

# Advances and challenges in the chemical kinetics of combustion

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## Abstract

Chemical kinetic modeling has become a more and more important tool in the analysis of combustion systems, and considerable progress has been made during recent decades. Notable successes have been achieved in the understanding of complex phenomena in practical combustion devices, but physical and chemical regimes of interest to combustion are so broad that substantial efforts are needed to provide reaction mechanisms with sufficient generality to be reliable predictive tools. These efforts must be amplified, because future global energy and environmental issues have imposed changes in the operating conditions of practical combustion devices. Research is now oriented on saving energy, in parallel with enhanced protection of our environment. To achieve these goals, the development of combustion technologies requires a more detailed understanding of the role of chemistry in practical devices.

Since it is expected that fossil fuels will remain the major energy source within the next two or three decades, the first step is to improve existing combustion systems in efficiency, in order to increase their productivity and their environment acceptability. In the same time, a diversification of the primary energy sources is necessary, by extending the use of other sources such as non-fossil fuels. The search for alternative primary energy sources is accompanied by the search of alternative energy conversion processes, and among them, innovative combustion technologies are expected to help, in the short to medium term, to fulfill requirements for CO<sub>2</sub> reduction and protection of the environment. Cleaner combustion technologies and renewable power-generation techniques, as well as high-performance propulsion systems are emerging, and the knowledge accumulated in the kinetic modeling of conventional fuels and combustion systems can be used and extended, as an interpretative and predictive tool for their design.

## Introduction

Facing energy demand which will result from the growth of population on the globe and enhanced living standards for an increasing number of inhabitants, with a minimum impact on the environment, represents a formidable challenge. In this perspective, some future requirements to our combustion community have been presented and discussed in recent plenary lectures at International Combustion Symposia [1,2].

Until now, fossil fuels have contributed to over 90% of energy expenses, and among them, oil played the dominant role. It is not surprising that chemists have tried, since more than one century, to elucidate the mechanisms of hydrocarbon combustion. These efforts were not only motivated by academic interest, but also, in the beginning of the last century, by the necessity of a better understanding of the combustion processes in internal combustion engines for an efficient control. More recently, the mechanisms of formation of combustion-generated pollutants have concentrated considerable attention.

It is expected that the use of oil and gas will not decline until the next two or three decades, and consequently current energy conversion technologies must be improved for a reduction of fuel consumption, and a protection of our environment. At the same time, it is necessary to make an optimal use of mixtures of carbonaceous fuels with alternative C-neutral and C-free

fuels, and to develop innovative combustion technologies capable of reducing CO<sub>2</sub> and pollutant emissions.

After a short review of recent achievements in the chemical kinetic modeling of hydrocarbon combustion, this presentation will examine how kineticists can participate in these new developments, in order to help our society in maintaining and improving our living standards.

## Detailed combustion mechanisms of hydrocarbons

At the last International Combustion Symposia, review papers have detailed recent progress and challenges in the chemical kinetic modeling of flames [3] and of hydrocarbon ignition in practical systems [4], as well as in chemical theory [5]. It is clear from these reviews that chemical kinetics can be used as a tool for improving present combustion systems and building new technologies of combustion.

Liquid practical fuels are complex mixtures of hydrocarbons belonging to the following families :

- linear or branched alkanes (paraffins)
- cycloalkanes with one or two rings (naphtenes)
- alkenes
- aromatics with one or several rings

To this list one must add oxygenates which are introduced as additives in gasoline and diesel fuel.

The challenge of modeling the combustion of practical fuels will be examined in the next paragraph. Nevertheless the preliminary task is to model the oxidation and combustion of individual hydrocarbons

which are initially present in the fuel, and of other molecules not present in the fuel but formed as intermediates (dienes, alkynes, aldehydes). This is why many kinetic studies of the oxidation and ignition of these hydrocarbons have been performed, since the elaboration by Semenov of the branched chain reactions theory. The development of numerical modeling allowed the elaboration of comprehensive detailed mechanisms which have been constructed in a hierarchical manner, starting with hydrogen-oxygen-carbon monoxide chemistry, followed by elementary reactions of C<sub>1</sub>, C<sub>2</sub> hydrocarbons, and so on.

### 1. Alkanes

Alkanes are the main components of practical fuels, this is why a good prediction of their combustion properties is crucial. A very large data base (issued from experimental and modeling studies) has been accumulated on the combustion of lower alkanes, methane and ethane, (the major components of natural gas), and chemical mechanisms have been validated even under extreme pressures of several hundreds bars [6,7].

Concerning higher alkanes, n-hexadecane, the reference fuel for the cetane index, is the largest one for which a detailed ignition mechanisms has been developed [8], but an experimental study of its oxidation has only being carried out recently [9], allowing the validation of new mechanisms [9,10].

Among all combustion mechanisms of hydrocarbons, those for alkanes are the more reliable. However even for the simpler and most studied one, methane, it has been shown [11] that because of present uncertainties in both thermodynamic and kinetic parameters of its combustion mechanism, the precision on computed flame velocities of lean to rich mixtures lies in the 10-20% range. Of course, the situation is worse for higher hydrocarbons, in spite of considerable progress in the modeling of C<sub>7</sub> and C<sub>8</sub> hydrocarbons in a wide range of temperatures and pressures using semi-detailed [12,13] or detailed [14,15,16] mechanisms. In fact an accurate prediction of ignition characteristics of branched alkanes, which is of practical importance for the prediction of fuel properties in internal combustion engines, needs further detailed experimental and theoretical studies [16].

### 2. Alkenes and alkynes

Alkenes are present in significant proportions (limited to 18% by volume) in gasoline, but they are only very minor components of kerosene and diesel fuel. However, they are the major primary intermediates in the combustion sequence of hydrocarbons, and for this reason, their oxidation mechanism is a sub-set of the combustion mechanism of alkanes. Whereas lower alkenes, in particular ethene, have been the subject of most of the studies performed in the past, recent research efforts are now concentrated on the reactions of higher alkenes, because they play an important role in the formation of the end products of long linear alkanes [9,10,17].

Another reason to increase our knowledge of the combustion mechanisms of alkenes and alkynes, is their important role in the formation of pollutants such as PAH and soot.

### 3. Cycloalkanes

Cycloalkanes (naphtenes) constitute an important fraction of practical liquid fuels, mainly diesel fuel and kerosene. Cyclohexane has been shown to produce significant amounts of air toxics, namely 1,3-butadiene and benzene within a gasoline single cylinder engine [18]. In addition, cycloalkanes are suspected to increase PAH and soot emissions in diesel engines. In this respect, the sooting tendency of cycloalkanes and particularly decaline (which has two rings) in a laminar diffusion flame, was found to be higher than that of linear and branched alkanes, but lower than that of aromatics [19].

Most chemical kinetics studies have been limited to cyclohexane and methyl-cyclohexane. The highest substituted cycloalkane which has been the subject of a detailed modeling study is n-propylcyclohexane [20]. Up to now, no detailed mechanism has been proposed for the combustion of bicycloalkanes, which are abundant in diesel fuel.

### 4. Aromatics

Because of their high resistance to knock, aromatic hydrocarbons constitute a large fraction of premium gasoline, although their concentration in European gasoline has been limited, since year 2000, to 42% by volume and is planned to be limited to 35% by year 2005. Their concentration in jet fuels (jet A1) is limited to 25%. In diesel fuel, their amount is lower than in gasoline, but they include a significant proportion of poly-aromatics, which are now limited to 11% by mass in European diesel fuels.

Most kinetic studies on the combustion of aromatics have been devoted to benzene and toluene, and more studies are necessary on C<sub>7+</sub> substituted mono-aromatics in a wider temperature range. Concerning polycyclic-aromatics, too many uncertainties remain on the important reaction paths and rate expressions of their combustion, to build comprehensive mechanisms. But because of the key role of aromatic hydrocarbons in the process of auto-ignition and in the formation of soot and other pollutants, a better description of their combustion mechanism, over the wide range of temperatures and pressures existing in automotive and aeronautic engines, is of primary importance. This task is necessary to obtain valuable interpretative and predictive tools.

### 5. Oxygenated hydrocarbons

Some oxygenated compounds are toxic by-products of hydrocarbon oxidation and combustion : among them one should cite aldehydes, which are important chemical intermediates. Other oxygenated compounds are currently used as fuel additives (alcohols, ethers) and are considered as potential alternative fuels or fuel-additives.

Concerning oxygenated compounds which are formed as intermediates in the combustion of hydrocarbons, their nature depends on the temperature

regime where oxidation takes place. The more complex situation is at temperature lower than about 850K, where the reactions of alkyl-peroxy radicals lead to high initial yields of oxygenates such as aldehydes, ketones, alcohols and O-heterocyclic compounds.

Among oxygenated molecules used as fuels or additives, only some of them (methanol, ethanol, methyl- and ethyl- tertio butyl ethers, and dimethyl ether) have been widely studied for the validation of detailed comprehensive oxidation mechanisms, but the variety of oxygenated compounds in biofuels will enlarge the field of investigations.

### **Kinetic modeling of the combustion of gaseous and liquid practical fuels**

Such a modeling represents a real challenge, not only because liquid practical fuels are complex mixtures of several hundreds of hydrocarbons, but also because the exact composition of the more complex of them (kerosenes and especially diesel fuels) is difficult, or even impossible to determine in details. For liquid commercial fuels, the most precise information is generally the hydrocarbon classes distribution. For this reason, and to avoid the enormous task of describing individually the combustion mechanism of every compounds, simpler hydrocarbon blends ("surrogate fuels") are used as models to mimic the real fuel. In a recent paper [21], Dagaut has presented examples of achievements in the modeling of the oxidation of commercial fuels like natural gas, jet A1 aviation fuel, and diesel fuel.

#### **1. Natural gas**

Natural gas is a much simpler mixture than liquid practical fuels : methane is the major constituent (from about 80% to more than 98% by volume) and a few other hydrocarbons are found, mainly ethane and propane. It is well known [22] that ignition characteristics of methane are considerably modified by the addition of a few percents of ethane or propane. The variability of the composition of natural gas with its source in the world [22] may cause problems in diesel engine operation, therefore kinetic models capable of predicting, with sufficient accuracy, the modifications of ignition characteristics of natural gas with its composition, will be helpful.

Experimental and modeling studies of the oxidation of natural gas in a jet-stirred reactor [23] and of its ignition in a constant-volume bomb [24] showed that kinetic mechanisms for the oxidation and ignition of methane-ethane-propane mixtures can be used to reproduce the characteristics of real natural gas fuels.

#### **2. Gasoline**

As mentioned above, the main constituents of premium gasoline are monoaromatic hydrocarbons, branched alkanes, and, to a lower extent, alkenes. The number of carbon atoms of most of these hydrocarbons lies between 4 and 10, and their H/C ratio is 1.7-1.9 [25]. To determine the knock resistance of gasoline, two octane number scales ("research", RON, and "motor", MON) were defined with 0 for n-heptane and 100 for

iso-octane (2,2,4-trimethyl pentane), these two alkanes being chosen as Primary Reference Fuels (PRF) because they have comparable boiling points. Consequently, many experimental and modeling studies have been performed on these hydrocarbons and their blends, for a better description of the chemical processes leading to knock in spark-ignition engines.

Knock, or autoignition of unburned "end gases" in the combustion chamber is the result of the decomposition of hydrogen peroxide accumulated during precombustion phase [4]. The length of this precombustion phase (ignition delay if ignition occurs before consumption by the flame) depends on the heat release resulting from low temperature ("cool flames") reactions [4]. There is now broad agreement that chemical mechanisms used to predict the knocking tendency of a fuel must include low temperature reactions involving  $RO_2$  radicals and their oxidation products. For this reason, semi-detailed reaction mechanisms describing the oxidation of n-heptane/isooctane mixtures in the temperature range 550-1200 K have been elaborated [26,27]. These mechanisms can predict the non-linear correlation between octane number and reactivity of the P R F mixture.

However, other standard mixtures including toluene in addition to n-heptane and isooctane, have been adopted for a better precision in the determination of octane numbers [25]. In fact it has been recognized since a long time that there are some difficulties in the use of the octane numbers : octane number in gasoline do not obey to a linear blending law [28]. In addition, the "sensitivity", which is the difference between the RON and the MON varies from one class of hydrocarbons to another, alkanes having a lower sensitivity than alkenes and aromatics [29]. These facts reflect the complexity of the chemical kinetics of hydrocarbon ignition, and show that chemical kinetic modeling of the ignition behavior of gasolines should use other surrogates than the PRF mixture. An interesting alternative is reported by Edwards and Maurice [30], in a paper on the use of surrogate mixtures to represent aviation fuel : a gasoline surrogate can be obtained by addition of an aromatic and an alkene to the PRF mixture.

#### **3. Kerosene aviation fuel**

Kerosene for civil aircraft engines, Jet A-1 (or Jet A in the US) has the same composition as JP-8 (used by USAF), which has special additives. Its general characteristics [25] are the followings :

- the carbon number of its constituents lies between 9 and 13, with H/C between 1.9 and 2.1
- the percentage by volume of each chemical family is 50-65% for alkanes, 20-30% for cycloalkanes, and 10-20% for aromatics.

Other sources, mentioned in [30], give a similar composition, with an approximated global formula being  $C_{11}H_{21}$ . An important characteristic is the absence of alkenes and the very low concentrations of two-ring cycloalkanes and aromatics [25].

Experiments performed in Orléans on the oxidation of a TR0 (JP-8) kerosene in a jet-stirred reactor [31,32] and on premixed laminar flames [33,34] have been used for the validation of reaction mechanisms based on representative fuels or mixtures. Guéret et al [31] used a quasi-global mechanism based on a surrogate mixture composed of n-undecane, n-propylcyclohexane, and 2,2,4-trimethyl-benzene to reproduce their results. Further experiments on TR0 kerosene were performed at pressures up to 40 atm. [32], and it was shown [35] that a detailed mechanism for the oxidation of n-decane could reproduce the experimental profiles of major chemical species, but the concentrations of aromatics were largely underpredicted.

Vovelle et al. [33] showed that a mechanism involving an aromatic (toluene) in addition to n-decane was necessary to model their low-pressure kerosene flame. Later, the 1 atm rich flame of Douté et al. [34] was modeled by Lindstedt and Maurice [36], using a surrogate model of 89 mole % n-decane and 11 mole % of various aromatics : benzene, toluene, ethylbenzene/naphthalene. Results of the computation showed that the structure of the flame was well reproduced by the detailed mechanism, and that all alkylbenzenes used to represent the aromatic fraction of kerosene, allowed a good prediction of benzene profiles in the flame. In another computational study, Patterson et al. [37] used a semi-detailed mechanism for the combustion of a mixture of 89% n-decane and 11% toluene to reproduce the jet-stirred reactor data at 10 and 40 atm [32] and the structure of the 1 atm flame [33]. Reasonable agreement was obtained between computation and experimental data from both experiments.

The interest of including a cycloalkane, as a third component in the jet-A1 surrogate, is still an open question, since the sooting tendency of this class of hydrocarbons is intermediate between those of alkanes and monoaromatics [19]. A recent modeling study by Dagaut [21] used a surrogate model of 74% n-decane, 11% n-propylcyclohexane and 15% n-propylbenzene by volume and showed good agreement between experimental and computed profiles, even for benzene, toluene and cyclopentadiene. Violi et al. [38], extending to cycloalkanes a previous semi-detailed mechanism for alkanes and simple aromatics, used a JP-8 surrogate composed of n-dodecane, isooctane, methycylhexane, benzene and toluene to reproduce the structure of the flame of Douté et al. [34]. The predictions of the model are correct, although the computed concentration of benzene is lower than the experimental one by a factor of two. Another objective, in the choice of this surrogate mixture, was to reproduce the boiling-point curve of a real JP-8 kerosene, because in several applications it is necessary to reproduce not only the chemical properties but also some physical properties of practical fuels [30].

#### 4 Diesel fuel

Diesel fuel is composed of higher hydrocarbons ( $C_{10}$  to  $C_{20}$ ) than kerosene, with 50-65% alkanes, 20-30% cycloalkanes and 10-30% aromatics by volume [25].

But the complexity with diesel blends is that they include two-ring cycloalkanes (decalines), two-ring aromatics (indanes, indenenes, tetralines and naphthalenes), and some three-ring aromatics (fluorenes, anthracenes, phenantrenes). Although these multi-ring compounds are not the major constituents of diesel fuel, some of them (polyaromatics) have an important impact on soot formation. An example of detailed analysis of a diesel fuel is given in Fig. 1.

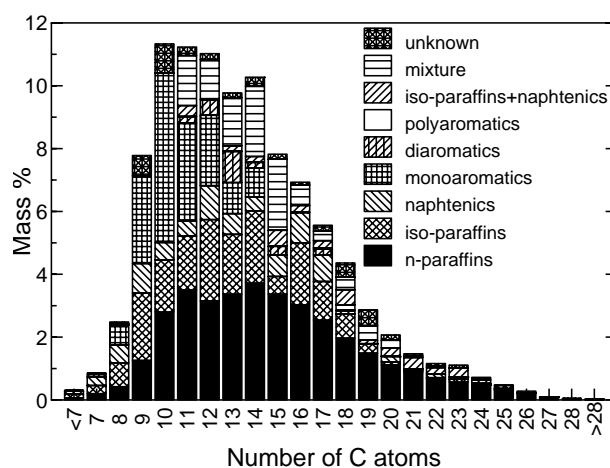


Fig. 1. Example of composition of a commercial diesel fuel, from Dagaut [21].

The quality of combustion in diesel engines is partially dependent on the ignition capability of the fuel by compression, given by its cetane number. The PRF chosen to scale this number are n-hexadecane ("cetane") whose CN is 100, and 2,2,4,4,6,8,8-heptamethylnonane with a CN equal to 15. The same difficulties arise with the cetane number as with the octane number in gasoline, because the two alkanes chosen as PRF are not sufficient to represent the complexity of the oxidation mechanisms of the different classes of hydrocarbons in the mixture.

Because of its more complex composition, kinetic modeling of the combustion of diesel fuel is even more difficult than that of other liquid commercial fuels. The simplest fuel used to represent diesel fuel was n-heptane [39,40], since its cetane number is 56, which is nearly equivalent to that of commercial diesel fuels. Other kinetic modeling studies with detailed chemical mechanisms have used surrogate mixtures containing an alkane and an aromatic : n-heptane and toluene [41] or n-decane and  $\alpha$ -methyl-naphthalene [42]. The reason is that the presence of an aromatic hydrocarbon ensures a better prediction of soot emission.

Dagaut [21] showed the results of a modeling study using a mixture of n-hexadecane, iso-octane, n-propylcyclohexane and n-propylbenzene, to reproduce the results of an experimental study of the oxidation of a diesel fuel in a jet-stirred reactor. A further refinement has been recently introduced by adding to this mixture

methylindene and  $\alpha$ -methylnaphtalene, and Fig. 2 shows an example of comparison between computation and experiment.

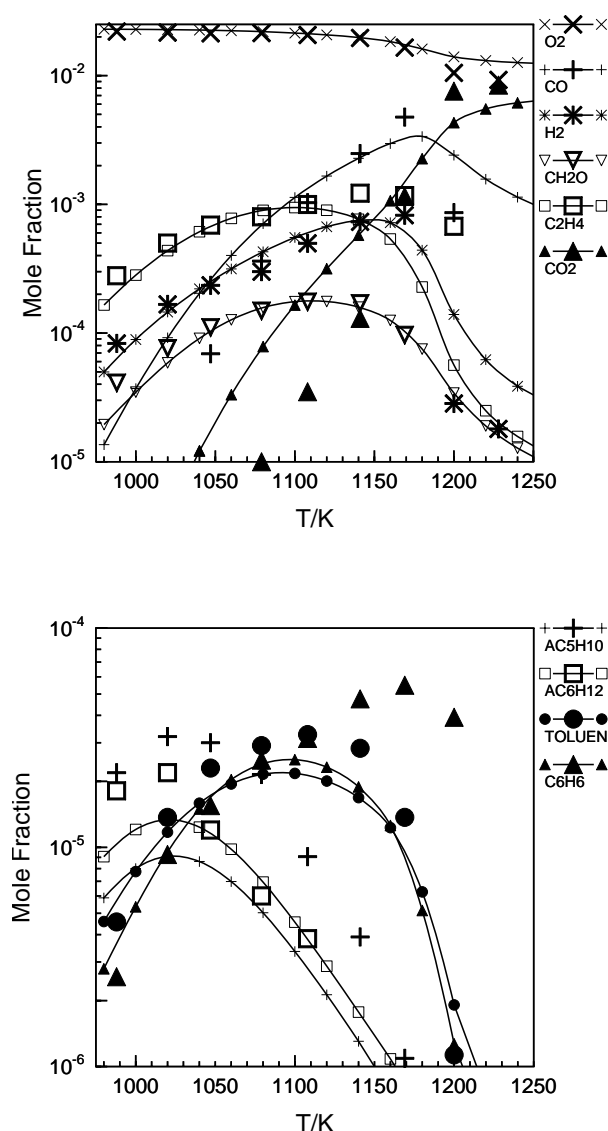


Fig. 2. The oxidation of a diesel fuel in a JSR at 1 atm (0.05% of fuel,  $\Phi=0.5$ , 1s). Comparison between experimental data (large symbols) and modeling results (lines) and small symbols.

### Kinetic modeling of conventional combustion systems

Performances of current combustion systems (internal combustion engines, gas turbines, burners) have been improved considerably in the last decades. However the increasing severity of regulation rules concerning air toxics, and the necessity of further reductions in fuel consumption, require continuous efforts for additional technological improvements. This can be obtained by a better understanding of the physical and chemical mechanisms governing the combustion processes in different configurations. Concerning internal combustion engines, more research

is needed for a better description of the chemical reactions leading to ignition, flame propagation in the cylinder, and pollutant formation.

#### 1. Mechanisms of ignition in engines

Auto-ignition is the normal ignition mode in diesel engines, but can damage gasoline engines when leading to severe knock. As mentioned above, the more advanced chemical mechanisms of ignition of hydrocarbons concern normal alkanes, and further experimental and theoretical studies are necessary on the ignition mechanisms of branched alkanes, alkenes cycloalkanes, aromatics, and mixtures representative of real fuels for an accurate prediction of ignition characteristics of gasoline and diesel fuel in engine conditions.

Spark ignition involves several phases : breakdown, plasma phase and initial combustion phase. Since the development of the flame kernel has a non negligible influence on the combustion which follows, the description of this early stage, occurring after initiation by the electrical spark, is necessary. It has been shown recently [43] that the chemical mechanism for the early development of the flame kernel must involve not only neutral species but also ions, which increases considerably the complexity of chemistry.

#### 2. Formation and destruction of pollutants

The impact of nitrogen oxides on air quality through smog, acid rain formation, and ozone depletion, has been known for several years. Several NO<sub>x</sub> abatement techniques in combustion have been proposed, among them *reburning*, a low-cost and effective one for stationary combustion systems [44,45]. In spite of the considerable amount of kinetic studies on the subject, the description of NO<sub>x</sub> formation and reduction through reburning in flames is complex, because of the numerous reactions between radicals issued from the combustion, and nitrogen compounds. This is why these reactions remain the topic of many experimental and theoretical kinetic studies.

Another major challenge in the kinetic modeling of combustion is the prediction, in practical combustion devices, of another class of toxic air contaminants : soot particles and Poly Aromatic Hydrocarbons (PAH). In fact, despite of general agreement on the main features of the processes involved, many important details of PAH and soot formation are still poorly understood. Recent reviews [46,47,48] have discussed the main aspects of chemical reactions and physical processes responsible for this formation, and summarized the present understanding and points of controversy. It appears that some steps of the chemical mechanism, as for example the formation of the first aromatic ring, depend on temperature and pressure, and also on the nature of the initial hydrocarbon. To face the ever increasing demand for more refined predictions for a better control of soot and PAH emissions, and because of the large size of reaction mechanisms, continuous effort is needed in the construction of thermodynamic and kinetic data bases.



poor ignition characteristics, corrosiveness, instability [64,65]. Further treatments will be necessary to improve these properties [64].

In any case, a variety of liquid fuels issued from biomass will be commercialized in the future, at a larger scale than at present. The composition of such biofuels is more or less complex, but their characteristic is to be oxygenated, which is not the case of petroleum derived fuels. Numerous kinetic studies will be necessary for the description of their combustion chemistry.

Another possibility to obtain liquid fuels from biomass is the gas to liquid (GTL) conversion of the syngas obtained by thermal gasification of biomass. This syngas can be fed into the classical Fisher-Tropsch process which involves the F-T reactor giving heavy paraffins, and hydrocracking, isomerization and fractionation to produce the final fuel. The fuels obtained by the F-T process are high quality gasoline or diesel fuel. Their composition is simpler than that of oil esters and pyrolysis oils, since they contain almost exclusively alkanes [25]. Thus the kinetic modeling of their combustion presents no supplementary difficulties.

### **Kinetic modeling of emerging new combustion technologies**

Improving the efficiency of combustion systems to reduce carbon dioxide emissions in conventional combustion systems has generally for consequence an increase in NO<sub>x</sub> emissions. To overcome this contradiction, it was necessary to introduce innovative technologies allowing at the same time a higher efficiency of combustion and pollution minimization.

Several emerging combustion concepts are based on a reduction of the temperature to minimize the formation of thermal NO. This is obtained through the dilution of the combustible mixture by air or by exhaust gases. Dilution by air, i.e. burning at lean flammability limit, is used in Lean Premixed Prevaporized (LPP) combustion chambers for gas turbines, while dilution by hot combustion gases is used in flameless (or mild) combustion in furnaces. Dilution by air or by Exhaust Gas Recycling (EGR) is used to control Homogeneous Charge Compression Ignition (HCCI), which is an alternative to conventional internal combustion engines. Since these new combustion devices operate under different conditions from those of conventional combustion systems, new modeling efforts have been made to describe the chemistry of combustion in such environments, i.e. with high excess air or in the presence of exhaust gases.

#### **1. Lean premixed combustion**

A critical requirement of lean premixed combustion is to avoid self-ignition of the flammable mixture, thus an accurate prediction of the auto-ignition limits of the fuels used in LPP chambers is the condition for the development of this process. For this reason, further experimental and modeling studies on the auto-ignition of practical fuels for turbines must be carried out.

#### **2. Flameless oxidation**

"Flameless oxidation" [66], also called "diluted", "mild", or "high temperature air" combustion, has been acknowledged as one of the most promising technology for energy saving and reduced levels of pollutant emissions in stationary combustion systems. This mode of combustion can be obtained by intense internal flue gas recirculation, to heat and dilute the combustion air. This strong recirculation results in a substantial reduction of the oxygen concentration, and consequently of nitric oxide emission. Semi-industrial scale experiments have shown the advantage of this technique, but the basic chemical-physical phenomena are far from being fully understood.

Several modeling studies including detailed kinetic mechanisms have been performed on natural gas forced internal recirculation burners [67,68]. However, further experimental and numerical chemical kinetic studies in simpler configurations are necessary for a better understanding of the influence of combustion products on the oxidation process. The results obtained in a recent kinetic modeling study [69] of the influence of dilution of air or fuel by burned gas, on the mechanisms of nitric oxides formation and destruction, must be validated by an experimental study, and extended to other laboratory configurations.

#### **3. Homogeneous Charge Compression Ignition**

HCCI allows high thermal efficiency, low NO<sub>x</sub> and soot production and low fuel consumption in internal combustion engines. This mode of ignition is quite different from those in spark-ignited and in diesel engines : a premixed, very lean mixture of fuel and air is introduced into the engine chamber and compressed by the piston, and thus ignites homogeneously near TDC. Recent optical investigations [70,71] have shown that HCCI combustion is characterized by distributed reactions and not by flame propagation. The consequence is that it is controlled primarily by chemical kinetics.

Several more or less refined models described in [4] have been used to predict combustion duration and composition of the bulk gases in HCCI engines. One of the practical difficulties in this technology is to control ignition, since octane or cetane numbers are not good indicators of the ignition behavior of conventional fuels in HCCI engines. Several parameters can be varied in practice for this control : equivalence ratio of the mixture, injection time, initial temperature, compression ratio, fuel composition and EGR.

A recent computational study [72] showed that the sensitivity of the ignition time in HCCI engines to changes in operating conditions, is dependent on the type of fuel. It can be noticed that most of the modeling studies involving detailed or reduced mechanisms in HCCI engines, have been performed on natural gas or the PRF for gasoline. However, since PRF have been shown not to be sufficiently representative of commercial fuels in conventional engines, more representative mixtures should be considered for a better prediction of the influence of fuel composition on ignition in HCCI engines.

Another important point to elucidate, for a complete understanding of the effect of EGR on ignition, is the impact of NO on the combustion of hydrocarbons. In an experimental study performed in a jet-stirred reactor on this topics [73], the reactions describing qualitatively the interactions of NO and hydrocarbons at low temperature have been presented (Fig. 4). A detailed

chemical model developed by Favarelli et al. [74] on the interactions between NO and hydrocarbons, was able to reproduce quantitatively experimental results obtained in several laboratories. Such studies need to be extended to a wide variety of fuels and operating conditions.

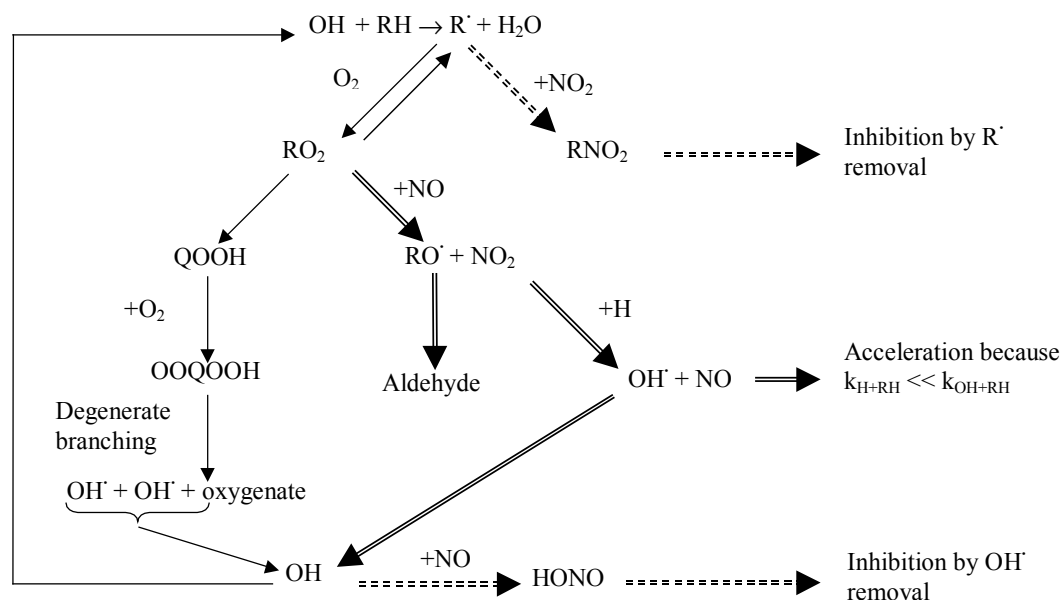


Fig. 4: Reaction diagram summarizing the interactions of NO with the low temperature oxidation chemistry of alkanes ( $T < 750\text{K}$ ), from Moréac et al. [73].

#### 4. Plasma based or plasma assisted processes

Non thermal plasmas are used in an increasing number of applications, one of them, still under evaluation, being diesel exhaust treatment for NO<sub>x</sub> removal [75,76]. In a plasma discharge, energetic electrons (few to tens of eV) are created, and by collision with molecules, reactive species such as ions, free radicals and metastable molecules, are produced. A recent paper [76] showed that during non-thermal plasma treatment of diesel exhaust, unburned hydrocarbons are mainly oxidised by O(<sup>3</sup>P) atoms, and to a lesser extent by OH radicals. But a detailed plasma chemistry model must include, in addition to radical and molecule reactions, electron-impact reactions and ion-molecule processes [76].

Another potential application of non-thermal plasmas is the stabilisation of flames : experiments performed in Kurchatov Institute and in the Institute of Physics and Technology in Moscow [77,78] showed that a plasma discharge broadens the ignition limits of flames.

#### 5. Catalytic combustion

Catalytic combustion is a low emission alternative to gas-phase combustion, and the conditions for its use in gas turbines have been enumerated in [79]. In fact, catalytic combustors mostly include, in addition to a heterogeneous combustion phase, a homogeneous one,

this is why one generally uses the term : "catalytically stabilized combustion" [80]. Detailed mechanisms have been elaborated [81,82,83], allowing a better knowledge of the conditions of ignition at the surface of the catalyst, but further experimental and modeling studies are necessary, in particular for a better prediction of the effects of pressure [84]. In addition, the range of catalyst materials investigated should be extended, and other fuels than hydrogen and methane should be considered, in order to provide a valuable tool for designing practical applications.

#### 6. Microcombustion

Micropower generation using combustion benefits from the potential advantage of liquid hydrocarbons over batteries, because of their high specific energy [85]. Miniaturization of microcombustors leads to a high surface-to-volume ratio which is in favor of catalytic combustion [85,86,87], but low temperature gas-phase reactions may occur as well [86]. Further studies on low temperature homogeneous/heterogeneous reactions systems with or without catalysts are necessary, for a better understanding of the chemical processes involved in the combustion chamber of a microcombustor.

#### Tools and continuing challenges

Since the Eighteenth International Symposium on Combustion, where early developments of detailed kinetic mechanisms have been presented [88,89],



several invited papers at the following symposia have summarized the progress and needs in the kinetic modeling of combustion processes [3,4,5,90,91]. All these papers have emphasized the necessity of reliable kinetic and thermodynamic data bases. However, the number of reactions and species involved in large reaction mechanisms is such that these data cannot be individually measured, but be mostly calculated. And the progress of theoretical chemistry and mathematical modeling is expected to lead to an "explosion of knowledge and predictive power" [91]. However, uncertainties remain on many sensitive reactions involving small molecules or radicals [11,90]. Because of the hierarchical character of the combustion mechanism of hydrocarbons, such uncertainties limit the accuracy of the kinetic models for the combustion of practical fuels, and continued efforts in this area are crucial. At the same time, a close interaction between theory and experiment is observed, and should intensify in the future [5].

Major difficulties in the modeling of chemical reactions in practical combustion devices concern reactions involving a solid phase, such as the formation and oxidation of soot particles [48] and the combustion of coal and biomass [50]. Surface combustion chemistry in general is much less well understood than gas-phase chemistry [90], and the elaboration of detailed mechanisms describing catalytic combustion or microcombustion will progress more slowly.

Kinetic data are also lacking for reactions involving electronically excited species responsible of chemiluminescence in flames, and reactions of non neutral species in plasmas.

More generally, the construction of detailed mechanisms needs accurate thermodynamic and kinetic data bases, but the manipulation of large mechanisms involves numerous steps which can be helped by mathematical tools. Such mathematical tools can be used for the construction of the mechanism [8,17,90] : Tomlin et al. [92] have reviewed the expert systems for automatic generation of chemical mechanisms. Another mathematical tool, which is extremely useful for the validation of the detailed mechanism by comparison with experimental data, is sensitivity analysis [90,92].

Once validated for a sufficiently wide range of conditions and combustion devices, the chemical mechanism may be used for practical design problems, but its inclusion into multi-dimensional codes for practical CFD computations generally necessitates a simplification. This topic is beyond the scope of the present paper and will be examined in another presentation, but several references cited herein [3,90,92]] deal with this subject which is frequently associated with kinetic modeling.

Finally, progress in the chemical kinetic modeling of combustion depends on continued advance in theoretical chemistry, diagnostic techniques, and mathematical tools for the elaboration, handling and reduction of chemical mechanisms

## Conclusion

With the elaboration of more and more complex comprehensive mechanisms, the chemical kinetics of combustion has achieved considerable progress. These efforts must continue for a deeper understanding of chemical processes occurring in practical combustion devices. Placed in the context of our changing world, the kinetics of combustion is actively involved in the formulation of appropriate tools for the improvement of conventional combustion systems, the use of alternative fuels, and the development of innovative technologies, in order to meet future requirements concerning energy and environment.

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