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Detailed Kinetic Modeling of Gasoline Surrogate Mixtures

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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, a recently revised 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. Simulation results are discussed focusing attention on the mixing effects of the fuel components.

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. 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 behaviour of complex mixtures. One of the major challenges in this field is now the definition and the development of appropriate surrogate models able to mimic the actual behaviour 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 behaviour can be effectively reproduced by simpler fuel surrogates containing a limited number of components. Aside the most commonly used surrogates containing iso-octane and n-heptane only, the so called Primary Reference Fuels (PRF), new mixtures have recently been suggested to extend the reference components in surrogate mixtures to also include alkenes and aromatics. The use of representative species for all the main classes of hydrocarbons makes possible to reproduce very effectively 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 revised 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 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.

The kinetic mechanism

During the last year, we extensively reviewed our detailed kinetic mechanisms for n-heptane, iso-octane and toluene based on recent findings in the literature on reaction paths and rate constants. We also compared of predictions of the mechanisms to experimental data in the literature. The main goal is the definition of a comprehensive and reliable database of mechanisms that can be merged together to simulate the behavior of complex fuel surrogates. The mechanism presented in this paper represents an important achievement in this direction.

An important improvement to the mechanism involved the revision of the decomposition rates and the thermal properties of several radicals including the iso-octyl isomers and the neo-pentyl. 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. The isomerization rates of the alkyl-peroxyl radicals were also updated slightly reducing the reference values of the activation energies used for this class of reaction by 400kcal (i.e. 24400→ 24000 for the ROO<=>QOOH on a primary hydrogen involving a 6 member transition state). 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.

The increased reactivity has been compensated by reinforcing the reaction pathway of the direct elimination, ROO=>alkene + HO_2.

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

Other recent improvements brought into the mechanism include the introduction of the low temperature chemistry of the linear isomers of hexene, important components in gasoline fuels.

The toluene mechanism published in 2001 [1] was also recently updated by Sakai et al [2] including new reaction pathways proposed by recent studies. A further revision was carried out in the past months in collaboration with Milano's group.

The n-heptane, iso-octane and toluene mechanisms were then merged into a detailed kinetic model for the simulation of surrogates including about 1550 species and 8000 reactions. The general structure of the resulting mechanism is based on a C1-C4 core and three main blocks: the first one includes all the main reaction pathways for the saturated and non-saturated linear hydrocarbons up to C7, the second one contains the same classes of reactions for branched hydrocarbons from C5 to C8, 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 peroxyl radicals of the different fuels.

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 [3]. A detailed description of each submechanism will be soon available in publications now under preparation and in [4-8]

Results and Discussion: Pure components

The first set of comparisons 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 this class of fuel [9-14].

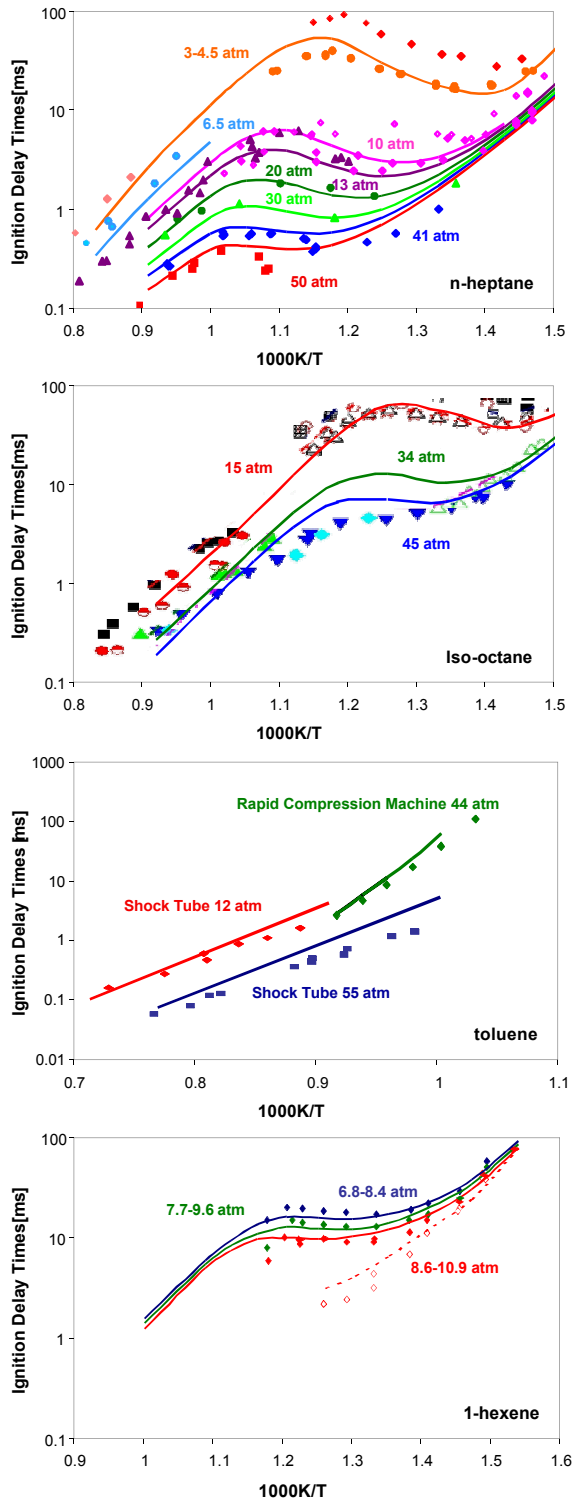

Figure 1: Experimental and calculated ignition delay times of PRFs (n-heptane, iso-octane) [9-14], toluene [15-16] and 1-hexene [17] in a wide range of operating conditions. Data collected in shock tube and rapid compression machine.

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 [15-16]. 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, evidence 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. [17]. Further details about olefin mechanism validation can be found in [6] where a complete discussion of the mechanism and a more extensive validation for this relatively recently studied fuel are presented.

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 briefly discussed at first. The next paragraphs show 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 [18]

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

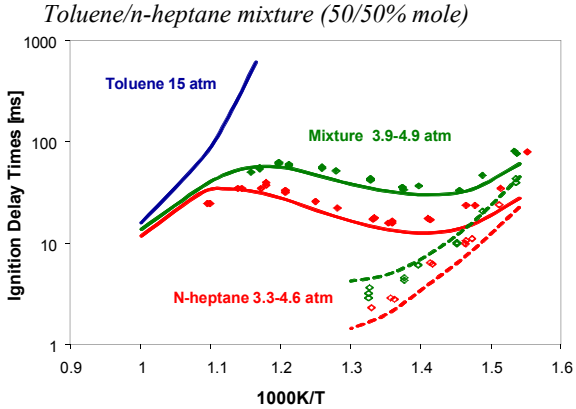

Figure 2: Ignition delay times (solid) and cool flames (dotted) of the toluene/n-heptane mixture and its pure components

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 methyl group acts 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 synergic 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 radicals to form 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 here 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 in the iso-octane/ toluene mixture because of the high concentration of iso-octane (Fig. 3).

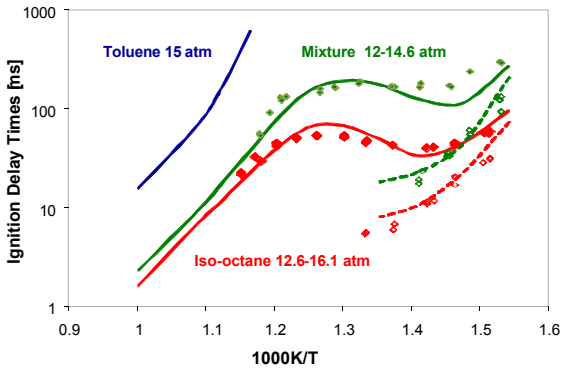

Figure 3: Ignition delay times (solid) and cool flames (dotted) of the toluene/iso-octane mixture and its pure components

The presence of toluene once more significantly delays both the cool flame 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)

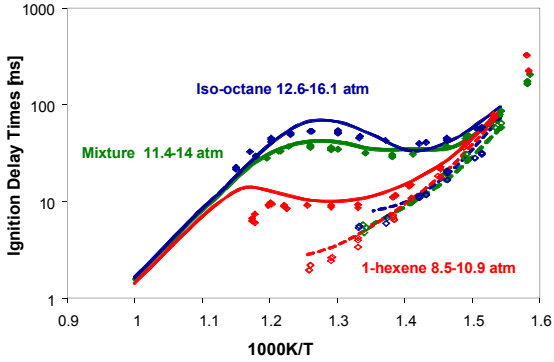

Figure 4: Ignition delay times (solid) and cool flames (dotted) of the 1-hexene/iso-octane mixture and its pure components

1-hexene is a relatively long chain alkene with a relevant saturated portion on the 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 anyway confers to this hydrocarbon some alternative reaction pathways: the possible formation of resonantly stabilized radicals and the high activation energy necessary to extract the vinyl hydrogen sites, make 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)

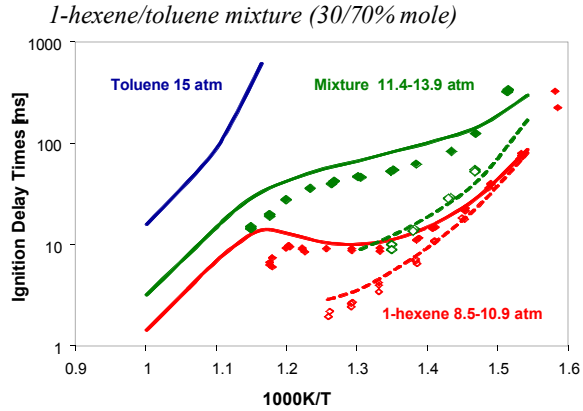

Figure 5: Ignition delay times (solid) and cool flames (dotted) of the 1-hexene/toluene mixture and its pure components

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, 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.

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 of this lack in reactivity might be the underestimation of this reaction pathway in the mechanism. Further investigations will help in discerning on this point.

The suppression of the NTC behavior performed by 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 structure having shorter alkylations) and typically tend to increase the octane sensitivity of gasoline blends [19].

Surrogate mixture

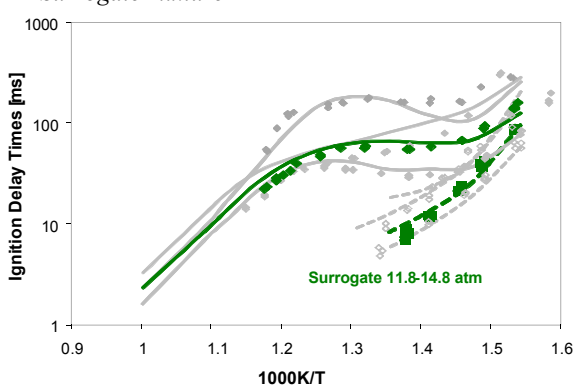

Figure 6: Ignition delay times (solid) and cool flames (dotted) of the surrogate mixture. Gray lines correspond to the curves of the binary mixtures

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 JSR in comparison with experimental data collected by Yahyaoui et al. [20] (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 8 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.

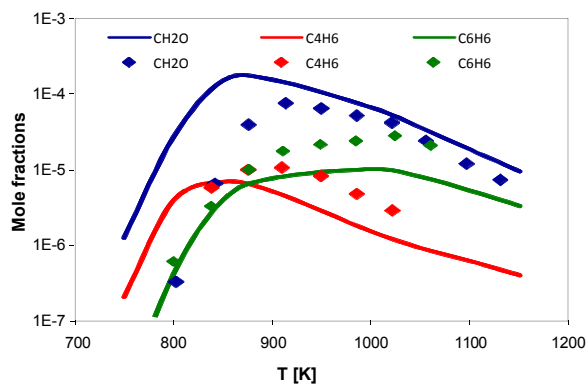

Figure 7: Experimental and calculated species profiles in a JSR (10MPa, τ=0.5s)

Conclusions

Some of the most relevant and recent improvements implemented in the NUI/LLNL kinetic mechanisms have been briefly described. New versions of the LLNL kinetic mechanisms 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 conditions.

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 fuel in internal combustion engines.

Acknowledgments

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References

[1] Pitz W.J., Seiser R., Bozzelli J.W., et al., in: Chemical Kinetic Characterization of the Combustion of Toluene, Proceedings of the Second Joint Meeting of the U.S. Sections of the Combustion Institute (2001)

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

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

[4] Curran, H.J., Gaffuri, P.,. Pitz, W.J, Westbrook, C.K.: Comb. Flame, 129: 253-280 (2002)

[5] Curran, H.J., Gaffuri, P., Pitz, W.J., Westbrook, C.K., Comb. Flame, 114: 149-177 (1998)

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

[7] Curran, H. J., W. J. Pitz, C. K. Westbrook, C. V. Callahan, and F. L. Dryer, Proc. Combust. Inst. 27: 379-387 (1998)

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

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

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

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

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

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

[14] K. Fieweger, R. Blumenthal, G. Adomeit, Comb. Flame 109: 599–619 (1997).

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

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

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

[18] Vanhove, G., Petit G., Minetti R., Comb. Flame 145: 521–532 (2006)

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

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