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Multicomponent Droplet Evaporation using Group Contribution Methods with Application to Fuel Blends

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Abstract: Current studies of multicomponent droplet evaporation do not successfully capture the evaporation characteristics of fuel blends. Reasons for this are the usage of averaged properties of fuel-components and the lack of data for physical properties of fuel components -- especially for cycloparaffins and substituted aromatics which form a significant portion of the mixture. We present an approach based solely on functional groups that are present in the components of the fuel. In the description of the multicomponent evaporation, we incorporate a non-ideal evaporation formulation while still providing computationally efficient calculations. This allows the evaluation of evaporation and combustion characteristics of virtually any fuel blend based only on the intrinsic primary and secondary functional groups. Studies of various fuel blends and surrogates, including Jet-A, JP-8 and gasoline are performed and results are compared against experimental data. Due to the generalized nature of this approach, the proposed method provides an effective alternative for existing computational techniques dedicated to multicomponent droplet evaporation; further work involving the utilization of this approach in various combustion codes can be performed.

Keywords: *Multicomponent, Group Contribution, UNIFAC, Aviation Fuels*

1. Introduction

Computational approaches to multicomponent droplet evaporation introduce challenges in generalizing to arbitrary fuel blends due to the vast number of assumptions that are being introduced to describe evaporation and composition. Some models [3] simplify on the computational cost by using a distribution-weighted average of component properties without a physical justification for the choice of the distribution. Other methods [2,3,6,11] arbitrarily generalize existing physical property correlations to fractional carbon numbers. In addition to this, current literature is restricted to specific families of components which is an infeasible approach for aviation fuel blends which not only have a high species count but also contain components belonging to widely different families of organic compounds. This motivates a generalized approach where the lack of experimental data is taken to be inevitable and physical properties must be calculated from first principles.

Measurements from distillation and chromatography provide information regarding the molecular weight and functional groups present in compounds, constituting a particular fuel blend. The results presented utilize the fuel descriptions provided in [12]. Also, [1] and [4] describe methods to estimate physical properties of a compound based on the functional groups

present in it. To evaluate how suitable the above methods are in calculating multicomponent fuel evaporation characteristics, we need to utilize a highly accurate evaporation model. UNIFAC [5] is a method used to calculate interaction coefficients and is also based solely on the functional groups present in each component. Note that the method described in [1] is compatible with the UNIFAC model and thus enabled the two to be coupled in the simulation code used for obtaining results. Preliminary evaporation studies have been performed on Jet-A and JP-8.

2. Basic Equations and Approximations

A computational study was performed using the UNIFAC non-ideal evaporation model. Despite the usage of an interpreted language (MATLAB), runtime is of the order of a second for droplet evaporation in fixed ambient conditions, making it a feasible candidate for other codes like reactive flow solvers which utilize an evaporation module. The focus in the following section will however be only on evaluating the effectiveness of this group contribution method in predicting droplet evaporation characteristics of fuel blends.

The evaporation rate is calculated on a per-component basis. A one-dimensional version of this equation is presented in [6] and is commonly referred to as DCM (Discrete Component Model). The current approach is also the multicomponent model implemented in ANSYS Fluent.

$$\frac{dm_i}{dt} = -4\pi r^2 (MW_i) k_c (C_{i,s} - C_{i,\infty}) \quad (1)$$

where r is radius of the droplet, MW is the molecular weight of species and k_c is the mass transfer coefficient, which in turn is given by

$$k_c = (Sh)(D_i)/2r \quad (2)$$

where Sh is the Sherwood number (can be expressed as a function of Reynolds and Prandtl number), D_i is the diffusion coefficient of species. Also, for a droplet temperature T_d , the concentration of species i at the surface $C_{i,s}$ is evaluated as

$$C_{i,s} = \gamma_i x_i p_{sat,i} / RT_d \quad (3)$$

where $p_{sat,i}$ is the saturated pressure, γ_i is the activity coefficient ($p_{real}/p_{theoretical}$) and x_i is the mole fraction of species. Similarly, $C_{i,\infty}$ stands for the far-field equilibrium concentration of the droplet species in the gas phase.

The change in temperature is calculated using the following equation.

$$\frac{dT}{dt} = \sum_i \frac{dm_i}{dt} L_{v,i} + \frac{2\pi(Nu)k_{air}(T_{amb} - T)}{m_d c_{l,m}} \quad (4)$$

where $L_{v,i}$ is the latent heat of evaporation, Nu is the Nusselt number (which can also be expressed as a function of the Reynolds and Prandtl number), k_{air} is the thermal conductivity of the surrounding medium (air in this case), T_{amb} is the ambient temperature, m_d is the mass of the

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droplet and $c_{l,m}$ is the mole fraction weighted average liquid specific heat capacity of the drop. Time integration was done using 'ode23' since the equations are stiff, especially as temperature of drop approaches the ambient temperature. The Prandtl number was assumed to be a constant, with a value of 0.7 and the following correlations from [7] have been used for calculating the Nusselt and Sherwood numbers:

$$Nu = 2 + \frac{0.555Re^{0.5}Pr^{1/3}}{1 + 1.232(RePr^{4/3})^{0.5}} \quad (5)$$

$$Sh = 2 + 0.6Re^{0.5}Pr^{1/3} \quad (6)$$

One of the key ideas we present is to use UNIFAC to calculate the activity coefficient γ . This quantity is a function of the entire mole fraction vector and thus makes this a non-linear problem. In addition to this, we require the physical properties as functions of temperature based only on the knowledge of functional groups and this is achieved using group contribution method [5], which also bases itself on the same functional group definitions as UNIFAC.

There is no known accurate method to estimate binary diffusion coefficients using the primary and secondary functional groups of [1]. For this purpose, the method due to Lee and Wilke [8] is used which yields D_i as a function of the Van der Waals Radius σ and Lennard-Jones Potential ϵ . An intermediate step for calculating the collision integral Ω_D is from [9]

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} \quad (7)$$

where $T^* = \epsilon/k_B T$. Table 1 summarizes the coefficients used in (7)

A	1.06036
B	0.15610
C	0.19300
D	0.47635
E	1.03587
F	1.52996
G	1.76474
H	3.89411

Table 1 : Coefficient set for calculating the collision integral described in [9]

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The binary diffusion coefficient is calculated as:

$$D_{AB} = \frac{[3.03 - (0.98/M_{AB}^{1/2})](10^{-7})T^{3/2}}{PM_{AB}^{1/2}\sigma_{AB}^2\Omega_D} \quad (8)$$

M_{AB} denotes the harmonic mean of molecular weights and σ_{AB} similarly stands for the harmonic mean of the Van der Waals radius. The pressure P is in bar, the molecular weight MW in g/mol and the temperature in K.

The use of Lennard-Jones parameters and Van der Waals radius is not highly restrictive when evaporation is followed by combustion as these parameters are available as part of mechanism data. Also, sensitivity of the evaporation rate to Lennard-Jones parameters has been provided below and thus, it can be observed that similar evaporation results can be obtained even if one is forced to use a more limited parameter set.

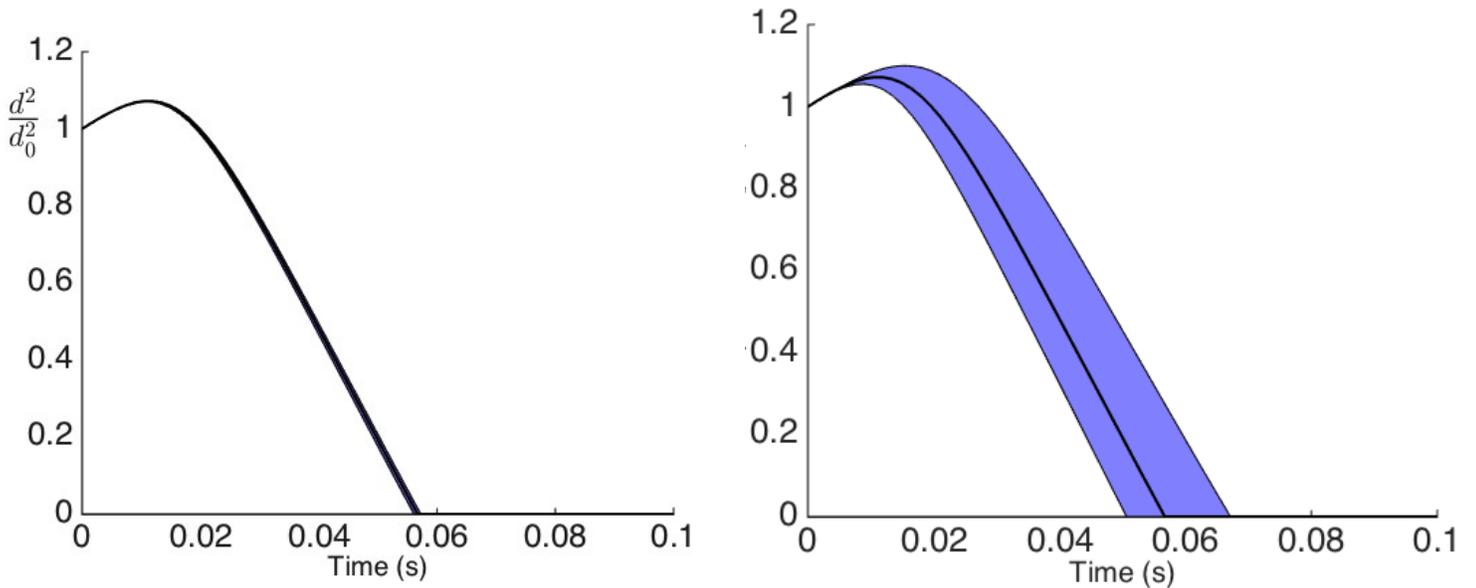


Figure 1: Sensitivity analysis based on computational results from group contribution using UNIFAC activity coefficients with Lennard-Jones potential and Van der Waals radius of $\frac{1}{2}$ and 2 times the input values. Initial droplet diameter = $100\mu\text{m}$, ambient temperature = 800K , initial droplet temperature = 300K and ambient pressure = 1bar

UNIFAC is based on splitting the activity coefficient calculation into a combinatorial (γ_i^c) and residual component (γ_i^r). Both contributions are totally determined by the three parameters, viz., group surface area parameter R , group volume contribution Q and the binary interaction parameter which is related to the interaction energy a_{mn} . The resulting equation for the activity coefficient is then written as:

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$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \quad (9)$$

where

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + L_i - \frac{\phi_i}{x_i} \sum_{j=1}^n x_j L_j \quad (10)$$

θ_i and ϕ_i are the molar weighted segment and area fractional components for component i in the system. The model is fairly insensitive to the co-ordination number z and is taken to be 10 for all calculations [5]. This in turn helps to calculate the compound parameter L_i . The following equation summarizes how each of these terms is calculated.

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^n x_j q_j}; \quad \phi_i = \frac{x_i r_i}{\sum_{j=1}^n x_j r_j}; \quad L_i = \frac{z}{2}(r_i - q_i) - (r_i - 1); \quad z = 10 \quad (11)$$

q_i and r_i are calculated from the group surface area Q and volume contributions R as well as the number of occurrences of the functional group on each molecule $\nu_{i,k}$

$$r_i = \sum_{k=1}^n \nu_{i,k} R_k; \quad q_i = \sum_{k=1}^n \nu_{i,k} Q_k; \quad (12)$$

The residual activity coefficient (γ_i^r) is calculated from the following equation

$$\ln \gamma_i^r = \sum_k^n \nu_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (13)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \sum_m \Theta_m \Psi_{mk} - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (14)$$

In (14), Θ_m is the summation of the area fraction of group m . The group interaction parameter is a measure of the interaction between different functional groups. This requires X_m , the group mole fraction as given by the following equations:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; \quad X_m = \frac{\sum_j \nu_{j,m} x_j}{\sum_j \nu_{j,n} x_j} \quad (15)$$

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Note that $\Gamma_k^{(i)}$ is calculated using the same equations, except that it corresponds to a solution consisting only of components of type i . The binary interaction parameters are calculated using the following equations. a_{mn} is well documented and can be obtained from [13].

$$\Psi_{mn} = \exp \left[\frac{-a_{mn}}{T} \right] \quad (16)$$

We require the saturation vapor pressure for a given component $p_{sat,i}$ before solving for droplet radius and temperature as a function of time. This is done using the Lee-Kesler method [14]. Note this in turns entails the requirement of acentric factor ω , the critical pressure P_c and critical temperature T_c , which can be easily estimated using the group contribution method. The equations for the Lee-Kesler are as follows:

$$\ln P_r = f^{(0)} + \omega \cdot f^{(1)} \quad (17)$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \cdot \ln T_r + 0.169347 \cdot T_r^6 \quad (18)$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \cdot \ln T_r + 0.43577 \cdot T_r^6 \quad (19)$$

Here $P_r = \frac{P}{P_c}$ and $T_r = \frac{T}{T_c}$ denote the reduced pressure and temperature respectively.

The data for the group contribution method can be found in [15] and the equations are written as:

$$T_c = 181.128 \ln \left[\sum_k N_k(tc1k) \right] \quad (K) \quad (20)$$

$$P_c = \left[\sum_k N_k(pc1k) + 0.10022 \right]^{-2} + 1.3705 \quad (bar) \quad (21)$$

$$\omega = 0.4085 \ln \left[\sum_k N_k(w1k) + 1.1507 \right]^{(1/0.5050)} \quad (22)$$

$$\Delta H_{v298} = 6.829 + \left[\sum_k N_k(hv1k) \right] \quad (kJ/mol) \quad (23)$$

$$V_{liq298} = -0.00435 + \left[\sum_k N_k(vliq1k) \right] \quad (cm^3 mol^{-1}) \quad (24)$$

$$C_p^0 = \left[\sum_k N_k (CpA1k) - 19.779 \right] + \left[\sum_k N_k (CpB1k) + 22.5981 \right] \theta + \left[\sum_k N_k (CpC1k) - 10.7983 \right] \theta^2 \quad (J/mol - K) \quad (25)$$

In (25), $\theta = (T - 298)/700$. The correlations are applicable in a wider range than prescribed but will not conform to the 5% error tolerance with respect to experiments [1]. Note that the current code implementation utilizes only first order functional groups. The number of occurrences of a functional group N_k is obtained from the fuel description.

Note that density is also a function of temperature and needs to be accounted for if one wishes to predict the initial increase in radius of droplet during evaporation as seen in (Fig 1). The group contribution method by [1] only yields specific volume at 298 K. [10] describe a method to compute the density at any specific temperature using the specific volume at 298 K.

$$V_s = V_{s,298} (0.29056 - 0.08775\omega)^\phi \quad (26)$$

$$\phi = \left(1 - \frac{T}{T_c}\right)^{2/7} - \left(1 - \frac{298}{T_c}\right)^{2/7} \quad (27)$$

3. Results and Discussion

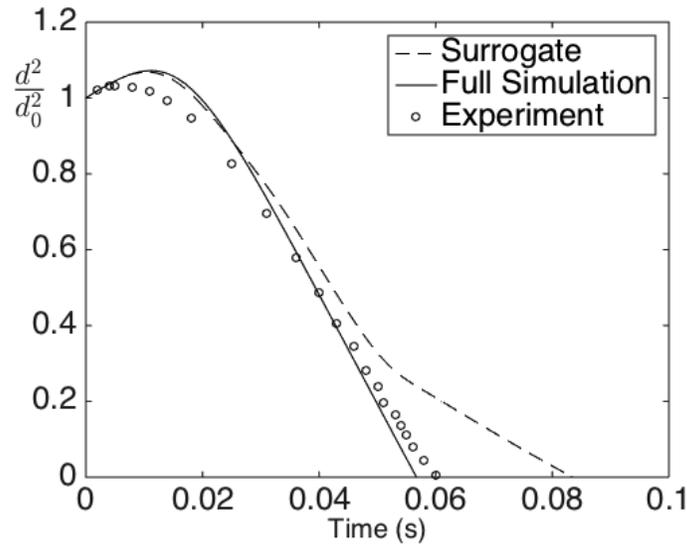


Figure 2: Comparison between quiescent Jet-A experimental evaporation data [2], computational results from group contribution using UNIFAC activity coefficients utilizing the full and surrogate (Jet A POSF 4658 2nd generation) description presented in [12,16]. Initial droplet diameter = 100 μ m, ambient temperature = 800K, initial droplet temperature = 298 K and ambient pressure = 1 bar

Figure 2 shows reasonable agreement between experimental data and the proposed method for evaporation calculations. Further relaxation of assumptions is possible and since Jet-A predominantly consists of non-polar molecules, the same simulation was run with both non-ideal and ideal model, the latter just assumes an activity coefficient of 1 for every component. An error of 0.8% was observed in the evaporation time for the same case. Thus, it is suggested that an ideal evaporation model be used when computational cost is a constraint.

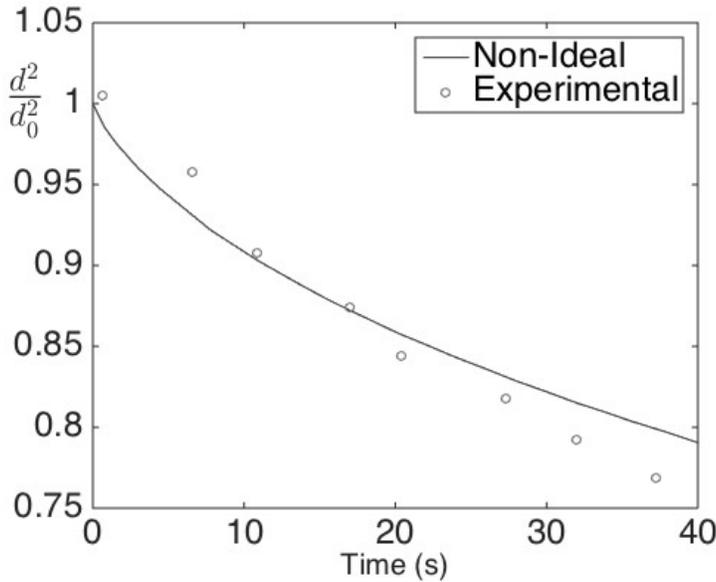


Figure 3: Comparison between JP-8 experimental evaporation[2] and computational results from group contribution using ideal evaporation. Initial droplet diameter = $639\mu\text{m}$, ambient temperature = 298K, initial droplet temperature = 298 K, ambient pressure = 1 bar, relative velocity = 3m/s

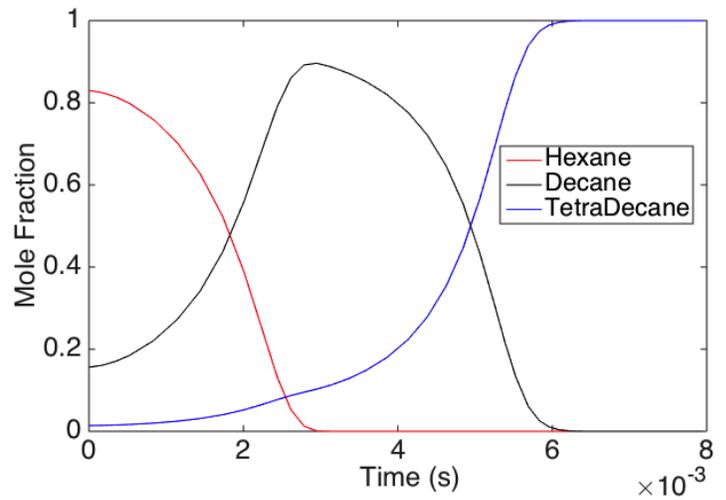
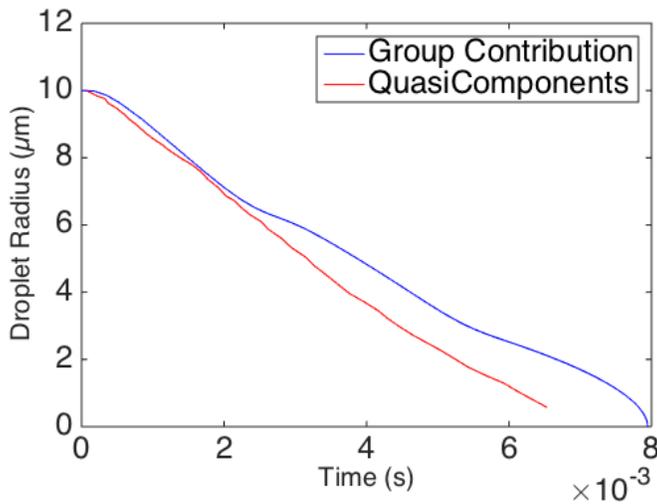


Figure 4: Computational results for 3-component gasoline evaporation surrogate[11] from group contribution using ideal evaporation with 3-quasicomponent model data [11]. Initial droplet diameter = $20\mu\text{m}$, ambient temperature = 450K, initial droplet temperature = 298 K, ambient pressure = 3 bar, relative velocity = 10m/s

4. Conclusions

The difficulties in performing computational studies for droplet evaporation of aviation fuel blends have been presented and a novel method has been described. The proposed method only requires the knowledge of the functional groups present in the mixture, making it generalizable to virtually any fuel blend. Evaporation of Jet-A, JP-8 and gasoline has been presented along with corresponding experimental data and was shown to have good agreement. The redundancy of a detailed non-ideal evaporation model in case of aviation fuels has also been presented. Due to the low computation cost, further studies utilizing the group contribution method as part of the simulation code can be performed.

5. Acknowledgements

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