dot{m}^* \\ \dot{V}^* \end{bmatrix} \quad (15)$$

Direct Injection Engine Model

In order to predict how the dynamic temperature and pressure inside of a direct injection engine may affect the relative timescales of the ethanol evaporation, an isentropic Otto cycle was used to provide ambient pressure and temperature as a function of time. Dimensions representative of a 2.0L DISI 4-cylinder engine were used at an assumed rotational velocity of 1000 revolutions per minute. These dimensions allowed the volume of air within the piston to be determined as a function of time, assuming constant radial velocity. Therefore, the pressure and the temperature in the cylinder were calculated based on an isentropic ideal gas. This ramped temperature droplet model does not account for cooling of the combustion chamber by the droplet evaporation and remains an open model with diffusivity along an infinite scale. Table 1 provides the engine dimensions and conditions used to calculate the transient temperature/pressure traces.

Table 1. Engine operating parameters

Bore	83.5 mm
Stroke	91.2 mm
Connecting Rod	159.6 mm
Compression Ratio	13.0:1
Rotation Velocity	1000 RPM
Pressure at BDC	101.325 kPa
Temperature at BDC	315 K
Initial droplet diameter	40 μm

RESULTS

Distillation Model

Comparisons between the measured and predicted distillation curves and HOV for E15 are shown in Figure 1. Results from simulations assuming ideal interactions and non-ideal interactions determined using the UNIFAC approach are provided for comparison. It should be noted that the use of UNIFAC resulted in a 45 fold increase in computation time compared to the ideal distillation model. The predicted distillation curves and HOV accounting for non-ideal interactions agree well with data from the ADC experiments. Assuming ideal interaction behavior for these fuel blends, however, significantly under predicts the HOV and over predicts boiling temperatures in the early part of the distillation. Not shown here, the ideal interaction assumption did accurately predict experimental measurements performed on the neat FACE B (E0).

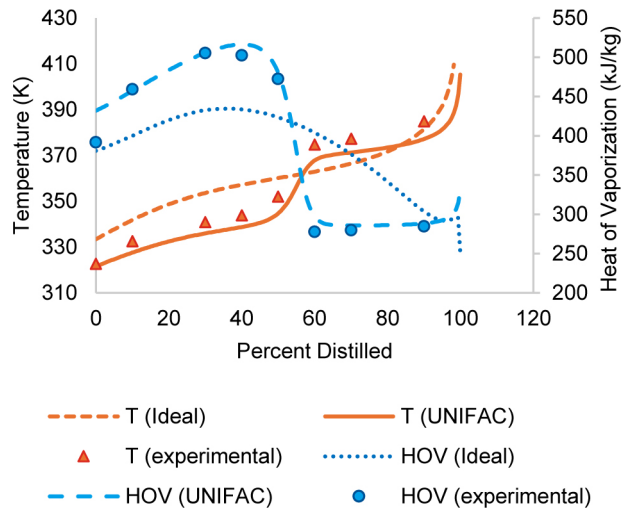


Figure 1. A comparison of experimental HOV and temperature results to models of ideal vapor pressure and UNIFAC vapor pressure for distillation of E15 at 81.2 kPa.

Despite the good overall agreement, there is a noticeable over prediction in the HOV for the initial sample of condensate. This is likely a result of the sampling process during the experiments not being able to collect the highly volatile species which are the first compounds to distill, namely n-butane. Nevertheless, the initial boiling temperature is accurately predicted based on the composition of the neat fuel blend, which implies that the composition at this point is properly reflected by the UNIFAC model. While the distillation model with UNIFAC followed the experimental trends