

QUASI AUTOMATED APPROACH FOR CONSTRUCTION OF REDUCED CHEMICAL KINETIC MECHANISM FOR AUTOXIDATION OF BLEND OF CONVENTIONAL AND ALTERNATIVE FUELS

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Abstract. Quasi-automated approach was used to expand pseudo detailed mechanism for aviation fuel autoxidation. This was achieved by inclusion of a mixture of 5 normal alkanes (C10 to C14) as the initial condition in "Reaction Mechanism Generator (RMG)" instead of solely one normal alkane (C12) as used in manual construction of pseudo detail mechanism. An industrial solvent composed of approximately equal amount of (C10 to C14) known as "Banner Solvent" was thermally stressed in a near isothermal plug flow reaction in order to generate chemical kinetic experimental data for the mixture. The detailed RMG generated mechanism composed of 918 reaction steps involving 61 chemical species originated from 5 hydrocarbon constituents and molecular oxygen was in a good agreement with the experimental results. By the application of species lumping the detailed mechanism was significantly reduced to only 33 reaction steps initiated from two lumped groups of normal alkanes. The reduced mechanism was validated with the experimental results of Banner solvent and neat diesel autoxidation obtained from near isothermal plug flow reactor. Since RMG presents a number of numerical issues in dealing with heteroatomic species, the authors customized the RMG libraries in order to overcome such limitation for hydroperoxide species. Quantum chemistry method, B3LYP/6-311G(d,p)/IEFPCM was used to estimate the rate parameters of antioxidant reactions. This is a work in progress and continues to combine the resultant reduced mechanism with the reduced mechanism for cyclo alkane in order to construct more representative kinetic schemes for blend of conventional and aviation fuel.

Keywords: Fuel thermal stability, Chemical Kinetics, Automated Chemical Kinetic Mechanism Generation

INTRODUCTION

Publicly available kinetic mechanisms for autoxidation of petroleum based jet fuels are constructed based on reactions and species generated from a single surrogate hydrocarbon in the range of aviation fuel cut, for instance normal dodecane. One of these mechanisms, the pseudo detailed mechanism, presents the most sensitive and representative reactions and chemical species amongst thousands of other reaction pathways and species found in thermally degraded aviation fuel spectrum. With a great deal of success in prediction of autoxidation reactions and surface deposition in mild and rigorous aero engine representative conditions, the same mechanism falls short of being consistent with conditions where blends of conventional and alternative fuels are used. This is primarily because of inherent dissimilarity in the autoxidation propensity of major hydrocarbon building blocks shaping the blends. The results of a preliminary experimental work carried out in our lab in small scale thermal oxidation test device, Petroxy, indicates the propensity and type of autoxidation reactions between normal alkanes, cyclo alkanes and iso alkanes is substantially dissimilar. This dissimilarity for n-dodecane (n-C₁₂) and decalin (cyclic hydrocarbon) is shown in Figure 1. These preliminary results indicate that pseudo detailed mechanism which is put together based on only one hydrocarbon presents limitation for the application to condition where blend of conventional and alternative fuels are used. Our approach for construction of more updated liquid phase autoxidation mechanism is to include at least two or three monocomponent hydrocarbons (depending on the in question blend of aviation fuel) as representative of two or three different classes of building blocks (representative of normal, iso and cyclo alkanes) together with dioxygen (dissolved oxygen) corresponding to the amount of oxygen in air saturated fuel in a system composed of as many reactions as possible between chemical species which are stem from hydrocarbon building blocks in the reaction medium. The choice of monocomponent hydrocarbons will be based on the major constituents of jet fuel. Addition of more building blocks results in significant increase of possible chemical reactions and chemical species (intermediate and stable products). Therefore, further attempt is required to reduce the detailed mechanism in order to be significantly less computationally expensive for the application in "Computational Fluid Dynamic (CFD)" and at the same time to maintain the main chemistry of the in question system. The manual generation of chemical kinetic mechanisms in general begins with the selection of important species which usually include reactants and products

as well as significant intermediate species that are necessary to calculate the generation of key products or other key quantities. The type of reactions that can occur between these coupled groups of chemical species must then be specified along with appropriate thermochemistry data. Although, the identity and the reaction patterns for most of the species in the range of aviation fuel are fairly understood, inclusion of all these species and reactions requires expertise in kinetic mechanism generation techniques. However, manual construction of mechanism for a mixture of monocomponent hydrocarbons (the surrogate fuels representative of aviation fuel) is a tedious and error prone process. For this reason the automated reaction generation is required. Therefore "Reaction Mechanism Generator (RMG)" computer code was used as an automated tool for kinetic mechanism generation. RMG is an open source code developed by Prof. W. Green research group at "Massachusetts Institute of Technology (MIT)". RMG was originally developed in Java language by Jing Song in 2004 following approaches pioneered by NetGen at and ExxonMobil Mechanism Generator(XMG)ⁱⁱ however, a better readability, better error handling and broader access to variety of existing chem-informatics libraries is achieved by Python version of RMG known as RMG-Py. Over the years, several detailed kinetic mechanisms generated by RMG have been published in open literature, including models for butanolⁱⁱⁱ, ketone biofuels^{iv}, JP-10^v jet fuel all in high temperature oxidation and combustion regime.

RMG-Py was used^{vi} in our research group for construction a detailed mechanism for diesel autoxidation process. The detailed mechanism was reduced through an algorithmic approach based on chemical species. Comparison between the detailed and reduced kinetic mechanisms is shown in Figure 2. The reduced mechanism was numerically integrated and compared with the result of neat diesel autoxidation which proved a good agreement for the first phase autoxidation process as shown in Figure 3. The rate parameters for the competing reaction of antioxidant with normal alkanes substrates in H-abstraction by peroxy radicals was calculated using quantum chemistry method B3LYP/6-311G(d,p)/IEFPCM as shown in Figure 4 and Figure 5.

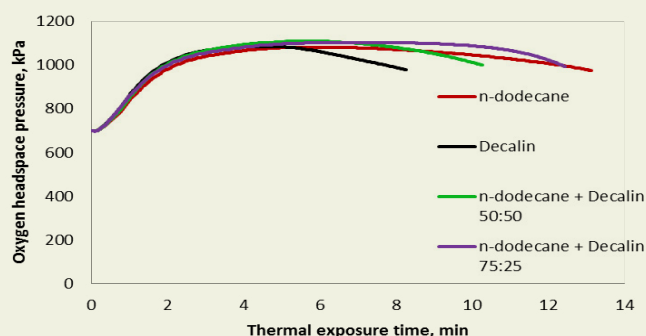


Figure 1: Dissimilar autoxidation propensity between normal alkane and cyclic hydrocarbon obtained in a small scale thermal oxidative test device (Petroxy)

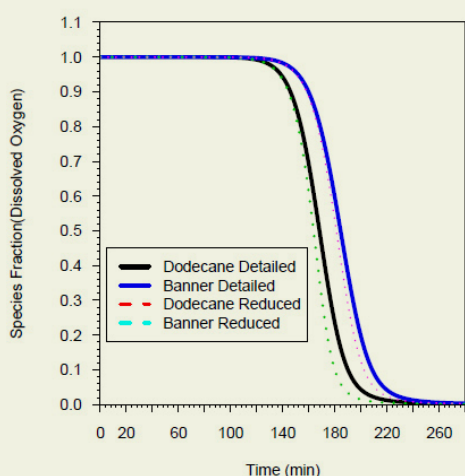


Figure 2: Comparison between calculated rate of autoxidation using reduced and mechanisms for normal dodecane and mixture of 5 hydrocarbons resembling banner solvent

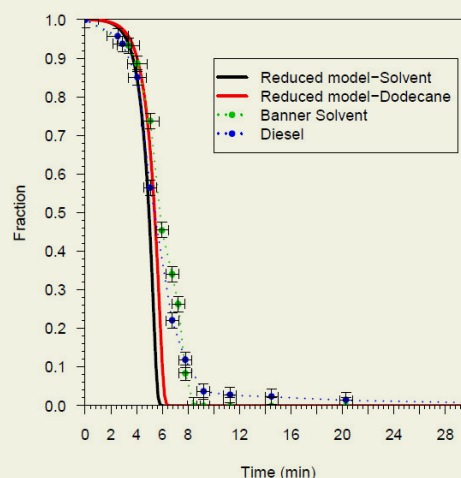


Figure 3: Validation of reduced with the experimental results of autoxidation of neat diesel and Banner solvent

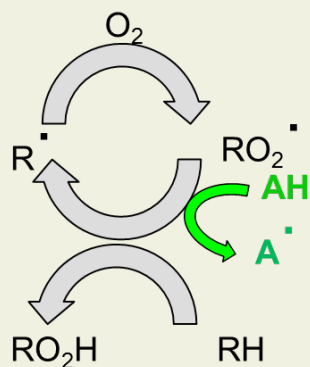


Figure 4: Competing reactions between Antioxidant(AH) and hydrocarbon substrates(RH) in H-abstraction reaction by RO_2

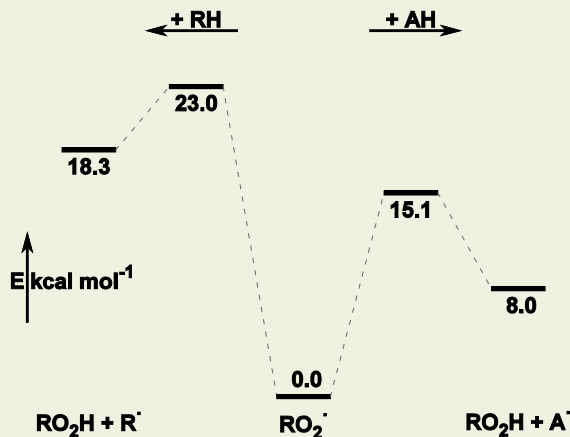


Figure 5: Calculated activation energy of the reaction of antioxidant with RO_2 radicals

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