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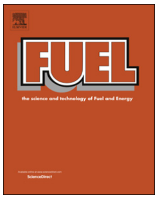

Full Length Article

Pyrolysis of binary fuel mixtures at supercritical conditions: A ReaxFF molecular dynamics study

Chowdhury Ashraf, Sharmin Shabnam, Abhishek Jain, Yuan Xuan, Adri C.T. van Duin*

Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

Combustion devices such as rocket engines, gas turbines and HCCI engines frequently operate at a pressure higher than the critical pressure of the fuel or the oxidizer. This significantly limits the transferability of existing chemical kinetics models as they are developed and validated at low pressure/temperature conditions, considering only temperature dependence on the reaction rates while neglecting pressure dependence on combustion pathways. Since the experiments are difficult to perform at the supercritical region, in this study, we demonstrate the capability of ReaxFF reactive force field method simulations to study combustion kinetics of fuels and fuel mixtures at these conditions with an objective to investigate how the presence of a highly reactive fuel can alter the properties of a much less reactive fuel during pyrolysis. We consider two different fuel mixtures, namely JP-10/toluene and n-dodecane/toluene and find that they behave differently at different mixing conditions and densities. We also compare our results with continuum simulation results using a detailed chemical kinetic model and elaborate why the continuum results fail to capture the phenomena predicted by the ReaxFF simulations. Lastly, with the help of product distribution of decomposition of different fuel components, we explain the reasons behind the observed behavior. Additionally, this study enables us to identify the pressure/temperature regime and the mixing conditions where the simple first order kinetics and Arrhenius type relations do not prevail. This study reveals that the overall pyrolysis characteristics of a fuel mixture do not only depend on the activation energy of its most reactive component. In fact, the product of pyrolysis plays a more significant role in helping other, less reactive, molecules to decompose. Overall, ReaxFF force field based molecular dynamics simulations can provide important atomistic insights on the pyrolysis properties of fuel mixtures at supercritical conditions.

1. Introduction

With the current advancement of materials research, new materials are being developed which can withstand extremely high pressures and temperatures. This will lead to the development of next generation high-pressure jet engines, the primary goal of which will be to increase both fuel efficiency and flexibility and decrease the carbon footprint. However, designing and optimizing the performance of these high-pressure jet engines will require a detailed understanding of the chemical kinetics and reaction mechanisms of the fuels that will be used for operation. This will include the conventional jet fuels as well as the alternative fuels which are expected to play a critical role in next generation aviation technology [1]. These alternative fuels will be produced from sources different from conventional jet fuel sources and should have combustion characteristics similar to the conventional fuels but at a lower cost and better emission control [2]. Thus, the concept of ‘fuel design’ might appear attractive in foreseeable future.

Many existing combustion devices such as rocket engines, gas turbines and HCCI engines are already operating at pressures higher than the critical pressure of either the fuel or the oxidizer. For example, the pressure inside rocket engine that is using H_2 as fuel can go as high as 100 atm [3], which is well above the critical pressure of both the fuel (H_2, 13 atm) and oxidizer (O_2, 50 atm) [4]. As the next generation engines will operate at even higher pressures, optimizing their performances related to fuel efficiency will be a daunting task which will pose two major challenges. Firstly, most of the chemical kinetic models are developed for single component fuels [5–12] while the ‘real fuels’ those are available in nature, are mostly a mixture of various hydrocarbons ranging from paraffin to aromatics. Developing a chemical kinetic model covering all the different fuel types is rather complex. In fact, for this enormous intricacy, researchers have come up with the concept of blending a few hydrocarbons together to mimic the chemical and

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* Corresponding author.
E-mail address: acv13@psu.edu (A.C.T. van Duin).

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physical properties of real fuels. This concept of 'surrogate fuel' is widely popular among the researchers [13–15], however, the combustion characteristics of the surrogate fuels are strongly dependent on the type of hydrocarbons present and their percentage in the mixture. Additionally, the surrogate fuel models incorporate intricate reaction mechanisms of both pyrolysis and oxidation of hydrocarbons and their intermediates which makes it nearly impossible to validate through experiments. Secondly, as most combustion devices work at extremely high-pressure condition, application of available chemical kinetic models [16] will be significantly limited as they are developed only considering temperature dependence on the reaction rates via simple Arrhenius-type rate laws while neglecting pressure dependence on pyrolysis and oxidation pathways. This pressure dependence can significantly alter the chemical properties at high pressure, thus it prohibits transferring of these models directly from low pressure to high pressure regime.

During high pressure combustion, turbulent mixing plays an important role as the heavy fuel molecules initially dissociate to smaller molecules and radicals at one place and mixes with the oxidizer at another place. Despite its significant importance, recent experimental studies [17–21] are only limited to binary species mixing instead of multiple components, deviating significantly from the real fuel scenario. Additionally, performing experiments at supercritical conditions is difficult and most of these studies are limited to qualitative visualization rather than the quantitative analysis that is required for kinetic model verification. For that reason, some of these studies are only limited to very simple fuels such as N_2, H_2 and O_2, as they require rather straightforward kinetic models [17,22,23]. Recently, various computational fluid dynamics (CFD) methods have been emerged as a potential solution to deal with the complexity of experiments as they study the coupling between the physical (diffusion, turbulence) and chemical (reaction) processes. Using both direct numerical simulation (DNS) and large eddy simulation (LES) method within CFD framework, researchers have studied multi species high pressure turbulence mixing [24], Combining this model with rate of single-step chemical reaction consistent with ignition prediction [25], researchers have investigated diffusion [26], and turbulent reaction rate [27] of high pressure mixing, length of the potential core of round fluid jet entering high pressure chamber [28] and the Soret and Dufor cross diffusions [29] in turbulent mixing. Though the pressure considered typically ranges from 60 atm to 100 atm, these studies mainly considered the physical aspects of turbulent mixing while considering very simple kinetic models partly because of non-availability of reliable chemical kinetic models at supercritical conditions, and partly to avoid the complexity of using intricate chemical models.

Recently, to address the limitations of surrogate fuel models and to avoid the complexity of incorporating large intricate chemical models in CFD simulations, researchers have come up with an alternative approach by decoupling pyrolysis from oxidation in high temperature combustion process. Named as Hybrid Chemistry (HyChem) model [1,30,31], this approach considers that, with a given lower heating value and hydrogen to carbon ratio, any fuel mixture first undergoes pyrolysis process at high temperature and generates smaller intermediates which then experience the oxidation process. Thus, studying the oxidation mechanism of those major intermediates which are much smaller in size and mostly independent from initial fuel composition would be enough to study the combustion properties of the fuel mixture. The current HyChem formulation considers only seven intermediates (C_2H_4, C_3H_6, C_4H_8 (both 1-butene and *iso*-butene), CH_4, C_6H_6, C_7H_8) and contains experimentally derived lumped pyrolysis model and detailed foundational oxidation chemistry model. The preliminary results from this simplistic model show good agreement with experimental results in terms of combustion properties, yet this method is still to be validated against high pressure combustion as most of the rate parameters are derived at experimental conditions. Also, at high pressure condition, the assumption of decoupling pyrolysis with oxidation might not hold for some hydrocarbon mixtures.

Since experiments are difficult to conduct at supercritical pressure/temperature regime, and the quality of CFD simulations are highly dependent on the chemical kinetic model one chooses to implement, we need a computationally feasible method which can simulate complex combustion reactions at these conditions without requiring any user input of possible reactions. This will allow us to develop chemical kinetic models at these conditions and study the effect of pressure in simple Arrhenius type kinetics along with temperature. Recently, quantum mechanical (QM) based *ab initio* methods are implemented to accurately predict the reactions for such systems. *Ab initio* simulations solve Schrodinger equation for reaction energies and barriers and highly accurate but are limited to shorter system size and simulation cost due to the higher cost of computation [32]. To deal with the limitation of QM based methods, empirical methods like tight binding [33] or force field (FF) based methods have been developed which are both computationally inexpensive and can provide a reasonable approximation of QM results. A number of reactive potentials have been developed to study hydrocarbon combustion including first [34] and second-generation [35] reactive empirical bond order (REBO), charge-optimized many body (COMB) potential [36,37], modified embedded-atom method (MEAM) [38] and the ReaxFF reactive force field [39] which allow to dynamically simulate bond formation and bond breaking, thus simulating chemical reactions of complex chemical system. In particular, the ReaxFF based molecular dynamics simulations have been used extensively to investigate complex combustion phenomena [40–47].

Since ReaxFF force field is trained against quantum mechanical data and does not require any user input for possible reaction pathways, it can be a useful tool to study pyrolysis of fuel and fuel mixtures at supercritical condition. Recently, Song et al. [48] studied the blending effect between decane and toluene in high temperature oxidation. However, our focus is at relatively low temperature pyrolysis of fuel mixtures only which might help us to differentiate between pyrolysis and oxidation temperature domain. As such, in another recent study, we considered the effect of blending a highly reactive fuel (n-dodecane) with a less reactive one (toluene) on fuel pyrolysis and observed that simple Arrhenius type relation does not hold when high percentage of more reactive fuel is introduced in the mixture at high pressure/density condition, the details of which will be published separately as a part of our ongoing work. Here, we investigate how the fuel structure may play a role in pyrolysis properties of fuel mixtures. For comparison, we kept toluene as the less reactive fuel in both the mixtures which is then blended with either n-dodecane or JP-10 (Fuel molecules considered in this study are shown in Fig. 1). Next, we studied how these two-different fuel mixtures behave during the thermal degradation procedure

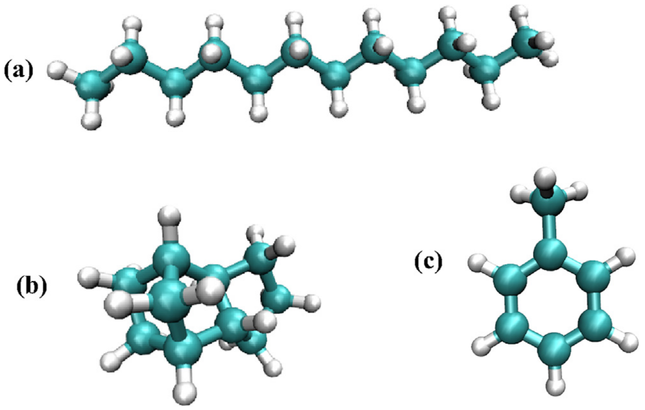

Fig. 1. Fuel molecules considered in this study (a) n-dodecane, (b) JP-10 and (c) toluene. Cyan and white spheres represent carbon and hydrogen atoms respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)