

PROGRESS IN THE DEVELOPMENT OF COMBUSTION KINETICS DATABASES FOR LIQUID FUELS

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ABSTRACT

This paper describes the present situation regarding chemical kinetic databases for the simulation of the combustion of liquid fuels. Past work in the area is summarized. Much is known about the reactions of the smaller fragments from combustion processes. In order to describe real liquid fuels there is the need for an understanding of how the larger organic fuels are broken down to these fragments. The type of reactions that need to be considered are described and the breakdown of heptane is used as an example.

Keywords: Combustion, Liquid fuels, Hydrocarbons, High temperature, Chemical kinetics, Databases, Pyrolysis, Oxidation, Decomposition

1 INTRODUCTION

For the foreseeable future combustion of fossil fuels will remain a major source of world's energy. However the desired increase in efficiency is not necessarily compatible with the equally important need to decrease emissions that can result in severe health effects (Glassman, 1996). For example, recent work has focussed increasing attention of particulate emissions from transportation fuels (Yanowitz, Graboski & McCormick, 2002) As a result there has been much interest in arriving at a better understanding of the details of the combustion process. The expectation is that it may be possible to find optimum conditions in existing systems or even completely new configurations where both needs are met.

In recent years computer simulations have proved to be a powerful new tool for the conceptualization and optimization of complex physico-chemical processes (Peter, 1994). It can supplement and to some degree substitute for direct physical testing with all its attendant costs and uncertainties. Particularly important have been developments in computational fluid dynamics (Maas and Pope, 1992) which has led to codes that can handle increasing amounts of chemistry. Combustion phenomena are a complex mixture of fluid dynamics and chemistry. Mixing is particularly important since it controls the local stoichiometry. Thus the powerful combination of fluid dynamics and chemistry means that it is increasingly possible to simulate the behavior of real systems. It may well be that in the near future computer simulation of combustion system will become a standard design tool.

Intrinsic to the use of simulation is the existence of a database of basic information that together with the boundary conditions that define inlet conditions and the geometry of the system dictate all subsequent behavior. This paper will be concerned with the state of the database. We will begin by defining its scope and nature. We will then use heptane as an example to illustrate the technical considerations that must be used to develop the database. Finally we will consider the extension of such work to more realistic systems.

2 SCOPE

The focus of the work will be on liquid fuels. This means hydrocarbon fuels with boiling points somewhat higher than ambient and corresponds to intermediate sized compound with more than seven carbon atoms. We will be concerned with chemical changes of the fuel. This further restricts the work to reactions in the gaseous state. A major problem with most of the liquid transportation fuels is the large variety of starting reactants. A gas chromatogram of a real fuel will reveal hundreds of peaks. Further, the composition of

“same” fuel will vary month to month. However the types of compounds that are present is strictly limited. As a result investigators have been using simulants containing a more modest selection of starting compounds. This is illustrated in Table 1 for JP-8 the standard jet engine fuel. Although this is a vast

Compounds	Mole percentage	Compounds	Mole percentage
Methyl cyclohexane	5	1-methyl-naphthalene	5
Cyclooctane	5	Isooctane	5
Butylbenzene	5	Decane	15
Tetralin	5	Dodecane	20
Meta-xylene	5	Tetradecane	15
1,2,4,5tetramethylbenzene	5	Hexadecane	10

Table 1. Chemical composition of a mixture designed to simulate the stability behavior of JP-8 (Edwards, Harrison and Maurice, 2001)

improvement over the hundreds of compounds actually present, the enumeration of the breakdown of these products into their thermodynamic end states and possible side products is still a daunting but manageable problem.

Thermodynamically, the end products from any combustion process are CO_2 , H_2O , H_2 , and solid carbon, where the latter two species are from fuel rich situations. The details of how the thermodynamic end states are reached are dictated by the chemical kinetics of the overall process. This information is contained in the rate constants and parameters for the elementary processes. In the familiar Arrhenius or modified Arrhenius form they are dependent only on the temperature which is a reflection of the reacting molecules being in Boltzmann distributions. For practical purposes these rate constants or expression are either unimolecular or bimolecular and are fundamental properties of the molecules of interest or their interactions with each other. As such there is only one set of correct values. This is the chemical kinetic database of concern in this discussion. It is important to distinguish between these rate constants or expressions that describe such processes and the more global quantities derived from a set of observations on a particular system. Such rate constants may be system specific and therefore must be used with care when confronting conditions out of the range from which they are derived.

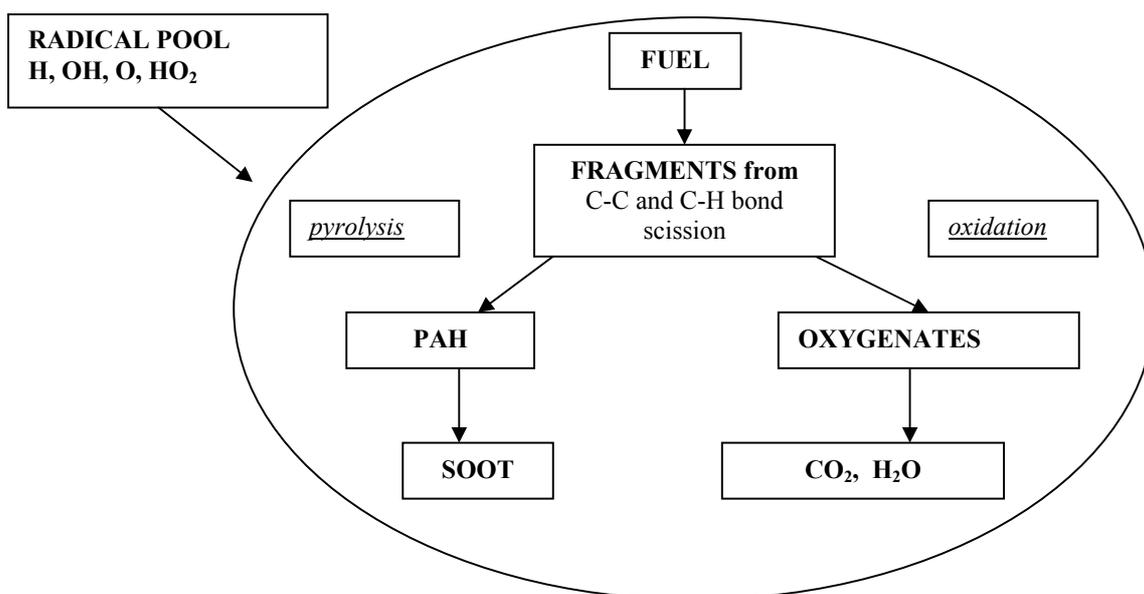


Figure 1. Overall processes occurring during the combustion of hydrocarbon fuels

In the context of the two types of reactions of interest it should be noted that true bimolecular processes (for example metathesis reactions) in general do not change the number of carbon atoms in the reacting species. This is because most of the reactions of interest simply shuffles the hydrogen atoms. Unimolecular reactions lead to the breakdown of the fuel molecules to smaller moieties. The reverse of unimolecular reactions are special types of bimolecular processes that are related to the former by detailed balance. They can therefore be covered in the former category. It will be seen subsequently that these two types of reactions are of key importance for the present purposes. It should be noted that due to the high temperatures of combustion processes in general, the Boltzmann distribution of reacting species may be perturbed. The consequence is that rate constants may also be pressure and indeed, in some conditions, time dependent. Methods for treating such phenomenon have been developed (Gilbert & Smith, 1990; Tsang, 2001). This will be used in the subsequent sections.

Figure 1 contains a schematic of the processes occurring during the combustion of any fuel. Note the initial necessity of breaking down the fuel to smaller fragments before the formation of the ultimate products. It is clear that the first products are radicals. Except for certain resonance stabilized species their decomposition rates are so fast that there is rapid formation of smaller unsaturated compounds. These smaller compounds can then be oxidized to their thermodynamic endstates or be pyrolyzed leading to the formation of polynuclear aromatic hydrocarbons and ultimately soot. All of these reactions are occurring in a pool of radicals. The importance of these radical reactions is dependent on the physical and chemical situations in the reacting system. Of key importance is the competitive nature of the cracking and oxidation processes. Thus one or the other may dominate in different region of the same combustor.

It is thus possible to describe the overall process in terms of relatively independent data modules on kinetic processes. Many of these exist. There has been much work on the oxidation of small hydrocarbons. Particular attention is called to the database GRIMECH (Smith, Golden, Frenklach, Moriarty, Eiteneer, Goldenberg, Bowman, Hanson, Song Gardiner, Lissianski & Qin, 1999) which contains the reactions of importance for methane oxidation and has also considerable data on the oxidation of ethane and propane. It also contains reactions of a number of C₂ or C₃ unsaturates. These represent probably the highest quality existing chemical kinetic database of pertinence to combustion. There also exist databases on the oxidation of larger linear alkanes (Curran, Gaffurri, Pitz & Westbrook, 1998; Lindstedt & Maurice, 1995; Bakali, Delfau, & Vovelle, 1999; Fournet, Warth, Glaude, Battin-LeClerc, Scacchi & Come, 2000). These are of somewhat lower quality and are deficient with respect to pyrolytic processes. Thus they cannot be applied to soot formation processes.

Probably the true scientific frontier in combustion kinetic databases is the description of soot formation processes (Frenklach, Clary, Yuan, Gardiner & Stein, 1986; Richter & Howard, 2000; Marinov, Castaldi, Melius & Tsang, 1997). Although there remain important uncertainties, all of these databases do fit certain sets of observations. However most of these begin with unsaturated compounds such as ethylene or benzene. Thus for the description of the combustion of real fuels it is necessary to reduce these compounds to a set of these unsaturates. This then represents the area where attention must be focussed in order to extend available databases to cover the type of fuels of interest. In the following we will describe the reactions necessary to reduce larger hydrocarbon into forms that can be fed into existing models.

A major problem in the construction of these mechanisms is that chemical kinetics is still a research area. New experimental results as well as theoretical constructs are constantly produced. Thus there is a continual need to update the databases. Indeed there is very little question that the latest mechanisms (Curran, Gaffuri, Pitz & Westbrook, 1997; Bakali et al., 1999; Fournet et al., 2000) should be preferred over older works or compilations (Warnatz, 1984; Westbrook, Warnatz & Pitz, 1988; Allara & Shaw, 1980). For the reader, who wishes to bring a particular database up to date, the reader is referred to the

NIST Kinetics Database (NIST, 2000), standard reviews as those found in the Journal of Physical and Chemical Data (Baulch, Cobos, Cox, Frank, Hayman, Just, Kerr, Murrells, Pilling, Troe, Walker & Warnatz, 1995) and original articles in the literature (Sumathi,

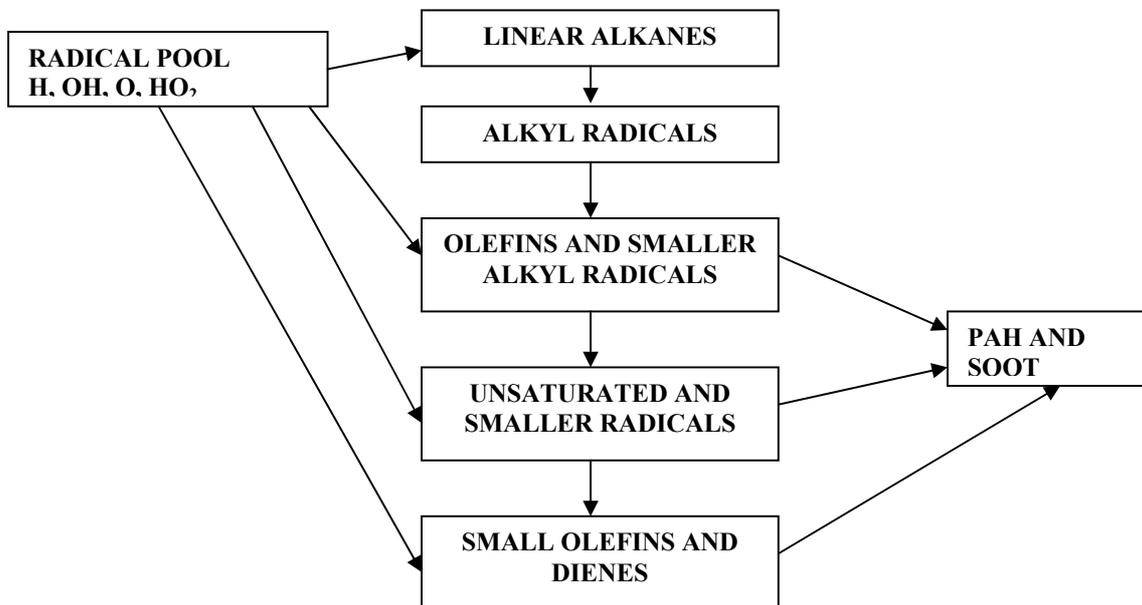


Figure 2. Sequence of reactions from the cracking of an alkane fuel

Carstensen & Green, 2001). The new elements introduced in the current work are the derivation of isomerization rate constants from experimental observations and taking into account, energy transfer effects. It should nevertheless be remembered that published mechanisms do fit some sets of experimental results. Thus changing the values of the elements in the data base must be done with care so that the original agreement is not lost or some rationale is provided for the nature of the original fits with the experiments.

Implicit in the above is the assumption that the thermodynamic properties of all reactants and intermediates are well established. This is probably not a problem for the usual liquid fuels and the associated intermediates important during oxidation. A more serious problem is the thermodynamic properties of the larger aromatics and associated reactive intermediates. Here there is the need for a great deal of definitive work. Of particular concern is the uncertainty of the theoretical procedures that have proved to be so powerful for small molecular entities when applied to larger systems.

3 HEPTANE PYROLYSIS

Examination of the data in Table 1 shows that the largest component of fuel mixtures are the linear alkanes. They are also the compounds that contain the largest number of carbon atoms. The general picture can be found in Figure 2. The first step in the breakdown of these molecules involves either bond breaking or radical attack on the fuel molecules. Rate constants for these processes are in general well established. The organic radicals created can now decompose. It is known that these will degrade extremely rapidly. For reactions involving a single reaction channel, exact values of the rate constants may not be necessary. However in the case of multiple channels, branching ratios become very important. Of particular importance are isomerization of the radicals. This leads to the introduction of new species. There is not much experimental data on these isomerization reaction. The accuracy of predictions are uncertain. The

initial cracking process leads to a large number of olefins before further cracking leads to the small molecules and intermediates whose rate constants can be found in other modules. It should also be noted that the cracking reactions are of particular importance in the soot formation mechanism since they furnish the boundary conditions for use in existing soot formation models where unsaturated compounds are the starting species.

In order to illustrate some of the scientific issues, we use the cracking of heptane as an example. It should be noted that at the high temperatures of interest energy transfer effects must always be considered. Thus, although they are a necessary data input, the high pressure rate expressions are not sufficient. The other inputs due to the reversibility of the isomerization process are the thermodynamic properties of the molecules and radicals under consideration. For the latter we follow the procedure outlined by Pitzer (1944) on the effect of adding methylene groups to a smaller hydrocarbon. We then make minor adjustment of the vibrational frequencies to match the entropies in standard tables (Stull, Westrum & Sinke, 1969). Radical entropies were determined following the procedure of Benson (1974) on the effect of removing a hydrogen atom from a hydrocarbon structure. Heats of formation of the molecules were taken from standard tables (Stull, Westrum & Sinke, 1969). For the radicals we use standard values of 420.5 kJ/mol for the bond dissociation energy of a primary C-H bond and 410 kJ/mol for a secondary C-H bond (Tsang, 1999; Tsang, 1996).

Rate expressions for the bond breaking processes for heptane can be deduced from previous studies (Tsang & Kiefer, 1995). Pressure effects can be accounted for by using the treatment given in standard texts (Gilbert & Smith, 1990). It is a result of decomposition occurring from a new non-equilibrium steady state distribution of molecular energies. This treatment is appropriate for the decomposition of all the stable species. Of particular pertinence is the case of the 1-olefins that are the immediate products from radical decomposition. The challenging scientific issue is the decomposition of the radicals that are formed. These radicals all have low thresholds for decomposition as well as isomerization. Thus energy transfer effects will be especially important and leads to new effects that have been ignored by previous investigators. Rate constants are large. Note that if there were only one channel, no problem would arise since the reaction mechanism would be unchanged.

Figure 3 is illustrative of the complexity of the situation. Our procedure involves first estimating high pressure rate expressions for the radical decomposition reactions and then carrying out kinetic studies to obtain the cracking pattern for the decomposition of 1-heptyl radicals from the pyrolysis of n-heptyl iodide radicals in single pulse shock tube experiments (Tsang & Lifshitz, 2001). The conditions are set so that only the radical decomposition can occur and branching ratios are determined from the olefin yields.

Using the procedure designed to take into account energy dependent effects, we then determine the high pressure rate expressions for isomerization on the basis of the experimental branching ratios. The high pressure rate expressions can then be used to project results over all temperatures and pressures. A serious problem is the high temperature situation where rate constants are no longer constant (Tsang, Bedanov & Zachariah, 1996) due to the occurrence of a dynamic situation arising as the molecular energy distributions change. Fortunately at these high temperatures only the branching ratios are of importance. There is nevertheless an intermediate temperature region where we have not found it possible to express results in standard formats.

The 1-olefinyl radicals of concern are those involving four to six carbon atoms with the radical sites in the 3, 4, 5, and 6 positions. The treatment is similar to that for the heptyl radicals, except that the isomerization possibilities are much decreased. We have found that the literature data for the reverse radical addition reaction to dienes (Kerr & Parsonage, 1972) as well as chemical activation results (Carter and Tardy, 1974) on the addition of hydrogen atom to pentadienes particularly useful in providing a fixed point for estimation. There are however similar problems regarding the presentation of results under conditions where rate constants are no longer constant. The overall effect of this treatment is to present to soot models a mixture made up of ethylene, propene, 1,3-butadiene, allyl and various small radicals.

processes. In these cases some success have been achieved through the use of an average value. This is clearly a continuing research area.

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