ELSEVIER

Catalysis Today 52 (1999) 153–163

CATALYSIS TODAY

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Kinetic modeling of acid-catalyzed oil refining processes

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Abstract

In this paper the kinetic modeling of acid-catalyzed oil-refining processes is based upon the elementary steps of carbenium-ion chemistry. This completely avoids the lumping of species and reactions practised today. A number of reasonable assumptions, the introduction of the single-event concept, the Polanyi relation and thermodynamic constraints keep the number of kinetic parameters within tractable limits. The approach is applied to the simulation of a riser reactor for the catalytic cracking of gasoil. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Kinetic modeling; Carbenium ion; Zeolites

1. Introduction

Oil refining processes like catalytic reforming, cracking, hydrocracking, alkylation are carried out on acid catalysts, generally zeolites or alumina, loaded or not with metals. These processes involve reactions which modify the composition of oil fractions derived from the crude oil by atmospheric and vacuum distillation: naphtha, gasoil, vacuum gasoil (VGO), resid or, in the case of alkylation, gases from the other processes mentioned above. The transformation of these fractions aims at improving the quality in the sense of satisfying the product specifications set by their application (octane number, e.g. for gasoline) or to increase the yield of commercial products (gasoline, kerosine, diesel).

The fractions dealt with contain hundreds of components in measurable quantities and the same is true for the commercial products. Their composition varies with the origin and type of the crude oil, so that the process operating conditions have to be adapted to satisfy the rigorous product specifications. This has led to extensive experimentation in pilot units, generally of a rather empirical nature and requiring extrapolation to the industrial scale based upon rules of a heuristic nature which are part of the art developed inside the various companies. Clearly, this is a situation where modeling could significantly contribute. A comprehensive and reliable model could reduce the experimentation, improve the extrapolation, guide the plant operation and serve as a basis for its control. But it is evident also that the development of such a model is an overwhelming task, in particular because of the complexity of the feedstocks and of their transformations. Early attempts reported in the literature describe the process in terms of so-called lumps: the 3-lump model of Weekman and Nace [1] and the 10-lump model for catalytic cracking of Jacob et al. [2]. The 3-lump model considers gasoil, gasoline and coke+light gases in a triangular reaction network. The 10-lump

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PII: S0920-5861(99)00073-5

model consists of gasoline, cokes, light and heavy fuel oil. The light fuel oil (boiling range 220–350°C) contains light paraffins and naphthenes, aromatic rings in this range and side chains. The heavy fuel oil (boiling range 350–550°C) contains the heavy representatives of the above types of lumps. The reaction network now consists of 19 reactions. The kinetic equations are of the monomolecular type, but corrected by a single denominator accounting for the strong adsorption of the heavy aromatics. The influence of basic components and of coke formation is accounted for in a rather empirical way.

2. Analytical problems

A description of the composition mainly based upon boiling range and some very broad families of hydrocarbons or chemical groups of these is too crude a basis for a reliable model of the process, accurately predicting the properties of the products without resorting to extensive empirical correlations. Over the years the chemical analysis of the feedstocks has tremendously improved. Gas chromatography presently permits a component analysis of a gasoline. The combined GC-MS technique allows rapid analysis of VGO. Table 1 shows the hydrocarbon analysis of a partially hydrogenated VGO by means of a combined GC-MS technique [3].

This is an analysis that falls within the standard capabilities of the research departments of the oil companies. Further information can be obtained by HRMS. Padrta et al. [4] have reported analyses reaching as high as C_{60}. HRMS allows the identification of naphthenes with 1–6 rings and aromatic hydrocarbons and heteroaromatic molecules with 1–12 rings. NMR analysis constrains the iso-paraffin distribution per C-number since it provides information on the amounts of primary, secondary, tertiary and quaternary C-atoms. It also places constraints on the structure of the alkylsubstituents in the aromatic rings.

3. New developments in the kinetic modeling of complex processes

Today the modeling approach proposed by Liguras and Allen [5], Klein et al. [6], Quann and Jaffe [7,8],

Table 1
Detailed characterization of a hydrogenated VGO by means of GC-MS

*n*C	NPA (wt%)	IPAR (wt%)	MNA (wt%)	DNA (wt%)	TNAP (wt%)	QNA (wt%)	MAR (wt%)	DAR (wt%)	TAR (wt%)
14							1.24	0.047	
15	0.002						2.33	0.539	
16	0.016	0.002	0.004				2.71	1.51	
17	0.077	0.002	0.032	0.021			2.32	1.42	0.323
18	0.167	0.039	0.128	0.131	0.022		1.61	0.915	0.689
19	0.365	0.152	0.339	0.312	0.109	0.018	0.718	0.335	0.189
20	0.729	0.333	0.614	0.613	0.247	0.196	0.246	0.168	0.117
21	1.01	0.570	1.03	1.05	0.541	0.447	0.086	0.113	0.070
22	1.43	0.910	1.47	1.38	0.650	0.723	0.012	0.020	0.010
23	1.56	1.27	1.92	1.77	0.873	0.793			
24	1.86	1.60	2.38	2.22	1.24	0.873			
25	2.07	1.72	2.79	2.46	1.37	0.693			
26	1.65	1.45	2.59	2.27	1.09	0.533			
27	1.27	1.36	2.38	2.11	0.897	0.439			
28	0.900	1.11	2.07	1.93	0.615	0.395			
29	0.538	0.723	1.55	1.52	0.403	0.235			
30	0.343	0.426	1.15	1.14	0.163	0.118			
31	0.183	0.268	0.712	0.608	0.090	0.082			
32	0.115	0.163	0.405	0.248	0.092	0.060			
33	0.040	0.070	0.236	0.015	0.125	0.047			
Sum	14.3	12.2	21.8	19.8	8.52	5.65	11.3	5.06	1.40

NPA, IPAR: *n*- and *i*-paraffins; MNA, DNA, TNAP, QNA: mono-, di-, tri-, quater-naphthenes; MAR, DAR, TAR: mono-, di-, and tri-aromatics.

Froment and co-workers [9–13] starts from a much more detailed characterization of the feedstocks than in the 3- and 10-lump models. In the present paper the model development starts from a GC-MS analysis of the type shown in Table 1. The number of components or lumps identified in this oil fraction amounts to 127. Each "component" generates a complex reaction network. The number of molecular species generated in the network of catalytic cracking of a simple molecule like *n*-butylcyclohexane amounts to 1090. Determining the kinetics of all the reactions in which these species are involved is evidently an impossible task. Also, since the rate coefficient for a certain type of reaction increases with the C-number and the rate depends on the adsorption of the components of the reacting mixture, the work would have to be done over for each new feedstock. Considering the molecule as a whole in an approach called here "molecular level modeling" is not realistic. What has to be done is to decompose molecular reactions called "isomerization" or "cracking", e.g. into their "elementary steps" in terms of the underlying chemical mechanism, which involves carbenium ions. Fig. 1 shows elementary steps of isomerization in naphthenes, e.g. involving hydride- and methyl-shifts or a protonated cyclopropane intermediate when branching occurs.

Carbenium ions crack through the scission of C–C bonds in β-position with respect to the C-atom carrying the positive charge. In carbonium ions, produced by hydride abstraction from a saturated molecule leading to an unstable structure with a pentavalent C-atom, the protolytic scission occurs in α-position. The catalytic cracking network of *n*-butylcyclohexane contains 111 naphthenic molecules and 571 naphthenic carbenium ions. The former are involved in 1214 elementary steps (138 exocyclic protolytic scissions, 511 endocyclic protolytic scissions and 565 hydride abstractions), the latter in 2320 elementary steps (hydride-, methyl- and alkyl-shifts, PCP-branchings, aromatizations, β-scissions, deprotonations, etc.)

It should be clear by now that even if the number of elementary steps is gigantic, they belong to a very limited number of types. The kinetic modeling now becomes feasible, provided an experimental data based on the catalytic cracking of judiciously selected model components is available.

The approach is very similar to what has become widely accepted in thermal cracking [14–16] and polymerization [17] where the reaction is decomposed into elementary steps of radical chemistry (initiation, H-abstraction, radical decomposition, termination, etc. in thermal cracking); (initiation, chain growth by propagation, termination, etc. in polymerization). In reforming and in hydrocracking the acid catalyst is loaded with metals which promote dehydrogenations of saturated components into olefins and of these into di-olefins which react more rapidly than paraffins. Under normal conditions the rate determining step in the isomerization and cracking reaction is located on the acid sites. The (de)hydrogenation steps may then be considered to reach pseudo-equilibrium, so that no rate equations need to be determined for these steps.

In what follows the steps which have to be taken to develop a kinetic model for the catalytic cracking of a complex oil fraction and to apply it to an industrial unit will be briefly outlined.

4. Computer generation of networks of elementary steps

In what precedes, mention was made of the number of species and elementary steps comprised in the network of the catalytic cracking of as simple a molecule as *n*-butylcyclohexane. It is clear that such a network can only be generated by computer.

Clymans and Froment [18] and Baltanas and Froment [19] generated the elementary steps by means of Boolean relation matrices, in combination with an auxiliary vector further characterizing the chemical species. Fig. 2 represents a Boolean relation matrix of 2-methyl-3-hexyl-carbenium ion. The matrix element on the *i*th row and the *j*th column is "one" when there is a bond between carbon atoms *i* and *j*, if not a value "zero" is assigned to that element.

The number of ones on a row indicates if a C-atom is primary, secondary, tertiary or quaternary. The position of the positive charge is given in the auxiliary vector which also characterizes the nature of the C-atom (1: bridge-head aromatic, 2: bridge-head cyclo olefinic, 3: bridge-head naphthenic, 4: aromatic, 5: cyclo-olefinic, 6: naphthenic, 7: acyclic olefinic, 8:

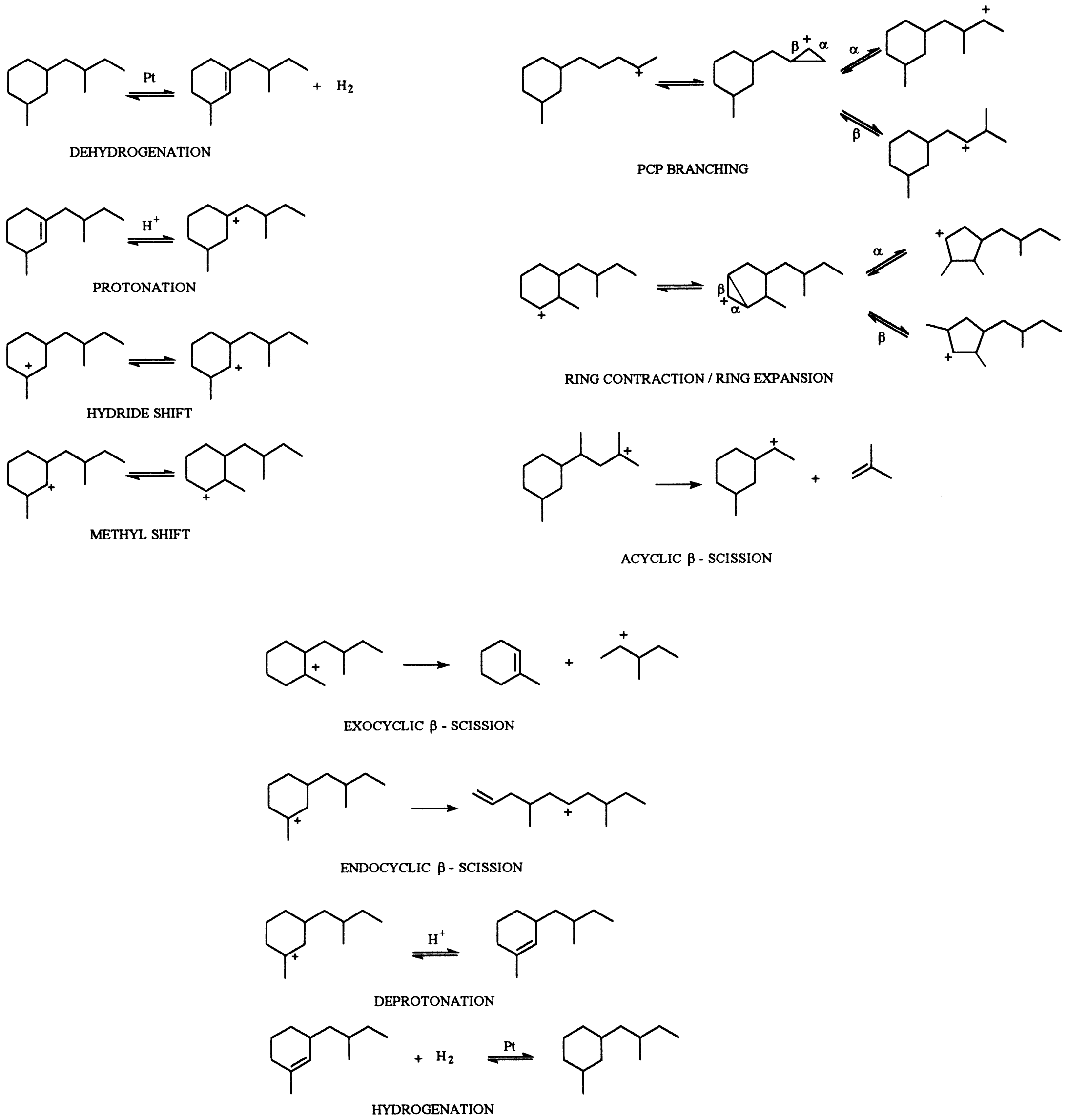


Fig. 1. Elementary steps for the isomerization and hydrocracking of naphthenes.

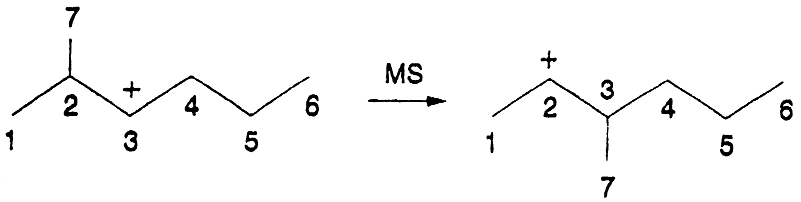
acyclic paraffinic). A standardized numbering of the C-atoms is a prerequisite, of course.

The isomer 3-methyl-2-hexyl carbenium ion is obtained from the first by a methyl-shift. In the Boolean relation matrix $\boldsymbol{B}_1$ the elements (2,7) and (7,2) are set zero, whereas in $\boldsymbol{B}_2$ the elements (3,7) and (7,3) are set to one. The position of the positive charge is adapted in the auxiliary vector and the location of the tertiary C-atom is changed. The β-neighbors of each C-atom can be identified from the matrix

$$\boldsymbol{M} = \boldsymbol{B}_1 \cdot \boldsymbol{B}_1 - \boldsymbol{I},$$

where $\boldsymbol{I}$ represents the identity matrix. Higher order relations (γ-positions, etc.) are identified from

$$\boldsymbol{M}_n = \boldsymbol{B}_{1(n-1)} \cdot \boldsymbol{B}_1 - \boldsymbol{B}_{1(n-2)}.$$



$$B_1 = \begin{array}{r|cccccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & \ldots & \mathrm{NMAX} \\ \hline
1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\
2 & 1 & 0 & 1 & 0 & 0 & 0 & \textcircled{1} & 0 & \ldots & 0 \\
3 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & \ldots & 0 \\
4 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & \ldots & 0 \\
5 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & \ldots & 0 \\
6 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \ldots & 0 \\
7 & 0 & \textcircled{1} & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\
8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\mathrm{NMAX} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0
\end{array}
\quad \xrightarrow{\mathrm{MS}} \quad
B_2 = \begin{array}{r|cccccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & \ldots & \mathrm{NMAX} \\ \hline
1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\
2 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\
3 & 0 & 1 & 0 & 1 & 0 & 0 & \textcircled{1} & 0 & \ldots & 0 \\
4 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & \ldots & 0 \\
5 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & \ldots & 0 \\
6 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \ldots & 0 \\
7 & 0 & 0 & \textcircled{1} & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\
8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\mathrm{NMAX} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ldots & 0
\end{array}$$

$$H_1 = \begin{array}{|ccccccc}
3 & & & & & & \\
1 & 3 & 2 & 2 & 2 & 1 & 1 \\
8 & 8 & 8 & 8 & 8 & 8 & 8
\end{array}
\qquad
H_2 = \begin{array}{|ccccccc}
2 & & & & & & \\
1 & 2 & 3 & 2 & 2 & 1 & 1 \\
8 & 8 & 8 & 8 & 8 & 8 & 8
\end{array}$$

Fig. 2. Representation of a methylshift from 2-methyl-3-hexyl- into 3-methyl-2-hexyl-carbenium ion by means of Boolean relation matrices and auxiliary vectors where 3 and 2 indicate the C-atom with the positive charge.

Elimination of a C–C bond in ***M***, representing β-scission results into two separate matrices representing the two products of the scission.

For species with a large number of C-atoms the Boolean relation matrices become very sparse, but they still occupy considerable computer memory. Therefore, the species of the network are stored on the basis of the auxiliary vector, whereas the elementary steps are based upon the matrix representation.

The network generation involves all the species, molecules and ions, and their elementary steps yielding intermediates and products.

The number of species in the network tremendously increases with the number of C-atoms of the components in the feed. A C_{20}-*n*-paraffin generates 417 iso-paraffins, 6417 olefins, 6938 acyclic carbenium ions, etc., a C_{40}-*n*-paraffin 4237 iso-paraffins, 151 057 olefins, 155 889, acyclic carbenium ions, etc. The CPU-time required for the generation of the complete reaction network starting from a given feed component and utilizing the rules of carbenium- and carbonium-ion chemistry becomes excessive beyond 20 C-atoms. From a scrutiny of the evolution of the network and the species with the C-number, recursive formulas were derived which permit to predict the number and identity of, e.g. the iso-paraffins with 40 C-atoms, without proceeding through the rigorous network generation.

5. Kinetic parameters

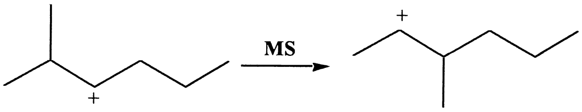
The next step towards the modeling of the catalytic cracking is the definition of the kinetic parameters. These have to be defined through the elementary step approach explained above, so as to limit their number.

A more refined view on these elementary steps is now required. A hydride – or a methyl shift, e.g. can involve a shift from a primary to a secondary carbenium ion, with a rate coefficient $k'_{\mathrm{HS}}(\mathrm{p,s})$ or $k'_{\mathrm{MS}}(\mathrm{p,s})$. To reduce the number of rate coefficients, methyl- and primary carbenium ions are disregarded because they are much less stable than s, t and q- ions. For the isomerizations, including these by PCP-branching, it can now be assumed that the rate coefficient is independent of the number of C-atoms and of the structure of the carbenium-ion. In other words: the energy level of a carbenium-ion is defined only by its type (s or t). This reduces the number of rate coefficients for the elementary steps of isomerization to 12 ($k'_{\mathrm{HS}}(\mathrm{s};\mathrm{s})$; $k'_{\mathrm{HS}}(\mathrm{s};\mathrm{t})$; $k'_{\mathrm{HS}}(\mathrm{t};\mathrm{s})$; $k'_{\mathrm{HS}}(\mathrm{t};\mathrm{t})$, etc.)

Care has to be taken here. In spite of the depth at which the chemical transformation are analyzed the rate coefficients of the elementary steps are not yet completely unambiguous.

6. From elementary steps to single events

Consider, e.g. the methyl-shift leading from the 2-methyl-3 pentylcarbenium ion to the 3-methyl-2 pentylcarbenium ion for which in terms of elementary step kinetics the rate coefficient would be written: $k'_{\mathrm{MS}}(\mathrm{s};\mathrm{s})$



Yet, intuitively, from left to right two methyl-groups can shift, but only one from right to left. In other words: a different value would be calculated for $k'_{\mathrm{MS}}(\mathrm{s};\mathrm{s})$ depending upon which isomer would be chosen in the experimental work. Evidently, characterizing a carbenium ion only by its type (p, s, t or q) is not sufficient. Its structure also has to be accounted for.

According to transition state theory, the rate coefficient of the transformation of A into a product through an intermediate activated complex may be written:

$$k' = \frac{k_{\mathrm{B}}T}{h}\exp\left(\frac{\Delta S^{0\neq}}{R}\right)\exp\left(\frac{-\Delta H^{0\neq}}{RT}\right), \tag{1}$$

where k_{B} is the Boltzmann constant and h the Plank constant. The standard entropy of a component consists of translational, vibrational and rotational contributions. The latter, selected here as representative for the structure, consist of an intrinsic term $\hat{S}^0$ and a term related to the symmetry number of the species, σ:

$$S^0 = \hat{S}^0 - R\ln(\sigma). \tag{2}$$

The change in standard entropy due to symmetry changes associated with the formation of the activated complex is given by

$$\Delta S^{0\neq}_{\mathrm{sym}} = R\ln\left(\frac{\sigma_r}{\sigma^{\neq}}\right). \tag{3}$$

Chirality is accounted for through the introduction of a global symmetry number, defined by

$$\sigma_{\mathrm{gl}} = \frac{\sigma}{2^n}, \tag{4}$$

where n is the number of chiral centers in the species.

Explicating now $\Delta S^{0\neq}$ in (1) by means of (3) leads to

$$k' = \frac{k_{\mathrm{B}}T}{h}\left(\frac{\sigma_{\mathrm{gl,r}}}{\sigma_{\mathrm{gl},\neq}}\right)\exp\left(\frac{\Delta S^{0\neq}}{R}\right)\exp\left(\frac{-\Delta H^{0\neq}}{RT}\right) \tag{5}$$

or

$$k' = n_{\mathrm{e}}k \tag{6}$$

with

$$n_{\mathrm{e}} = \frac{\sigma_{\mathrm{gl,r}}}{\sigma_{\mathrm{gl},\neq}}. \tag{7}$$

The rate coefficient of an elementary step, k' is a multiple of that of a single event, k. The number of single events is represented by n_{e}. Application of the theory to the methyl shift mentioned above shows that from left to right the elementary step consists of two single events, whereas from right to left $n_{\mathrm{e}}=1$.

The computer calculation of the number of single events in an elementary step requires the knowledge of the configuration of the transition state. Present day quantum chemical packages like MOPAC or GAMESS, in particular the ab initio versions, lead to values for the energy level of the transition state which are in agreement with the scarse experimental data. The nature of the link of the carbenium ion to the zeolite is a problem. From IR-spectroscopy, high resolution MAS^{13}C-NMR and ab initio quantum chemical calculations, Kazansky [20,21] concluded that alkylcarbenium ions are rapidly converted into surface alkoxy groups which are covalently bonded to the surface oxygen ions. The global symmetry number of such a configuration is different from that of a free carbenium ion, but the effect of the zeolite is the same for the reactant and the transition state, so that the number of single events, which is the ratio of the global symmetry numbers, is the same as that calculated from the free configurations.

What has been achieved by splitting off the number of single events from the rate coefficient of an elementary step, i.e. by the introduction of the concept of single event rate coefficient, is to account for the effect of structure on the change of entropy. The possible effect of the structure on the standard enthalpy of activation for the formation of the activated complex is not accounted for.

Only now, with the introduction of the single event concept, it can be guaranteed that only four rate coefficients (single event) per type of isomerization are sufficient.

7. Further reduction of the number of single event rate coefficients

Since the number of olefins becomes overwhelming when the number of carbon atoms is large it is inevitable to introduce assumptions for the single events involving olefins, like protonation and alkylation, e.g. for these events it is assumed that the rate coefficient does not depend on the olefin. Justification for this is the structure of the activated complexes which are close to that of the reacting olefin.

Thermodynamic constraints further contribute to the reduction of the number of independent single event rate coefficients. Assuming, e.g. that the deprotonation rate coefficients are also independent of the olefins would lead to values that are thermodynamically inconsistent. The following relation can be derived [10]

$$k_{\mathrm{De}}(\mathrm{m};\mathrm{O}_j) = k_{\mathrm{De}}(\mathrm{m};\mathrm{O}_\mathrm{r})K_{\mathrm{isom}}(\mathrm{O}_\mathrm{r} \Leftrightarrow \mathrm{O}_j), \tag{8}$$

where m stands for s or t and $\mathrm{O_r}$ for a reference olefin with the double bond in such a position that both a secondary or a tertiary carbenium ion can be formed by protonation. Consequently, for a given C-number there are only two independent single-event rate coefficients: $k_{\mathrm{DE}}(\mathrm{s;O_r})$ and $k_{\mathrm{DE}}(\mathrm{t;O_r})$. This reduces the number of single event rate coefficients for deprotonation in the catalytic cracking of *n*-octane, e.g. from 85 to 7 (2 for $\mathrm{C_8}$-, 2 for $\mathrm{C_5}$-, 2 for $\mathrm{C_4}$- and 1 for $\mathrm{C_3}$- carbenium ions).

8. Accounting for the identity of the carbenium ions

The single event rate coefficients discussed here account for the type of the carbenium ion (s,t) involved in the single event but also for the identity, i.e. the structure of the carbenium ion. This is done through the effect on the variation of the entropy, expressed in terms of the change of symmetry associated with the transition from the reactant to the activated complex. Is this the complete picture? Also, is there no effect of the number of carbon atoms in the ion?

Some insight into these aspects may be gained from the relation between the activation energy of an elementary step and the reaction enthalpy proposed by Polanyi [22] and which is written for an exothermic step

$$E_\mathrm{a} = E_0 - \alpha|\Delta H_\mathrm{r}| \tag{9}$$

and for an endothermic step

$$E_\mathrm{a} = E_0 + (1-\alpha)|\Delta H_\mathrm{r}|. \tag{10}$$

The Polanyi parameters E_0, called "intrinsic activation energy" and α, called "transfer coefficient" take on unique values for a given type of elementary step or single event (protonation, H- or Me-shift, etc.)

The activation energy E_a enters into the Arrhenius-type expression for the temperature dependence of the single event rate coefficient

$$k = A^* \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{11}$$

in which A^* is a modified frequency factor, since the structure effect on ΔS^0 has been accounted for by factoring out the number of single events, n_e.

The Polanyi-relation reduces right away the number of parameters in the kinetic model: there are only two parameters E_0 and α per type of single event, compared to four frequency factors and four activation energies as mentioned in Section 5. The value of ΔH_r for a certain type of single event can be reliably calculated when the standard heat of formation of reactant and activated complex are accurately known. But the activation energy E_a can only be calculated when E_0 and α are known for the various types of single events. These have to be estimated from experimental data on the rates of transformation of judiciously chosen components. It should be added here that α is usually quite different from the value of 0.5, which is often used in the literature in the absence of specific information.

Park and Froment [23] calculated ΔH_r values for a set of alkylations $\mathrm{R}_i^+ + \mathrm{O}_j$, using Pople's STO-3G minimal basis ab initio approach. Experimental data were available for the estimation of E_0 and α. The influence of the number of C-atoms in the olefin and of the structure of the olefin and carbenium ion for a given C-number were found to be of the order of 8%. The main effect comes from the type of the carbenium ion (s or t), as emphasized in the preceding.

9. Rate equations at the single event level

Consider by way of example the rate of an elementary step consisting of the β-scission of a paraffinic secondary carbenium ion R_1^+ into an acyclic olefin and an acyclic paraffinic carbenium ion R_2^+. The rate equation can be written

$$r_\beta = n_\mathrm{e} k_\beta(\mathrm{s};\mathrm{s}) \mathrm{C}_{\mathrm{R}_1^+}. \tag{12}$$

The inaccessible concentration of R_1^+ can be expressed in terms of accessible partial pressures of paraffins and olefins through a pseudo-steady state balance considering its rate of formation and disappearance. The formation occurs by protonation of olefins, protolytic scission of paraffins and hydride transfer between the paraffin P_1 and adsorbed carbenium ions, the disappearance by deprotonation and hydride transfer from paraffins. The equation for $C_{\mathrm{R}_1^+}$ can be written:

$$\begin{aligned}\mathrm{C}_{\mathrm{R}_1^+} = \frac{1}{N}\Bigg[&\left(k_\mathrm{pr}(s)(1 - C_{\mathrm{B}^+}) \sum_j (n_\mathrm{e})_\mathrm{pr} K'(\mathrm{O}_j \Leftrightarrow \mathrm{O}_\mathrm{r}) p_{\mathrm{O}_j}\right) \\ &+ k_\mathrm{protol}(s)(1 - C_{\mathrm{B}^+}) \sum_j (n_\mathrm{e})_\mathrm{protol} p_{P_j} \\ &+ k_\mathrm{ht} C_{\mathrm{B}^+} (n_\mathrm{e})_\mathrm{ht} p_{P_1}\Bigg],\end{aligned} \tag{13}$$

where $N = (n_\mathrm{e})_\mathrm{av.De} k_\mathrm{De}(\mathrm{s}) = k_\mathrm{ht} \Sigma_{j=1} (n_\mathrm{e})_{ht} p_{P_j}$

K' is the equilibrium constant for the isomerization between O_j and O_r. $(n_\mathrm{e})_\mathrm{av.De}$ represents an average of n_e for the deprotonation events of R_1^+ and C_B^+ is the relative concentration of Brønsted sites covered by carbenium ions, so that

$$\mathrm{C}_{\mathrm{B}^+} = \sum \mathrm{C}_{\mathrm{R}_1^+}. \tag{14}$$

Elimination of $\mathrm{C}_{\mathrm{R}_1^+}$ between (12) and (13) yields the rate equation for this type of single events, expressed in terms of accessible partial pressures in the gas phase.

In hydrocracking of lighter fractions, which occurs at lower temperatures than catalytic cracking, the physisorption of the components in the zeolite cages have to be explicitly accounted for [12].

10. Rate equations for a partially lumped model

Since the network generation starts from individual components and considers all possible elementary steps the number of species thus obtained is extremely large (for n_e=40 it amounts to 5 160 748). In setting up the kinetic model lumping is inevitable, were it only to come to a reasonable set of equations and a tractable output. The lumps should in the first place be chosen in terms of the present day analytical capabilities, as exemplified by the feedstock analysis given in Table 1. In doing so the initial values of the partial pressures which enter into the rate equations are available.

Assigning a partial pressure to the components inside a lump can only be exact when equilibrium between them is guaranteed. Rate equations for the transformation of lump L_1 into a lump L_2 can then be derived. This rate is the sum of rates of all the elementary steps which convert all the carbenium ions and molecules of L_1 into carbenium ions and molecules of L_2. By way of example the rate of isomerization by PCP-branching of a paraffinic lump L_1 into lump L_2 is written:

$$\begin{aligned}r_\mathrm{PCP}(\mathrm{L}_1 \to \mathrm{L}_2) = &\sum_{\mathrm{s,s}} \mathrm{C}_{\mathrm{R}_i^+}(\mathrm{s}) n_\mathrm{e} k_\mathrm{PCP}(\mathrm{s};\mathrm{s}) D(\mathrm{s}) \\ &+ \sum_{\mathrm{s,t}} \mathrm{C}_{\mathrm{R}_i^+}(\mathrm{s}) n_\mathrm{e} k_\mathrm{PCP}(\mathrm{s},\mathrm{t}) D(\mathrm{s}) \\ &+ \sum_{\mathrm{t,s}} \mathrm{C}_{\mathrm{R}_i^+}(\mathrm{t}) n_\mathrm{e} k_\mathrm{PCP}(\mathrm{t};\mathrm{s}) D(\mathrm{t}) \\ &+ \sum_{\mathrm{t,t}} \mathrm{C}_{\mathrm{R}_i^+}(\mathrm{t}) n_\mathrm{e} k_\mathrm{PCP}(\mathrm{t};\mathrm{t}) D(\mathrm{t})\end{aligned} \tag{15}$$

where n_e is the number of PCP single events for (s;s), (s;t), etc. transformations and D(s) and D(t) represent the fraction of secondary or tertiary carbenium ions which desorb by hydride transfer. By eliminating the carbenium ion concentrations by equating the rate of formation and disappearance of the carbenium ions (quasi-steady state approximation) and by accounting for the total site balance leads to the following equation:

$$\begin{aligned} r_{\mathrm{PCP}}(\mathrm{L}_1 \rightarrow \mathrm{L}_2) = & (LC)_{\mathrm{PCP}}(\mathrm{s};\mathrm{s}) \cdot F_{\mathrm{PCP}}(\mathrm{s};\mathrm{s}) \cdot p_{\mathrm{L}_1} \\ & + (LC)_{\mathrm{PCP}}(\mathrm{s};\mathrm{t}) \cdot F_{\mathrm{PCP}}(\mathrm{s};\mathrm{t}) \cdot p_{\mathrm{L}_1} \\ & + (LC)_{\mathrm{PCP}}(\mathrm{t};\mathrm{s}) \cdot F_{\mathrm{PCP}}(\mathrm{t};\mathrm{s}) \cdot p_{\mathrm{L}_1} \\ & + (LC)_{\mathrm{PCP}}(\mathrm{t};\mathrm{t}) \cdot F_{\mathrm{PCP}}(\mathrm{t};\mathrm{t}) \cdot p_{\mathrm{L}_1}. \end{aligned} \tag{16}$$

The factors F_{PCP}(m;n) contain various single event rate coefficients. $(\mathrm{LC})_{\mathrm{PCP}}$(m;n) are so-called lumping coefficients. These depend on the network of elementary steps and the choice of the lumps only, not on the single event rate coefficients.

For carbon numbers exceeding 20, the network generation becomes very time- and memory-consuming. The shortcut recursive formulae used to obtain the number and identity of descendants were also used to calculate the lumping coefficients. Fig. 3 shows the LC for the isomerization of *n*-paraffins into *i*-paraffinic lumps for (s;s) PCP-isomerization as a function of the carbon number. The curve calculated from the recursive formulae perfectly overlaps with that generated by the rigorous method so that extrapolation to the higher carbon numbers is justified.

The kinetic model for VGO-cracking contains 646 components and lumps: 40 normal- and 39 iso-paraffins; 40 normal- and 37 iso-olefins; cyclopentane; 35 mono-, 31 di-, 27 tri-, 23 tetranaphthenes with saturated side chain; 35 mono-, 31 di-, 27 tri-, 23 tetra-aromatics with saturated side chain; 33 mono-, 29 di-, 25 tri-, 21 tetra-aromatics with olefinic side chain; 36 mono-, 31 di-, 27 tri-, 23 tetra-cyclic olefins; 6 naphthenomono-, 5 naphthenodi-, 5 naphthenotri aromatics with saturated side chain; 6 naphtheno-mono-aromatic, 5 naphtheno-diaromatic- and 5 naphtheno-triaromatic cyclic olefins.

There are 44 169 reactions at the molecular level between these species (be it a component or a lump). Each reaction at the molecular level contains all the elementary steps occurring in the molecules or ions leading from reactant to product species. For a lump all possible components are considered in the conversion, i.e. the lump is not represented by a pseudo-component, except in the calculation of the thermodynamic properties by Benson's group contributions.

11. Application of the single-event kinetic model to riser catalytic cracking of vacuum gasoil

In a riser reactor the feed is injected at the bottom, it is vaporized by the hot catalyst recycled from the

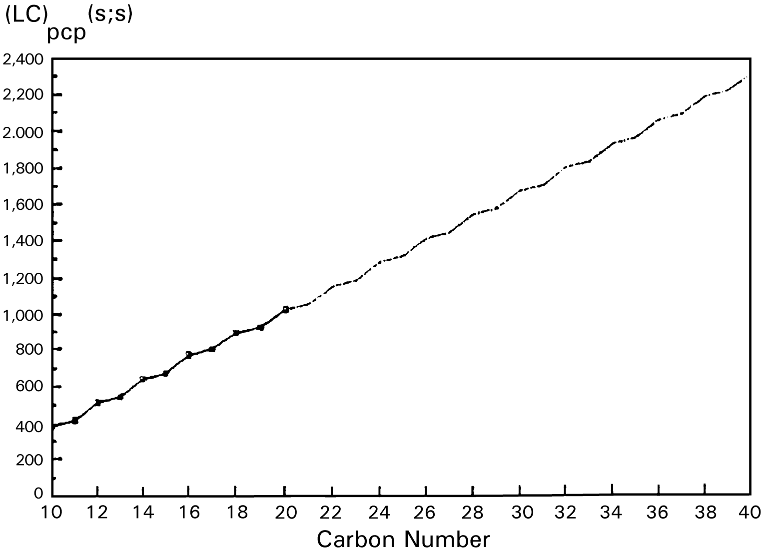


Fig. 3. Lumping coefficient for the isomerization of *n*-paraffins into isoparaffinic lumps by (s;s) PCP-isomerizations vs. the lump carbon number.

regenerator and flows upwards while reacting on the entrained catalyst. The reactor model used in the simulation of a typical commercial riser is a one-dimensional heterogeneous model with plug flow and slip between the phases [24]. Fig. 4 shows the evolution of groups of the lumps considered here and traditionally used to represent the effluent of a catalytic cracking reactor: LPG, gasoline, light and heavy fuel oil, encountered already in the 10-lump model of Jacobs et al. [2]. The heavy fuel oil (HFO) yield monotonically decreases over the riser with its height of 50 m and diameter of 1.24 m. The light fuel oil (LFO) yield initially drastically decreases and then shows a very broad maximum. The gasoline yield monotonically increases, initially very rapidly. The LPG-yield continuously rises.

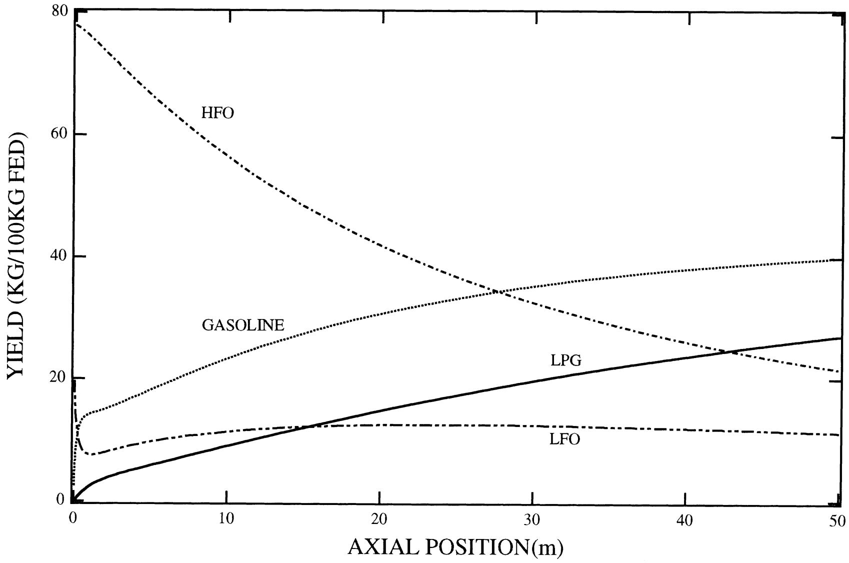


Fig. 4. Evolution of LPG, gasoline, light and heavy fuel oil along the riser for catalytic cracking.

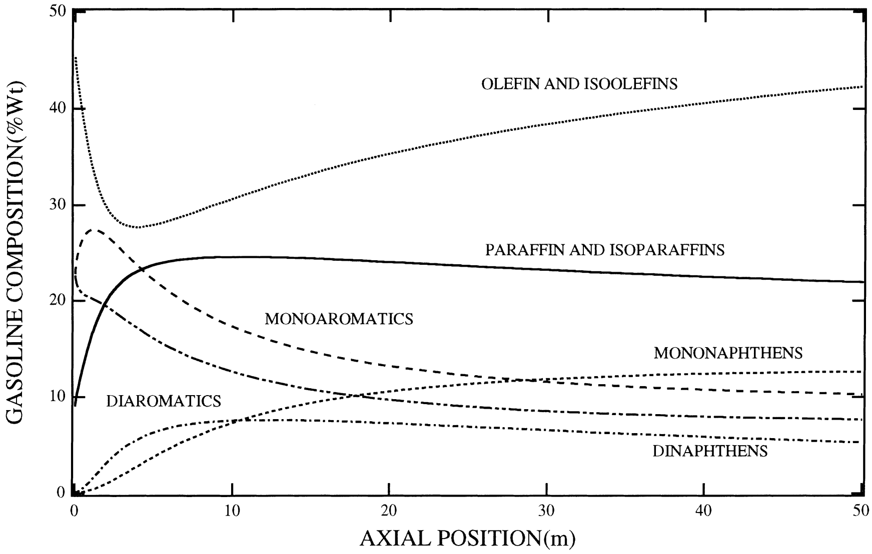


Fig. 5. Evolution along the riser of the gasoline composition.

Fig. 5 shows the evolution of the composition of the gasoline along the riser. This composition is also expressed in terms of a number of lumps, built up from a large number of molecules. It should be clear by now that the lumps defined here are only used to represent the results in a concise way.

12. Conclusion

The single event approach allows to develop a detailed kinetic model for reactions on acid catalysts leading to invariant rate coefficients, i.e. not depending on the feedstock composition. These can be determined from experiments with relatively simple but judiciously chosen components whose reactions imply basic features of carbocation chemistry. The application of the kinetic model in the simulation of commercial processes yields a wealth of information, valuable in guiding the process operation and the optimization of the catalyst. Lumps are introduced to account for the limitations of present day analytical tools only. Groups of these lumps yield an output interface with various levels of sophistication depending upon the tasks and objectives of the users. A basis is now available for extending the approach to even more complex feeds. Modern catalytic cracking also processes feedstocks ranging into the resid oil fraction. Also, catalyst deactivation by coke formation has to be accounted for. The rate of coke formation is probably best dealt with along the lines presented here for the "main" reactions [25]. The feedstocks also contain basic nitrogen compounds, and nickel- vanadium- and iron- containing compounds whose reactions lead to catalyst deactivating substances. These reactions too can be described in terms of detailed mechanisms so as to save experimental efforts.

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