Detailed Chemistry of Pyrolysis and Combustion Processes

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ABSTRACT

Nowadays complex and detailed kinetic schemes are largely available and diffused in the scientific community and they constitute a formidable tool for the design, simulation and optimization of pyrolysis processes and combustion devices. Main goal of this paper is to present the state of the art of these detailed models in the pyrolysis and combustion processes. The careful analysis of the chemical mechanism with the ability to single out the different classes of elementary reactions is the first step towards the development of complex kinetic schemes, constituted by several hundreds of species involved in thousands of elementary reactions. Only on this basis it is then feasible to build up the automatic generation of the reaction schemes through properly conceived computational program and/or expert systems. The successive critical point is the validation of the kinetic model and the assessment of its reliability in predictive terms. This paper presents and shortly discusses a few recent examples, both in pyrolysis and in combustion processes, in order to indicate the possibility as well as the limits of these detailed kinetic schemes.

INTRODUCTION

Since several years the use of detailed and complex reaction schemes to describe pyrolysis and combustion processes has become very distribute in the scientific and technical community. At the beginning of the seventy’s, the use of a detailed kinetic scheme constituted by more than thousands elementary reactions [1] in order to describe the steam cracking process for ethylene production was strongly innovative and largely ignored by the scientific community [2]. Nowadays, the improved computing facilities and mainly the availability of Chemkin package [3] and similar kinetic compilers and processors made these complex kinetic schemes very friendly to use and they allow to study process alternatives as well as to design and optimize combustion and pyrolysis devices. The main focus of this paper is the discussion on some critical features in the development and validation of these complex reaction schemes.

Both in pyrolysis and in combustion processes, the complexity of the reacting system is due not only to the large number of elementary reactions involved but also to the difficulty in the proper characterization of the reacting mixture. This is true in steam cracking process of liquid feedstocks, such as naphtha and gasoil, and is also true in the combustion of gasoline, diesel oil or jet propeller fuels. The first step before the analysis of the elementary reactions involved is the reliable characterization of the fuel or the pyrolysis feedstock. For this reason, it is nowadays of interest to study well defined mixtures of reference components (surrogate fuels) in order to analyse the combustion behaviour of practical fuels in a reproducible way [4].
A relevant feature of the detailed reaction schemes is their modular and hierarchical structure [5]. This aspect allows to study pyrolysis or combustion reaction schemes starting from the simpler systems and progressively extending the simulation capability of the model to new and more complex situations. The H2-O2 system is the simpler combustion sub-model and it is always active in all the combustion environments. Similarly, the pyrolysis kinetic model is hierarchically preceding the combustion models of the same species. For this reason, pyrolysis reactions will be treated first, followed by the combustion ones in the coming paragraphs.

**PYROLYSIS SYSTEM**

It is well established that the steam cracking of hydrocarbons follows a radical chain mechanism. In fact, only the mechanistic radical kinetic schemes can provide reliable description of the pyrolysis process. In a simple way, a chain radical mechanism can be summarized as follows:

1. Initiation and termination (or recombination) reactions
   - Unimolecular: \( \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3 \rightleftharpoons \text{C}_2\text{H}_5\cdot + \text{C}_2\text{H}_5\cdot \)
   - Bimolecular: \( \text{CH}_3\text{-CH}_3 + \text{CH}_2=\text{CH}_2 \rightleftharpoons \text{C}_2\text{H}_5\cdot + \text{C}_2\text{H}_5\cdot \)

2. Propagation reactions
   - H-abstraction (or H-metathesis) on molecules
     \( \text{CH}_3\cdot + \text{CH}_3\text{-CH}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5\cdot \)
   - Addition of radicals on unsaturated molecules and alkyl radical decomposition
     \( \text{CH}_3\cdot + \text{CH}_2=\text{CH}-\text{CH}_3 \rightleftharpoons \text{CH}_3\cdot\text{-CH}_2\text{-CH}\cdot\text{-CH}_3 \)
   - Alkyl radical isomerization via (1-4) and (1,5) H-transfer
     \( \text{CH}_3\cdot-(\text{CH}_2)_3\text{-CH}_2\text{-CH}_3 \rightleftharpoons \text{CH}_3\cdot-(\text{CH}_2)_3\text{-CH}\cdot\text{-CH}_3 \)

It is relevant to observe that also some molecular reactions can play a significant role. Typical examples are cyclo-alkane and olefin isomerization as well as dehydrogenation via four and six center reactions:

\[
\begin{align*}
\text{CyC}_6\text{H}_{12} & \Rightarrow \text{CH}_2=\text{CH}-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{CH}_3=\text{CH}=&\text{CH}-\text{CH}_3 & \Rightarrow & \text{CH}_2=\text{CH}-\text{CH}_2\text{-CH}_3 \\
\text{CH}_2=\text{CH}-\text{CH}_2\text{-CH}_3 & \Rightarrow & \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{H}_2
\end{align*}
\]

There is a large abundance of groundwork in scientific literature both in the fundamental and the applied chemical kinetics

As already observed, the steam cracking of naphtha and gasoil to produce light olefins is a process where the chemical complexity is dictated both by the characterization of the hydrocarbon mixture and by the complete definition of the kinetic mechanism. Due to the large number of involved species and to the necessity to account for all the relevant interactions between different species, the number of elementary reactions becomes very
large. For this reason, it is necessary, from one side, to classify the reactions and to apply automatic procedures in order to build up the kinetic scheme. From the other side, it is also useful to adopt carefully evaluated simplifications. As a simple example of the complexity of the pyrolysis mechanism, Figure 1 shows the complete reaction path of H-abstraction reactions on n-octane. When faced with these large hydrocarbon molecules in the typical range of pressure and temperature, a very important simplification regards the fate of the large intermediate radicals. They can be directly isomerised and decomposed to their final products. To this end, only the few reference kinetic parameters of Table 1 need to be applied [6]. The complex kinetic scheme of Figure 1 can be simply reduced to this simple, equivalent or lumped reaction:

\[
R^* + nC_8H_{18} \rightarrow RH + 0.107 CH_3 + 0.268 C_2H_5 + 0.379 nC_3H_7 + 0.246 1C_4H_9 + \\
+ 0.264 C_2H_4 + 0.348 C_3H_6 + 0.228 1C_4H_8 + 0.187 1C_5H_{10} + 0.103 1C_7H_{14}
\]

This stoichiometry, directly obtained at 1040 K by MAMA Program [7], is only weak temperature dependent and it lumps all the elementary reactions of Figure 1. R and RH stand for all the possible H abstracting radicals and for the corresponding saturated species. The reference kinetic parameters of Table 1 allows to directly deduce all the stoichiometries and kinetics of H-abstraction reactions of n- and iso-alkanes.

<table>
<thead>
<tr>
<th>H-Abstraction Reactions</th>
<th>Primary H atom</th>
<th>Secondary H atom</th>
<th>Tertiary H atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary radical</td>
<td>$10^{8.0}$ exp (-13.5/RT)</td>
<td>$10^{8.0}$ exp (-11.2/RT)</td>
<td>$10^{8.0}$ exp (-9/RT)</td>
</tr>
<tr>
<td>Secondary radical</td>
<td>$10^{8.0}$ exp (-14.5/RT)</td>
<td>$10^{8.0}$ exp (-12.2/RT)</td>
<td>$10^{8.0}$ exp (-10/RT)</td>
</tr>
<tr>
<td>Tertiary radical</td>
<td>$10^{8.0}$ exp (-15/RT)</td>
<td>$10^{8.0}$ exp (-12.7/RT)</td>
<td>$10^{8.0}$ exp (-10.5/RT)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isomerization Reactions</th>
<th>(Transfer of a Primary H-atom(^a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4 H Transfer</td>
<td>10.2 exp (-14.5/RT)</td>
</tr>
<tr>
<td>1-5 H Transfer</td>
<td>10.2 exp (-14.5/RT)</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Alkyl Radical Decomposition Reactions to form Primary Radicals</th>
</tr>
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<tbody>
<tr>
<td>Primary radical</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>$10^{14.0}$ exp (-30/RT)</td>
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</tbody>
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<th>Corrections in Activation Energy to form:</th>
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<tr>
<td>Methyl radical</td>
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<td>+2.</td>
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Table 1 - Reference kinetic parameters for pyrolysis reactions
\(a\). Corrections for secondary and tertiary H-atoms are the same as for H-abstractions.
\(b\). Rate values for secondary and tertiary radicals are obtained by adding 1 and 1.5 kcal/mol to the activation energies.

Naphtha and gasoil feeds, usually characterized in terms of boiling curves and PONA index, are complex mixtures of a large number of different isomers. The analysis and comparison of different virgin feeds shows that significant regularities in the internal distribution of the different isomers can be singled out, fairly independent from the crude origin. In this way a simplified description of the feed can be obtained on the basis of a limited number of equivalent or ‘lumped’ components with a fixed internal distribution of pure isomers. In this way a simplified but still reliable detailed composition of naphtha and gasoil feeds can be obtained and, more important, the total number of species and reactions is strongly reduced. As an example of this simplification procedure, the ‘pseudo’ component isoC8 is obtained by grouping the all different isomers with their relative weights, where the three mono-methyl-heptanes sum up to about 70% of the whole fraction. The corresponding H-abstraction reaction presents the following stoichiometry:
This reaction is equivalent to more than 300 elementary reactions and also results in a significant reduction of species still maintaining a high level of accuracy in the prediction of the different pyrolysis products.

The difference in primary products from homologous species decreases when the carbon number $N_C$ becomes larger than 10-12, like in the case of kerosene and gasoil. Therefore, only reference components can be selected inside each family obtaining in this way a good compromise between computation efforts and prediction accuracy. As a further example of the complexity of the overall reacting system, let's consider the cyclo-alkane species. They are abundant in liquid hydrocarbon feeds and they are constituted both by 5 and 6 ring components. Figure 2 shows the primary reaction paths of cyclo-hexyl radical [8].

New reference reactions appear in this scheme, namely the ring opening as well as the cyclo addition reactions of hexenyl radicals to form cyclopentane and cyclo-hexane structures. While the opening of the ring can refer to the reference values of the $\beta$-decomposition reactions, the following kinetic parameters are selected for cyclo-addition-reactions:

$$k_{cy5} = 10^{11} \exp(-13000/RT) \ [s^{-1}]$$
$$k_{cy6} = 10^{10.2} \exp(-7500/RT) \ [s^{-1}]$$

As a result of these successive cyclo addition and decomposition reactions all the different isomers of hexenyl radicals are generated. For instance, starting from cyclo-hexyl, methyl-cyclopentyl as well as hexenyl and methyl-cyclopentyl radical are formed. The number of skeleton isomers rapidly increases with the carbon number and becomes about $10^6$ for $N_C = 16$. It is evident the need to apply careful and strong simplifications when describing the pyrolysis of liquid feedstocks. This need is present not only when considering intermediate pyrolysis products but also when describing a detailed composition of gasoil starting from commercial and industrial indexes such as gravity, boiling curve and H/C data. The huge number of different isomers contained in the feed means that the lumping approach must be forced by selecting only the following classes of model components:

- **n- and iso-alkanes**
  - $C_{n}H_{2n+2}$
  - $C_{n}H_{2n}$

- **cyclo-alkanes**: mono-naphthenes
  - di- and poly-
  - $C_{n}H_{2n-2}$, $C_{n}H_{2n-4}$, $C_{n}H_{2n-6}$

- **aromatics**: alkyl-benzenes
  - alkyl-tetralines and -indanes
  - $C_{n}H_{2n-6}$
  - $C_{n}H_{2n-8}$
alkyl-naphthalenes, -phenanthrenes \[ C_{n}H_{2n-12} \]
alkyl-crysenes \[ C_{n}H_{2n-24} \]

Only a few reference components were selected for each family in the range between 15 and 35 carbon atoms. Despite of these simplification, the pyrolysis model is able to give accurate and reliable yields predictions [9]. As an example, Figure 3 reports the comparisons between model predictions and experimental data for the following heavy hydrotreated gasoil:

<table>
<thead>
<tr>
<th>Boiling range (TBP)</th>
<th>250-510 °C</th>
</tr>
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<tbody>
<tr>
<td>H/C (atomic ratio)</td>
<td>1.95</td>
</tr>
<tr>
<td>Sulphur (wt%)</td>
<td>0.01</td>
</tr>
<tr>
<td>Average molecular weight</td>
<td>300</td>
</tr>
</tbody>
</table>

**Figure 3: Hydrotreated gasoil pyrolysis.**
Comparison of predicted and experimental yields vs CH4 (wt%)

**COMBUSTION SYSTEM**

When considering the combustion of hydrocarbon fuels, the development of the detailed kinetic mechanism maintains the same kinetic approach. The system becomes more complex due to the presence of the oxygen and still there is the need of a hierarchical modularity for a progressive extension of the overall kinetic scheme. Of course, reactions of methane (formaldehyde and methanol), ethane and \( C_{2} \) species followed by heavier species should be added sequentially to the core CO-H\(_{2}\)-O\(_{2}\) sub mechanism. New reactions and species are added at each step and the resulting mechanism has to be tested through comparisons with experimental data.
This hierarchy is a typical advantage of mechanistic kinetic models: once the elementary reactions are progressively defined for certain sets of components, the introduction of new species requires only the definition of the primary propagation and decomposition reactions towards intermediate and final products already considered. As for the case of pyrolysis process, the kinetic analysis of the interactions of smaller species is a key feature in the development of the whole kinetic scheme. The hierarchical and modular structure of the model allows also simple extensions to different problems. This is the case of NOx. The impact on the whole scheme of the NOx reaction subsystem is negligible, but a correct evaluation of NOx requires the precise determination of several radicals (like OH•, H•, HO2•, O• and CH3•) considered in the main mechanism. A simple example of primary propagation and oxidation reactions of n-pentane is shown in figure 4.

From here it is possible to single out the different classes of primary propagation reactions for the oxidation process. Rate parameters for all of these reaction classes are reported in Table 2 and are based only on a limited set of reference kinetic parameters deduced from the available literature [10]. Expert systems and computer programs for the generation of kinetic mechanisms of these primary oxidation reactions for both pyrolysis and oxidation have been generated. These tools perform at their best for complex and large molecules, such as n- and iso-alkanes, which decompose via a defined set of reaction classes. Naturally, the procedures can then be readily modified if changes in the understanding of the process lead to a modification of the rules and reaction classes. As already mentioned, it is important to underline that this automatic generation is very useful only for the extension of the kinetic schemes. The critical points in mechanism development remain the careful analysis and proper definition of the species and reactions involved in the core of the kinetic mechanism.
With reference to the kinetic parameters of Tables 1 and 2, it is feasible to generate all of the primary decomposition and oxidation steps of normal and branched paraffins [10]. The oxidation of n-dodecane (n-C_{12}H_{26}) involves 256 primary propagation reactions. The pyrolysis subsystem is constituted by 32 elementary reactions. As an overall, 72 intermediate radicals retain the n-C12 structure and it is possible to distinguish 6 alkyl, 6 peroxy, 30 hydroperoxy-alkyl and 30 hydroperoxy-alkylperoxy radicals. Due to this complexity, it is very convenient and efficient to reduce and simplify the overall scheme to the lumped mechanism shown in Figure 5. This oxidation scheme is a convenient simplification of both the intermediate components and reactions. When compared with the lumped decomposition reaction of octyl radicals considered in the pyrolysis scheme, it is clear how large alkyl radical interactions with the oxygen in the mixture give rise to a greater complexity of the resulting mechanism. The lumped scheme maintains the description capabilities of the detailed kinetic schemes. Furthermore, this reduction is directly deduced on the basis of the theoretical distributions of the primary products predicted with the complete kinetic model as generated by MAMOX++ program [10]. In order to complete the extension of the whole kinetic model to n-dodecane, only seven new lumped species were introduced. Namely the four lumped radicals of Figure 5 and only one pseudo species each for dodecenies, cyclic ethers and ketohydroperoxides components. At high temperatures, β-decomposition reactions of alkyl radicals prevails. Branching reactions are dominant at low temperatures. As a consequence, cyclic ether and conjugate olefin selectivities reach their maximum in the intermediate region. This temperature dependence and the pressure effect are properly maintained by the lumped model.
The primary combustion reactions of cyclo-alkanes require further reference kinetic parameters, due to the presence of the ring inside the molecule. For this reason it is necessary to investigate the isomerization reactions of cyclo-alkane peroxy radicals to form the alkyl-hydroperoxy radicals and their successive paths. A paper on this subject will be presented at this meeting [11]. ‘Ab initio’ calculations are performed in order to clarify and quantify the excess of energy and the entropy corrections due to the presence of multiple rings in the transition state.

Once again, the description of the successive reactions of intermediate species exploits the hierarchical modularity and the lumping procedures. As already mentioned, these simplifications are more relevant when the interest lies in the oxidation and combustion of real mixtures of heavy hydrocarbons, such as kerosenes and diesel or jet fuels, where a large number of isomer species are already involved as reactants. The use of surrogate blends [12], comprised of a relatively small number of pure hydrocarbons and blended to simulate the combustion performance of practical fuel, has the advantage of allowing fuel composition to be accurately controlled and monitored. In addition to provide a model fuel for the study of the effect of fuel properties and chemical composition on combustor performance, the compositional control afforded by a surrogate fuel is also attractive for the development and verification of computational codes for combustor design. Surrogate mixtures are desirable for experimental and computational tractability and reproducibility. The type of surrogate mixture used is dependent ideally upon the fuel properties that are being simulated: surrogates may be tailored to reproduce the physical, chemical, or more comprehensive behavior of a fuel in a given application. A physical surrogate is designed to reproduce physical properties such as density, thermal conductivity, heat capacity, viscosity, surface tension, and volatility. A chemical surrogate, on the other hand, has similar hydrocarbon types and distribution, and reproduces chemical properties such as pyrolysis or oxidation stability, ignition temperature, rates of reaction, sooting tendency. In the previous referred paper [12], a formulation procedure was described for blending pure hydrocarbons (n-dodecane and n-tetradecane, iso-octane, methyl-cyclo-hexane, xylenes and tetralin) in such a way as to produce a fuel surrogate that matches the distillation curve as well as the sooting propensity of a JP-8. Hence, the surrogate provides an attractive baseline fuel of controlled composition and manageable complexity from which to explore fuel property and chemical composition effects. In a parallel way the whole kinetic model was extended to include the new reference fuel components, making also more effective and reliable the model validations.

A couple of two recent applications of the whole oxidation scheme will be presented at this meeting and they respectively refer to the autoignition characteristics of different fuels in CFR engines [13] and to the sooting tendency and burning rates of ethanol droplets [14]

CONCLUSION

Reliable mechanistic kinetic models are available to simulate pyrolysis and combustion of hydrocarbon mixtures. The definition of the core mechanism is always the crucial and fundamental step. The classification of the different primary reactions involved, the definition of their intrinsic kinetic parameters, the automatic generation of the detailed primary reactions and the proper simplification rules are important steps in the successive extension of the core mechanism. These assumptions are more relevant when interest lies in the pyrolysis and combustion of real mixtures, such as naphthas, gasoils and automotive fuels, where a large number of isomer species are involved both as reactants and products. The primary and successive reactions allow a complete validation of the small set of fundamental kinetic parameters on the basis of comparisons with experimental data. Due to the complexity
of these kinetic schemes, a correct validation must take into account the widest ranges of operating conditions.

In spite of the different models present in the technical literature not all the problems have yet been solved and much theoretical and experimental work remains to be done. New experimental data will allow further improvements in the kinetic assumptions or suggest new hypotheses for a deeper understanding of the detailed chemistry of pyrolysis and combustion processes.

REFERENCES


