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Distillation-Resolved Evolution of Key Combustion Properties

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Abstract: Many studies demonstrate successful emulation of pre-vaporized real fuel combustion through use of fuel surrogates. These surrogates may be described by a multiplicity of non-unique multicomponent formulations, each with pre-vaporized combustion behaviors that are essentially equivalent to the target real fuel and each other. However, many combustion applications employ fuel sprays, leaving some question as to the validity of pre-vaporized assumptions for these conditions. In the present work, a batch distillation model for ideal liquids is developed to predict the evolution of surrogate fuel combustion properties such as autoignition propensity (represented by an effective RON or DCN), hydrogen-carbon-oxygen atomic ratios, average molecular weight (MW), etc. Simulations reveal that, among several effectively equivalent pre-vaporized surrogates, large disparities may exist in one or more combustion properties as the fuels distill. For example, three multicomponent 95 RON gasoline surrogates show distillation-resolved RONs spanning, respectively, 91.0, 93.5 and 94.0 to 120.0, each with a sustained depression from the pre-vaporized 95 RON target over ~60-70% of the distillation curve. A jet fuel example is also considered herein. Whether or not preferential vaporization effects are attenuated by the complex combustion environments encountered in many applications remains an open question; however, present results indicate a significant potential for chemical property stratification in spray combustion environments.

Keywords: *Preferential Vaporization, Batch Distillation, Spray Combustion, Surrogate Fuel*

1. Introduction

Real fuels used in many propulsion applications are generally complex mixtures that may contain a large number of individual chemical species in varying proportions. Each of these species can be characterized by its own specific rate of oxidation that depends on imposed combustion conditions as well as chemical coupling with a spatiotemporally varying pool of combustion reaction intermediates. Such complexity would appear to render intractable the high fidelity emulation of many combusting flow properties (whether in the physical or computational domain) [1]. However, creating fuel blends composed of a limited number of distinct chemical species as real fuel "surrogates" has been shown in many cases to provide satisfactory emulation of real fuels over a restricted range of combustion conditions (e.g., [2-4]). When using surrogate fuels, computational modeling can benefit from the reduced computational requirements, while experimental fuel research can benefit by having a predictable and consistent test fuel [1, 2].

Extensive research has been conducted on surrogate formulation techniques. Of this, several approaches focusing on matching some ensemble of combustion properties (CPs) shared by a

particular real fuel and its surrogate have been advanced for the case of properties associated with pre-vaporized combustion (e.g., [2, 4-7]). However, the pre-vaporized fuel assumption underpinning these approaches disregards distillation effects (among other phenomena associated with multi-phase combustion) on combustion performance.

This omission of a distinct physical process contributing to overall fuel combustion may significantly influence the ability of a surrogate to emulate its corresponding real fuel, as evidenced by several previous studies that address fuel distillation effects [8-10]. Many of these studies couple distillation into relatively complex CFD models for spray combustion, providing detailed resolution of local heat fluxes, droplet size distributions, droplet/gas interface locations, local species concentrations, etc. Despite high resolution ability (and attendant high computational overhead), these simulations provide limited insight as to

- (1) the effects of distillation on combustion behavior for two or more effectively equivalent pre-vaporized combustion surrogates that differ significantly in distillation behavior, and
- (2) simple surrogate formulation rules that permit distillation effects to further constrain the limited set of pre-vaporized combustion property targets (CPTs).

To provide insight for item (1), the present work demonstrates a simple (low computational overhead) model that resolves a surrogate fuel's previously lumped (via pre-vaporized assumption) CPs along its distillation trajectory. Here CPs are used with a degree of informality (e.g., use of effective RON to indicate ignition propensity of a particular mixture); however, these serve as meaningful proxies for key combustion behaviors such as ignition, soot formation, etc. Item (2) is addressed elsewhere [11].

2. Approach

The model used in this work considers coupling between combustion and distillation during multi-phase, multicomponent fuel combustion by inferring CP evolution from the equilibrium-limited distillation of a representative spherical fuel droplet (Figure 1a). Notionally, the droplet vaporizes in effective isolation, though with sufficient external convection to negate significant barriers to heat and mass transfer. Combustion phenomena are governed by the CPs associated with type and abundance of chemical species deposited in the distilled vapor (Figure 1c).

The model simulates ideal multicomponent mixture batch distillation (Figure 1b) that satisfies Raoult's law for vapor-liquid equilibrium and uses species-specific partial pressures determined from the Antoine equation. This batch distillation computation results in three distinct, co-evolving chemical compositions as represented in Figure 1 for a ternary fuel surrogate mixture: a residual liquid (droplet) composition corresponding to the fuel's residue curve, a vapor composition in the envelope surrounding and in equilibrium with this droplet, and a virtual composition for fuel that would be captured during ASTM D86 distillation [12]. We treat this latter fuel as a "virtual" product of distillation since, in practice, it will be consumed during combustion; nevertheless, we include it here since it is considered by others [11]. Following the work of (e.g., [4, 13]), linear blending rules are applied to determine CPs (e.g., TSI or RON) corresponding to the separate liquid and vapor compositions as they evolve during distillation.

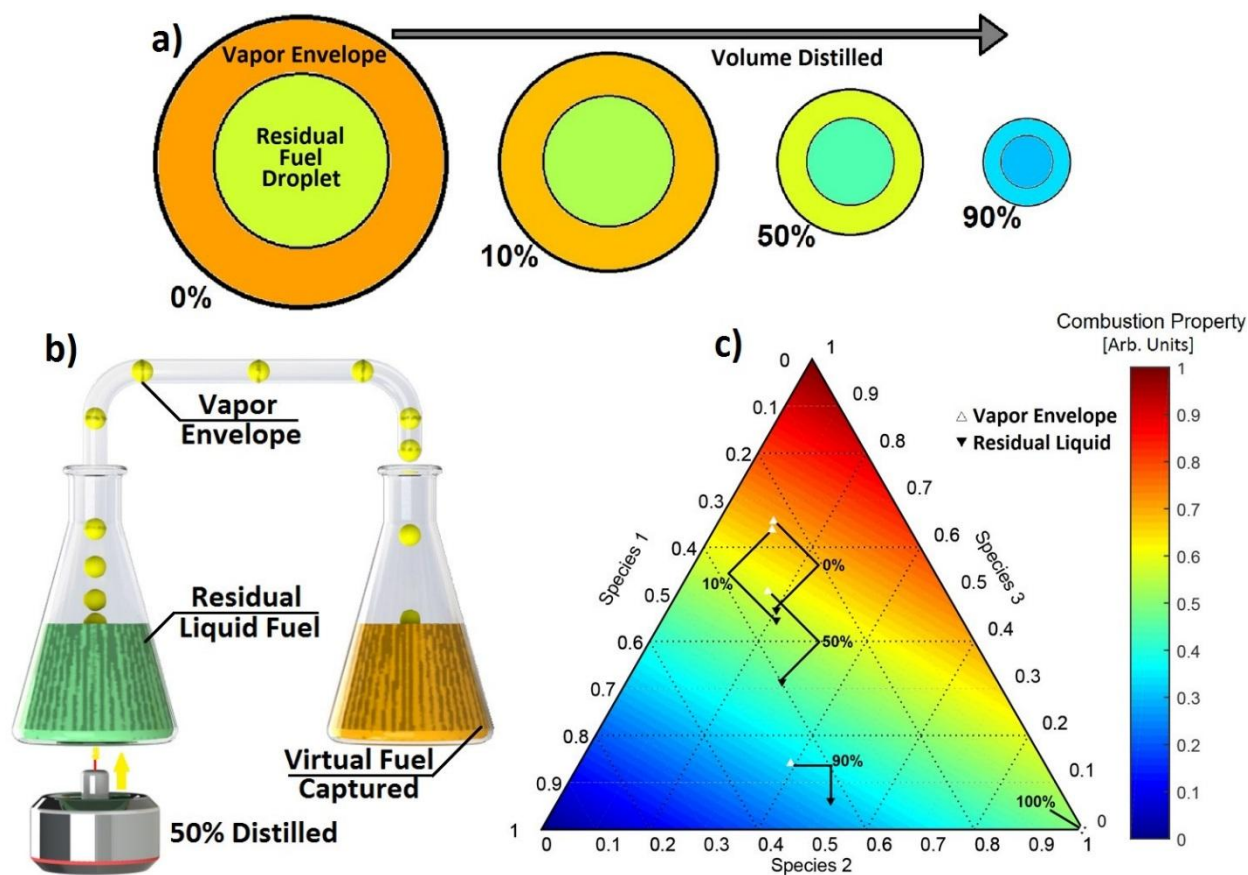


Figure 1: Distillation and combustion property (CP) determination scheme employed by present model: a) representative spherical droplet progressing into residual liquid fuel droplet and vapor envelope phases through equilibrium-limited vaporization; b) batch distillation equivalent of droplet evolution, including a virtual captured fuel phase; c) representative distillation-resolved CP trajectories for residual liquid and vapor envelope phases of a representative ternary mixture/surrogate.

For atmospheric pressure, the simulated distillation process is analogous to distillation by the ASTM D86 method [12], which applies to a wide variety of liquid fuels, including the gasoline and aviation kerosene surrogates considered later. In addition to previously considered pre-vaporized combustion CPs, this framework for distillation-resolved CP determination can also provide “volatility” CPs such as the IBP or T50 to be used for fuel/surrogate characterization and constraint.

We acknowledge a variety of limitations for the model framework (e.g., assumption of no flash boiling, chemical equilibrium, “combustion” indicated by lumped CPs), but deem these to be acceptable with respect to the model’s

- (a) substantial simplicity relative to multi-dimensional, multi-phase, multicomponent, multi-physics simulations of droplet/spray combustion (e.g., [8, 9, 14-17]),
- (b) ability to semi-quantitatively demonstrate CP stratification for surrogates as they distill, and
- (c) ability to demonstrate qualitative non-equivalence of surrogate CP evolution among surrogates that are otherwise effectively equivalent in the pre-vaporized case.

Items (b) and (c) are highlighted in the next section through examples for both gasoline and aviation kerosene surrogates.

3. Results

To illustrate distillation-resolved discrepancies in the behavior of effectively equivalent surrogates developed (primarily) through consideration of pre-vaporized combustion targets, the three multi-component surrogates (Sur95t, Sur95o and Sur95f) defined by Pera & Knop [4] to emulate 95 RON gasoline are considered here. Simulated atmospheric pressure distillation and CP computation results are presented in Figure 2 for the distilled vapor envelope surrounding the notional residual liquid droplet indicated in Figure 1.

Regardless of particular surrogate formulation, panels a), c), and d) of the figure demonstrate stratification of some of the key Pera & Knop CPs along the distillation coordinate. Under pre-vaporized conditions, each of these CPs (effective RON, MW, and H/C) is nearly the same constant target value shared among surrogates and the emulated real gasoline. Similarly, and to varying degree, each panel of Figure 2 demonstrates differences in respective CP evolution among the essentially equivalent (pre-vaporized) surrogates.

Of the CPs indicated in Figure 2, octane number sensitivity (S) was not a target of the Pera & Knop surrogate formulation approach and MW matching permitted a large degree of variability about the real fuel target. For these reasons as well as the relatively similar behavior in H/C evolution among the Sur95 surrogates and the presently intended study of CP dependence on distillation curves indicated by Figure 2e, we concentrate present discussion on effective RON evolution of the distilled vapor envelope. Figure 2a indicates that effective RON values are up to 4 units below the 95 RON target during distillation of the first 60-70% of the initial volume of fuel. Assuming a crude d^2 law transformation between droplet volume and time coordinates holds, this represents about 70-80% of the overall vaporization time of the droplet and implies effective RON (i.e., characteristic ignition delay time) stratification along

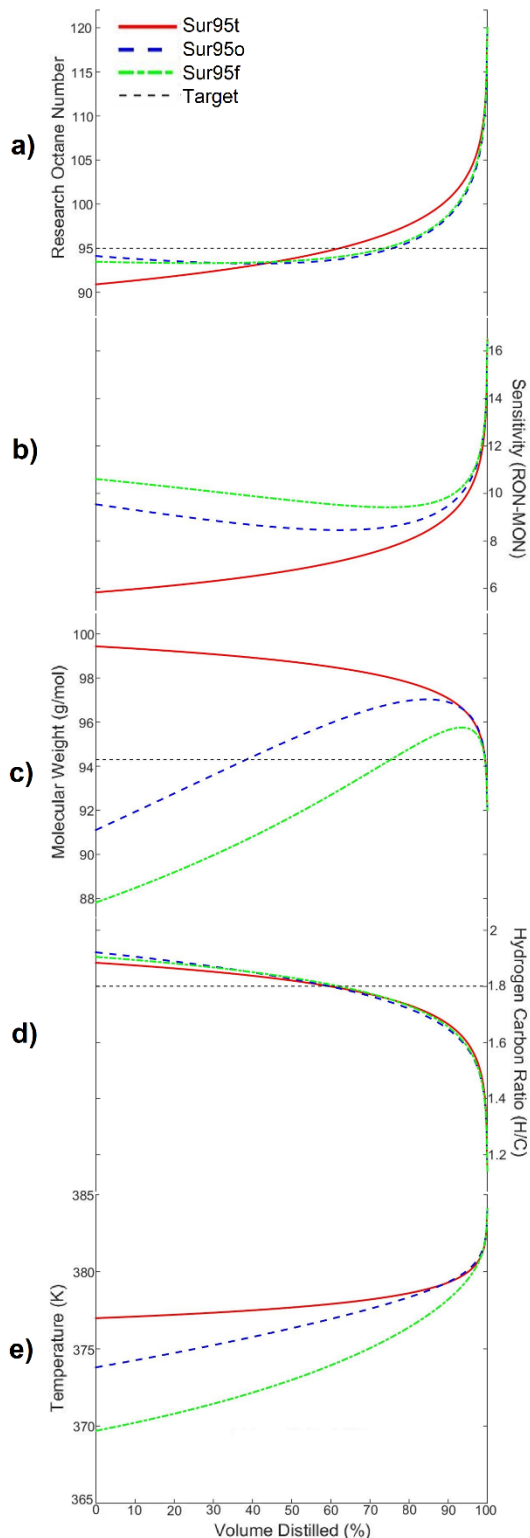


Figure 2: Distilled vapor envelope evolution of a) RON; b) ON sensitivity (S); c) MW; d) H/C ratio; and e) bubble temperature during distillation of three effectively equivalent gasoline surrogates.

the path swept out by the vaporizing droplet. Since the effective RON proxy for characteristic ignition time corresponds to gas phase mixtures with faster ignition rates, present results suggest that over much of the droplet lifetime, a relatively greater ignition susceptibility may prevail for the distilled vapor envelope relative to the average pre-vaporized mixture.

As observed in Figure 3 for aviation kerosene surrogates, CP stratification around the target pre-vaporized value as well as inter-surrogate non-equivalence applies to varieties of fuel other than gasoline. The figure describes the distillation trajectories of derived cetane number (DCN) and H/C for three effectively equivalent pre-vaporized surrogates of POSF 10325 jet fuel [11]. These surrogates are composed of varying proportions of n-dodecane (nC12), n-hexadecane (nC16), iso-octane (iC8), iso-dodecane (iC12), and 1,3,5-trimethylbenzene (135TMB), which have been defined elsewhere to match the pre-vaporized POSF 10325 jet fuel DCN, H/C, and TSI to within reasonable measurement uncertainties [11].

In these cases, preferential vaporization of relatively light surrogate fractions (e.g., iC8 and 135TMB) leads to large initial deviations in DCN and H/C from respective target values. Later in the distillation trajectory, the relatively heavy residual fractions (e.g., nC12 and nC16) likewise lead to large deviations from pre-vaporized CP targets. Moreover, the three “effectively equivalent” surrogates (under pre-vaporized conditions) exhibit qualitatively different CP evolution when compared to each other. For example, Surrogate 2 exhibits non-monotonic evolution in DCN unlike Surrogates 1 and 3, while Surrogate 3 exhibits monotonically increasing H/C evolution unlike Surrogates 1 and 2.

The degree to which these inconsistent CP evolutions may differentiate effectively equivalent surrogates in applied combustion settings is presently unclear. However, non-contrived examples provided in Figures 2 and Figure 3 make apparent some representative magnitudes of deviation (i.e., stratification) from pre-vaporized real fuel CP target values, as well as non-equivalence among surrogates developed to be “effectively equivalent” in their emulation of the pre-vaporized target real fuel.

4. Conclusions

The preceding simulation results yielded by a simple ideal mixture distillation/linear blending rule model demonstrate that distillation effects may lead to stratification of key combustion properties (e.g., RON, DCN, MW, H/C, etc.) about the lumped, pre-vaporized “average” target values used to formulate some real fuel surrogates. Physical reasoning also suggests this distillation effect may lead to spatial stratification of relative ignitability, local stoichiometry, etc.

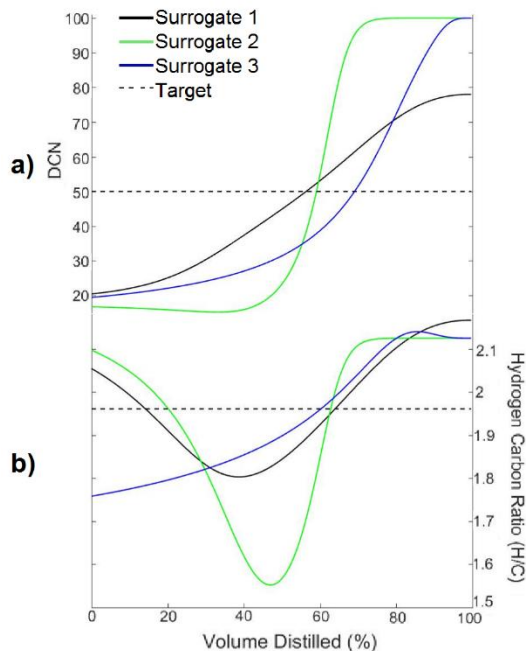


Figure 3: Distilled vapor envelope evolution of a) DCN and b) H/C ratio for three effectively equivalent pre-vaporized surrogates for POSF 10325 aviation kerosene.

in practical applications involving fuel spray/atomization. Moreover, non-equivalent combustion property evolutions are evident among “effectively equivalent” pre-vaporized surrogates for the same real fuel.

In sum, these observations appear to demand greater constraint than the isolated use of pre-vaporized combustion property targets for the formulation of surrogates. However, this conclusion warrants further support from additional, related studies with finer resolution and more robust assumptions than employed here since present results are semi-quantitative at best.

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