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A high temperature model for the combustion of methylbutanoate

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Methylbutanoate, a C_4 methyl ester, possibly represents the simplest surrogate that captures the chemical effects of the ester moiety in biodiesel and biodiesel surrogates. An updated chemical kinetic model has been used to characterize the ignition and flame characteristics of MB. The mechanistic elements within this model that relate to the MB and smaller ester/oxygenate sub-mechanisms are drawn from the prototypical Fisher et al. model and from more recent theory and modeling efforts. The MB model development which is based on an iterative procedure involving global sensitivity analyses to identify elementary reactions that govern ignition and subsequent high level ab-initio based theoretical updates to these reaction rates will be discussed. Furthermore the applicability of this detailed model over a spectrum of conditions of significance to 3D engine modeling will also be discussed.

1. Introduction

Biodiesel is one among several alternatives that either when used as a neat fuel or in blends with conventional fuels offers substantial emissions advantages in compression ignition engines [1, 2]. Biodiesel is typically produced by the reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and a by-product glycerin. More exotic sources such as algae have also been shown to produce biodiesel albeit in limited quantities [3]. Biodiesel is technically defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751 [4]. More commonly, typical biodiesel derived from soybean oil (primary source in US) or rapeseed oil (major source in Europe) consist of varying amounts of C_{16}-C_{18} saturated and unsaturated methyl esters.

The need for an energy scenario dominated by alternative fuels coupled with stringent emissions compliance legislations in future transportation systems have led to a substantial redirection of efforts over the past few years within the basic combustion research community to focus simultaneously on both clean burning fuels and more efficient engines [5]. This is very evident in the biodiesel combustion kinetics and chemistry arena which has witnessed a steep rise in the number of experimental and modeling studies on methylesters oxidation and pyrolysis [6] in the

past five years. This rapid growth in methylester combustion studies still reveals the poorly characterized elementary kinetics database that is exemplified in the most recent evaluation of chemical kinetics data by Baulch et al. [7] that does not make a single recommendation for elementary reaction rate parameters for a methyl ester molecule. Consequently in the earliest combustion mechanism/model for a methylester that was developed by Fisher et al. [8] for the combustion of MB, the core mechanism incorporating the MB unimolecular and bimolecular reactions were assigned rate coefficients based on analogies with the corresponding alkane (n-butane). MB despite being a poor surrogate for real biodiesel represents a good chemical kinetics surrogate for targeted elementary kinetics studies. Furthermore from a 3D diesel engine modeling perspective, MB represents a candidate species that can be blended in varying amounts with a straight chain n-alkane such as n-heptane to represent a surrogate that mimics the chemical properties of real biodiesel. This approach has been utilized to some degree of success [9,10] in recent diesel engine modeling efforts. Of course an added advantage from a chemical kinetics perspective is that this allows a more careful probe and characterization of the elementary kinetics governing ignition in these relatively smaller molecules rather than larger/real biodiesel components.

The Fisher et al. [8] MB model incorporated 279 species and 1259 elementary reactions. This early modeling study on MB combustion formed the basis for more recent modeling studies [11-16]. While some of these recent modeling studies [14] have replaced the analogy based rate estimates in the Fisher et al. [8] model with theory based rate estimates for some of the important elementary reactions, the theoretical methods used are fairly low-level with substantial uncertainties in their estimates. Consequently we have used linear and global sensitivity analyses on literature models for MB combustion to identify key elementary reactions governing ignition in a high pressure, fuel-rich environment that is relevant to CI engine applications. Subsequently high-level ab-initio electronic structure theory was used to characterize the energetics for these reactions for theoretical chemical kinetics predictions for reaction rates for replacement in a MB model that is hierarchically assembled as part of this work.

2. Simulation Results, Discussions and Model Development

Ignition delay measurements represent excellent targets to assess the overall predictive capability of detailed chemical kinetic models. These are 0D measurements, and consequently with transport or diffusion related uncertainties absent the observed reactivity trends are governed entirely by the combustion chemistry. Ignition delay measurements have been reported in shock tubes [12, 13,16,17,18] and rapid compression machines (RCM's) [19] at pressures ranging from 1-20 atm and for equivalence ratios 0.3-2 over a wide T-range 900-1700 K. The literature MB models are able to match reasonably well the lower pressure (<5 atm) ignition delay data for stoichiometric and fuel lean conditions at high-T (>1200 K). Figure 1 depicts comparisons of current literature models [8,13,16] to ignition delay data at 4 atm obtained by Bergthorson et al. [18]. It is quite clear from Fig. 1 that these literature models [8,13,16] are in reasonable agreement with the experimental ignition delay data. Simulations in the 1-4 atm pressure regime for stoichiometric and fuel lean mixtures reveal similar trends with the literature models in reasonable agreement with the data. The Fisher et al. model [8] appears to best match the experimental ignition trends under these conditions.

We have also assessed the capability of literature models to predict ignition at higher pressures (20 - 50 atm) and for fuel-rich (Φ = 2-5) conditions. These are more representative of real-world compression ignition (CI) engine conditions, however very limited ignition delay measurements exist for MB combustion under high-pressure fuel rich conditions. Fig. 2 represents the data [18] and predictions made by current models [8,13,16] for fuel rich (Phi=2) ignition at 10 atm for MB/O_2/Ar mixtures. Unlike the lower-pressure simulations wherein reasonable agreement was observed, the 10 atm simulations indicate that the detailed models predict longer ignition delays than those observed in the experiments with the predictive quality of the Fisher et al. model being the best. The 0D ignition simulations in Figure 2 reveal that the detailed models may well need revisions to predict ignition phenomena particularly in higher pressure/fuel-rich combustion regimes.

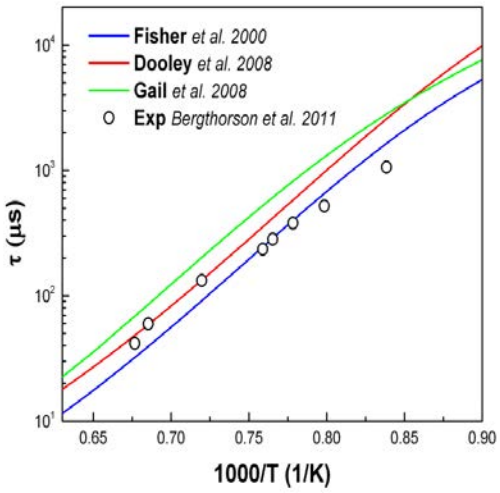

Figure 1: P=4 atm, Phi=0.5 Data from Ref. 18

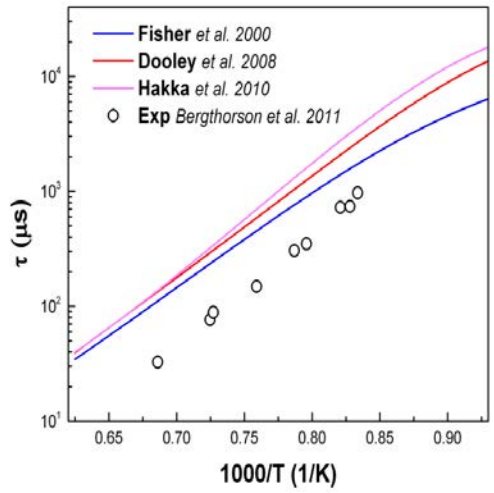

Figure 2: P=10 atm, Phi=2, Data from Ref. 18

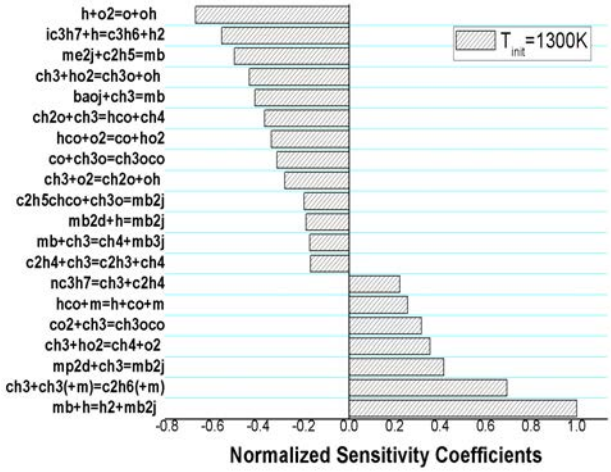

Figure 3: Local sensitivity analysis, ignition delays, P = 10atm, Phi = 2 [18]

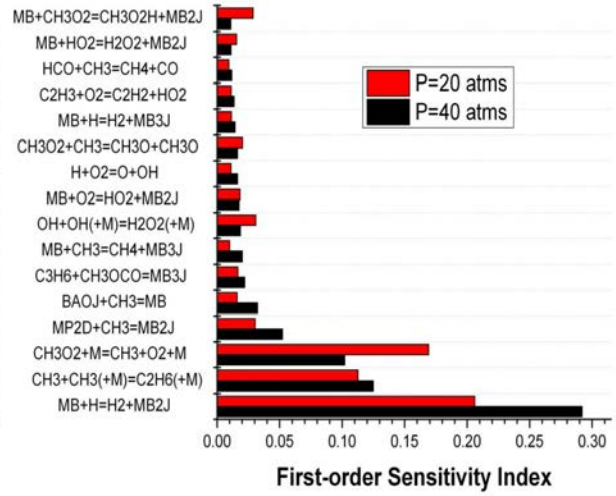

Figure 4: Global sensitivity analysis, T=1300 K.

Local and global sensitivity analyses to ignition delays were performed with the Fisher et al. model [8] to highlight some of the key steps that affect ignition at higher pressures (10 atm). Figure 3 depicts the local sensitivity analyses at 1300 K for a typical representative experiment with the same conditions as in Fig. 2. While some of the key chain branching steps like H + O_2 → O + OH, CH_3 + HO_2 → CH_3O + OH and C-C bond fissions in MB are observed to promote ignition, the abstraction reaction MB + H (most sensitive to ignition in this case) retards ignition delays by competing with the promoting chain branching steps for reactive H-atoms. Global sensitivity analyses to ignition delays were also performed using the Fisher et al. [8] over a wide range of P (10-50 atm), T (800-1300 K), and Φ (1-5) conditions to identify potentially important reactions that affect ignition over such wide combustion regimes. Figure 4 represents a global sensitivity analysis [20] performed for Φ = 2 at 1300 K. The results of these simulations were studied using the high-dimensional model representation (HDMR) [21,22], which decomposes the variance in the resulting output (for example, ignition delay times) in terms of components in each of the reactions. We have found that this technique is very useful for picking out reactions which need further study and is a very useful approach for the theoretical validation of chemical-kinetic mechanisms [23]. The trends observed in the local sensitivity analyses are mirrored in the global analyses and ignition under these conditions is largely sensitive to MB + H. Figure 5 is a representation of the global sensitivity analyses at lower initial temperatures, 800 K for a Φ = 2 MB/O_2/Ar mix. Under these lower-T conditions ignition is governed primarily by the initiation reaction of MB by O_2 and MB + HO_2.

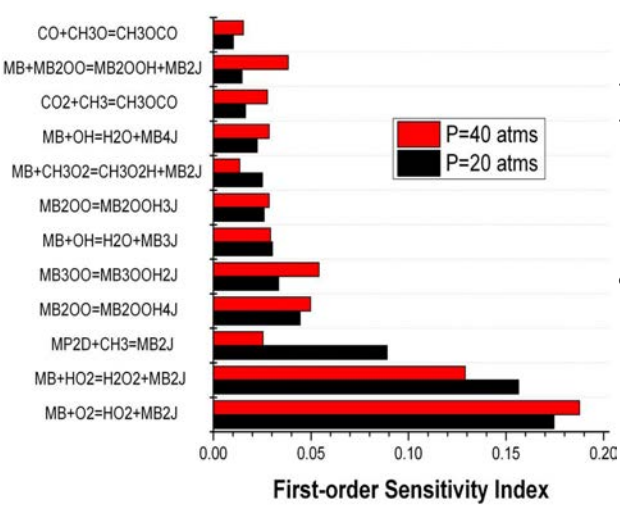

Figure 5: Global sensitivity analysis, T=800 K.

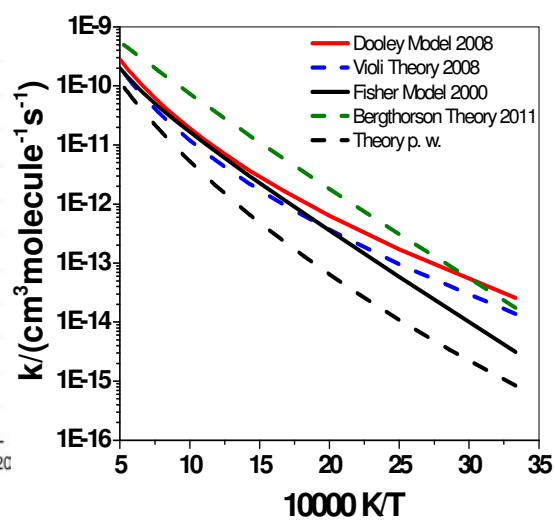

Figure 6: Arrhenius MB + H → products.

There are very limited studies for the rate coefficients for MB + H [24] and no literature estimates for MB + HO_2/O_2. Figure 6 summarizes the total rate coefficients for MB + H used in two of the models [8,13] along with two available theoretical predictions [18,25]. The two models assign rate coefficient estimates by analogy from the corresponding alkane, n-butane, and differ by an order of magnitude at room-T but under combustion conditions (500-2000 K) differ by approximately a factor of 2 or lower. The DFT based theoretical predictions of Huynh and Violi [25] are in reasonable agreement with the rates used in the two models (less than a factor of two deviations in the 500-2000 K regime). However, the more recent higher level CBS-QB3 based estimates of Akih-Kumgeh and Bergthorson [18] are factors of 3-4 higher than the values

predicted by Huynh and Violi [25] or used in the models. It is quite clear that substitution of these rate coefficients [18] in current models will retard ignition substantially rather than promoting it.

Consequently we have utilized high-level ab-initio electronic structure methods to obtain reliable energetics for the reaction, MB + H, MB + HO_2 and MB thermal decomposition reactions. The rovibrational properties of the reactants, saddle points for the transition states, and products for each of these channels were determined at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory. Higher level energy estimates for these stationary points were obtained using the CCSD(T)/cc-pV∞Z method where the infinite basis set limits are estimated from an extrapolation of results obtained from sequences of cc-pVnZ where n=(D,T,Q) basis sets [26,27]. The energetics for the saddle points and reaction enthalpies at the CCSD(T)/cc-pV∞Z level of theory using either the MP2/6-311++G(d,p) or the B3LYP/6-311++G(d,p) geometries differ by no more than 0.4 kcal/mol. Since B3LYP is known to underestimate imaginary frequencies [28] we have used the molecular parameters at the MP2/6-311++G(d,p) level of theory for the rate constant calculations for the abstraction reactions. Preliminary estimates for rate constants for the thermal decomposition reactions were obtained through an in-house RRKM code. Of course a more sophisticated VRC-TST [28] treatment may well be warranted for the radical-radical reactions which is outside the scope of this study. The T1 diagnostic which is a measure of the multi-reference character was <0.018 for the transition states in the abstraction and molecular decomposition reactions which suggests that there is no need to consider multireference effects. The Gaussian 09 [29] software package was used to perform the electronic structure calculations reported here. The rate coefficients for MB + H and MB + HO_2 were estimated using transition state theory [30]. Tunneling corrections were obtained from one-dimensional asymmetric Eckart barriers [31-33]. While an enhanced treatment of tunneling [34] may well be warranted to model this reaction at low temperatures (<300 K), the Eckart correction provides a computationally cheaper and accurate compromise for the conditions of importance to this study (300-2000 K). Low frequency modes are treated as hindered rotors. Variational corrections are expected to be insignificant in these reactions as is typical for reactions with significant barriers.

The barrier heights for the H abstractions by H-atoms from secondary C-H bonds have lower barrier heights than abstractions from primary C-H bonds in MB with the lowest lying channel leading to the MB2J radical and H_2. In contrast with this the formation of a hydrogen bonded complex lowers the barrier height of the secondary C-H bond leading to the MB3J radical + H_2O_2 preferentially in the MB + HO_2 system potentially changing the dominant reaction pathways at higher pressures. Figure 6 summarizes the total rate constants obtained from the present theoretical kinetics for MB + H. The present theoretical predictions approach the Huynh and Violi [25] predictions at T>1000 K with substantial deviations observed at lower-T from the previous studies. As such the present theoretical estimates for MB + H show promise for enhancing ignition for conditions depicted in Figure 2. The theoretical predictions for MB + HO_2 are the only such theoretical estimates in the literature and are probably more uncertain than the MB + H estimates.

A detailed mechanism describing the combustion of MB and consisting of 269 species interacting through 1617 reversible elementary reactions was assembled in an hierarchical manner. Of course in any hydrocarbon/oxygenates combustion any such hierarchy will

necessarily involve the H_2/CO oxidation subset, and in the specific case of MB, initiation, propagation and termination reactions of $CH_2O/CH_3OH/CH_4/C_2$-C_4 hydrocarbons/C_1-C_2 methylesters/MB. The H_2/CO subset is derived from prior work [35] with updates to CO+HO_2 [36], OH+HO_2 (refit to low-T data and [37]), H_2O_2+OH [38] and H_2O decomposition [39]. Updates to the CH_2O and CH_3OH subsets were also performed in lieu of recent experiments and theory on a number of elementary reactions of relevance to these systems. Chemistry relevant to reactions of CH_4, C_2H_2-C_2H_4-C_2H_6 and C_3 hydrocarbons are derived from prior work [40] which is an update based on the Pope and Miller hydrocarbon model [41] without the precursor soot chemistry. Large parts of the CH_2OH, CH_3O, CH_3CO, CH_2CHO, $^{1,3}CH_2$ and CH chemistry are derived from the Baulch [7] or the Tsang and Hampson reviews [42] with the incorporation of recent elementary theoretical and experimental studies where available for the methylester chemistry [6 and references within]. The theoretical updates made to the core MB mechanism are being evaluated and tested against a variety of combustion targets with the eventual goal of a comprehensive model that can then be reduced for engine simulations.

CI engine processes are multi-physics, multi-scale and highly coupled in nature and are characterized by turbulence, two-phase flows, and complicated spray physics. Furthermore, turbulence-chemistry interactions, moving boundaries (piston and valves), heat-transfer (conduction, convection, and radiation), and complex combustion chemistry of fuel oxidation and emission formation make engine simulations a computationally daunting task [43,44]. Accounting for detailed combustion chemistry in the order of hundreds of species and thousands of reactions is perhaps beyond the current computational capabilities. After assembling the detailed reaction mechanism for MB, the mechanism will be reduced for CI engine simulations.

3. Concluding Remarks

Local and global sensitivity analysis have been applied to literature models for MB combustion with the view of identifying key elementary reactions that affect ignition under practical diesel engine conditions. These simulations reveal that ignition delays in a high pressure fuel rich environment are sensitive to the reaction rates of MB + H and MB + HO_2. These two abstraction reactions along with MB thermal decomposition reactions have been theoretically characterized using high-level ab-initio electronic structure methods. A detailed chemical kinetic model has been assembled for MB combustion that incorporates these updates to the core MB mechanism as well as updates to the sub-mechanisms incorporating small molecule chemistry. This detailed model will be validated against available literature targets for MB combustion.

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