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A comprehensive detailed kinetic mechanism for the simulation of transportation fuels

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Abstract: This work presents a recently compiled comprehensive model for transportations fuels resulting from the collaboration of three research groups: LLNL, NUI Galway and KAUST. In the past 5 years new fundamental calculations led to significant improvements in the fidelity of detailed kinetic models of important surrogate components (e.g. n-heptane, iso-octane, toluene…) improving predictions of the combustion behavior of pure components and mixtures. By extending the newly adopted reaction rate rules, mechanisms for components that were not included in the previous LLNL gasoline and diesel surrogate mechanisms were developed (e.g. polyalkylated aromatics, cycloalkanes, components from bio-logical sources…). The major features of this updated and extended model are presented together with validation comparisons, examples of applications and future directions.

Keywords: Detailed kinetics, transportation fuels, fuel surrogates

1. Introduction

Thanks to the increasing accessibility to high performance computing, it is becoming common practice for industry to incorporate detailed kinetic calculations in the design of combustion systems.

Compared to semi-empirical and highly reduced models, detailed kinetics allows extrapolating predictions to a wide range of conditions. Furthermore, it enables to simulate different fuel compositions, a powerful feature when the focus is the study of candidate fuel components under consideration for future engine applications.

This work presents a detailed kinetic mechanism for transportation fuels developed through the cooperative effort of LLNL, NUI Galway and KAUST combustion teams. This comprehensive mechanism includes revised versions of previously published models as well as some novel mechanisms recently developed by our groups. In the current model, compared to the previously published LLNL gasoline model, the number of available fuel components is expanded significantly and a broad range of distillation temperatures and structures are covered. Particular relevance is given to oxygenate components in the gasoline boiling range and their blending behavior.

The next paragraphs detail the fundamental features of the mechanism, providing a sample of the validation comparisons performed, and illustrate an example of application to the prediction of blending behavior of fuel components.

2. The kinetic mechanism: general features

The kinetic mechanism here presented is based on principles of hierarchy, self-consistency and modularity. The mechanism core is the recent extensively validated base chemistry compiled by the NUI Galway combustion group, the AramcoMech 2.0. The AramcoMech 2.0 covers the combustion chemistry of C0 to C4 hydrogen/carbon compounds as well as ethanol, methanol and dimethyl ether. Compared to its previous version (AramcoMech 1.3), this mechanism incorporates updated rates emerging from extensive studies on the chemistry of small olefins (e.g. [1]). These updates impacted positively predictions at high temperature conditions, where large fuel molecules rapidly decompose into C2-C4 unsaturated species (e.g. high temperature ignition, flame speed and structure...).

The C0-C4 mechanism has been extended to lager alkanes up to C7 species. Long chain saturated species are characterized by low temperature oxidation pathways leading to degenerate chain branching. While this chemistry has been the subject of investigations for decades, it is only in recent years that quantomechanic calculations provided more precise estimates of the reaction rates involved in the process. The recent studies by Bugler et al, and Zhang et al. [2-4] carried of a critical review of these recent fundamentally calculated rates and validated self-consistent comprehensive models based on them. Adopting the same principles, a collaborative effort involving NUI Galway, LLNL and KAUST carried out a comprehensive study on iso-octane and updates based on recently calculated reaction rates have been proposed [5].

Beside saturated species, the mechanism here discussed features a recently updated toluene model based on the work by Zhang et al. Contrarily to most of the kinetic mechanisms available for toluene, Zhang experimental and modeling work focused on the reactivity of toluene in blends, allowing to probe the reactivity of the aromatic component in the low temperature region (650K-950K), where the pure component is too refractory to be tested rapid compression machines [6]. In this work, Zhang’s mechanism underwent minor updates to correct transcription errors affecting the original version.

Mixtures of primary reference fuels (n-heptane and iso-octane) and toluene are often used within the engine community to mimic the reactivity of gasoline fuels but typically fail to reproduce physical and chemical properties such as distillation curve, density, sooting tendency or H/C ratio. A better characterization of the fuel can be achieved through the use of more complex mixtures including olefins, naphthenes and oxygenates. The mechanism here discussed expands the possibility of modelers by including the detailed oxidation chemistry of C6 linear olefins, diisobutylene [7] and cycloalkanes from C5 to C7 [8].

Collectively these models provided the basis for expanding the mechanism to heavier hydrocarbons in the jet and diesel fuel range.

The n-alkane mechanism developed by Westbrook et al. [9] was updated including rates and chemical pathways adopted for the C5-C7 alkanes. In order to enlarge the palette of components available for surrogate formulations, additional compounds from the list presented in the CRC AVFL-18 report [10] as candidate surrogate components for Diesel fuels have been added to the model: α-methylnaphthalene, trans-decalin, tetralin, trimethylbenzenes (?) and *n*-butylbenzene are examples of species available in the current model. Similarly to what has been done for the saturated species, these models use reaction rates consistent with the ones adopted for their counterparts in the gasoline boiling range.

A number of mechanism for oxygenated species were also included. The previously published mechanisms for higher alcohols (C3-C5 isomers) were merged with the gasoline portion of the mechanism and revalidated against older predictions. The previously published mechanism for small esters was thoroughly revised and updated using recently calculated reaction rates from quantomechanic calculations. Finally, validation targets for ethyl and methyl acetate were expanded to include ignition delay time data.

A detailed kinetic model for anisole, an oxygenated aromatic considered to be representative of bio oils derived from fast pyrolysis, has been developed and incorporated in the model. Further details on this mechanism are available in a paper by Wagnon et al. to be presented at this same meeting.

Finally, in order to provide NOx formation predictions and capture NO sensitization effects for engine combustion application, the detailed kinetic model for gas phase nitrogen reactions from Politecnico di Milano [11] was added to the mechanism.

Comprehensively, this detailed kinetic model covering both Diesel and gasoline components includes about 10000 and 30000 reactions. The portion of the mechanism covering gasoline components gasoline, together with the bio-derived fuel components, includes about 2300 species and 10000 reactions.

3. The kinetic mechanism: selected validation comparisons

The significant updates introduced in the gasoline mechanism led to improved agreement with literature and newly collected experimental data.

Figure 1a and 1b respectively compare the simulated ignition delay times (solid lines) of n-heptane and iso-octane against literature experimental data (symbols). Results obtained with the previously published kinetic mechanism are presented with a dashed line.

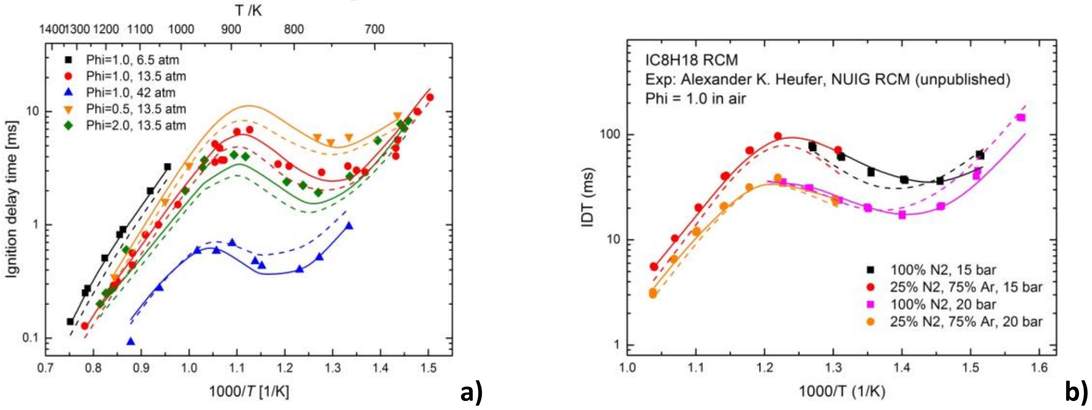

Figure 1: Predicted ignition delay times of PRFs (a: n-heptane, b: iso-octane) versus measurements (n-heptane data are from Ciezky and Adomeit, 1993). Dashed lines show predictions obtained with the LLNL mechanism currently available on the LLNL website

It can be noticed how the new mechanism exhibits an improved pressure dependence predicting a significantly enhanced reactivity at 40 atm and longer ignition delay times at 3-15 atm.. These changes can be attributed to the new rates adopted for the low temperature chemistry and updates in the thermochemical properties, which were calculated in THERM using a revised version of the group contribution database. These changes have important implication in the simulation of engine combustion where the in-cylinder pressure at top dead center easily exceeds 25atm, a pressure condition for which the two models respond similarly.

Another important element covered by the mechanism validation was the study of fuel component mixtures. Beside validation on pure components, great emphasis was given to the study of binary and multicomponent blends, an effective way to investigate the reactivity of refractory fuels such as aromatics in the low temperature region.

Figure 2a shows the calculated ignition profiles obtained for a 50/50 by mole mixture of toluene and n-heptane. Solid lines indicate predictions obtained with the current model, symbols are recent experimental data collected in the NUI Galway RCM. Dashed lines indicate calculations obtained using the previously published mechanism.

Once more the mechanism captures correctly the experimental trends exhibiting an improved pressure dependence (mostly due to the changes in the n-heptane chemistry).

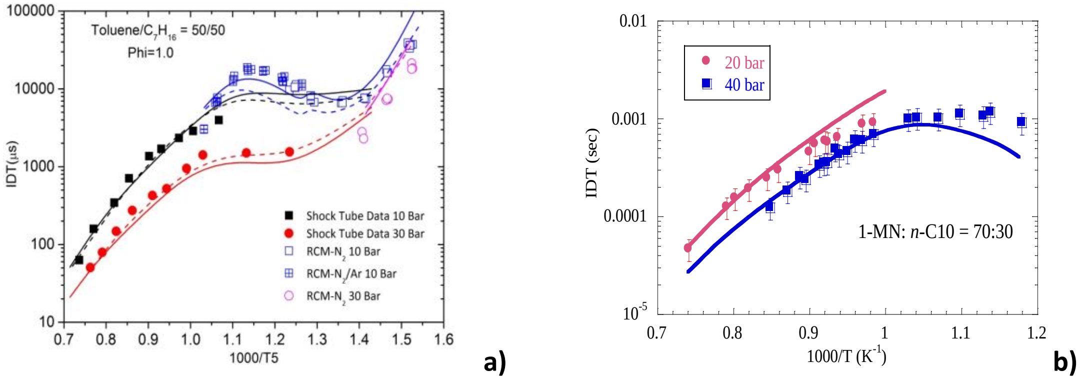

Figure 2: Predicted ignition delay times of n-alkanes/aromatic mixtures: a) n-heptane/toluene blend, b) n-decane/ alpha methylnaphthalene. Dashed lines in panel a) shows predictions obtained with the LLNL mechanism currently available on the LLNL website

In a similar fashion, figure 2b shows the comparison between simulations and recent Shock Tube experiments collected at Rensselaer Polytechnic Institute (Wang et al., 2010) for a binary mixture relevant to jet and diesel fuels. Focusing on the blending behavior of a reactive fuel component (n-dodecane) and an aromatic species, these experiments (indicated by symbols) allows to verify that the model can correctly capture the behavior of multicomponent surrogates relevant to transportation application. The mechanism validation is an ongoing process which is broadening month after month through the collection of new data provided by the NUI Galway and KAUST facilities, as well as from external collaborators (e.g. UConn, NREL, …)

4. Applying the kinetic mechanism to octane number estimates

An interesting application of the described kinetic mechanism is the evaluation of the blending behavior for a variety of fuels containing oxygenate compounds. This effort fit within the scope of the Co-Optima effort carried out by nine US National laboratories, including LLNL, and supports the computational and experimental search for more efficient combustion strategies for automotive application where fuel and engines are considered as a whole system subject to optimization. The methods used to estimate the octane numbers of mixtures from their ignition delay times in constant volume calculations is described in Mehl et al. [12].

In this work, the original correlations have been reformulated using a broader set of mixtures as training set. Also, because of the greater importance of the research octane number versus motor octane number in modern engines, the correlation between AKI and ignition delay time has been replaced by a similar one indicating the RON value.

The updated kinetic model and correlations were used to explore the blending behavior of some oxygenate components of interest in a 4 component base fuel mimicking the composition of a high octane BOB (before oxygenate blending) with a RON of 91.

Increasing fractions of oxygenate components were added to the base fuel and, using the correlations, their RON and sensitivities (not discussed here) were estimated. The same blends were independently tested in a standard CFR engine to measure their octane numbers [13]. Figure 3 shows the predicted RONs (solid lines) and measured ones across a wide region of blending ratio.

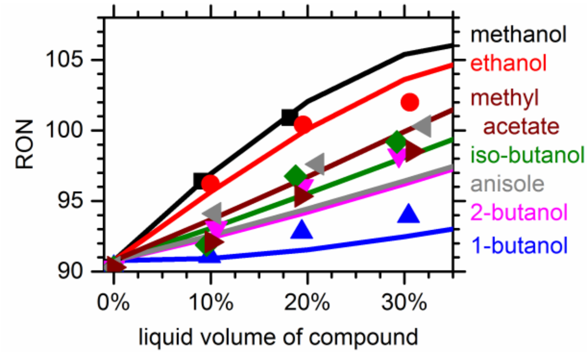

Figure 3: RON predictions for blends including increasing amount of oxygenate species (lines) vs experiments (symbols)

The model captures the relative effectiveness in increasing the antiknock performances of most of the considered fuel additives and, even more interestingly, replicates correctly the synergistic (e.g. methanol) vs antagonistic (n-butanol) blending behavior of different fuels, noticeable through the convexity of the presented curves. Similar tests have been successfully carried out for other fuel components and demonstrates how the presented model can be effectively applied to the study of complex blends and compositional effects in engines.

5. Conclusions

This work presents a comprehensive model for transportation fuels resulting from a multi-year collaboration of three combustion research groups (LLNL, NUI Galway and KAUST). The model discussed in the paper includes the most recent mechanisms by these groups for fuel components ranging from natural gas to diesel. The mechanism features rates obtained through extensive critical reviews of current fundamental calculations and provides predictions showing improved agreement with literature data. New experimental data were also obtained to validate the model at less investigated conditions. Thanks to the large number of components included in the mechanism, this comprehensive model allows to investigate the blending behavior of an unprecedented variety of fuels.

6. Acknowledgements

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