

Automatic generation of combustion mechanisms

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Abstract

Due to the increase of species and reactions number with the size of initial fuels, automatic generation of kinetic mechanisms for combustion is no longer considered an option to manual construction. It has become a necessity. This is particularly true if the focus is on components such as alkenes or cycloalkanes, where the number of possible isomers/intermediates increases exponentially with the number of carbon atoms. The generation is the result of the application of defined rules, which are automatically executed by computer programs. The paper will focus the list of the elementary reaction steps and the rules to apply them, while the components representation, the algorithm for the homomorphism of molecules, lumping and the list of kinetic data will be addressed by references.

Keywords

Automatic generation, combustion mechanism, combustion kinetics

1. Introduction

A characteristic feature in the automatic generation is the ‘modularity’ of the reaction schemes. A generic scheme is seen as an open folder where each file stands for the reactions path of hydrocarbons having a certain carbon number. The files are piled on each other with ascending carbon number. The folder (in practice a kinetic database) is continuously updated with the addition of new elements. The automatic procedure takes advantage of such modularity, so that the creation of a C7-feedstock scheme, as shown in fig. 1, will mainly refer to

the new reactions associated to C7 molecular structures. The remaining reactions associated to lower carbon numbers are already stored inside the database.

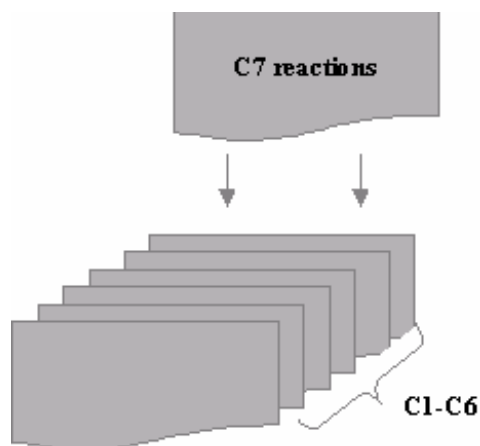


Fig. 1: Visualization of the modularity feature

Provided the evidence that today the kinetics of the combustion of fuels till C4 are available and consolidated in literature [1,2], it comes out that the automatic generation practically 'starts' and it is worth to be considered from C5 onwards. Due to limitation on the space of this paper, Table 1 reports the latest references related to the study of the combustion mechanisms of hydrocarbons, mainly linear or branched alkanes. A comprehensive list of references on this matter may be found in the dissertation of Muharam [11]. The oxidation of fuels

Tab 1: List of major references for the kinetic mechanisms of hydrocarbon combustion

Scheme	Authors	Year	Ref.
C5	Dagaut Cathonnet	1999	[3]
C6	Nehse et al	1996	[4]
C7	Westbrook et al.	2001	[5]
C8	Chen et al.	2000	[6]
C10	Ristori et al.	2001	[7]
C16	Touchard et al.	2003	[8]
Alkenes and/or Naphthenic	Buda	2006	[9]

belonging to the classes of alkenes and or naphthenic compounds, has a limited presence in literature.

This matter however is rapidly increasing due to the continuous use of large hydrocarbons as fuels. The mechanisms capable of describing the oxidations of alkene and naphthenic compounds are in the aims of this paper.

2. Automatic Generation

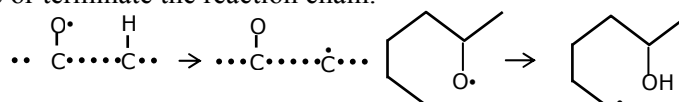
Several systems are available today for the automatic generation of kinetic mechanisms for the oxidation of hydrocarbons. Among them it is worth to mention MAMOX program, from the group of Milan ([1,2,10]. The Nancy group is proposing EXGAS system, which is continuously updated by a team working in this area since the 80's. The software for linear and branched alkanes is freely available for academic researchers

(Valérie.Conraud@ensic.inpl-nancy.fr). The group of prof. J. Warnatz (University of Heidelberg, Germany) created MOLEC, a program for the generation of chemical reaction equations: a comprehensive description is available in [11]. All these systems have in common a set of features, which constitute fundamental elements of their structure:

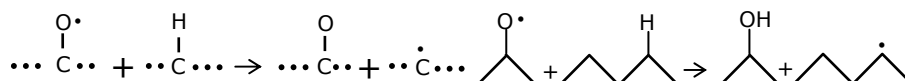
- components representation (this paper adopts the approach from [12])
- list of the elementary reaction steps and the rules to apply them
- algorithm for the homomorphism of molecules (that is a non-ambiguous and effective statement whether two molecule descriptions refer to the same component or not. This paper adopts the approach from [12])
- list of kinetic data
- optional postprocessors for the reduction of the produced scheme (This paper adopts the approach from [10])

3. "Bond Class" approach

It is commonly accepted that the kinetic of each reaction in the oxidation mechanisms of large species, depends on local properties of the bonds involved in the reactions: the magnitude of the influence is more or less equal to the bonds length. Therefore instead of describing the reactions in terms of involved species, it is possible and easier to generalise the description by focusing it at the bonds level. With this novel approach proposed by this paper the reactions will use the convention of referring to a "class of radical bonds" and a "class of component bonds". Also the reactions (initiation, propagation and termination) are distinguished in "unimolecular" and "bimolecular" reactions. A simple inspection of each reaction will be sufficient to find whether they initiate, propagate or terminate the reaction chain.



The above notation indicates a "unimolecular reaction": the internal H-abstraction of the bond CO• from C-H. Both bonds belong to the same radical component.



The above notation indicates the bimolecular H-abstraction of radical CO• from C-H bond of a component: the products are the radical (C•) and the hydroxide (C-OH).

Figures 2 and 3 report two matrixes, which summarize the set of possible unimolecular and bimolecular reactions. It is worth to point out, how the novel technology of representing these mechanisms in terms of "bond class" helps also the representation of the reactions, which is more compact and ready to one glance examination.

Columns and rows stand for bonds: columns for reactants and rows for



















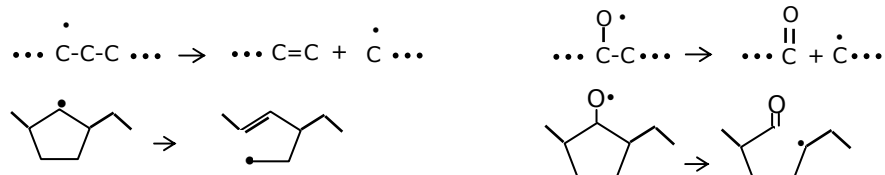
	C-H	C-OH	C-OOH	C-C	C-C	C-O	-OH	-OOH
H•	--- C•CO•							
OH•		--- C•CO•						
OOH•	--- COO•		--- C•CO•					
C•	C•CO•		COO•	C•CO•				
CO•	---	C•CO•						
COO•			C•CO•					
C-OH	CO•	CO•	CO•					
C-OOH	COO•		COO•					
C-C	--- C•COO•	C•	C•	C•				
O								
C•	---	---	---	C•				
C-O	--- CO•	CO•	CO•	CO•			C•	C•
								
								
								
								
								
								
								
								
								
								
								
								
								
								
								
								
								
								

Fig.2: Unimolecular reactions set

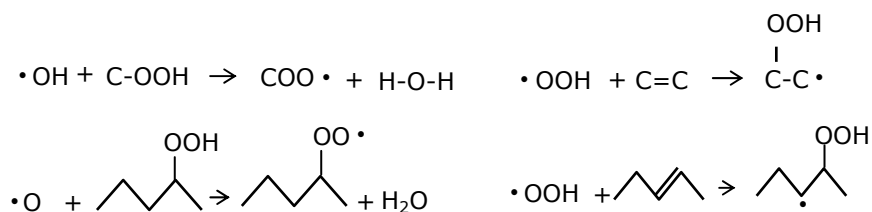
products. The bonds reported in the matrix elements are reactant bonds repeated in each column as many times as the bond products are. As an example the column C-C of figure 2, indicates two reaction types:



The same rules apply to the bimolecular reactions reported in figure 3.

	C-H	C-OH	C-DOH	C-C	C-O	O-O	R-C-O-O-R	C-CR
H-H	H ₂	H ₂	H ₂					
OH [•]	O ₂	O ₂	O ₂					
HOH	OH ₂	OH ₂	OH ₂					
HOOH	OOH ₂	OOH ₂	OOH ₂					
OOH [•]							C [•]	
C-H	C [•]	C [•]	C [•]					
C [•]	O ₂ H ₂ OH [•] CO [•] OOH [•] COO [•] C [•]							
CO [•]		O ₂ H ₂ OH [•] CO [•] OOH [•] COO [•] C [•]						
COO [•]			O ₂ H ₂ OH [•] CO [•] OOH [•] COO [•] C [•]			C [•]		
C-OH	CO [•]	CO [•]	CO [•]					
C-DOH	COO [•]	COO [•]	COO [•]					
O				O ₂				
C-C								
C								
C-C [•]				C [•]				
H				H [•]				
C-C [•]							C [•]	
C-C								
OH								
C-C [•]				OH [•]				
OC								
C-C [•]				CO [•]				
OOH				OOH [•]				
C-C [•]								
H								
C-O [•]				H [•]				
C								
C-O [•]					C [•]			
C-O-C							C [•]	
C-OH							H [•]	
C-O								O ₂
R [•]								O ₂
R-C-O								O ₂
R-C-C-O								O ₂

Fig.3: Bimolecular reactions set



So the column corresponding to the component C-OOH indicates the products of the reaction with OH radical in the rows reporting the radical name. Similarly the generic olefin reacts with the radical OOH as indicated by the intersection with the row reporting the radical name.

4. Conclusions

This paper has proposed a novel approach for representing the rules adopted by the automatic generation of combustion mechanisms. In particular the paper has focused: the list of the elementary reaction steps and the rules to apply them. It is believed that the solutions proposed might help the understanding of the subjects opened by the paper to those who face these kinds of problems.

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