European Symposium on Computer Aided Process Engineering – 15
L. Puigjaner and A. Espuña (Editors)

A kinetic generator of hydrocarbon pyrolysis mechanisms

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Abstract
This paper presents the approach and the results of a kinetic generator in the area of hydrocarbon pyrolysis mechanisms. Radical formation and successive radical decomposition are taken into account. Care is paid to the description of molecule identification procedure and to its homomorphism which enables unique and no ambiguous reactions. New results referring to the pyrolysis of olefins as well as cyclo-alkanes are reported on the basis of Rice, Kossiakoff-Rice and Dente-Ranzi theories.

Keywords: Pyrolysis, Automatic Generation, Detailed kinetics

1. Introduction

Various techniques have been adopted for the automatic generation of kinetic mechanisms in the pyrolysis of hydrocarbon species: graph theory and boolean algebra are the most useful tools frequently referenced in literature (Dente and Ranzi 1983, Clymans and Froment 1984, Hillewaert et al. 1988). Similar techniques have been also adopted for combustion mechanisms (Battin Leclerc et al. 2000, Neurock 2004) as well as for the description of coke deposit in pyrolsys coils (Wauters and Marin 2001). These techniques have been applied to the generation of detailed and lumped kinetic mechanisms to analyse the pyrolysis of linear or branched alkanes. Scarce attention has been devoted to the pyrolysis of alkenes and more complex species such as cyclo-alkanes or naphthenes which fall into the main scope of this paper.
This paper presents the approach and the results of a kinetic generator for the analysis of the primary distribution products from hydrocarbon pyrolysis. In a chain radical mechanism, the formation of large alkyl, cyclo-alkyl or alkenyl radicals is typically the result of initiation, H-abstraction, radical addition as well as successive radical decomposition reactions. Care will be paid to the description of molecule identification procedure which enables unique and no ambiguous reactions. A novel molecule homomorphism algorithm and database managements make more acceptable the problem of the huge growth of components in each decomposition step. New theoretical results referring to the pyrolysis of alkenes and cyclo-alkanes are reported on the basis of Rice-Herzfeld (RH), Kossiakoff-Rice (KR) and Dente-Ranzi (DR) theories.

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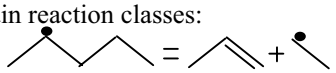
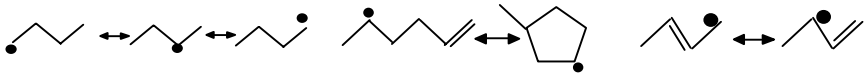
2. Kinetic Parameters and Kinetic Mechanism

This paper refers to the kinetic data reported by Ranzi et al. (1983, 1997) for the decomposition of normal and branched paraffins. Tab.1 reports the auxiliary data required by the analysis of cyclo-alkyl and alkenyl radical decomposition.

Although the formation of large hydrocarbon radicals follows different mechanisms, it can be easily demonstrated that the successive radicals decomposition is an autonomous process not influenced neither by the formation mechanism nor by the cracking mixture. As a consequence the evolution phase of a radical can be considered as a stand alone procedure which applies to any of the radicals while disregarding their formation. Radicals evolution involves two main reaction classes:

β-decomposition reaction, ex: 

isomerization reactions (internal H-abstraction reactions, 1-4 and 1-5 H transfer to form 5 or 6 membered rings and resonantly stabilized radical formation).



An example, a typical decomposition path of a n-octyl radical is reported in fig. 1

3. Kinetic generator

Aim of the kinetic generator (KG) is to produce the set and weights of the final products obtained by the decomposition of a radical mixture. In view of describing the minimum requirements of a KG, let us consider again the example of fig. 1. It is realised that KG needs :

a 'library of kinetic parameters' for the evaluation of the single reaction parameters ,

a 'proper molecule (radical/non radical) description' for the representation of each element in the whole reaction path,

Table1. Kinetic parameters for the pyrolysis of cyclo-alkane and alkenes.
(R=A exp-E/RT, Units are: kcal, mol ,l ,K, s)

H-Abstraction Reactions						
	Primary H atom		Secondary H atom		Primary allyl H atom	
	LogA	E	LogA	E	LogA	E
Primary alkyl radical	8.0	13.5	8.0	11.2	8.0	10.5
Primary alkenyl radical[a]	8.5	22.5	8.5	19.0	8.5	18.5
Isomerization Reactions of allyl radicals (Transfer of a Primary H-atom)						
	1-4 H Transfer		1-5 H Transfer		1-6 H Transfer	
Primary radical[b]	11.0	28.0	10.2	23.5	9.7	22.5
			5-membered ring		6-membered ring	
Cyclo-Addition Reactions			11.0	13.5	10.2	8.0
Cyclo-Alkyl Radical Decomposition Reactions (to form Primary Radicals)			13.7	28	13.7	31.5
Allyl Radical Decomposition Reactions-(to form dienes)					13.7	33.5

a. Corrections for secondary and tertiary radicals are the same as for alkyl radicals

b. E values for sec. and tertiary radicals are obtained by adding 1.5 and 2 kcal/mol.

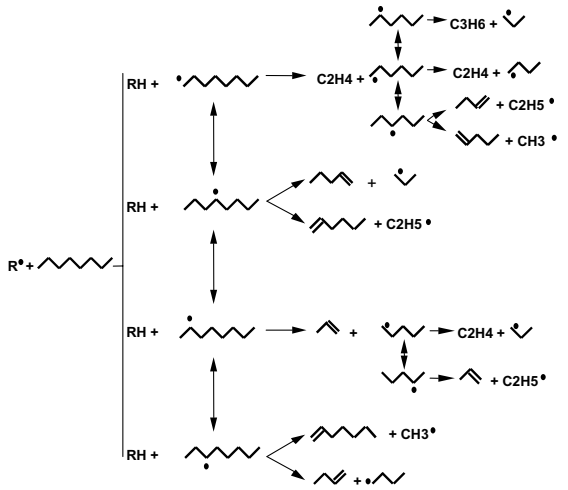


Figure 1. Decomposition paths of n-octyl radical

a ‘library of reaction types and rules’ which lists the possible formation and decomposition reactions and the rules for applying them plus the products which they form,

a ‘proper reaction path’ description which enables the recognition of the reaction type, its products as well as the sequence by which it is drawn into the path,

an ‘algorithm for molecule homomorphism’ i.e. a non ambiguous and effective statement whether two molecule descriptions refer to the same product or not

a ‘ numerical procedure’ which starting from the reaction path root, it completes it to the end and evaluates the weights of each final product. In doing this, the procedure should also offer the flexibility to follow different theoretical approaches such as Rice and Herzfeld (1934), Kossiakoff and Rice (1943) or Dente and Ranzi (1983).

Among the listed above items, the molecule description and homomorphism merit some additional attention. Dealing with hydrocarbons the molecule is univocally characterized by the carbon to carbon connections and the type of carbons involved. Tab. 2 reports the assumed correspondence between integer indexes and carbon types: they are used to represent a molecule, in a plane, as a sequence of integers.

Table 2. Correspondence between integer numbers and carbon types

	→ 21 22 23 22 2 1 1	
1 →— C	21 → C =	31 → C≡
2 →— C—	22 → —C =	32 → — C≡
3 →— C—	23 → —C =	42 → = C=
4 →— C—		

Rings also may be put into correspondence with integers which contain information about the ring members and their connections to the molecule chain. In this type of molecule representation, it is not necessary to further specify the connections between C and H atoms (see Wauters and Marin 2001).
The molecule homomorphism is based on a 'branch and chain' algorithm. A branch is a linear portion (including rings) which is connected to the molecule chain at its ends. A molecule is then divided into branches (see fig.2 a). Due to its linearity, it is assumed that the branch homomorphism, i.e. the statement whether two branches are identical, is a trivial problem. In facts two branches are checked for their length and position of possible unsaturated bonds. The molecule is represented as a graph whose nodes are the branches. The molecule homomorphism is then transformed into a graph homomorphism. Despite many algorithms present in literature, the one used by Steward (1965), (for the definition of an admissible output set of an algebraic system of equations) may be slightly modified to solve the problem at hand. For low interconnected graphs, substitution matrixes are an efficient way to represent them (see fig.2 a). The homomorphism of two graphs analyses their representation with the matrixes S1 and S2 which start at the first row and column with a branch-edge, i.e. one of the two extreme points of a branch which is not connected to any other branch. While S1 description is maintained fixed, S2 is rearranged from top to bottom with the aim of creating a chain equal to S2 (see fig.2 b). The rearrangement involves an exhaustive analysis of all the possible chains obtained by connecting each branch of S2 with admissible branches, i.e. those which are equal to the corresponding one in S1.

4. Performance of the kinetic generator

Most of literature data and results refer to the pyrolysis of linear/branched hydrocarbons. In such situations the whole set of compounds involved (intermediate and final) is limited to the order of hundreds. More complex is the situation when facing olefins or naphthenic compounds. Fig 3 refers to the pyrolysis of n-olefins. Similar results are obtained for naphthenic compounds. The reason of such 'explosive' number of components versus carbon number, stands essentially in the possibility to approach the number of all possible isomers (radicals and olefins) with carbon number less or

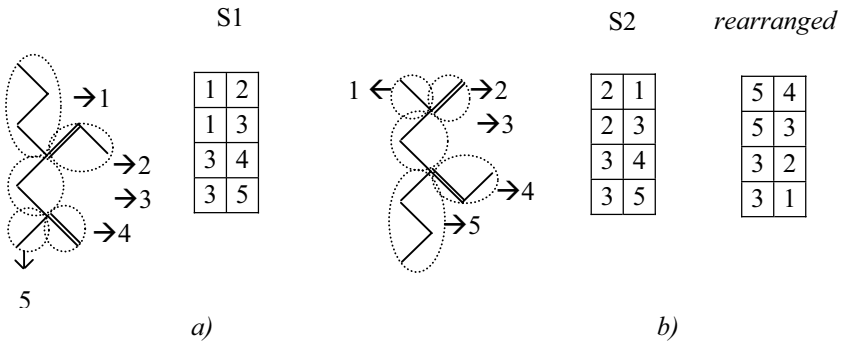


Figure 2. a) Molecule divided into branches and substitution matrix; b) Initial substitution matrix S2 of an equal molecule, and its content after rearrangement.

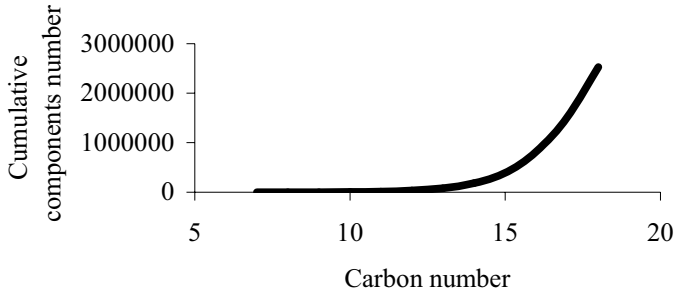


Figure 3. Components cumulated by the database vs Carbon number

equal to the initial one. Also the computing time for the creation of the reaction paths, suffers of serious limitations: while for n-octene is limited to few seconds, for a n-$C_{17=}$ lasts about 7 days (3.6 MHz, 1 G ram). Once a creation path has been created, it may be saved as a database and used by the numerical procedure for calculating the weights of final products. This phase does not need, in the worst conditions, more than few minutes.

It is evident, from the above considerations, that the results of a KG are of no practical use in the form they are obtained. It is neither of value nor of interest a kinetic model with millions of molecular species. It is more practical and of value to 'lump' the components with certain pre-assigned rules which satisfy the requirements, say, of a reactor model which will use them. From a computing point of view, it is supposed that a post-processor is linked to the KG with the purpose of 'lumping' the final products to a limited number of 'pseudo' components.

5. Kinetic Generator results

The set of key-final products of interest in pyrolsys prediction contains the major olefins and stabilized radicals (CH3, C2H5, …..). Let focus the attention on some of them obtained by the decomposition of n-olefins. Table 4 reports the results obtained at 1040K according with R, KR and DR approaches. It is worth to point out that the

Table 4. Product distributions of n-olefins decomposition at 1040 K, vs carbon number: KR= Kossiakoff –Rice, R=Rice, DR=Dente-Ranzi

	KR	R	DR	KR	R	DR	KR	R	DR	KR	R	DR	KR	R	DR
#C	*CH3*			*C2H5*			*C2H4*			*C3H6*			*C4H8*		
8	.139	.065	.085	.094	.029	.077	.109	.418	.216	.107	.077	.090	.062	.062	.074
10	.183	.032	.096	.264	.059	.234	.169	1.010	.203	.358	.118	.238	.230	.085	.148
12	.177	.026	.068	.260	.048	.232	.166	1.555	.199	.359	.095	.208	.234	.069	.114
14	.166	.022	.067	.258	.040	.231	.166	2.086	.186	.366	.080	.220	.243	.058	.130
16	.165	.019	.063	.263	.034	.226	.170	2.608	.178	.377	.069	.219	.250	.050	.128

practical absence of such data in literature does not allow any effective and direct comparison.

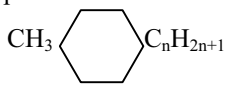
Table 5 refers to the decomposition of the homologous series of 1-alkyl-4-methyl-cyclohexane of the type:  with n=3 to 9

Table5. Primary distribution products from the pyrolysis of 1-alkyl-4-methyl-cyclohexanes decomposition at 1040 K, vs carbon number

	KR	R	DR	KR	R	DR	KR	R	DR	KR	R	DR	KR	R	DR
#C		*CH3*			*C2H5*			*C2H4*			*C3H6*			*C4H8*	
10	.353	.241	.320	.219	.167	.186	.147	.178	.093	.280	.290	.232	.030	.000	.008
11	.284	.243	.291	.199	.079	.078	.188	.254	.114	.258	.336	.238	.134	.081	.076
12	.338	.228	.285	.220	.023	.204	.187	.551	.201	.306	.347	.353	.146	.062	.073
13	.322	.218	.293	.245	.039	.205	.183	.753	.179	.337	.355	.358	.166	.057	.119
14	.306	.206	.285	.238	.036	.210	.188	1.069	.169	.353	.359	.327	.182	.053	.129
15	.298	.199	.274	.234	.034	.209	.191	1.261	.172	.359	.366	.326	.190	.049	.115
16	.299	.199	.269	.245	.032	.212	.195	1.568	.175	.374	.368	.343	.199	.046	.122

6. Conclusions

A kinetic generator of hydrocarbons pyrolysis mechanism has been described in details. The product distribution involves a number of components which rapidly increases whith the carbon number of the initial radical. This leads to the necessity of lumping the products to pseudo components. Novel results from the decomposition of n-olefins and naphthenic radicals are reported. Due to the lack of direct experimental information these results should be considered as a contribution to the reactors models used in several commercial applications.

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