High-pressure shock tube experiments of the ignition of 3-pentanone-doped n-heptane and iso-octane/air mixtures

Mustapha Fikri, Leonel R. Cancino, Michaela Hartmann and Christof Schulz
Institute for Combustion and Gasdynamics (IVG), University of Duisburg-Essen
Duisburg, Germany

1 Introduction

Innovative concepts for internal combustion engines such as homogeneous-charge compression ignition (HCCI) require a detailed knowledge about the gas mixture prior to ignition. The use of tracers and fluorescing fuel compounds for fuel-concentration visualization based on laser-induced fluorescence (LIF) has grown to be an important engineering tool over the last two decades and has proven indispensable in internal combustion engine research [1]. Consequently, special focus has been laid on the photophysics of these tracers to get quantitative data from fluorescence signals under varying ambient conditions, such as pressure, temperature, and oxygen partial pressure. However, tracers exhibit limited stability at high temperatures and partially decompose together with the base fuel in the pre-ignition phase. Thus, the addition of the tracers to fuels for LIF experiments has two important implications. On one hand, the measured fluorescence signals could be misinterpreted in case of the decomposition of the tracer, and, on the other hand, the tracer itself, depending on the conditions, can influence the ignition characteristics of the base fuel. Many tracer types have investigated as candidates. Based on selection according to matching boiling points and diffusion characteristics with those of the base fuel, 3-pentanone has been selected as one “standard tracer”. It also provides a satisfactory fluorescence quantum yield and its low sensitivity to the effects of oxygen quenching are advantageous for quantitative signal interpretation. A comprehensive review highlighting the different substances for the application of tracer LIF is given in [2].

The absorption spectrum of 3-pentanone in the UV is due to the existence of the chromophore ketone group allowing the ($n \rightarrow \pi^*$) transition. Modica et al. [3] investigated the LIF signal dependence of 3-pentanone on temperature, pressure, and concentration of the ambient gas. Einecke et al. [4] developed a two-line planar LIF-imaging technique of 3-pentanone, which is added to iso-octane as the primary fuel, to quantify the temperature distribution and temperature development in the unburned gas region of an SI engine. Neij et al. [5] used 3-pentanonre in order to map iso-octane fuel distribution at ignition in a spark-ignited engine using LIF. Han and Steeper [6] presented a method based on in-cylinder LIF measurements to identify the equivalence ratio in the presence of multi-component fuels. The technique was applied on different ketone tracers. Rothamer et al. [7] used dual-wavelength excitation of 3-pentanone in the ultraviolet to simultaneously measure exhaust gas residual mole fraction and temperature in an automotive HCCI engine where both fuel and air were seeded with a tracer.

Despite the multiple works that deal with the physics and the photophysics of tracer molecules, studies about the oxidation chemistry of tracer-fuel mixtures are not well known and are just appearing. Few papers address the interaction of fluorescence tracers and fuels. A recent theoretical study by Westbrook and Sick investigated the stability of biacetyl relative to reference fuels based on kinetics models, however, without experimental validation [8]. Recently, we performed shock-tube measurements of ignition delay times to assess the influence of toluene onto the ignition behavior of iso-octane and n-heptane and to further validate the existing TRF mechanism based on our previous

Correspondence to: mustapha.fikri@uni-due.de

experimental results for low toluene concentration in n-heptane or iso-octane/air mixtures [9]. Furthermore, numerical simulations were employed to study the decomposition of toluene under in-cylinder conditions and its significance as a representative for local fuel concentration or as an indicator for the time and the location of the onset of the heat release.

Fitzgerald et al. [10] showed in a direct injection HCCI engine, that for n-heptane the chemical effects of tracer addition are more pronounced because of low-temperature heat release. It was also shown that 3-pentanone advances iso-octane combustion while retarding the ignition of n-heptane. The impact of the tracer is modest for the chosen operating conditions since varying the intake temperature can easily compensate for it. Serinyel et al. [11] studied the oxidation of 3-pentanone/O_2 mixtures in argon at high temperature (1250–1850 K) and atmospheric pressure behind reflected shock waves. Laminar flame speed measurements were also taken in a spherical bomb and a kinetics sub-mechanism was developed. The influence of the stoichiometry was investigated and a correlation was derived. Unfortunately, this correlation does not account for the effect of pressure. Therefore, an extrapolation to higher pressures was not feasible. In addition, because Ref. [11] focused on the high-temperature range only, it was not possible to directly compare the data. Recently, Davidson et al. [12] investigated ignition delay times for a series of oxygenate species such as acetone, n-butanal, methyl butanoate, and 3-pentanone. Again, the measurements covered only the high-temperature and low-pressure ranges. These surveys identify the continuous need for additional experimental data to cover the entire range relevant to engine combustion.

In this work we extend the range of experimental conditions to lower temperatures and higher pressures to cover the conditions under which tracers are commonly employed and where their influence is supposed to be more significant. The experimental findings were compared with a blended model combining PRF and 3-pentanone chemistry.

2 Experiment

The shock-tube facility used for gathering the ignition delay time data is described in detail in [13-14] but is briefly summarized here for completeness. The shock tube has a constant inner diameter of 90 mm. The driver section is 6.4 m long and the driven section has a length of 6.1 m. The maximum test time is extended up to 15 ms by driver gas tailoring. All the experiments were conducted behind the reflected shock waves in the temperature range 690–1270 K and at two pressures of 20 and 40 bar. Mixtures of the base fuels n-heptane and iso-octane with 3-pentanone (hereafter 3-P) at a fixed ratio of 10% are selected and compared with the corresponding base fuels at two equivalence ratios ϕ = 0.5–1.0. The mixtures are prepared manometrically and settled for at least one hour to ensure homogeneous mixing. Earlier tests showed that with the fuel used here the measured ignition delay times did not depend on the mixing time as long as a minimum of 60 min is exceeded. The temperature and pressure behind the reflected shock wave were computed from the incident shock velocity. The estimated temperature uncertainty is less than 15 K. Emission from CH* chemiluminescence was monitored at the sidewall location with a Hamamatsu 1P21 photomultiplier tube with a 430±5 nm bandpass filter. The ignition delay times was defined as the interval between the rise in pressure due the arrival of the shock wave at the end-wall and the time with the maximum increase in chemiluminescence signal. A second photomultiplier detected the broadband emission of formaldehyde in the 400–450 nm wavelength interval to observe the first stage (cool flame) of the two-stage ignition that occurs at low and moderate temperatures. The fiber and photomultiplier is equipped with the respective bandpass filters for the wavelength interval given above and is operated at higher gain because of the weak signal in the first stage ignition. During second stage ignition, this detector also receives CH* signal light which is seen as a strong increase in signal that is not considered further. The principle of the determination of τ_{ign} from the CH* and pressure signals is shown in Figure 1 for an example signal trace for stoichiometric 3-pentanone/ iso-octane (10/90% per volume) ignition in air at p_5 = 40.0 bar and T_5 = 764 K.

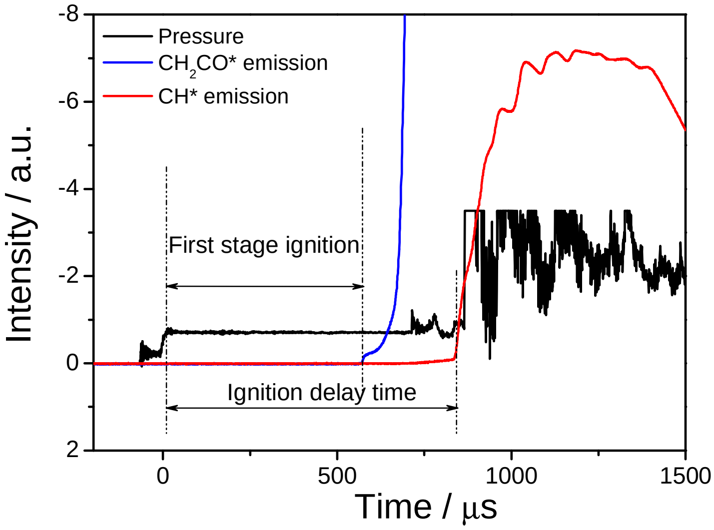

Fig. 1: Typical pressure, CH* (λ = 431 ± 5 nm) chemiluminescence and CH_2CO* (450 ≤ λ ≤ 500 nm) signals for a stoichiometric n-heptane/ 3-pentanone (90/10 vol. %)/air mixture with T_5 = 764 K and p_5 = 40.0 bar. Data traces after the initial rise after ignition do not have a quantitative meaning.

3 Chemistry modeling

In this work we propose a detailed kinetics model for mixtures of PRF fuels and 3-pentanone. The PRF model from Curran et al. [15] and the 3-pentanone model from Curran et al. [11] were assembled. The blending process of the kinetics model is described in earlier work [13,14]. The procedure is briefly described here. It is based on merging available chemical kinetics submodels for each chemical species present in the current study. When two species have the same empirical formula it is necessary to check their thermodynamic databases by comparing the enthalpy h, heat capacity c_p, and entropy S at several temperatures. If their thermodynamic properties return the same (or similar) values, then both chemical species are considered identical despite different names or abbreviations used in the original kinetics models. One of the duplicated species is then removed and the occurrences of that species are replaced by the equivalent one. Automatic mechanism checking is used to simplify the process. The original PRF model includes a number of reactions for 3-pentanone. In this work, we took the chemical species and elementary reactions from Curran et al. [11] that are not present in the PRF model and implemented them into the PRF model. The resulting blended model is composed of 1060 chemical species among 4347 elementary reactions. Additionally, all the pressure-dependent reactions in the C4 model from Curran et al. [11] were taken in the blended model.

4 Results and Discussion

Experimentally, the ignition delay times were evaluated from CH* emission for stoichiometric and lean mixtures in air using pure 3-pentanone (3-P), isooctane/3-P and n-heptane/3-P at 20 and 40 bar in the range of 690–1270 K. Ignition delay time calculations were carried out using CHEMKIN-PRO [16] under constant volume, constant internal energy assumption. The calculated ignition delay times were determined from the maximum O-atom concentration. For 3-P/air mixture, the ignition was calculated using the Curran mechanism which was published recently [11]. In the same fashion, the experimental ignition delay times were compared with the calculated ignition delay times from the blended mechanism [15]. Figure 2 shows the results of the simulated ignition delay times using the C4 model [11] and the blended model of this work (see text below). The former was validated against experimental data for high temperature and atmospheric pressure using Ar-diluted mixtures. The experimental data of this work (table 1), however, were determined at high pressure. Therefore, the values were scaled to atmospheric pressure using the pressure dependence ($p^{-0.52}$) found in [12] for acetone mixtures to allow for a rough comparison between both data sets. Figure 2 shows that both models (C4 and the blended model) predict faster ignition than the experimental data (1 bar and 42 bar). Our experimental data show a typical roll-off at low temperature. Serinyel et al. [11] studied the oxidation of 3-pentanone/O_2 mixtures diluted in argon at reflected shock pressures of 1 bar in the 1250–1850 K range at equivalence ratios of 0.5–2.0. They observed that rich mixtures ignite slower compared to lean ones. The chemical model that is the basis for the ignition delay time simulation, includes the pressure-dependent unimolecular decomposition of 3-pentanone, H(α,β)-abstraction reactions from 3-pentanone, and the decomposition of the fuel radicals (parent radical (-H)) as well as isomerization reactions. However, it does not contains addition reactions of free radicals with molecular O_2 forming alkyperoxy that are important at low and intermediate temperature. The primary reference fuel mechanism contains similarly all 3-pentanone submechanism, there are about 16 reactions involving H-abstraction (primary and secondary H-atom abstraction) with the active species as OH, HO_2, O_2, H, C_2H_3, C_2H_5, CH_3O and CH_3O_2.

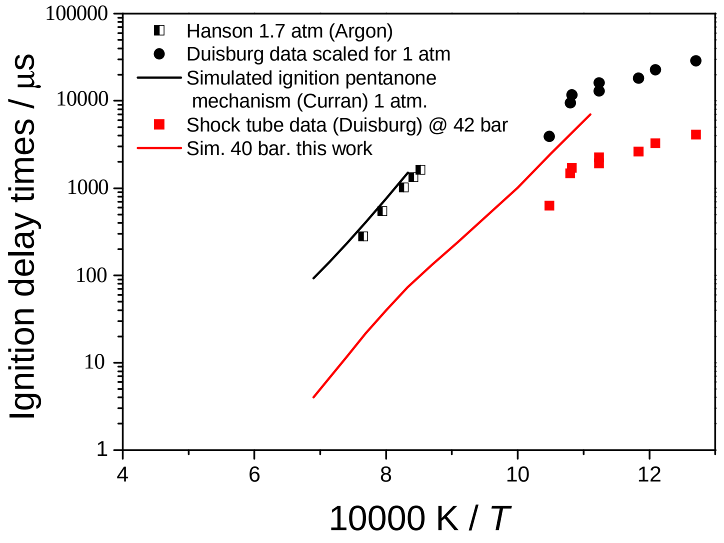

Fig. 2: Ignition delay times of stoichiometric 3-pentanone/air mixtures. Solid squares: Ignition delay times at 42 bar. Open circles: Ignition value scaled to 1 atm. Half filled squares: Experiments of Hanson at 1.6–1.8 bar [12] Lines: Calculated ignition delay times using the C4 mechanism for 1 bar [11].

Chemical effect of 3-pentanone on n-heptane

Figure 3 shows a set of measured and simulated ignition delay times of 3-pentanone and a mixture of 3-pentanone/n-heptane (10/90%) at stoichiometric and lean conditions ($\phi = 0.5$) and at two respective pressures of 20 and 40 bar. The figure also includes the ignition delay times for n-heptane at the corresponding pressures for a wide temperature range. A rough comparison of the ignition delay times of pure 3-pentanone and pure toluene published in [9] at 40 bar indicates that the latter exhibits a lower reactivity 1.7 times slower (having an activation temperature of 8157±761 K and 4619.8±442 K for 3-pentanone in the range of 787–1030 K) compared to 3-pentanone for similar experimental conditions. Considering the lean condition first, both data set at pure n-heptane for 20 and 40 bar exhibit the NTC regime expected for this kind of fuel. Second, the 3-pentanone-doped n-heptane mixture (40 bar) follows the same ignition trend as pure n-heptane, however, the absolute values are considerably slower than for pure n-heptane for $T_5 < 950$ K. For the 20 bar case, it seems that the ignition delay times of the mixture are faster than for the n-heptane at the same conditions. However, more data are needed especially in the low temperature range to reliably discern the effect of 3-pentanone in n-heptane mixtures at this conditions. Third, in the same manner, the first-stage ignition delay times of the mixtures (40 bar) are notably lower (about 36%) than for pure n-heptane keeping the same activation energy in the 740–880 K range. These findings are depicted in the insert of Fig. 3. We conclude, that for lean conditions at high pressure and low temperatures, 3-pentanone acts as an inhibitor for the first-stage ignition and for the second-stage ignition at intermediate temperatures. For high temperatures, the simulation does not resolve any substantial effect. Because of the lack of experimental high temperature data, this cannot yet be confirmed for these conditions. While the proposed model overestimates the ignition delay times it reproduces the trend of the experimental data. The behavior of the 3-P-doped n-heptane mixture observed experimentally is also reproduced in the simulations. 3-pentanone inhibits the reactivity of n-heptane in the low temperature range (950–750 K).

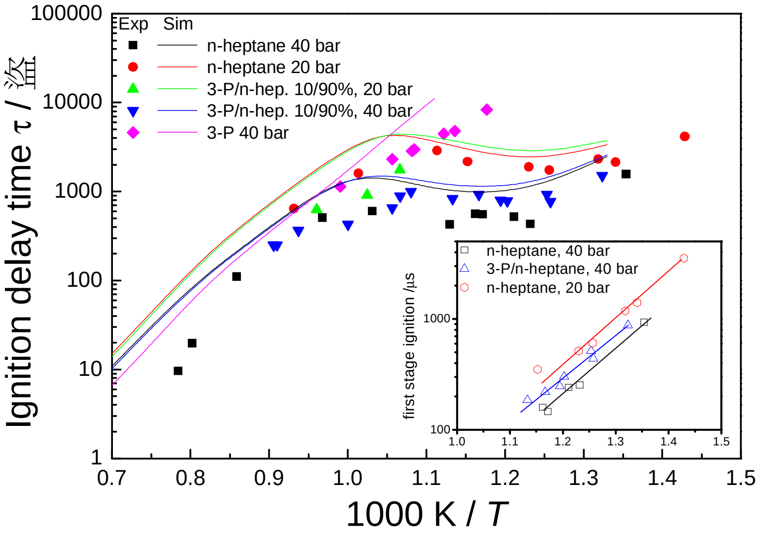

Fig. 3: Comparison of measured and simulated τ_{ign} for 3-P and 3-P/n-heptane (10/90% vol.) with n-heptane mixtures in air for p_5 = 20 and 40 bar and ϕ = 0.5. The insert shows the first-ignition.

The overall picture changes for stoichiometric conditions (Fig. 4). For 40 bar experiments, the addition of 10% 3-pentanone to n-heptane does not cause any apparent changes in the ignition delay times. This trend is also reflected in the simulation. The comparison of 3-P-doped n-heptane and pure n-heptane shows that the ignition delay times characteristics for the mixture follow the overall ignition chemistry of the main fuel. When 3-pentanone is used as an additive it does not globally affect the kinetics of the main fuel, here n-heptane. The simulation also reflects the same result for both pressures tested in this work. It shows that the difference of reactivity between pure n-heptane and 3-P-doped n-heptane diminishes and the fuel concentration of the main fuel compensate for the effect of 3-pentanone. In the experiments of Fitzgerald et al. [10], seeding n-heptane with 3-pentanone in an HCCI engine reduced the low-temperature heat release and delayed the main heat release.. However, the 3-pentanone concentration was 21% (base fuel: n-heptane), a value quite unusual for tracer-LIF measurements. Serinyel et al. [11] showed that the addition of 3-P to n-heptane mixtures (15/85% by vol) in O_2/Ar does not show any apparent effect on the ignition delay times of the base fuel. However, their results are inconclusive since the experiments were measured at high temperature and low pressure (1 bar) with high inert-gas dilution, far away from engine-like conditions where the low-temperature chemistry of the tracer and the main fuel interact.

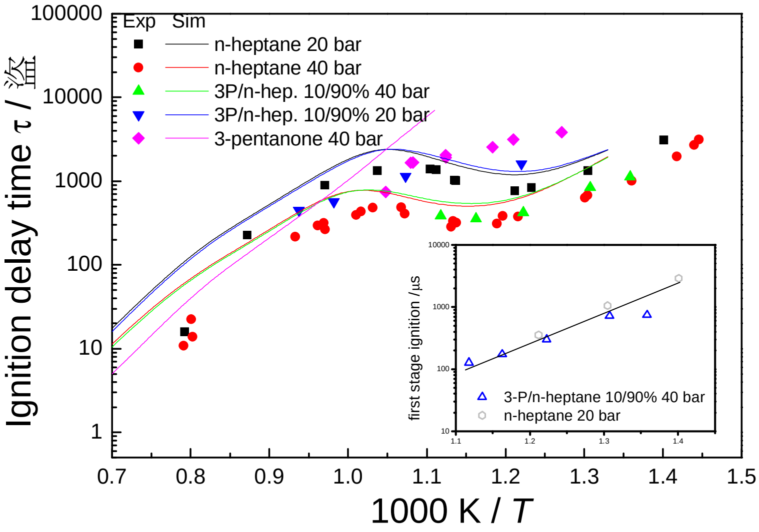

Figure 4: Comparison of measured and simulated τ_{ign} for 3-P and 3-P/n-heptane (10/90 vol.%) with n-heptane mixtures in air for p_5 = 20 and 40 bar and ϕ = 1.0. The insert shows the delay times of first-stage ignition.

The above finding is also reproduced by a (0-D) simulation (not shown here), which shows that the effect is rather pronounced at low temperatures and for tracer seeding level up to 20%. Further increase in tracer concentration increases the inhibiting effect of 3-pentanone. The reason for this inhibition factor is that the 3-pentanone chemistry interferes with the n-heptane chemistry. 3-pentanone decomposes faster and retards the production of the major radicals (OH, HO_2, H_2O_2), relevant in the low temperature range, with radical concentration of more than an order of magnitude than in case of pure n-heptane. As a result, ignition is delayed. In contrast to the 10/90% 3-P/n-heptane mixture, for pure n-heptane at 40 bar no first-stage ignition was observed.

Chemical effect of 3-pentanone on iso-octane

Figure 5 shows the comparison of measured and simulated ignition delay times for pure iso-octane, pure 3-pentanone and a mixture of iso-octane with an equivalent proportion of 10% 3-pentanone for p_5 = 40 bar and ϕ = 1.0 and 0.5, respectively. Both, experiment and simulation, show longer ignition delay times for lean mixtures, as expected for pure isooctane as well as for pure 3-pentanone Serinyel et al. [11] observed the reversed effect for diluted mixtures. For all measurements and simulations the shape of the curves are comparable. Moreover, no occurrence of the first stage ignition was observed. When comparing the experiments (ϕ= 0.5) for 3-P/iso-octane mixtures with pure iso-octane, in contrast to the prior finding regarding n-heptane, one clearly sees that 3-pentanone advances the ignition of iso-octane. The simulations for 3-pentanone-doped iso-octane with ϕ = 0.5 show no difference in the ignition delay times compared to the case with pure iso-octane until approximately 950 K. For lower temperatures the model does not foresee any ignition within our experimental time. The difference in τ_{ign} between 3-P-doped and pure iso-octane is more pronounced in the experimental results, especially in the low-temperature range. Similarly, as in the case of n-heptane, at high temperatures, the impact of 3-pentanone is negligible and cannot be resolved by the simulation.

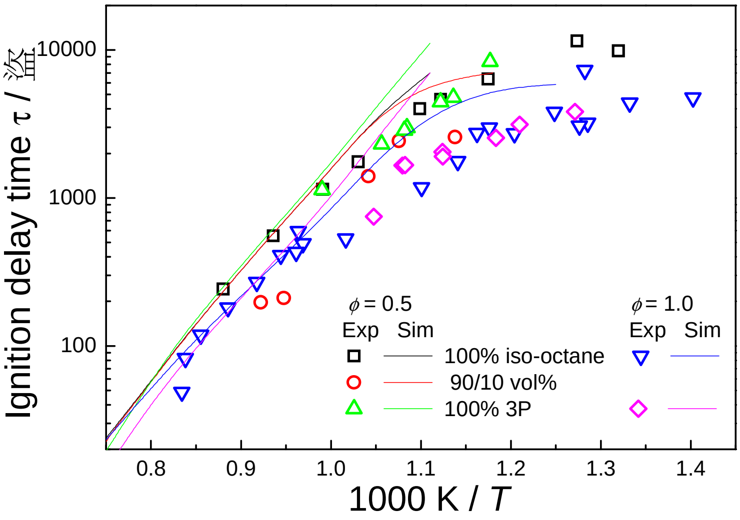

Figure 5: Comparison of measured and simulated τ_{ign} for 3-pentanone and 3-P/iso-octane (10/90 vol.%) and iso-octane mixtures in air for p_5 = 40 bar and ϕ = 0.5 and 1.0.

5 Summary and Conclusions

Ignition-delay times for 3-pentanone/iso-octane (10/90% by volume) and 3-pentanone/n-heptane mixtures (10/90% by volume) have been determined in a high-pressure shock tube under engine-relevant conditions (p_5 = 20–40 bar) for equivalence ratios ϕ = 0.5 and 1.0 over a wide temperature range 690 K < T_5 < 1270 K. The results were compared to ignition delay times of pure iso-octane and n-heptane fuels and to pure 3-P/air mixtures under identical conditions. Attempting to represent the experimental results numerically, a detailed kinetics model for PRF/3-pentanone mixtures is proposed. The model overpredicts the ignition delay times especially in the low temperature range. However, it is still able to reproduce the overall trend of the experimental data. As found in simulations and already confirmed by experiments, for lean condition 3-pentanone reduces the reactivity of n-heptane. For stoichiometric conditions, however, it does not alter the ignition delay by more than 11% at 850 K and 20 bar (with 10% 3-pentanone). The chemical effect of adding 3-pentanone to iso-octane is inverse, leading to retardation of the main ignition. Further investigation of the model is needed and the model used in this work needs further development to account for the low temperature chemistry.

Acknowledgements

Funding by the German Research Foundation (DFG) is gratefully acknowledged.

References

1. M. C. Drake; D. C. Haworth, Proc. Combust. Inst. 31 (2007) 99-124
2. C. Schulz; V. Sick, Progr. Energy Combust. Sci. 31 (2005) 75-121
3. V. Modica; C. Morin; P. Guibert, Appl. Phys. B 87 (2007) 193-204
4. S. Einecke; C. Schulz; V. Sick, Appl. Phys. B 71 (2000) 717-723
5. H. Neij; B. Johansson; M. Alden, Combust. Flame 99 (1994) 449-57
6. D. Han; R. R. Steeper, Proc. Combust. Inst. 29 (2002) 727-734

7. D. A. Rothamer; J. A. Snyder; R. K. Hanson; R. R. Steeper, Appl. Phys. B 99 (2010) 371-384
8. V. Sick; C. K. Westbrook, Proc. Combust. Inst. 32 (2009) 913-920
9. M. Hartmann; I. Gushterova; M. Fikri; C. Schulz; R. Schiessl; U. Maas, Combust. Flame 158 (2011) 172-178
10. R. P. Fitzgerald; R. R. Steeper; J. A. Snyder, SAE Int. J. Fuels Lubricants 1 (2009) 1491-1502
11. Z. Serinyel; N. Chaumeix; G. Black; J. M. Simmie; H. J. Curran, J. Phys. Chem. A 114 (2010) 12176- 12186
12. D. F. Davidson; S. C. Ranganath; K. Y. Lam; M. Liaw; Z. Hong; R. K. Hanson, J. Prop. Power 26 (2010) 280-287
13. L. R. Cancino; M. Fikri; A. A. M. Oliveira; C. Schulz, Energy & Fuels 24 (2010) 2830-2840
14. L. R. Cancino; M. Fikri; A. A. M. Oliveira; C. Schulz, Fuel http://dx.doi.org/10.1016/j.fuel.2010.11.003 (2010)
15. Curran H. J.; Pitz W. J.; Westbrook C. K.; Callahan C. V.; Dryer F. L., Proc. Combust.Inst. 27(1998) 379–87.
16. R. J. Kee; F. M. Rupley; J. A. Miller; M. E. Coltrin; J. F. Grcar; E. Meeks; H. K. Moffat; A. E. Lutz; G. Dixon-Lewis; M. D. Smooke; J. Warnatz; G. H. Evans; R. S. Larson; R. E. Mitchell; L. R. Petzold; W. C. Reynolds; M. Carcotsios; W. E. Stewart; P. Glarborg; C. Wang; O. Adigun, CHEMKIN-PRO Collection, Reaction Design, Inc., San Diego, CA (2009)