LLNL-PROC-422312

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Kinetic Modeling of Gasoline Surrogate Components and Mixtures under Engine Conditions

M. Mehl, W. J. Pitz, C. K. Westbrook, H. J. Curran

January 11, 2010

The 33rd International Symposium on Combustion
Beijing, China
August 1, 2010 through August 6, 2010

Kinetic Modeling of Gasoline Surrogate Components and Mixtures under Engine Conditions

Marco MEHL, William J. PITZ, Charles K. WESTBROOK

Lawrence Livermore National Laboratory, Livermore, CA 94550 - USA

and Henry J. CURRAN

National University of Ireland, Galway - Ireland

Corresponding author:
Marco Mehl
Lawrence Livermore National Laboratory
7000 East Avenue
Mail Stop L-367
Livermore, CA 94550
Tel: 925 423 6993
Fax: 925 424 4334
Colloquium: Reaction Kinetics

Paper length Calculation

Text					=	3713
Figures:	Size	Size+10mm	Columns	Caption		
Figure 1	93	103	2	40	=	493.2
Figure 2	43	53	1	23	=	139.6
Figure 3	43	53	1	23	=	139.6
Figure 4	44	54	1	23	=	141.8
Figure 5	43	53	1	23	=	139.6
Figure 6	43	53	1	19	=	135.6
Figure 7	41	51	1	20	=	132.2
	Number	Number+2				
References	25	27				471.96
				TOTAL	**=**	**5506.6**

Kinetic Modeling of Gasoline Surrogate Components and Mixtures under Engine Conditions

Marco MEHL, William J. PITZ, Charles K. WESTBROOK

Lawrence Livermore National Laboratory, Livermore, CA 94550 - USA

and Henry J. CURRAN

National University of Ireland, Galway - Ireland

Abstract

Real fuels are complex mixtures of thousands of hydrocarbon compounds including linear and branched paraffins, naphthenes, olefins and aromatics. It is generally agreed that their behavior can be effectively reproduced by simpler fuel surrogates containing a limited number of components.

In this work, an improved version of the kinetic model by the authors is used to analyze the combustion behavior of several components relevant to gasoline surrogate formulation. Particular attention is devoted to linear and branched saturated hydrocarbons (PRF mixtures), olefins (1-hexene) and aromatics (toluene). Model predictions for pure components, binary mixtures and multi-component gasoline surrogates are compared with recent experimental information collected in rapid compression machine, shock tube and jet stirred reactors covering a wide range of conditions pertinent to internal combustion engines (3-50 atm, 650-1200K, stoichiometric fuel/air mixtures). Simulation results are discussed focusing attention on the mixing effects of the fuel components.

Keywords: Kinetic modeling, gasoline surrogates, autoignition, blending effects

1. Introduction

Detailed kinetic models of pyrolysis and combustion of hydrocarbon fuels are nowadays widely used in the design of internal combustion engines and these models are effectively applied to help meet the increasingly stringent environmental and energy efficiency standards [1-3]. In previous studies by the combustion community, such models not only contributed to the understanding of pure component combustion, but also provided a deeper insight into the combustion behavior of complex mixtures. One of the major challenges in this field is now the definition and the development of appropriate surrogate chemistry models able to mimic the actual behavior of real fuels.

Real fuels are complex mixtures of thousands of hydrocarbon compounds including linear and branched paraffins, naphthenes, olefins and aromatics. It is generally agreed that their behavior can be effectively reproduced by simpler fuel surrogates containing a limited number of components. For example, a commonly used surrogate for gasoline fuels contains iso-octane and n-heptane, the so called Primary Reference Fuels (PRF) for gasoline. This gasoline surrogate fuel has been recently extended to also include alkenes and aromatics [4]. The use of representative species for all the main classes of hydrocarbons makes possible the reproduction of not just the auto-ignition propensity of gasoline or Diesel fuels, but also their physical properties and their combustion intermediates and products over a wide range of operating conditions.

In this work, a recently improved version of the kinetic model by the authors is used to analyze the combustion behavior of several components relevant to gasoline surrogate formulation. Particular attention is devoted to linear and branched saturated hydrocarbons (PRF mixtures), olefins (1-hexene) and aromatics (toluene). In internal combustion engines, fuel-air mixtures encounter a wide range of pressures and temperatures and it is important that chemical kinetic mechanisms be valid over these ranges. Model predictions for pure components, binary mixtures and multi-component gasoline surrogates are compared with recent experimental information collected in rapid compression machines, shock tubes and jet stirred reactors covering a wide range of conditions pertinent to internal combustion engines. Simulation results are analyzed focusing attention on the chemical kinetic interactions of the fuel components.

2. The kinetic mechanism

The kinetic model here discussed is based on previous works carried out by the NUI/LLNL research group. Its general structure is based on a C_1-C_4 detailed mechanism core and three main blocks: the first one includes all the main reaction pathways for the saturated and non-saturated linear hydrocarbons up to C_7, the second one contains the same classes of reactions for branched hydrocarbons from C_5 to C_8, the last includes the reactions of aromatic structures such as benzene and short chain alkyl aromatics (toluene, styrene, …). The interaction among the oxidation pathways of the different components of the mixture analyzed here are accounted for by the reactions of smaller radicals contained in the core mechanism and by a specific block of reactions involving the alkyl and alkyl peroxyl radicals of the different fuels.

In the past year, significant revisions of some important reaction rates included in the mechanism have been carried out. A thorough revision of the latest recommendations for many of these reaction rates allowed the performance of the model to be improved over a wide range of operating conditions. In the following paragraphs, the most relevant modifications will be briefly discussed and some comparisons with experimental information will be presented as a validation of the mechanism.

C_1-C_4 mechanism

A thorough revision of the mechanism core took was accomplished by the NUI research group. The chemistry of the small alcohols was analyzed and some reaction rates were updated on the basis of recent quantum mechanical calculations [5]. The abstraction reactions of HO_2 and CH_3O_2 radicals were also recently reevaluated [6]. One significant improvement is the achievement of the full thermodynamic consistency between the forward and reverse reactions included in the mechanism core. Further details on this section of the mechanism are available in [5-6]. These improvements significantly impacted flame speed predictions and ignition behavior in the high temperature region (1000K-1400K). The updated reaction rates of the peroxides abstractions were also used as a reference for the analogous reactions of higher hydrocarbons.

n-heptane

The reaction mechanism of the n-heptane was also revised: the reaction rates adopted for the HO2/CH3O2 abstraction reactions of the C_1-C_4 core mechanism have been applied here as well. The decomposition rates of the alkyl radicals and alkoxy radicals were also updated on the basis of the rules reported in [7].

Following the most recent literature recommendations, the isomerization rates of the alkyl radical (R) and of the hydroperoxy alkyl radical (OOQOOH) respectively to hydroperoxy alkyl radical (QOOH) and ketohydroperoxides have been energetically favored by 400 kcal/kmol compared with the older values (i.e. 24400 kcal/kmol → 24000 kcal/kmol for the ROO<=>QOOH on a primary hydrogen involving a 6 member transition state). The direct eliminations of HO_2 from the alkyl peroxy radical (ROO) have been enhanced to compensate for the increased reactivity. As a result the low temperature reactivity is more effective and the low temperature heat release requires lower induction times. On the contrary the formation of olefins from the ROO limits the heat release associated with the low temperature chemistry.

A large block of reactions was also implemented to account for the low temperature oxidation of unsaturated fuels such as hexenes and pentenes that are intermediates formed during n-heptane oxidation. The new reaction pathways included in the mechanism are described in [8].

iso-octane

The decomposition rates and the thermal properties of several radicals including the iso-octyl isomers and the neo-pentyl were reevaluated. The decomposition rates were derived by [7], while the thermal properties of the radicals were evaluated using the THERM program developed by Ritter and Bozzelli [3]. The abstraction reactions of H atoms from iso-octane by HO_2 and CH_3O_2 were updated according the same rules used for the linear alkanes. The isomerization rates of the alkyl-peroxyl radicals were also updated in terms of activation energy as reported for n-alkanes. The increased reactivity has been compensated by reinforcing the reaction pathway of the direct elimination: ROO=>alkene + HO_2.

These modifications significantly influenced the general reactivity of iso-octane and opened the possibility of getting a much better match with experiments over a wide range of operating conditions. This relatively small change significantly speeded up the low temperature oxidation processes and, more important, increased the importance of the O_2 addition steps in conditioning the ketohydroperoxide formation efficiency.

These refinements led to a stronger dependence of the system on pressure conditions, increasing the ignition delay times at low pressure and making them shorter at typical engine conditions.

Toluene

The toluene mechanism published in 2001 [10] was also recently updated by Sakai et al. [11] including new reaction pathways proposed by recent studies. A further revision was carried out in the past months in collaboration with Milano's combustion group. The updated C1-C4 mechanism has been integrated into the toluene mechanism and the submechanism specific to aromatics has been revised as well.

The toluene model has been analyzed according its internal hierarchy. The mechanism of cyclopentadiene has been revised and validated against Butler et al. work [12]. Similarly the reactions relevant to benzene and phenol have been extensively improved for better internal consistency. A careful validation of these submechanisms is extremely important because of the high concentration of the resonantly stabilized radicals formed along the toluene oxidation process. The main reaction pathways identified during this revision involve the interaction of benzyl radicals with HO2 radicals at intermediate temperatures, and the attack of the O radicals on the aromatic ring at high temperatures. Benzyl terminations also play an important role at relatively low temperatures. The interactions of toluene with other hydrocarbons at engine conditions are mostly related with the low-intermediate temperature reactions forming HO_2 mentioned above. Further details on this section of the model can be found in [13].The n-heptane, iso-octane and toluene mechanisms were merged into a detailed kinetic model for the simulation of gasoline surrogate fuels including about 1550 species and 8000 reactions.

The thermodynamic properties of all the species included in the mechanism were evaluated using the THERM program developed by Ritter and Bozzelli, implementing Benson's group additivity method [9]. The kinetic model here discussed is available upon request and will be soon available on the LLNL website [14].

3. Results and Discussion: Pure components

In the next paragraphs the calculated ignition delay times of pure components and their mixtures are compared with experimental rapid compression machine (RCM) and shock tube (ST) data.

RCM simulations have to account for the heat loss affecting the experimental measurements. Non reactive pressure traces were used to calibrate the heat loss coefficient. Shock tube data were simulated assuming the conditions behind the shock wave assuming constant volume conditions.

The first set of comparisons here presented involves n-heptane and iso-octane. These two fuels, generally referred as primary reference fuels, are the simplest and most used fuels in both experimental and theoretical engine studies. They are considered to be also the basis for more complex gasoline surrogates; therefore the capability of the model to reproduce their combustion feature is essential for any practical application.

Figure 1 shows the comparison between model predictions and experiments over a wide range of conditions for n-heptane and iso-octane. The recent modifications improved the agreement on a wide range of pressure moving from 3 up to nearly 50 atm covering both the high and the low temperature reaction domain. In particular this new version of the model is a solid step in the direction of mimicking the strong dependence of ignition delay times on pressure evidenced by many experimental evidences for these fuel components [15-20].

Toluene model has been also validated over a wide range of operating conditions, Figure 1 shows a few comparisons of modeling results with shock tube and rapid compression machine data [21-22]. It's interesting to notice how the slope of these sets changes depending on the experimental device used to measure them. As a matter of fact, RCM experiments are affected by a conspicuous amount of heat losses that effectively delay the ignition timing at lower temperature. These experimental results, supported also by experimental measurements, highlight the role of heat transfer and prove it to be a fundamental aspect to include when simulating these experiments.

Unfortunately a limited amount of experimental information is available for olefins. Figure 1 reports some comparisons carried out on RCM data collected by Vanhove et al. [23]. Further details about olefin mechanism validation can be found in [8] where a complete discussion of the mechanism and a more extensive validation for this relatively recently studied fuel are presented.

4. Results and Discussion: Binary mixtures and gasoline surrogates

In order to better understand the interactions among different components, the behavior of binary mixtures will be discussed at first. The next paragraphs discuss respectively the comparisons between calculations and experiments for a 50/50% mole toluene/n-heptane mixture (Fig. 2), a 35/65% mole toluene/isooctane mixture (Fig. 3), a 18/82% mole 1-hexene/iso-octane mixture (Fig. 4), a 30/70% mole 1-hexene/toluene mixture (Fig. 5) and a 47/35/18% iso-octane/toluene/1-hexene gasoline surrogate (Fig. 6) as long with the ignition delay times of the components of the blends. All the experimental data shown in the figures are taken from [24]

Toluene/n-heptane mixture (50/50% mole)

This first set of comparisons focuses on a stoichiometric toluene/n-heptane 50/50% mole mixture (Fig. 2). Though n-heptane is not present in the gasoline surrogate mixture we are going to discuss later, it is useful to consider this blend both because of the high level of confidence that characterizes the n-heptane mechanism and the representativeness of this hydrocarbon to the family of large alkanes.

N-heptane is a two-stage fuel showing a high reactivity, even at mild conditions, due to the numerous sites available for the formation of ketohydroperoxides, (strong branching agents) at low temperatures.

Toluene, on the contrary, is a single stage fuel with very limited reactivity at low temperatures. At low temperatures, the most favored abstraction reactions involve the formation of the resonantly stabilized benzyl radical. When in mixture, the easily abstractable H-atoms on the methyl group on toluene act as a radical scavenger depressing the reactivity of the system. These features make it a strong octane enhancer.

When n-heptane is mixed with toluene, the two stage behavior is maintained, even though a significant delay both in the cool flame and in the thermal ignition timing is observed.

This delay appears to result from many synergistic factors. For example, the radical scavenging effect of toluene reduces the speed of propagation reactions and stable radicals such as benzyl favor termination reactions.

The combination of these two factors results in a delayed and less pronounced heat release during the cool flame. When toluene is present, lower H_2O_2 are reached during the first phase of the combustion. Since the second stage of the ignition is triggered by the thermal decomposition of H_2O_2, lower concentration of this chemical species and milder conditions allow the reacting system to delay significantly the transition between low and the high temperature reactions, resulting in a longer lasting temperature plateau.

An important reaction for this system is also the interaction among HO_2 and the benzyl radical. This reaction is promoting, countering the scavenging effect mentioned earlier. It converts the slow reacting HO_2 and benzyl radicals to OH and benzoxy radicals that speed up the reactivity. The relative weight of the two processes however is suppression and the OH produced by the benzyl + HO_2 reaction is promptly consumed by the abstractions of the benzyl hydrogen.

Similar effects can be observed in the next toluene/alkane mixture discussed.

Toluene/iso-octane mixture (35/65% mole)

Even though branched alkanes are much less reactive than linear ones, iso-octane still shows some low temperature reactivity. The cool flame intensity is smaller if compared with n-heptane and the NTC covers a much narrower region. This is also due to the high number of primary hydrogen sites makes the internal isomerization reactions necessary to the formation of ketohydroperoxides slower than h-heptane. The scarce low temperature reactivity of iso-octane, however, is still able to produce cool flames (two-stage ignitions) in the iso-octane/ toluene mixture because of the high concentration of iso-octane (Fig. 3).

The presence of toluene once more significantly delays both the cool flame (or first stage of ignition) and the final ignition of the system. The delay between the cool flame (dotted curve) and the second stage (solid curve) appears to be particularly affected.

The model shows a very good agreement with experiments on cool flame estimations; however, some improvements are still necessary to get better prediction of the second stage ignition at very low temperature conditions.

1-hexene/iso-octane mixture(18/82% mole)

1-hexene is a relatively long chain alkene with a long saturated portion on one side of the double bond. For this reason it shows some of the features typical of alkanes such as a significant NTC behavior.

The presence of the double bond confers to this hydrocarbon some alternative reaction pathways: the possible formation of resonantly stabilized radicals and a high activation energy necessary to extract the vinyl hydrogen sites, making alkenes less reactive than their saturated homologues.

Moreover, the double bond may undergo radical additions that subtract highly reactive species from the system. This last reaction pathway requires very low activation energy and, being competitive with the abstraction reactions, slows down the reactivity at low temperature conditions.

Comparing the reactivity of 1-hexene and iso-octane (Fig. 4), the former shows similar ignition times at about 650K but much faster ones in the NTC region between 700K and 800K.

When the two fuels are mixed, it is possible to observe a reduction in the negative temperature coefficient of the alkane, while the low and high temperature reactivity is less affected.

Since the cool flames of the pure components and of the mixture show a similar timing, it is not obvious to infer what kind of interactions occurs among the two fuels during the early stages of the combustion.

A flux analysis performed just before the cool flame onset highlights how the 18% of 1-hexene is responsible for more than the 27% of the reactions involving OH, accounting for both abstractions and radical additions. The 66% out of this 27% is related to the double bond and the allyllic site. This result confirms the non linear effects caused by the addition of olefins to gasoline blends and the fact that it is possible to transfer some of the features of this family of compounds to mixture using a limited amount of alkenes.

Lastly, as evidenced for toluene, 1-hexene radicals and the allyl radicals generated by the decomposition of this fuel, contribute to the ignition process promoting the conversion of HO_2 to OH via the resonantly stabilized hexyl radical.

1-hexene/toluene mixture (30/70% mole)

The reactivity of the 1-hexene/toluene mixture is strongly influenced by the interactions of the fuel radicals. Both the two fuels produce large amount of resonantly stabilized radicals responsible for recombination reactions that slow interactions with other chemical species.

Because of the abundance of weak C-H bonds in this mixture, OH radicals abstract these H atoms and are promptly stabilized to water. As a result, highly stable allylic or benzyl radicals are formed and the reactivity is reduced. For the same reason H transfers among toluene and 1-hexene radicals are much easier than for any other of the considered mixtures.

1-hexene is responsible for the little low temperature reactivity shown by this blend (Fig. 5).

The high concentration of toluene totally suppresses the NTC behavior shown by 1-hexene and effectively delays both the cool flame and the high temperature ignition (2^{nd} stage ignition). However, toluene affects the high temperature ignition, much more than the cool flame ignition.

The model correctly reproduces the cool flame timing but tends to overestimate the total ignition delay. It is interesting to discuss what reactions might account for the missing reactivity. Both the fuels are sources of radicals able to interact with HO_2 and convert it to more reactive radicals. This mechanism is particularly relevant in the intermediate temperature region (750-850K), where the mechanism tends to underpredict the reactivity of the mixture. Olefins are known to produce a higher amount of HO_2 and diolefins than their saturated relatives. One possible explanation for the lack in reactivity predicted by the model might be the underestimation of the HO_2 activation pathway mentioned above. Further investigations will help in discerning on this point.

The suppression of the NTC behaviorby toluene and, in some cases, by 1-hexene is particularly evident in this mixture where both the fuels are present. When these fuel components are blended in a mixture they reduce the low temperature reactivity (this effect is less relevant in the case of 1-hexene but can be easily observed for structures having shorter alkylations) and typically tend to increase the octane sensitivity of gasoline blends [25].

Surrogate mixtures

The two ternary mixtures analyzed here contain iso-octane as main component, toluene and 1-hexene (47/35/18% mole). Gasoline surrogates generally contain a significant amount of n-alkanes. In this particular surrogate proposed by Vanhove et al., 1-hexene plays the role of both the saturated and unsaturated component because of its relatively long alkyl chain which can be effectively undergo the low temperature branching mechanism typical of alkanes.

The model makes a good job in reproducing all the main aspects of the ignition (Fig. 6). Once again the most reactive component (in this case 1-hexene) triggers the low temperature reactivity. The cool flame timing is indeed close to the one shown by the 1-hexene/iso-octane mixture. The high concentration of unsaturated components suppresses the NTC behavior of iso-octane reducing the low temperature reactivity of the mixture. This blend shows long delays between the cool flame and the high temperature ignition, a feature mostly conferred by the presence of toluene.

A second mixture having a similar composition has been tested in a simulated jet stirred reactor (JSR) in comparison with experimental data collected by Yahyaoui et al. [26] (Fig. 7). This last comparison is intended to confirm the reliability of the model not just for ignition delay predictions, but also in terms of species profiles and eventually pollutant emissions.

Figure 7 shows the species profiles versus temperature for a stoichiometric gasoline surrogate containing iso-octane/toluene/1-hexene (50/35/15% mole). Pressure conditions are similar to the ones considered in RCM experiments (1MPa), but the mixture is much more diluted (fuel concentration is 0.1% mole). The contact time is fixed at 0.5 s. The model effectively reproduces the profiles evidenced by the experiments providing a satisfactory indication both of the general reactivity and of the selectivity.

5. Conclusions

A thorough revision of the previously published LLNL mechanism was recently carried out. Significant changes have been introduced in the model on the basis of quantummechanic calculations and literature reviews. In this work the most relevant of these improvements have been briefly described. New versions of the LLNL kinetic mechanisms for pure components were merged into a kinetic mechanism suited to gasoline surrogate kinetic modeling. Experimental information provided the basis for discussing some of the main issues related to gasoline-like fuel. The mechanism has been used to simulate the ignition delay times of PRFs, 1-hexene, toluene and their mixtures in a rapid compression machine and a jet stirred reactor.

The model showed an overall good agreement with measured values over a wide range of pressures and temperatures relevant to internal combustion engine.

Computed results have been used to analyze the interactions occurring between the above mentioned components in simple and more complex mixtures identifying how the NTC behavior of the fuels is conditioned by the presence of different classes of compounds.

The radical scavenging effect of toluene and, to a lesser extent, of 1-hexene justifies the NTC attenuation observed in their mixtures while the activation of HO_2 radicals by allyl and benzyl radicals has been recognized as important in the transition from the low to the high temperature ignition.

The fundamental information provided by calculations can be a valuable help for a better understanding of the blending effects of hydrocarbons as well as a valuable tool for the analysis of combustion phenomena of real fuels in internal combustion engines.

6. Acknowledgments

The authors thank program managers Kevin Stork and Gurpreet Singh for their support. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

7. References

[1] Z. Liu; R. Chen, Combust. Sci. & Tech. 181 (6) (2009) 828-852.

[2] M. Pasternak, Fabian Mauss, Henry Bensler, SAE 2009-01-0676.

[3] C.V. Naik, W.J. Pitz, C.K. Westbrook, M. Sjöberg, J.E.Dec, J. Orme, H.J. Curran, J.M. Simmie; SAE transactions 114 (4) (2005) 1381-1387.

[4] W.J. Pitz, N.P. Cernansky, F.L. Dryer, F.N. Egolfopoulos, J.T. Farrell, D.G. Friend and H. Pitsch SAE 2007-01-0175.

[5] M.V. Johnson, S.S. Goldsborough, Z. Serinyel, P. O'Toole, E. Larkin, G. O'Malley, H. J. Curran, Energy & Fuels 23 (2009) 5886–5898.

[6] J. Moc; G. Black; J. M. Simmie; H. J. Curran, AIP Conference Proceedings, 1148 (2009) 161-4,

[7] H. J. Curran, Int. Journ. Chem. Kin**.** 38 (2006) 250-275.

[8] M. Mehl, G. Vanhove, W. J. Pitz, E. Ranzi, Comb. Flame 155 (2008) 756-772.

[9] E. R. Ritter, J. W. Bozzelli, Int. J. Chem. Kinet. 23 (1991) 767-778.

[10] W. J. Pitz, R. Seiser, J. W.Bozzelli J.W., Proceedings of the Second Joint Meeting of the U.S. Sections of the Combustion Institute (2001).

[11] Y. Sakai, A. Miyoshi, M. Koshi, W. J. Pitz, Proc. Combust. Inst. 32 (2009) 411-418.

[12] R.G. Butler, I. Glassman, Proc. Comb. Inst. 32 (2009) 395-402.

[13] M. Mehl, A. Frassoldati, R. Fietzek, T. Faravelli, W.J. Pitz, E. Ranzi, Fall Technical Meeting of the Western State Section of the Combustion Institute (2009).

[14] https://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion-mechanisms

[15] R. Minetti, M. Carlier, M. Ribaucour, E. Therssen, L. R. Sochet, Comb. Flame, 102 (1995) 298-309

[16] H.K.Ciezki, G. Adomeit, Comb. Flame 93 (1993) 421–433.

[17] B.M. Gauthier, D.F. Davidson, R.K. Hanson, Comb. & Flame 139 (2004) 300-311.

[18] G. Mittal and C. J. Sung, Comb. Sci. & Tech. 179 (2007) 497-530

[19] R. Minetti, M. Carlier, M. Ribaucour, E. Therssen, L.R. Sochet, Proc. Combust. Inst. 26 (1996) 747-753.

[20] K. Fieweger, R. Blumenthal, G. Adomeit, Comb. Flame 109 (1997) 599-619.

[21] G. Mittal and Sung, C.J. , Comb. Flame 150 (2007) 355–368.

[22] J. Vanderover and M. A. Oehlschlaeger, Proc. Combust. Inst. 32 (2009) 165-172.

[23] G. Vanhove, M. Ribaucour, R. Minetti, Proc. Combust. Inst. 30 (2005) 1065-1072.

[24] G. Vanhove, G. Petit, R. Minetti, Comb. Flame 145 (2006) 521-532.

[25] M. Mehl, T. Faravelli, F. Giavazzi, E. Ranzi, P. Scorletti, A. Tardani, D. Terna, Energy & Fuels, 20 (2006) 2391-2398

[26] M. Yahyaoui, N. Djebaïli-Chaumeix, P. Dagaut, C.-E. Paillard, S. Gail, Proc. Combust. Inst. 31 (2007) 385–391

Figures

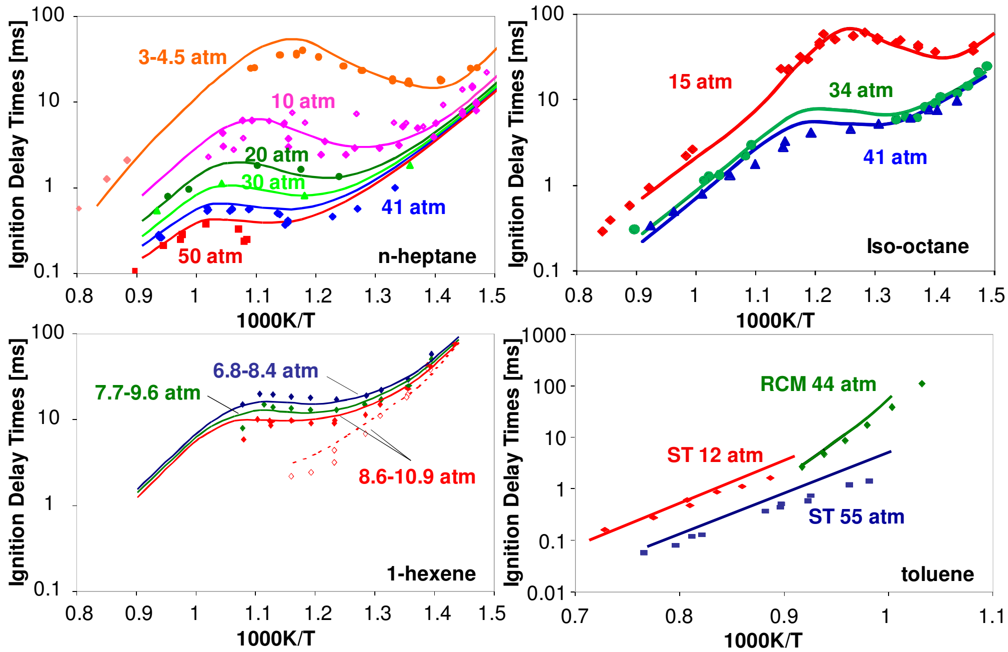

Figure 1: Experimental and calculated ignition delay times of PRF components (n-heptane, iso-octane) [9-14], toluene [15-16] and 1-hexene [17] in a wide range of operating conditions. Data collected in shock tube and rapid compression machine at stoichiometric conditions in air.

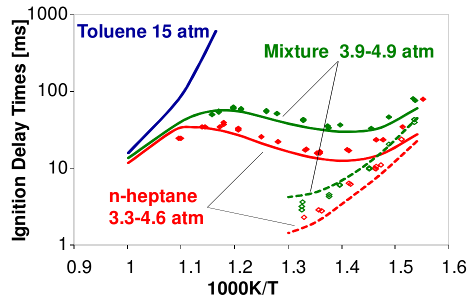

Figure 2: Ignition delay times (solid) and cool flames (dotted) of the toluene/n-heptane mixture and its pure components. Stoichiometric conditions in simulated air.

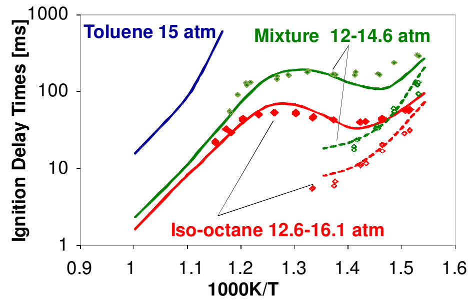

Figure 3: Ignition delay times (solid) and cool flames (dotted) of the toluene/iso-octane mixture and its pure components. Stoichiometric conditions in simulated air

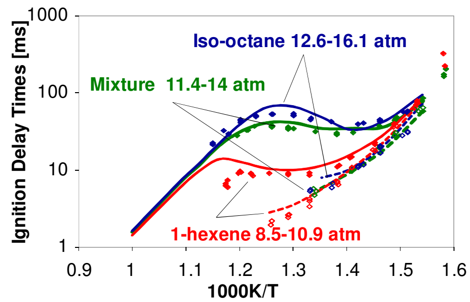

Figure 4: Ignition delay times (solid) and cool flames (dotted) of the 1-hexene/iso-octane mixture and its pure component. Stoichiometric conditions in simulated air

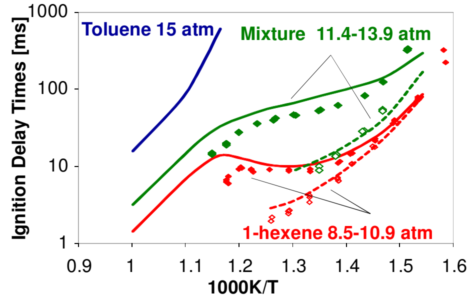

Figure 5: Ignition delay times (solid) and cool flames (dotted) of the 1-hexene/toluene mixture and its pure components. Stoichiometric conditions in simulated air

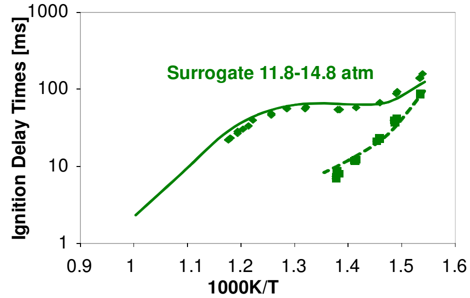

Figure 6: Ignition delay times (solid) and cool flames (dotted) of the surrogate mixture.

Stoichiometric conditions in simulated air

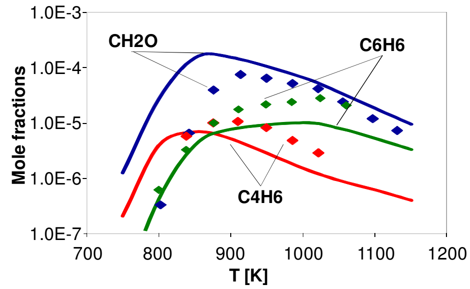

Figure 7: Experimental and calculated species profiles in a JSR of a *iso-octane/toluene/1-hexene (50/35/15% mole) surrogate blend: 10MPa, τ=0.5s, Φ=1*

Figure Captions

Figure 1: Experimental and calculated ignition delay times of PRF components (n-heptane, iso-octane) [9-14], toluene [15-16] and 1-hexene [17] in a wide range of operating conditions. Data collected in shock tube and rapid compression machine at stoichiometric conditions in air.

Figure 2: Ignition delay times (solid) and cool flames (dotted) of the toluene/n-heptane mixture and its pure components. Stoichiometric conditions in simulated air.

Figure 3: Ignition delay times (solid) and cool flames (dotted) of the toluene/iso-octane mixture and its pure components. Stoichiometric conditions in simulated air

Figure 4: Ignition delay times (solid) and cool flames (dotted) of the 1-hexene/iso-octane mixture and its pure component. Stoichiometric conditions in simulated air

Figure 5: Ignition delay times (solid) and cool flames (dotted) of the 1-hexene/toluene mixture and its pure components. Stoichiometric conditions in simulated air

Figure 6: Ignition delay times (solid) and cool flames (dotted) of the surrogate mixture. Stoichiometric conditions in simulated air

Figure 7: Experimental and calculated species profiles in a JSR of a iso-octane/toluene/1-hexene (50/35/15% mole) surrogate blend: 10MPa, τ=0.5s, Φ=1