A physics-based approach to modeling real-fuel combustion chemistry - I. Evidence from experiments, and thermodynamic, chemical kinetic and statistical considerations

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ABSTRACT

Real distillate fuels usually contain thousands of hydrocarbon components. Over a wide range of combustion conditions, large hydrocarbon molecules undergo thermal decomposition to form a small set of low molecular weight fragments. In the case of conventional petroleum-derived fuels, the composition variation of the decomposition products is washed out due to the principle of large component number in real, multicomponent fuels. From a joint consideration of elemental conservation, thermodynamics and chemical kinetics, it is shown that the composition of the thermal decomposition products is a weak function of the thermodynamic condition, the fuel-oxidizer ratio and the fuel composition within the range of temperatures of relevance to flames and high temperature ignition. Based on these findings, we explore a hybrid chemistry (HyChem) approach to modeling the high-temperature oxidation of real, distillate fuels. In this approach, the kinetics of thermal and oxidative pyrolysis of the fuel is modeled using lumped kinetic parameters derived from experiments, while the oxidation of the pyrolysis fragments is described by a detailed reaction model. Sample model results are provided to support the HyChem approach.

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1. Introduction

Chemical reaction modeling of combustion processes requires a set of pre-specified thermodynamic conditions as the initial or boundary conditions. These conditions include the temperature and pressure, and the chemical identity of the reactant molecules and their initial concentrations. Conventional, petroleum-derived gasoline, aviation jet fuels, rocket fuels and diesel fuels have compositions that are not precisely defined, at least not to the level that can be treated by detailed chemistry modeling using the fuel composition as a part of thermodynamic input. These distillate fuels are usually comprised of hydrocarbons ranging in carbon numbers from 4 to 12, 7 to 18, and 8 to 20 for gasoline, jet and diesel fuels, respectively (e.g., [1–3]). Major classes of hydrocarbon compounds found in these fuels include normal paraffins, *iso*-paraffins, cycloparaffins, alkenes and aromatics. As an example, Fig. 1 presents typical compositions of three jet fuels.

Compositional complexities in real fuels usually preclude the possibility of identifying explicitly the molecular structure and concentration of every fuel constituent. For modeling their combustion behaviors, the principal approach adopted over the last decade is the surrogate-fuel approach (e.g., [5–14]). This approach attempts to mimic real-fuel combustion behaviors using a surrogate fuel comprised of several neat compounds of well-defined structure and composition to represent the chemical functionalities of a real fuel. A key advantage of the surrogate-fuel approach is that it removes the difficulty associated with the inability to define the composition of a fuel, thus transforming it into a problem that can be tackled, at least in principle, from fundamental reaction mechanisms and rates. There are, however, some drawbacks to the surrogate approach.

First, while the development of detailed reaction models of individual surrogate components can be carried out, building a surrogate mixture to mimic a real fuel is empirical. Matching the physicochemical properties (e.g., H/C ratio, average molecular weight, smoke point, and cetane number) does not necessarily yield a surrogate that accurately duplicates the combustion behavior of the real fuel. Only a careful selection of surrogate

List of Symbols

A	Arrhenius prefactor
a	A stoichiometric coefficient in treating n-hexane pyrolysis
α	Stoichiometric coefficient in HyChem formulation, yield of H atom per fuel "molecule" from the thermal decomposition of the fuel "molecule"
B	"Activation energy" in modified Arrhenius equation
b_a	A dependent stoichiometric variable in HyChem formulation
b_d	A dependent stoichiometric variable in HyChem formulation
β	Stoichiometric coefficient in HyChem formulation, yield of H atom per fuel "molecule" from the β-scission the fuel "radical" upon H-abstraction
c_p	Specific heat
e_a	A dependent stoichiometric variable in HyChem formulation
e_d	A dependent stoichiometric variable in HyChem formulation
ϕ	Equivalence ratio of fuel–air mixture
G^{o}	Standard Gibbs energy
γ	Stoichiometric coefficient in HyChem formulation, yield of methane per fuel "molecule" (in addition to H-abstraction by the methyl radical)
H/C	Hydrogen-to-carbon ratio
H^{o}	Standard enthapy
H_v	Enthalpy of evaporation
$h^{\circ}_{f,298K}$	Standard-state enthalpy of formation
I/I_0	Ratio of transmitted-to-incident light intensities
K_{ext}	Counterflow flame extinction strain rate
k	Rate coefficient
L	Optical path length
LHV	Lower heating value
λ	Wavelength
λ_3	Stoichiometric coefficient in HyChem formulation, ratio of propene-to-ethylene yields
λ_4	Stoichiometric coefficient in HyChem formulation, ratio of butene-to-ethylene yields
$\lambda_{4,1}$	Stoichiometric coefficient in HyChem formulation, ratio of 1-butene-to-ethylene yields
$\lambda_{4,i}$	Stoichiometric coefficient in HyChem formulation, ratio of i-butene-to-ethylene yields
MW	Molecular weight
N	Absorbent number density
n_h	Number of hydrocarbon components in Monte Carlo simulations
n	Temperature exponent in modified Arrhenius equation
p	Pressure
p_5	Pressure behind reflected shock wave
σ_{λ}	Absorption cross section at wavelength λ
S^{o}	Standard entropy
S°_u	Laminar flame speed
$S_{u,ref}$	Reference velocity in laminar flame speed measurement
s^{o}	Molar specific, standard entropy
σ	Standard deviation
T	Temperature
τ_{ign}	Shock-tube ignition delay
T_u	Unburned gas temperature
T_5	Temperature behind reflected shock wave
t	Reaction time
χ	Stoichiometric coefficient in HyChem formulation, yield of benzene to the total yield of benzene and toluene

components and tuning of the surrogate mixture composition based on actual measured real-fuel combustion properties would recover the kinetic behavior over the range of conditions tested with real fuels. Since the condition space is usually large for practical combustors, experimental measurements must be extensive and are time consuming. Then, having tested the combustion behaviors of the real fuel over the range of relevant conditions, the need for the surrogate would itself diminish, since the combustion properties of the real fuel would have been known or acquired from the experiments. Second, typical surrogates are composed of four or five neat compounds (e.g., [10,12]). Usually, detailed reaction models are developed and tested against experiments for single-component fuels. Kinetic coupling of the fragments of fuel components may occur in some combustion reaction processes. Hence, surrogate reaction models assembled by combining submodels of single-component hydrocarbons may have to be tested for this coupling. To fully verify the model accuracy, a wide range of experiments and validation tests are again needed in order to explore kinetic coupling of surrogate constituents on an exhaustive, combinatorial basis. Third, developing detailed reaction models for large hydrocarbons is by no means as fundamental as one would hope. The number of reactions could reach several thousands for a single hydrocarbon. It is daunting, if not impossible, to treat the great many reaction pathways and rate parameters by first-principles or experimentation.

The three considerations discussed above suggest that the surrogate approach is overall an empirical approach. It is also inefficient, if not impossible, to capture the combustion chemistry of real fuels over a wide range of thermodynamic condition space. Even more importantly, jet and diesel fuels are usually injected into an engine as a spray. The breakup and evaporation of the spray is critical to the subsequent combustion process. To this end, it is impossible to develop a four- or five-component surrogate that can match the distillation curve closely and produce a fuel vapor mixture that matches the chemical properties of a real fuel. If, for example, the lowest boiling-point hydrocarbon in the surrogate mixture belongs to a particular class of hydrocarbon compounds (e.g., an n-alkane), the ignition behavior of the surrogate would be sensitive only to that class of compounds as the fuel starts to evaporate. Yet, the distribution of the evaporated compounds toward the low-temperature part of the distillation curve are in fact similar to the distribution of the hydrocarbon compound classes of the entire distillate fuel, as demonstrated by Bruno and coworkers [15].

The current study seeks to advance an alternative concept. The approach, called HyChem (Hybrid Chemistry), employs a physics-based understanding of the primary reaction pathways in fuel combustion. It combines an experimentally constrained fuel-pyrolysis model with a detailed, foundational chemistry model for the oxidation of pyrolysis products to describe and predict the combustion behaviors of real, multi-component fuels. Historically, ideas and elements of the HyChem approach have existed for some time. For example, lumped reaction models have been used in fuel combustion and chemical process research for a long time (see, for example, the pioneering work of Ranzi [16]). Williams and coworkers have advocated a "simplified" reaction modeling approach for some time now and demonstrated such an approach to modeling JP-10 combustion [17,18]. In the current paper, we provide experimental evidence as well as thermodynamic, chemical kinetic and statistical justifications to support the HyChem approach. We also