DETAILED KINETIC MODEL OF OXIDATION AND COMBUSTION OF N-HEPTANE USING AN AUTOMATIC GENERATION OF MECHANISMS

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Abstract

There is continued interest in developing a better understanding of the oxidation and combustion of large hydrocarbons, which are good representative for practical fuels used in automotive engines, for a wide range of operating conditions. This interest is motivated by the need to improve the efficiency and performance of currently operating combustion systems, the fuel economy, and the need to reduce pollutant emission. Normal-heptane is one of these hydrocarbons. In this work a detailed chemical kinetic model for the oxidation and combustion of n-heptane has been automatically developed using a computer code called MOLEC. The model consisting of 486 species taking part in 2008 elementary reactions was used to reproduce experimental results of n-heptane oxidation in shock tubes. The experimental study of the ignition delay times of n-heptane/O_2/Ar behind a reflected shock wave for equivalence ratios of 0.5-4.0 in a temperature range of 1300 K - 2000 K can be reproduced well by the model. Experimentally derived and numerically predicted ignition delays of n-heptane/air mixtures in a high-pressure shock tube in a wide range of temperatures, pressures, and equivalence ratios agree very well. Sensitivity analyses were performed for shock tube environment in an attempt to identify the most important reactions under the relevant conditions of study.

Keywords: Modelling, Oxidation, Combustion, Kinetics, Fuels

Abstrak

Dewasa ini di dunia muncul minat yang berkelanjutan dalam mengembangkan proses oksidasi dan pembakaran hidrokarbon panjang, yang merupakan representatif yang meyakinkan bagi bahan bakar praktis yang digunakan di dalam mesin kendaraan bermotor dalam rentang kondisi operasi yang lebar. Keminatan ini dipicu oleh keinginan untuk meningkatkan efisiensi dan kinerja sistem pembakaran yang digunakan saat ini, ekonomi bahan baker serta kebutuhan untuk mengurangi emisi polutan. Normal-heptane merupakan salah satu hidrokarbon ini. Di dalam riset ini sebuah model kinetika kimia detail untuk oksidasi dan pembakaran n-heptana dikembangkan secara otomatis dengan menggunakan sebuah kode komputer yang disebut MOLEC. Model yang terdiri dari 486 spesies yang berperanserta di dalam 2008 reaksi elementer digunakan untuk mereproduksi hasil-hasil eksperimen oksidasi n-heptana di dalam shock tubes. Hasil eksperimen ignition delay times n-heptana/O_2/Ar di dalam shock tube untuk rasio ekuivalensi 0,5-4,0 pada rentang temperatur 1300 K - 2000 K dapat direproduksi dengan baik oleh model. Ignition delay campuran n-heptana/udara hasil eksperimen dan hasil perhitungan numeris di dalam shock tube bertekanan tinggi dalam rentang temperatur, tekanan, dan rasio ekuivalensi yang luas sangat bersesuaian satu sama lain. Analisis sensitivitas dilakukan dalam upaya mengidentifikasi reaksi-reaksi yang paling penting di dalam kondisi kajian yang relevan.

Kata Kunci: Modeling, Oksidasi, Pembakaran, Kinetika, Bahan Bakar

1. Introduction

There is continued interest in developing a better understanding of the oxidation and combustion of large hydrocarbons, which are more representative for practical fuels used in automotive engines, for a wide range of operating conditions. This interest is motivated by the need to improve the efficiency and performance of currently operating combustion systems, the fuel economy, and the need to reduce pollutant emission.

Detailed chemical kinetic models can be used to predict and analyse the formation of a wide spectrum of observed products of oxidation and combustion, and to control physical processes such as flame speed and auto ignition time. To write detailed chemical kinetic mechanisms for the oxidation and combustion of large hydrocarbons for a wide range of temperatures and equivalent ratios, hundreds of elementary reactions have to be considered. Such large mechanisms have become difficult to write manually. Therefore, it is a convenient and rigorous way to write such large mechanisms by means of an automatic procedure, as showed by Tomlin *et al.* (1997).

Recent modeling studies of premixed systems such as stirred reactors and shock tubes have helped in the development of detailed chemical kinetic mechanisms describing the oxidation of large hydrocarbons as the primary reference fuels, or as practical fuel models used in automotive engines, such as n-heptane. The studies on the kinetic modeling of n-heptane oxidation and combustion have been performed by numerous researchers, but only a few have developed their mechanisms automatically.

Chevalier *et al.* (1992) and Nehse *et al.* (1996) have used a computer code to automatically generate the chemical kinetic mechanisms for n-heptane, but only to reproduce experimental measurements in high-pressure shock tubes at temperatures up to 1300 K. Come *et al.* (1996) have generated a chemical kinetic mechanism for n-heptane by means of a computer program. The results were generally in good agreement with experimental data, but none of these had the success that might have been expected at temperatures lower than 900 K. Therefore, the objective of this work is to provide a computer code to generate automatically large hydrocarbon mechanisms which is able to reproduce experimental measurements at wider range of temperatures.

2. Fundamental

Elementary reactions occur at a molecular level exactly in the way described by the chemical reaction equation. The reaction rate coefficient is given by the Arrhenius law

$$k = A' \exp\left[-\frac{E_a}{RT}\right] \qquad (1)$$

where A' is the pre-exponential factor and E_a is the activation energy. These quantities come from experiments or from statistical mechanics calculations. Not all molecular collisions will result in reaction, but only those with kinetic energy higher than the energy needed to break the bonds of the reactant molecules. This energy barrier is the activation energy. Its maximum value corresponds to the bond energies in the molecule. In dissociation reactions, for instance, the activation energy is approximately equal to the bond energy being broken. The value of activation energy may also be much smaller or even zero. The proportion of collisions occurring between molecules that have kinetic energy higher than E_a is given by $\exp(-E_a/RT)$. Since most elementary binary reactions exhibit Arrhenius behaviour over modest ranges of temperature, the temperature dependence can usually be incorporated with sufficient accuracy into the exponential alone. However, for the large temperature ranges found in combustion, "non-Arrhenius" behaviour of the rate coefficient tends to occur, particularly for processes that have a small energy barrier. Therefore, it is necessary to adopt a modified Arrhenius form which expresses the impact of temperature on the rate coefficient

$$k = AT^n \exp\left[-\frac{E_a}{RT}\right] \qquad (2)$$

where the power of T accounts for a temperature dependence of the pre-exponential factor, A'.

Mechanisms are systems consisting of a number of elementary chemical reactions with their rate coefficients determined by fundamental kinetic experiments or theoretical treatment. Detailed mechanisms are a centre feature of chemical kinetic models and developed as response to and validated by a set of experimental measurements. Consequently, the range of this experimental data set limits the range of applicability of the mechanisms.

Extrapolation of detailed mechanisms from one regime to others is difficult and frequently inaccurate. For instance, due to the fact that the chain branching reactions and many pathways are different in the two regimes, the mechanisms for a shock tube model are not correct if applied for hydrocarbon oxidation at low temperatures. The best solution is that the range of mechanism validation is expanded to a maximum practical

level by comparing it to a number of experimental data sets that permits to apply the so-called comprehensive mechanism in a wider range, providing a further knowledge that is not possible if directly obtained from experimental results.

The most important types of reactions found in oxidation and combustion of large hydrocarbons are: decomposition of hydrocarbons (e.g. alkanes, alkenes), H-atom abstraction by reactive radicals (e.g. O, H, OH, HO_2, CH_3), β-scission of radicals, internal H-atom abstraction (isomerization), addition to molecular oxygen, O-O bond scission, and radical addition to a double bond.

The rate coefficients of these types of reactions for hydrocarbons with more than four carbon atoms can be classified. They depend on the radicals abstracting a H atom from alkanes, alkenes, aldehydes, ketones or cyclic ethers (e.g. O, H, OH, HO_2, CH_3), the type of H atom being abstracted (primary, secondary or tertiary), the number of available equivalent H atoms, and the size of the intermediate ring structures (5-, 6-, 7- or 8-membered).

3. Methodology

A computer code named MOLEC, which can generate automatically mechanisms for the combustion and oxidation of large hydrocarbons, has been developed in the Warnatz group (Chevalier et al., 1990, 1992; Nehse et al., 1996). This system is based on simple rules, which appear from a very limited number of different types of reactions in the combustion and oxidation of large hydrocarbons.

Building on this observation, it is possible to formulate all possible reactions taking place in the combustion and oxidation of large hydrocarbons along with their rate coefficients using simple rules. Each rule represents a particular type of reaction.

Starting from elementary reactions between molecular reactants (fuel and oxygen), the decompositions, rearrangements and additions, which generate new species, are automatically evaluated. Due to the fact that the reaction mechanisms for the C_1-C_4 hydrocarbons already exists and that the rate coefficients of small species strongly depend on the chain length, the code considers only the reactions of species larger than C_4. The method of the MOLEC program is based on representation of molecules as binary trees and pattern matching. As a supporting system LISP (LISt Processing) is used because of its flexibility concerning the data structure, algorithm development and availability of a user interface design.

The C_5-C_{fuel} sub-mechanism produced automatically by the code has to be coupled to the handwritten C_1-C_4 sub-mechanism to compose a detailed mechanism for fuel oxidation, which is then solved numerically.

It is obvious that MOLEC can give a very detailed chemical kinetic mechanism. However, mechanisms provided by MOLEC were only able to reproduce experimental flame speeds and ignition delay times at temperatures up to 1300 K (Chevalier et al., 1990, 1992; Nehse et al., 1996). To avoid this disadvantage the code, therefore, was modified. The way to achieve this objective was through improvement of the existing rules such as cyclic-ether reactions and aldehyde reactions, inclusion of some additional rules to the code, such as ketone reactions, hydroperoxy cyclic-ether formations and additional reactions of alkenes, and inclusion of small oxygenates, produced by the code but not included in the handwritten C_1-C_4 sub-mechanism yet, to the handwritten C_1-C_4 sub-mechanism.

Reaction rules shown in Table 1 are ones included in MOLEC. This is sufficient to simulate many high temperature applications of the oxidation and combustion of alkanes and alkenes.

Table 1. Reaction Rules in MOLEC

No	Reaction
1	Unimolecular decomposition of alkanes
2	Abstraction of H atoms from alkanes
3	Decomposition of alkyl radicals
4	Isomerization of alkyl radicals
5	Oxidation of alkyl radicals to form alkenes
6	Decomposition of alkenes
7	Abstraction of allylic H atoms
8	Abstraction of vinylic H atoms
9	Abstraction of alkylic H atoms
10	Addition of H atoms to double bonds
11	Addition of CH_3 radicals to double bonds
12	Addition of O atoms to double bonds
13	Addition of OH radicals to double bonds
14	Addition of HO_2 radicals to double bonds
15	Retro-ene reactions
16	Isomerization of alkenyl radicals
17	Decomposition of allylic radicals
18	Decomposition of vinylic radicals
19	Decomposition of alkenyl radicals

At low temperature there is a so-called degenerate chain branching characterized by the fact that a main precursor of chain branching (here peroxy alkyl radicals, $RO_2^\bullet$) is decomposed at higher temperature ($T > 800$ K), leading to an inverse temperature dependence (the negative temperature coefficient, NTC) of the reaction rate. Reaction rules for low temperature are listed in Table 2.

Table 2. Reaction Rules for Low Temperature

No	Reaction
1	Addition of alkyl radicals to molecular oxygen
2	Isomerization of alkylperoxy radicals
3	Abstraction of H atoms from alkanes by alkylperoxy radicals
4	Reaction of alkylperoxy radicals with HO_2
5	Reaction of alkylperoxy radicals with H_2O_2
6	Homolytic O-O scission of hydroperoxides
7	Decomposition of alkoxy radicals
8	Addition o f hydroperoxy alkyl radicals to molecular oxygen
9	β-scission of hydroperoxy alkyl radicals formed by the (1,4) isomerization
10	Homolytic C -C scission of hydrop eroxy alkyl radicals formed by the (1.5) isomerization
11	Homolytic C -C scission of hydroperoxy alkyl radicals formed by the (1,6) and (1,7) isomerization
12	Homolytic O -O scission of hydroperoxy alkyl radicals with the radical site at a carbon atom linked to oxygen atom
13	Oxidation of hydroperoxy alkyl radicals
14	Formation of cyclic ethers from hydroperoxy alkyl radicals
15	Isomerization of peroxy hydroperoxy alkyl radicals
16	Homolytic O -O scission of dihydroperoxy alkyl radicals
17	Formation of hydroperoxy cyclic ethers from dihydroperoxy radicals
18	Decomposition of ketohydroperoxides
19	Decomposition of $O=R''O^{\bullet}$
20	Abstraction of H atoms from cyclic ethers
21	Decomposition of hydroperoxy cyclic ethers
22	Abstraction of H atoms from aldehydes or ketones
23	Decomposition of ketyl radicals

All reaction pathways at high and low temperature are schematically summarized in Figures 1 and 2, respectively.
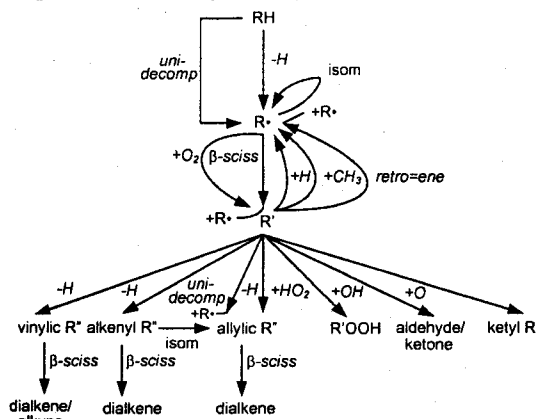
Figure 1. Scheme of High-Temperature Reaction Pathways (Muharam, 2005)

The C_5-C_7 sub-mechanisms generated by MOLEC were coupled with the handwritten C_0-C_4 sub-mechanism to build a detailed chemical
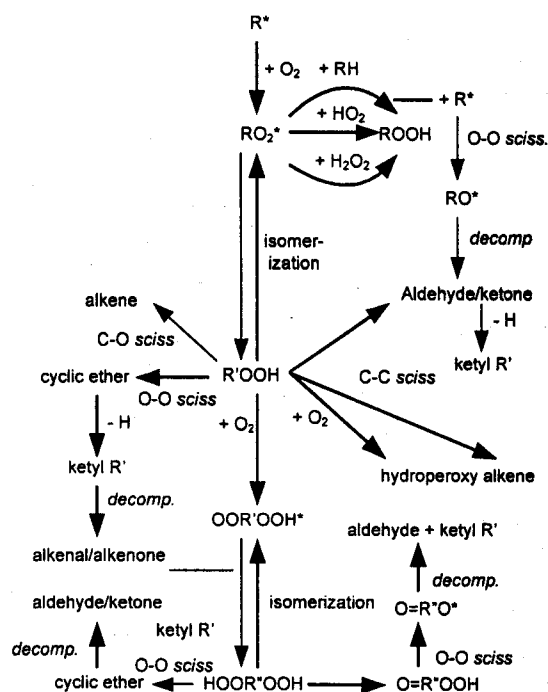

Figure 2. Scheme of Low-Temperature Reaction Pathways (Muharam, 2005)

kinetic mechanism for n-heptane oxidation consisting of 486 species taking part in 2008 elementary reactions. This mechanism is used to reproduce experimental results on n-heptane oxidation in a shock tube.

A study on ignition delay times of n-heptane/O_2/Ar mixtures behind reflected shock waves for equivalence ratios ranging from 0.5 to 4.0 in a temperature range of 1300 K - 2000 K has been carried out by Coats and Williams (1978). The experimental ignition delays together with the calculated ones are presented in Figure 3. As can be seen in this figure, good agreement between the experimental and calculated results is achieved for the stoichiometric and fuel-lean mixtures. However, the model rather overestimates the ignition delays of the fuel-rich mixtures. The fuel-lean mixtures burn more easily than the stoichiometric and fuel-rich mixtures under this pyrolysis condition. This trend is well reproduced by the model.

Ciezki and Adomeit (1993) have experimentally investigated specific aspects of auto-ignition of n-heptane in a high pressure shock tube at pressures ranging from 3.2 bar to 42 bar, but at rather lower temperatures ranging from 660 K - 1350 K for various mixture compositions. The ignition delay times observed together with numerically predicted are presented in Figures 4 to 6.
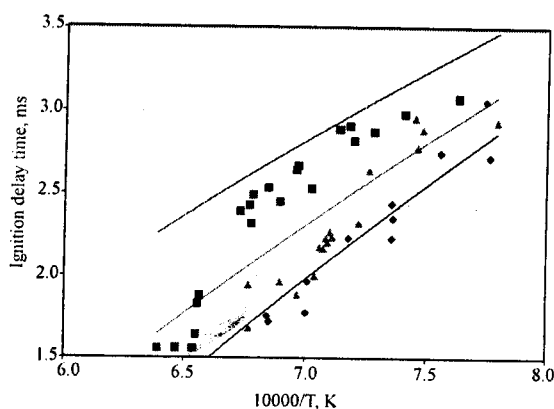
Figure 3. Ignition Delay Times of N-Heptane/O2/Ar Behind The Reflected Shock Wave. Diamond Symbols Indicate Equivalence Ratio = 0.5; Triangle, Equivalence Ratio = 1.0; Square, Equivalence Ratio = 2.0
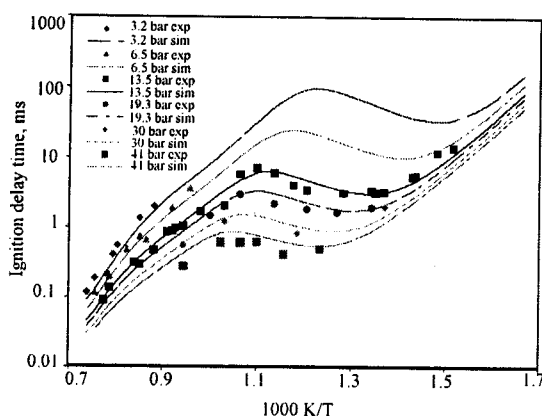
occurs between 950 K and 750 K and possesses a negative temperature coefficient. The magnitude of each NTC region at various pressures is accurately reproduced by the reaction mechanism. Furthermore, the shift of the NTC region towards higher temperatures with increasing pressure is also correctly reproduced. Linear lines can express the temperature dependence of the ignition delay time in the low-temperature region.

The experimental fact that the influence of pressure on the ignition delay is most pronounced in the NTC region is well reproduced by the model. In the low-temperature region pressure has the smallest influence on the ignition delay times. In the high-temperature region pressure has a varying degree of influence on the ignition delay times and the dependence becomes smaller with increasing temperature.
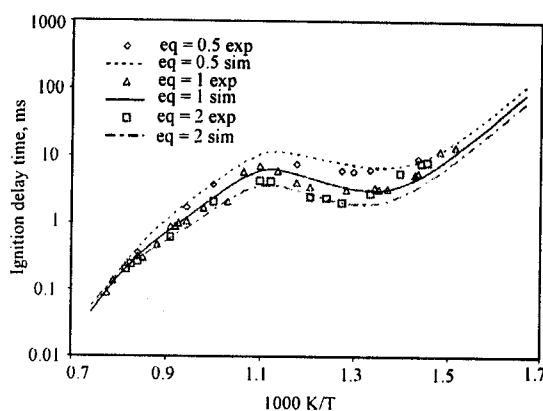

Figure 4. Ignition Delay Times of Stoichiometric N-Heptane/Air Behind The Reflected Shock Wave. Symbols Indicate The Experimental Results; Lines, Calculations

Figure 5. Ignition Delay Times of N-Heptane With Various Equivalence Ratios at 13.5 bar

In Figure 4 the ignition delay times of stoichiometic n-heptane/air mixtures is plotted logarithmically versus the inverse of the initial temperature behind the reflected shock wave at various initial pressures. In general, the calculations show excellent agreement with the experimental measurements. The decrease in the corresponding global activation energies with increasing pressure is well reproduced by the model within the investigated temperature range.

A somewhat linear temperature dependence of the ignition delay time in the Arrhenius plot is reproduced by the kinetic model in the high-temperature region. The S-shaped curves with maximum and minimum values are observed experimentally and computationally in the intermediate temperature region. At a pressure of 13.5 bar, for example, this non-linear temperature dependence of the ignition delay time

The effect of the composition of n-heptane/air mixture on the ignition delay time at 13.5 bar and 41 bar is plotted in Figures 5 and 6, respectively. The model can reproduce very well the ignition delay times for various equivalence ratios at 13.5 bar, but it shows a lower overall reactivity than the experiments at 41 bar. As can be seen in Fig. 5, at the constant initial pressure 13.5 bar and up to 1250 K the fuel-rich mixtures autoignite more easily than the lean-fuel mixtures. Above 1250 K, the contrary trend occurs: The fuel-lean mixtures burn faster than the fuel-rich mixtures, as shown in Figure 3. At the constant initial pressure 41 bar the temperature point at which the contrary trend occurs is shifted towards a higher temperature, as seen in Figure 6. The dependence of the ignition delay time on the equivalence ratio in the high-temperature region is small, but increases towards lower temperatures. In the transition region the dependence of the ignition delay time on the equivalence ratio reaches its maximum.
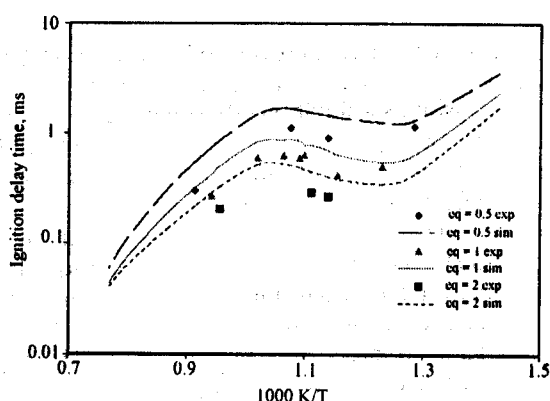
Figure 6. Ignition Delay Times of N-Heptane With Various Equivalence Ratios at 41 bar

Figure 7. Sensitivity Coefficients of A Stoichiometric N-Heptane/Air Mixture in A Shock Tube at A Pressure of 13.5 bar and An Initial Temperature of 600 K

A sensitivity analysis is used to identify rate-limiting reaction steps. This analysis will be performed in detail on each reaction in the mechanisms. In view of its greater impact on engine knock chemistry, only sensitivity analysis for shock-tube experimental results of Ciezki and Adomeit (1993) covering low-temperature kinetics will be discussed.

Numerical calculations for sensitivity analysis were carried out by changing the rate coefficient of a particular reaction and calculating the OH concentration. The difference between the OH concentration before and after changing the rate coefficient was then calculated. This result was compared to the largest difference obtained in the system. This is called sensitivity coefficient. A sensitivity coefficient might be positive or negative. A positive sensitivity coefficient indicates a higher OH concentration and an increased overall reaction rate, and a negative sensitivity coefficient indicates a lower OH concentration and a decreased overall reaction rate of the system. Sensitivity coefficients in a system are drawn in the form of a bar diagram. Only major oxidation pathways responsible for the fuel oxidation are shown. Figures 7 to 9 show this type of diagram. Emphasis was placed on determining the differences between reaction pathways at low, intermediate and high temperatures.

Figure 7 shows sensitivity coefficients of a stoichiometric n-heptane/air mixture in a shock tube at a pressure of 13.5 bar and an initial temperature of 600 K. From this figure, we observe that at low temperatures the ignition of normal alkane is governed by fuel-specific processes leading to very complex reaction systems, if the numerous isomeric structures are taken into account. It is clear that the overall rate of fuel oxidation is directly controlled by the fuel so that the ignition process of fuel-rich mixtures is faster than that of fuel-lean mixtures.
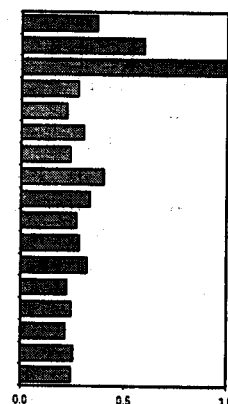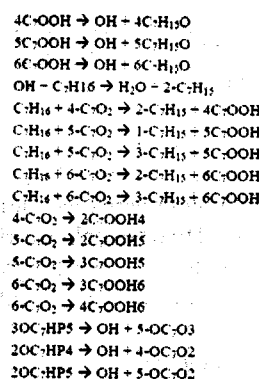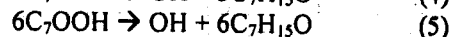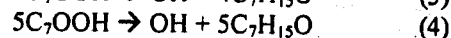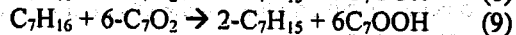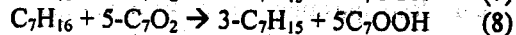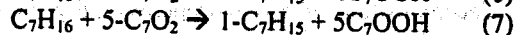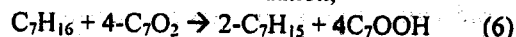
The type of reaction possessing the most effective (highest positive sensitivity) in promoting the overall rate of the fuel oxidation is homolytic O-O scission of hydroperoxydes to form alkoxy radicals and OH radicals,

$$4C_7OOH \rightarrow OH + 4C_7H_{15}O \qquad (3)$$
$$5C_7OOH \rightarrow OH + 5C_7H_{15}O \qquad (4)$$
$$6C_7OOH \rightarrow OH + 6C_7H_{15}O \qquad (5)$$
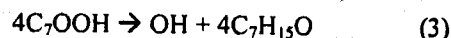
This type of reaction is chain branching because it produces two radicals from a stable molecule. Because of the high activation energy (170 kJ/mol), this reaction occurs quite slowly at 600 K. As the fuel oxidation proceeds, heat released is used to raise the temperature of the reacting system so that these stable hydroperoxyde molecules decompose more easily. This dynamic behaviour ensures a greater reactivity of the system and is responsible for cool-flame ignitions at low temperatures.
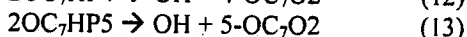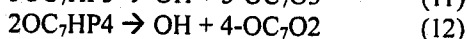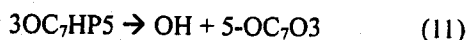
Alkyl radicals produced through initiation steps in the fuel oxidation undergo addition to molecular oxygen, leading to the formation of alkylperoxy radicals at low temperatures. We observe a low sensitivity to this reaction. However, the subsequent reaction involving alkylperoxy radicals, i.e. external H-atom abstraction from fuel to yield hydroperoxydes, possesses a positive high sensitivity coefficient. Thus, it promotes the overall rate of the fuel oxidation,

$$C_7H_{16} + 4-C_7O_2 \rightarrow 2-C_7H_{15} + 4C_7OOH \qquad (6)$$
$$C_7H_{16} + 5-C_7O_2 \rightarrow 1-C_7H_{15} + 5C_7OOH \qquad (7)$$
$$C_7H_{16} + 5-C_7O_2 \rightarrow 3-C_7H_{15} + 5C_7OOH \qquad (8)$$
$$C_7H_{16} + 6-C_7O_2 \rightarrow 2-C_7H_{15} + 6C_7OOH \qquad (9)$$
$$C_7H_{16} + 6-C_7O_2 \rightarrow 3-C_7H_{15} + 6C_7OOH \qquad (10)$$
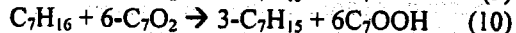
This high positive sensitivity coefficient is easily understood as the subsequent reaction, i.e. decomposition of hydroperoxyde molecules, is a chain branching process as explained above.
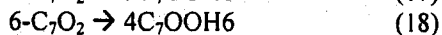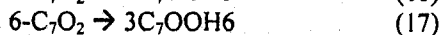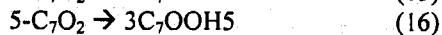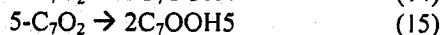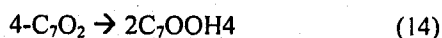
H-atom abstraction from fuel by hydroxyl radicals has also a high positive sensitivity coefficient because the hydroxyl radical is the most reactive radical and possesses a high concentration during ignition delays.

Another chain branching, i.e. decomposition of a ketohydroperoxyde molecule leading to the formation of two radicals, a carbonyl radical and a hydroxyl radical, is the next greatest in promoting the overall rate of the fuel oxidation at low temperatures,

$$3OC_7HP5 \rightarrow OH + 5\text{-}OC_7O3 \qquad (11)$$
$$2OC_7HP4 \rightarrow OH + 4\text{-}OC_7O2 \qquad (12)$$
$$2OC_7HP5 \rightarrow OH + 5\text{-}OC_7O2 \qquad (13)$$

In the symbol of ketohydroperoxyde molecules above, $3OC_7HP5$ for instance, 3 refers to the site at which the keto group is attached and 5 refers to the site at which the hydroperoxy group is attached. In the symbol of carbonyl radicals, 5-OC_7O3 for example, 3 refers to the site at which the keto group is attached and 5 refers to the site at which the oxo group is attached. Similar to decomposition of hydroperoxyde molecules, this type of reaction has a high activation energy that is difficult to overcome. However, as the fuel oxidation proceeds, heat released is used to raise the temperature of the reacting system so that these ketohydroperoxyde molecules decompose more easily.
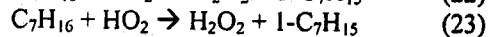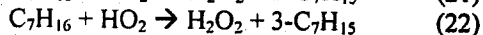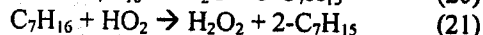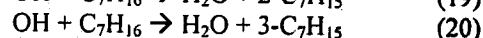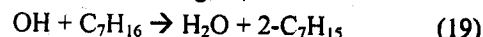
Internal H-atom abstraction of alkylperoxy radicals also shows a positive sensitivity coefficient. Thus, its influence on the reactivity of the system is positively large,

$$4\text{-}C_7O_2 \rightarrow 2C_7OOH4 \qquad (14)$$
$$5\text{-}C_7O_2 \rightarrow 2C_7OOH5 \qquad (15)$$
$$5\text{-}C_7O_2 \rightarrow 3C_7OOH5 \qquad (16)$$
$$6\text{-}C_7O_2 \rightarrow 3C_7OOH6 \qquad (17)$$
$$6\text{-}C_7O_2 \rightarrow 4C_7OOH6 \qquad (18)$$

This type of reaction competes with external H-atom abstraction from fuel via alkylperoxy radical attack described above, produces hydroperoxy alkyl radicals, which in turn undergo second addition to molecular oxygen to yield peroxy hydroperoxy alkyl radicals. After isomerization of peroxy hydroperoxy alkyl radicals, the successive reactions, i.e. decomposition of a dihydroperoxy alkyl radical and decomposition of a ketohydroperoxyde molecule, occur and lead to the production of two reactive hydroxyl radicals. These types of reactions lead to an increased reactivity of the fuel oxidation.
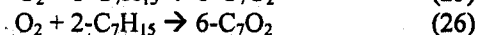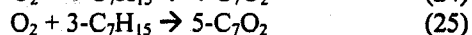
Sensitivity analysis at the onset (750 K), within (800 K) and at the end (900 K) of the NTC region of a stoichiometric n-heptane/air mixture in a shock tube at a pressure of 13.5 bar is exhibited in Fig. 8. From this figure it is clear that the most positive sensitivity coefficient in the NTC region is shown by the chain branching reaction, H_2O_2 +M(1) $\rightarrow$ OH +OH +M(1). Thus, it has the greatest effect in controlling the reactivity of the fuel combustion. The fuel-specific reactions still dominate during the ignition process. H-atom abstraction from fuel via alkylperoxy radical attack, which is a rate-limiting reaction step at 600 K, is not preferred any more in the NTC region. Therefore, the subsequent reaction, i.e. decomposition of hydroperoxy molecules, is not a main chain branching process. H atoms in the fuel are mainly abstracted by the OH radicals at the onset of the NTC region and by the HO_2 radicals at the end of the NTC region,

$$OH + C_7H_{16} \rightarrow H_2O + 2\text{-}C_7H_{15} \qquad (19)$$
$$OH + C_7H_{16} \rightarrow H_2O + 3\text{-}C_7H_{15} \qquad (20)$$
$$C_7H_{16} + HO_2 \rightarrow H_2O_2 + 2\text{-}C_7H_{15} \qquad (21)$$
$$C_7H_{16} + HO_2 \rightarrow H_2O_2 + 3\text{-}C_7H_{15} \qquad (22)$$
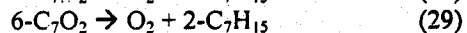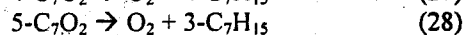$$C_7H_{16} + HO_2 \rightarrow H_2O_2 + 1\text{-}C_7H_{15} \qquad (23)$$

This phenomenon can be described as follows: Although it is not a main pathway, H-atom abstraction from fuel via alkylperoxy radical attack still has a significant effect on the overall rate at 750 K. Therefore, in addition to the decomposition of H_2O_2, decomposition of hydroperoxyde and ketohydroperoxy molecules still has a significant contribution to the OH radical concentration. If temperature increases, alkylperoxy radicals decompose back to alkyl radicals. This leads to an inverse temperature dependency of the reaction or a degenerate chain branching where the OH radical concentration decreases. Due to its high concentration at 900 K, the rather unreactive HO_2 radical, produced directly from the bimolecular initiation step, takes over the role in abstracting H atoms from the fuel so that the fuel oxidation proceeds more slowly than that at 750 K.

Alkyl radicals can undergo addition to molecular oxygen to produce alkylperoxy radicals in the NTC region. This type of reaction has a high positive sensitivity coefficient,

$$O_2 + 4\text{-}C_7H_{15} \rightarrow 4\text{-}C_7O_2 \qquad (24)$$
$$O_2 + 3\text{-}C_7H_{15} \rightarrow 5\text{-}C_7O_2 \qquad (25)$$
$$O_2 + 2\text{-}C_7H_{15} \rightarrow 6\text{-}C_7O_2 \qquad (26)$$

However, since the inverse reaction, i.e. decomposition of hydroperoxy alkyl radicals to alkyl radicals,

$$4\text{-}C_7O_2 \rightarrow O_2 + 4\text{-}C_7H_{15} \qquad (27)$$
$$5\text{-}C_7O_2 \rightarrow O_2 + 3\text{-}C_7H_{15} \qquad (28)$$
$$6\text{-}C_7O_2 \rightarrow O_2 + 2\text{-}C_7H_{15} \qquad (29)$$

possesses a negative sensitivity coefficient with the nearly same order of magnitude to the forward reaction, this type of reaction gives little effect on the reactivity of the fuel oxidation.

The next high positive sensitivity coefficient is exhibited by internal H-atom abstraction of alkylperoxy radicals to yield hydroperoxy alkyl radicals. The fate of these hydroperoxy alkyl radicals has been described above.
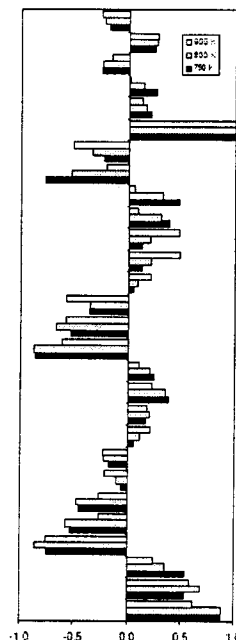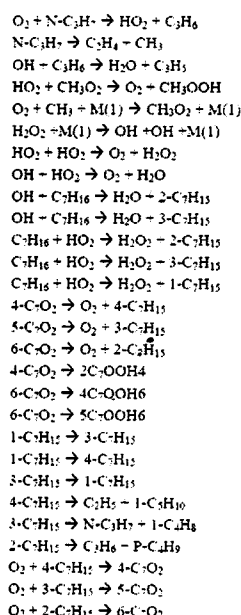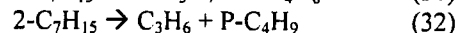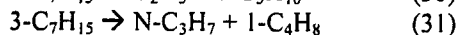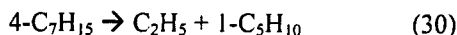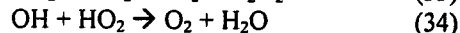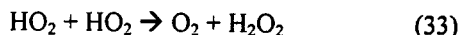

Figure 8. Sensitivity Coefficients of A Stoichiometric N-Heptane/Air Mixture in A Shock Tube at A Pressure of 13.5 bar and Initial Temperatures of 750, 800 and 900 K.

Decomposition of alkyl radicals through scission to produce small alkyl radicals and olefins shows a high negative sensitivity coefficient and is a competitor to addition of alkyl radicals to molecular oxygen in consuming alkyl radicals,

$$4\text{-}C_7H_{15} \rightarrow C_2H_5 + 1\text{-}C_5H_{10} \qquad (30)$$
$$3\text{-}C_7H_{15} \rightarrow N\text{-}C_3H_7 + 1\text{-}C_4H_8 \qquad (31)$$
$$2\text{-}C_7H_{15} \rightarrow C_3H_6 + P\text{-}C_4H_9 \qquad (32)$$

This type of reaction has a large inhibiting effect on the overall rate of the fuel oxidation and plays an important role in producing NTC behavior as its inhibiting effect increases with increasing temperature, while the promoting effect addition of alkyl radicals to molecular oxygen decreases with increasing temperature.

The next-highest negative sensitivity coefficients are shown by the reactions consuming two alkyl radicals,

$$HO_2 + HO_2 \rightarrow O_2 + H_2O_2 \qquad (33)$$
$$OH + HO_2 \rightarrow O_2 + H_2O \qquad (34)$$

These reactions have inhibiting effects on the overall rate of the reaction. The inhibiting effect of the self-reaction of hydroperoxyl radicals is pronounced at 900 K, while that of the reaction between hydroxyl and hydroperoxyl radicals is pronounced at 750 K. This behavior happens because the HO_2 concentration becomes dominant and the OH concentration decreases with increasing temperature.
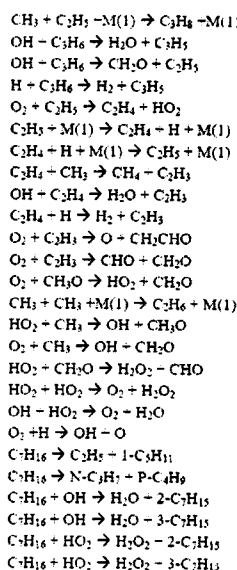

Figure 9. Sensitivity Coefficients of A Stoichiometric N-Heptane/Air Mixture in A Shock Tube at A Pressure of 13.5 bar and An Initial Temperature of 1200 K.

Figure 9 depicts sensitivity coefficients of a stoichiometric n-heptane/air mixture in a shock tube at a pressure of 13.5 bar and an initial temperature of 1200 K. This figure is totally different to that at 600 K (Figure 7). The ignition is mainly governed by chain branching processes, which are rather fuel-unspecific. The most positive sensitivity coefficient is shown by the chain branching reaction

$$O_2 + H \rightarrow OH + O \qquad (35)$$

Thus, this reaction controls the overall rate of fuel oxidation. The next highest positive sensitivity coefficients are

$$HO_2 + CH_3 \rightarrow OH + CH_3O \qquad (36)$$
and
$$OH + C_2H_4 \rightarrow H_2O + C_2H_3 \qquad (37)$$
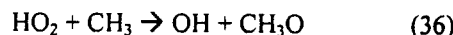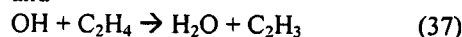
These reactions are not fuel-consuming reactions. The relative high importance of reactions involving HO_2, CH_3 and C_2H_5 radical in controlling the overall rate of the reaction is due to the fact that the concentrations of these rather unreactive radicals are relatively high at higher temperatures.

5. Conclusions

A mechanism generator code to automatically generate reaction mechanisms for the oxidation and combustion of large hydrocarbons has been successfully provided in this work. This code can be used to simulate ignition delay times at a wide range of temperatures.

Experimentally derived and numerically predicted ignition delays of n-heptane/air mixtures in high-pressure shock tubes in a wide range of temperatures, pressures and equivalence ratios agree very well. The negative temperature coefficient region is shifted towards lower temperatures as pressure is increased. The overall reactivity of the mixtures increases with increasing pressure. The fuel-rich mixtures burn more easily than the fuel-lean mixtures in the low- and intermediate-temperature regimes. In the high temperature regime a contrary trend occurs. At a constant initial pressure of 13.5 bar and above 1250 K the fuel-lean mixtures autoignite more easily than the fuel-rich mixtures.

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