KINETIC METHODS IN PETROLEUM PROCESS ENGINEERING

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Abstract

Kinetic modelling of petroleum processes is particularly difficult given the complexity of the feedstocks. Different lumping strategies are proposed according to the petroleum cuts type. As a paradox, a microkinetic method does allow a "late" lumping method for the case of distillates and bifunctional heterogeneous catalysis. The construction of a so-called "single-events" model consists in: (a) an automated generation of the complete network of reaction elementary steps; (b) a reduction in the number of kinetic constants; (c) a rigorous *a posteriori* relumping. Furthermore, an alternative late lumping method, not requiring network generation, has been developed. The extrapolation ability of the model is demonstrated by simulations of Fischer–Tropsch waxes hydrocracking. Finally, the perspectives of kinetic modelling by single-events are given.

I. Introduction

Thermodynamics (far from and close to equilibrium) is the mother of all sciences (Prigogine, 1996). Applied to gas–liquid equilibria, it was expressed very generally as follows: the equations of state f(P, V,T,N,parameters) $=$ 0. The latter could be, e.g., cubic or based on statistical physics. These equations of state are sufficiently generic to serve as a calculation basis for practically all separation unit operations (distillation, adsorption, extraction). It led to the development of commercial flowsheeting[1] software capable of simulating process diagrams, and the sequencing of their steps, for virtually all hydrocarbon-containing mixtures. In these programs, however, the reaction section modules available to "Process Engineering" professionals remain extremely poor and simplified.

The design of chemical reactors (Trambouze *et al.*, 1984) is based primarily on the laws of chemical kinetics. These laws are only general as regards their elementary steps, by definition of first order with respect to the reaction intermediates. When these elementary steps are poorly understood, which is the case in particular for heterogeneous reactions, no general expression is available which would make calculations of the degree of conversion of reactions even slightly generic. This situation explains why simulation methods have not been developed for chemical reactors as systematically as for the other unit operations; the reactors remain based on the use of apparent kinetics, with no intrinsic physical meaning, and contingent on each particular application.

Nevertheless, Chemical Kinetics is the key for development of processes in general (Froment and Bischoff, 1990), and more especially for the development

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[1] FLOWSHEETER = Process diagram calculation software package. Examples: ASPEN^{TM}, PROII^{TM}, HYSIS^{TM}.

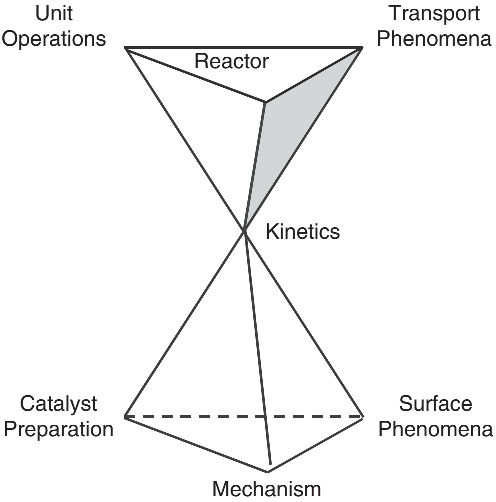

FIG. 1. Catalytic reaction engineering.

of *catalytic processes*. This essential science bridges the gap between two major disciplines: Catalysis and Process Engineering. It is a fundamental activity founded on the description that can be made of the catalytic act (physico-chemistry of solids, surface sites, elementary reaction mechanisms). Combined if necessary with the transfer laws, chemical kinetics is the applied tool enabling this contact catalysis (design, dimensioning and extrapolation of catalytic reactors) to be implemented, Fig. 1 (Marin *et al.*, 2000).

It allows the transition from the nanoscale of molecular processes to the mesoscale of unit operations (Charpentier, 2000).

The methodology of the kinetic approach is well understood when a molecular analysis of the feedstock is available. This is usually the case for the manufacturing processes of the major petrochemical intermediates. Although generally costly and time consuming, a complete kinetic study is possible if the method is systematically applied to each constituent identified at molecular level in the feedstock. The domain of refining is much more complex and the method is difficult to apply.

Refining operations (of which at least 80% are catalytic processes) are designed to transform and purify various petroleum cuts, derived from primary distillation, into the various fuels and refined products. As a reminder, a list of the main refining units is shown as a simplified refining scheme in Figs. 2 and 3.

Petroleum cuts, derived from crude oils, mainly consist of a continuum of paraffins,[2] naphthenes[3] and aromatic compounds, which are traditionally

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[2] Paraffin = alkane.

[3] Naphthene = (alkyl-) cyclo-alkane.

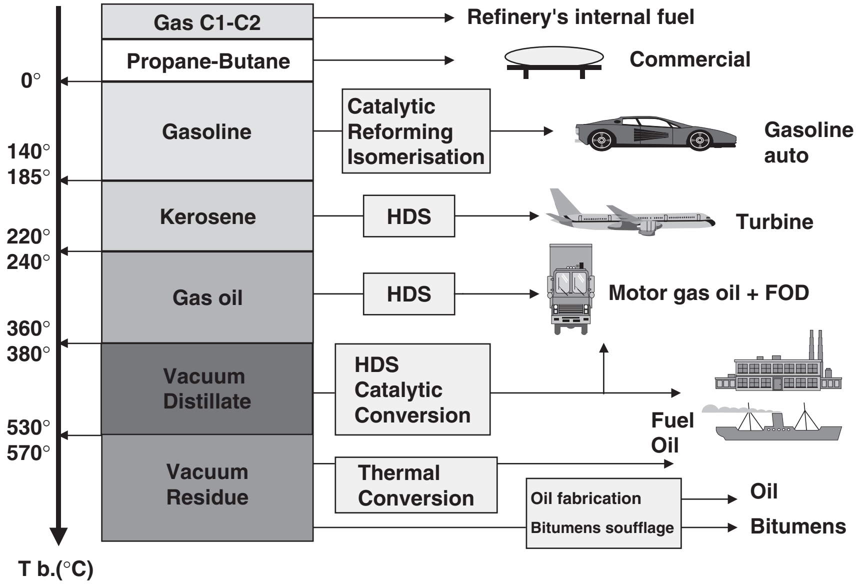

FIG. 2. Refining.

classified, depending on their distillation intervals, into various "gasoline", "diesel", "distillate" and "residue" cuts, from the lightest C5 compounds to the heaviest C50 + compounds, Fig. 4.

Petroleum cuts are extremely complex mixtures, however, which may contain several thousand chemically different molecules. Table I (Read, 1976) indicates the number of possible isomers according to the number of carbon atoms, thereby giving an idea of the complexity of the mixtures involved.

Analysis of feedstocks and effluents undeniably represents the main "bottleneck" for kinetic modelling of complex mixtures.

In addition to traditional monitoring analyses and standardised measurement of the various petroleum properties, modern analytical models now also include determination of the chemical composition of feedstock and recipes.

(1) In Fig. 5, the advanced (but difficult) analytical techniques developed at the IFP[4] (Fafet and Magné-Drisch, 1995) involve preparative liquid chromatography to separate the saturated and aromatic extracts, on adsorbents such as silica gels [the S.A.(R.(A.)) method[5]].
(2) Each extract is then analysed separately by coupling gas chromatography (GC) to mass spectrometry (MS).

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[4] IFP = Institut Français du Petrole, BP.3, F-69390 Vernaison, France.

[5] S.A.(R.(A.)) = Saturates, Aromatics, (Resins, (Asphaltenes)).

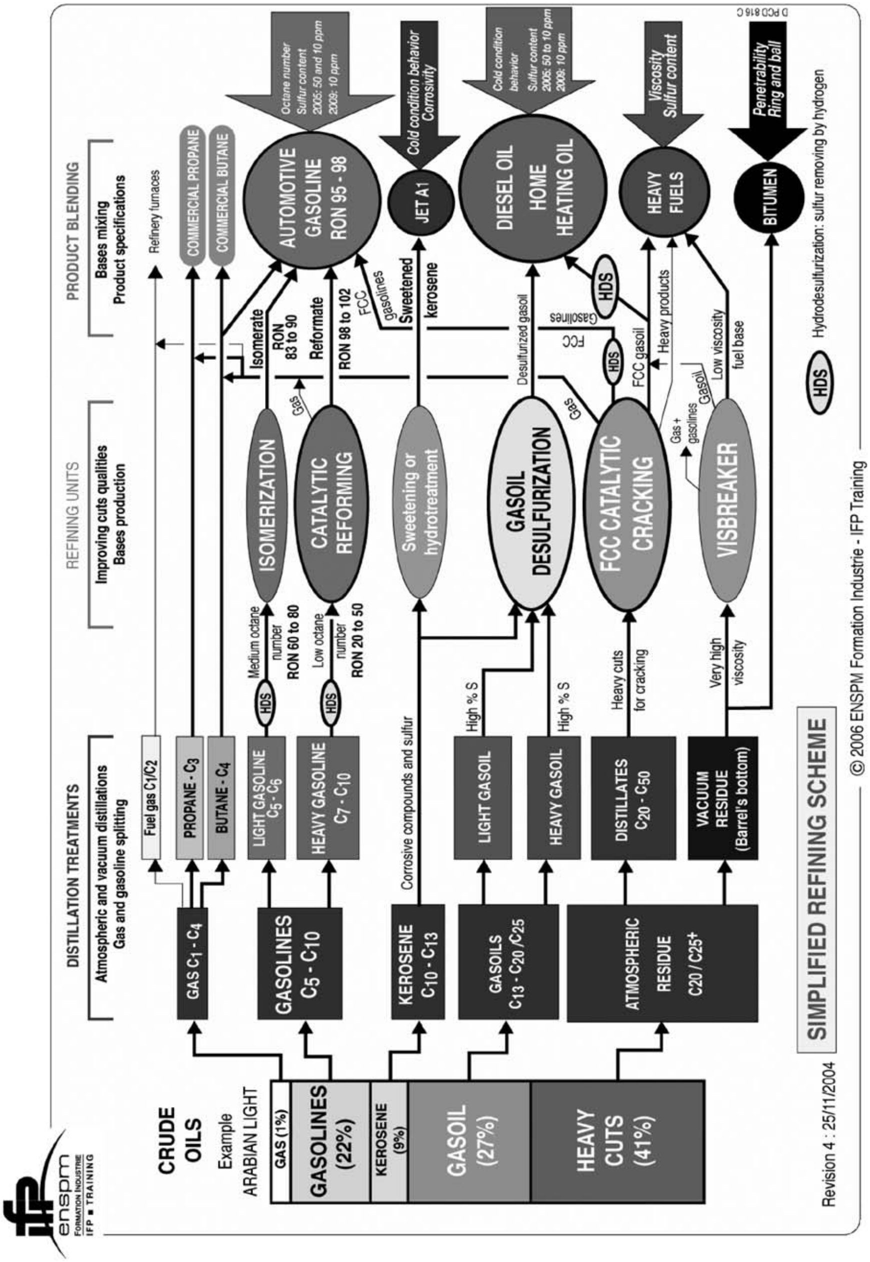

FIG. 3. Simplified refining scheme.

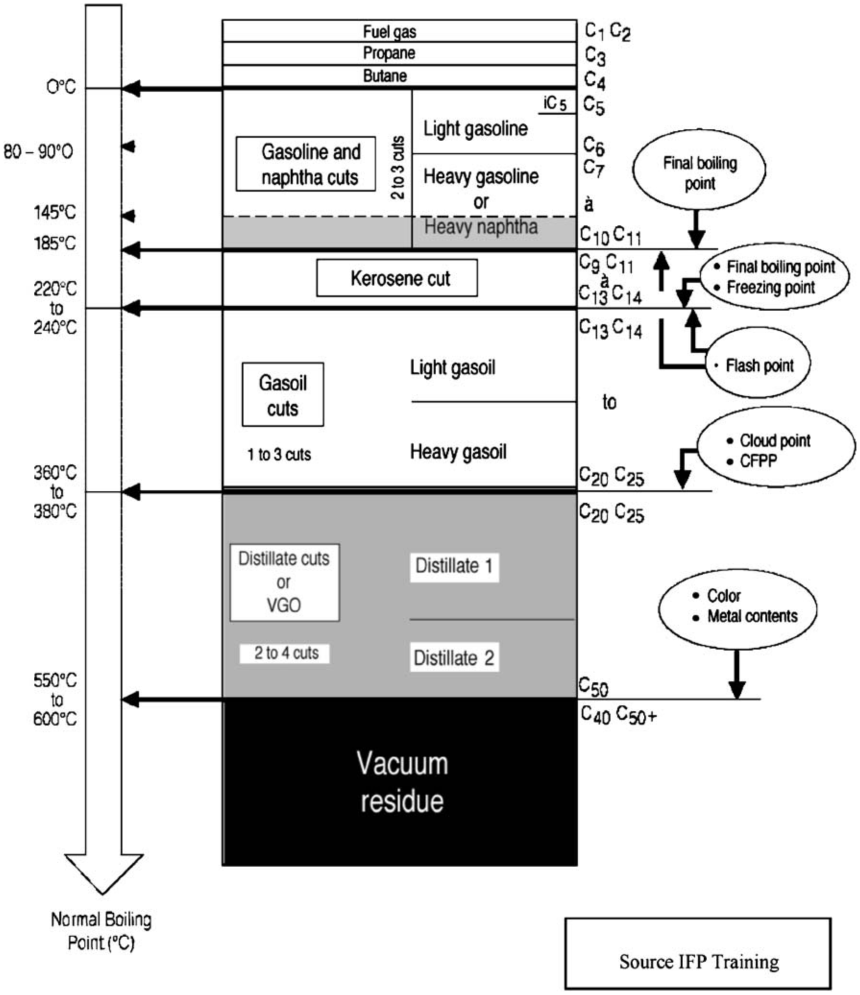

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FIG. 4. Crude oil fractionation—volatility and cut points constraints.

This method gives the distribution by family (paraffins, isoparaffins, naphthenes with one or more rings, etc., aromatics) and by number of carbon atoms (up to a maximum of C33 for saturated compounds and up to C22 for aromatic compounds).

For example, Fig. 6 provides the weighted analysis, as detailed as possible (Hillewaert, 1986), obtained for a vacuum gas oil (VGO) after partial hydrogenation, with a density at 300 K of 0.832 kg/m^3 and a distillation interval ranging from 300 to 480+.[6]

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[6] 480+ = Petroleum cut whose distillation interval exceeds a temperature of 480°C.

TABLE I
STRUCTURAL ISOMERS OF DIFFERENT HYDROCARBON TYPES

Carbon number	Paraffins	Olefins	Alkylbenzenes
5	3	5	–
10	75	377	22
15	4,374	36,564	2,217
20	366,319	4,224,993	263,381
25	36,797,588	536,113,477	33,592,349

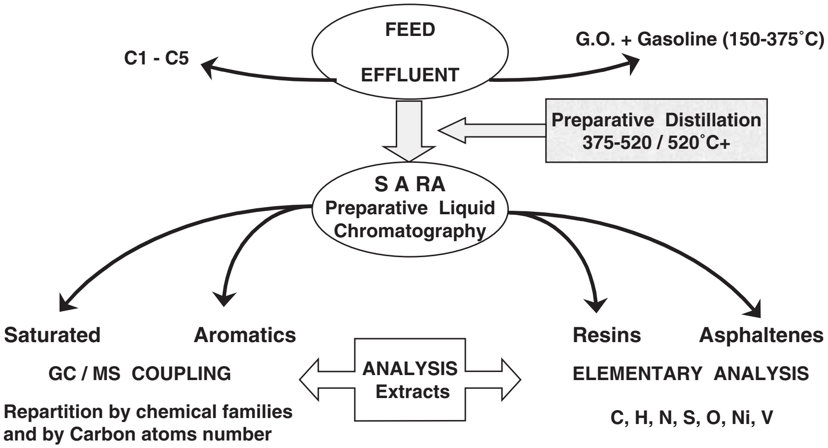
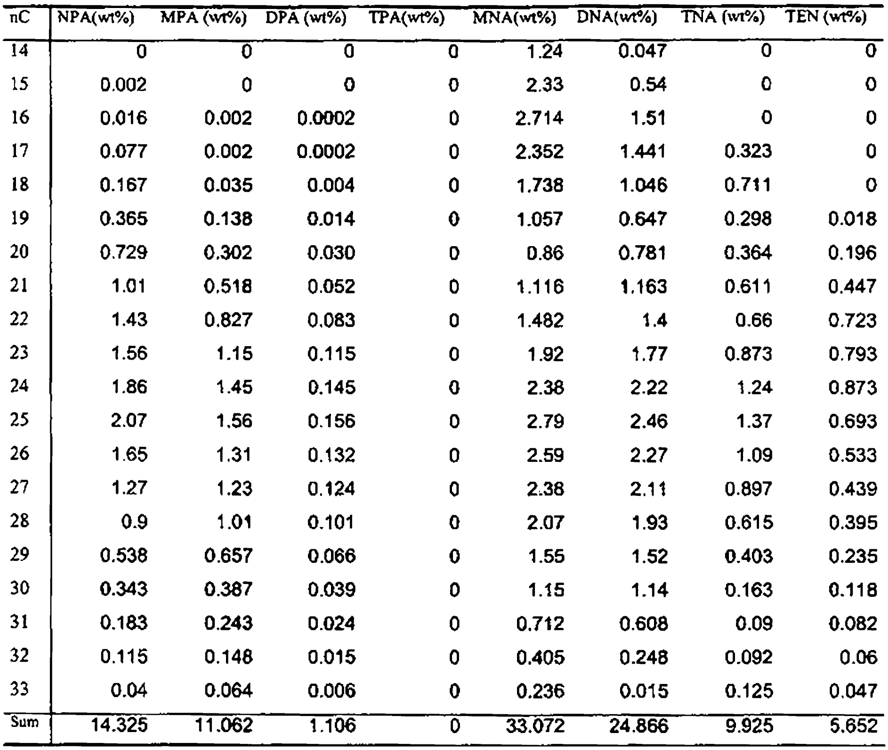


FIG. 5. Analytical set.

Despite their sophistication, it is clear that these advanced analysis methods can only be applied to the various light, middle and heavy "distillates", according to their origin ("atmospheric", "vacuum"). For petroleum cuts involving "residues", this type of pseudo molecular description cannot be obtained, so a way must be found to "reconstruct" it.

Since there is no detailed analysis at molecular level, kinetic modelling of complex mixtures raises a problem of methodology which clearly demands a scientific approach (Astarita and Sandler, 1991; Sapre and Krambeck, 1991). Petroleum cuts contain so many molecules and isomers, with such large variations in structure and chemical composition that their physico-chemical properties vary almost continuously with the number of carbon atoms.

Several attempts have been made to construct a "kinetics of continuous reactions" (Aris and Gavalas, 1966; Astarita and Ocone, 1988). These mathematical developments mainly use either distribution functions to represent variations in molecule reactivity according to their chain lengths or boiling points for example (Aris, 1989), or the method of moments (Kodera *et al.*, 2000;



nC	NPA(wt%)	MPA (wt%)	DPA (wt%)	TPA(wt%)	MNA(wt%)	DNA(wt%)	TNA (wt%)	TEN (wt%)
14	0	0	0	0	1.24	0.047	0	0
15	0.002	0	0	0	2.33	0.54	0	0
16	0.016	0.002	0.0002	0	2.714	1.51	0	0
17	0.077	0.002	0.0002	0	2.352	1.441	0.323	0
18	0.167	0.035	0.004	0	1.738	1.046	0.711	0
19	0.365	0.138	0.014	0	1.057	0.647	0.298	0.018
20	0.729	0.302	0.030	0	0.86	0.781	0.364	0.196
21	1.01	0.518	0.052	0	1.116	1.163	0.611	0.447
22	1.43	0.827	0.083	0	1.482	1.4	0.66	0.723
23	1.56	1.15	0.115	0	1.92	1.77	0.873	0.793
24	1.86	1.45	0.145	0	2.38	2.22	1.24	0.873
25	2.07	1.56	0.156	0	2.79	2.46	1.37	0.693
26	1.65	1.31	0.132	0	2.59	2.27	1.09	0.533
27	1.27	1.23	0.124	0	2.38	2.11	0.897	0.439
28	0.9	1.01	0.101	0	2.07	1.93	0.615	0.395
29	0.538	0.657	0.066	0	1.55	1.52	0.403	0.235
30	0.343	0.387	0.039	0	1.15	1.14	0.163	0.118
31	0.183	0.243	0.024	0	0.712	0.608	0.09	0.082
32	0.115	0.148	0.015	0	0.405	0.248	0.092	0.06
33	0.04	0.064	0.006	0	0.236	0.015	0.125	0.047
Sum	14.325	11.062	1.106	0	33.072	24.866	9.925	5.652

FIG. 6. Composition of a hydrogenated VGO (NPA, MPA, DPA, TPA: normal-, monobranched-, dibranched and tribranched paraffins; MNA, DNA, TNA, TEN: mono-, di-, tri-, tetra-naphtenes).

Wang *et al.*, 1995). Strictly speaking, it is therefore a continuous approximation of a discrete system. Although interesting and skilful, these formal approaches only apply to certain cases of thermal cracking reactions in homogeneous phase. The analytical solutions found remain limited, however, to reaction networks, which are purely parallel or purely consecutive, as well as to reaction orders assumed to be simple. In order to generalise them to the mechanisms and complexity of surface reactions, the distribution functions to be used should not be empirical (Gamma Laws, etc.) but should systematise the available chemical knowledge of these reaction networks. The "single-events" detailed kinetic modelling method, which we will describe below, would form a preliminary means of constructing distribution functions respecting the physico-chemical understanding acquired of the relative reactivities for these reaction sets.

The approach chosen, privileged by the IFP "Kinetics and Modelling" group, aims to be much more respectful of the chemistry and reaction mechanisms involved.

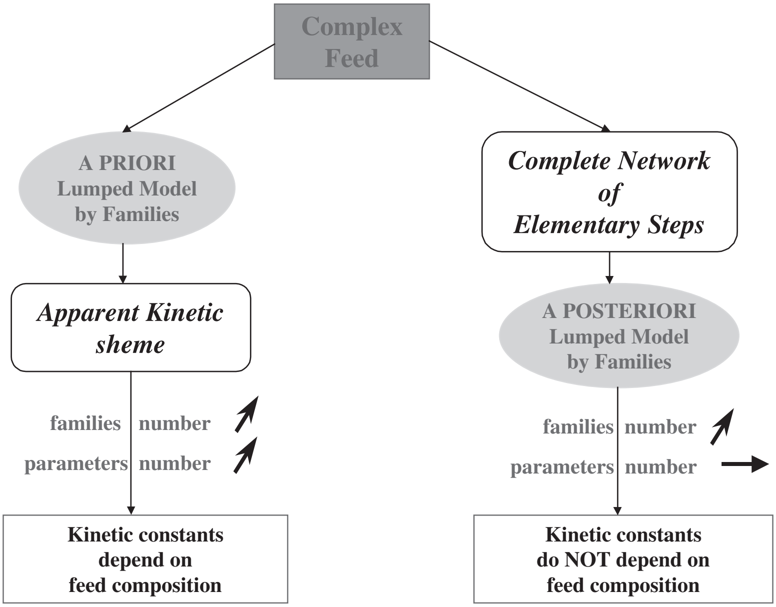


FIG. 7. Kinetics modelling.

Since modelling complex processes involves numerous reactions and molecules, a certain degree of simplification is required; the objective is always to reduce the number of compounds by *lumping*. However, like (Nigam *et al.*, 1991), we identify two different *lumping* approaches, Fig. 7.

(1) Early lumping:

This approach is applied naturally by the chemist on the basis of his know-how and/or intuition. Several models in the literature describe lumping operations carried out according to distillation cuts (Verma *et al.*, 1996), structural considerations (Quann and Jaffe, 1992) or functional considerations (paraffins, olefins, nitrogenated or sulphurated molecules). Lumping, often based on the available analyses, considerably reduces the number of constituents and can be used to produce a kinetic model comprising few parameters.

The problem with this type of model is that it frequently depends on the composition of the feedstock; in this case, an expensive experimental data bank is required to obtain a set of kinetic parameters which, to say the least, are apparent and dependent on the feedstock composition.

In addition, since it is always tempting to refine the model by subdividing the lumped families, the number of kinetic constants between all these lumpings increases at an almost exponential rate with the number of pseudo-constituents considered, since they are apparent constants.

To model hydrotreatment (HDT) processes, however, we have extended this approach to all reactions hydrodesulphurisation (HDS), hydrodenitrogenation (HDN) and hydrogenation of aromatics (HDA), since it is the only one possible in the case of sulphide catalysis (Bonnardot, 1998; Magné-Drisch, 1995).

(2) Late lumping:

In more favourable cases, for example acid and/or bifunctional catalysis, we will see that a different approach can be considered.

There is in fact sufficient knowledge available on the elementary steps involved in the reaction mechanisms to allow automatic generation of the entire network and the reaction intermediates, which run into several tens of thousands (Baltanas and Froment, 1985). In retrospect, and given a few fairly reliable assumptions, *late lumping* of the species and the reaction intermediates is possible (Vynckier and Froment, 1991).

In addition, the apparent kinetic constants between these families so lumped are *strictly* expressed according to a small number of elementary and fundamental kinetic constants. Their number remains finite, irrespective of the number of carbon atoms in the molecule; furthermore, due to their intrinsic nature, it may be possible to determine them from simple model molecules.

This method is therefore doubly *generic*:

(a) Firstly, it can be used to *extrapolate* the kinetic constants according to the length of the hydrocarbon chains.

(b) Secondly, it can be generalised to all processes using acid catalysis, in other words 80% of the refining operations.

We decided to validate it under *conditions representative* of various industrial processes: isomerisation, catalytic reforming, hydrocracking and fluid catalytic cracking (FCC).

(3) Reconstruction of feedstocks; case of heavy cuts:

The two previous techniques are obviously limited when it comes to refining heavy feedstocks (520 +); in practice, they can only be applied to distillates.

With heavy cuts containing residues, there is insufficient analytical data to provide the detailed composition of feedstock and effluents. The aim (Neurock *et al.*, 1989, 1990, 1994) in this case is therefore to artificially reconstruct an equivalent molecular population, whose global properties (density, viscosity, etc.) are the same as those measured on the actual feedstock.

The studies conducted at the IFP by the "Kinetics and Modelling" research group are structured around the three previously defined axes, summarised in Fig. 8.

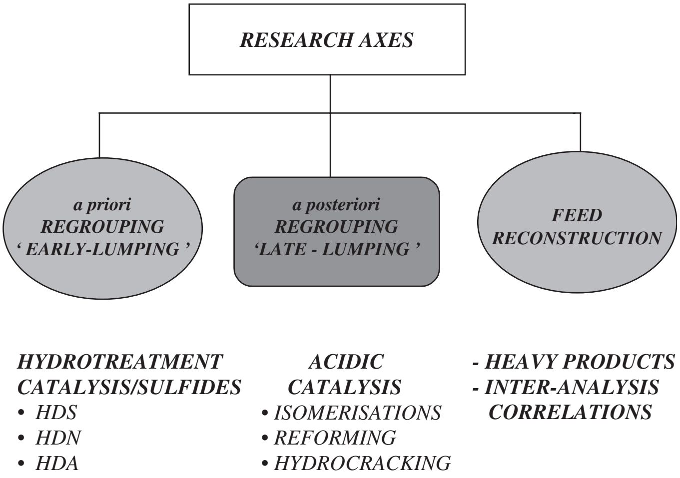


FIG. 8. Research axes.

II. Kinetic Modelling by Single-Events

A. INTRODUCTION

The creation of models that are as representative as possible is a major step in the industrial development of refining processes. The models created can be used firstly to optimise the operating conditions: "design" of the unit, choice of reactor, determination of optimum running conditions. Secondly, they can be used to predict the performance of the unit.

To optimise the modelling studies—which may be lengthy and costly—detailed predictive models must be developed which can be adapted to evolutions in the process, i.e. be extrapolated to different feedstocks, different operating conditions, etc.

Modelling based on the single-events theory[7] and developed in radical chemistry, or in acid catalysis, meets these requirements since it allows detailed prediction of the yields output from the units. This methodology, developed in the "Laboratorium voor Petrochemische Techniek" at Ghent University (Froment, 1991), consists in constructing a reaction network which, although exhaustive, is described by a limited and uncoupled number of kinetic constants independent of the number of atoms in the molecules. The behaviour of complex feedstocks can therefore be predicted on the basis of studies conducted on model molecules. This method can be applied to several refining processes, as demonstrated by a series of studies currently in progress at the IFP

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[7] = "Single-Events MicroKinetics" (SEMK) method.

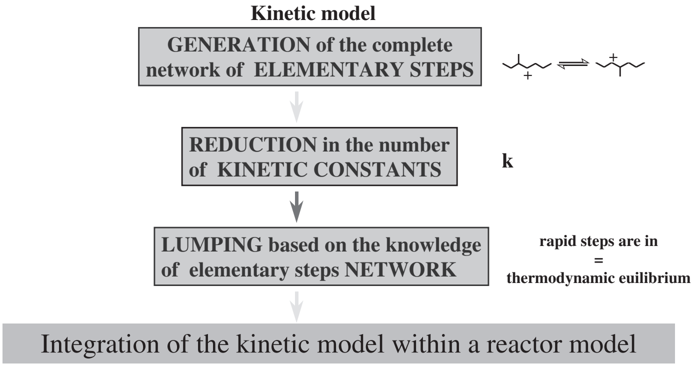


Fig. 9. "Single-Events" modelling.

(isomerisation, reforming, hydrocracking, etc.) (Cochegrue, 2001; Schweitzer, 1998; Valery, 2002).

The "Single-Events" methodology can be used to produce a highly detailed representation of the reaction mechanisms occurring in the acid phase of the catalyst. It can be used to describe all the reactions involving carbocations adsorbed on acid sites and derived from paraffins and naphthenes in the feedstock. The rates of formation and disappearance of all the hydrocarbons are expressed according to the kinetics of formation and disappearance of these carbocations and can be lumped by chemical family, if necessary. Figure 9 schematically represents the different stages of the methodology.

B. BIFUNCTIONAL CATALYSIS MECHANISMS

Most refining catalysts consist of two active phases: a metallic phase and an acid phase, Fig. 10.

- *The metallic phase* protects the catalyst and allows the formation of unsaturated reaction intermediates for the acid phase.
- *The acid phase* forms carbocations whose carbon skeletons undergo modifications (ring opening/closing, cracking, isomerisation, etc.), Fig. 11.

All reactions involving primary ions are neglected, considering their low thermochemical stability compared with secondary and tertiary carbenium ions.

For example in Fig. 12, the *n*-hexane hydrocracking reaction network—the last which can be drawn entirely by hand—contains 6 paraffins, 14 olefins and 10 carbocations, and involves the following elementary reactions:

- 14/14 hydrogenations/dehydrogenations
- 18/18 protonations/deprotonations

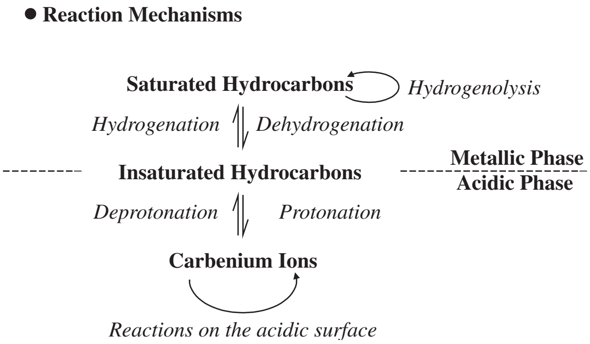


FIG. 10. Bifunctional catalysis—reaction mechanisms.

- **Reaction Mechanisms**
  - Saturated carbenium ions
    - Rearrangement or shift reaction (HS, MS, ES, intra ring alkyl shift (IRAS))
    - Isomerisation by the intermediaries PCP
    - Beta Cracking (acyclic, exocyclic, endocyclic)
    - Deprotonation

  - Unsaturated carbenium ions
    - Allylic Resonance
    - Rearrangement or shift reaction (HS)
    - Cyclization
    - Deprotonation

FIG. 11. Acidic phase—reaction mechanisms.

- 8 hydride shifts (HS)
- 4 methyl shifts (MS)
- 20 isomerisations by a protonated cyclopropane (PCP)
- 2 isomerisations by a protonated cyclobutane (PCB)
- 1 β-scission cracking reaction

III. Generation of Reaction Networks

Generation is carried out according to chemical criteria. A molecule undergoes a sequence of reactions which leads to new products, respectively undergoing

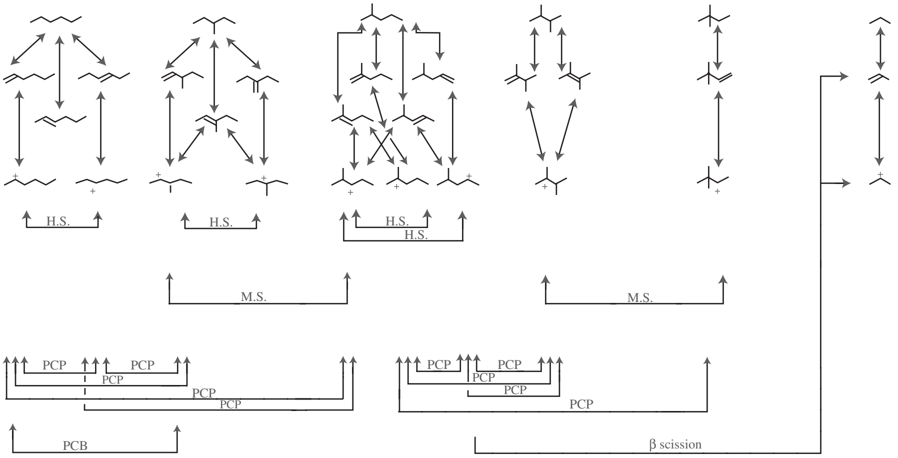


FIG. 12. Elementary steps network for *n*-hexane cracking.

- **Computing by generation algorithm**
  - ☞ **Repeating a limited number of elementary steps (tree-form scheme)**
  - ☞ **Avoiding duplication of same reaction pathways**

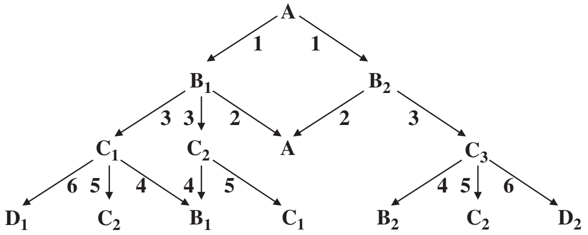


FIG. 13. Elementary steps network generation.

another sequence depending on their type and structure. We then obtain a tree structure. As an example in Fig. 13, from a body A, we obtain the following generation:

This method can be used to take into account all types of reaction which are chemically possible. Although there are thousands of elementary steps, the reaction network actually consists of repetitions and combinations of a limited number of reaction types.

A computer tool is required to construct a network of complex reactions. The algorithm used for this purpose precludes possible duplication of reaction species and pathways during their generation.

A. Computer Representation of Species and Chemical Reactions

The hydrocarbon species are represented by Connectivity Matrices (Clymans and Froment, 1984). The carbon–hydrogen bonds are not shown explicitly. In contrast, the carbon skeleton (containing no hetero atoms) can be mathematically represented by Boolean matrices. If carbon 1 is bonded to carbon 2, matrix elements (1;2) and (2;1) are assigned a value of 1. This is illustrated in the example shown in Fig. 14.

B. Results Obtained for Computer Generation of Networks from *n*C8 to *n*C15

The Fig. 15 indicates the change in the *number of species* generated (paraffins, olefins, ions, in Fig. 15a) and the *number of reactions* (hydrogenations, protonations, HS, MS, ethyl shiftes (ES), PCP branching, PCB branching, beta scissions, in Fig. 15b) according to the *number of carbons* of a single hydrocracked normal paraffin.

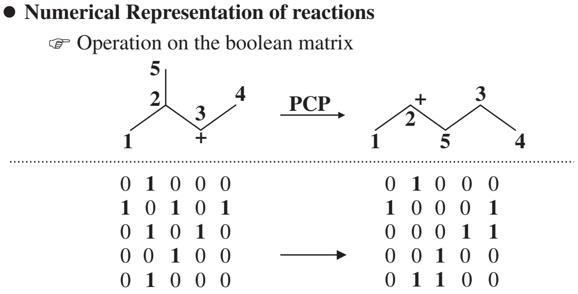
The above examples concern only aliphatic molecules. Cyclic molecules have similar curves. With cyclic molecules, however, there are more products and more reactions.

IV. Kinetics by Single-Events

The concept of single-events lies upstream from the notion of elementary step.

A. Single-Events Microkinetic Concept

The reaction network consists of elementary steps. Each step is the result of one or more "single-events" (Baltanas *et al.*, 1989; Vynckier and Froment, 1991).



$$\begin{matrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{matrix} \longrightarrow \begin{matrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 \end{matrix}$$

Fig. 14. Network generation by computer.

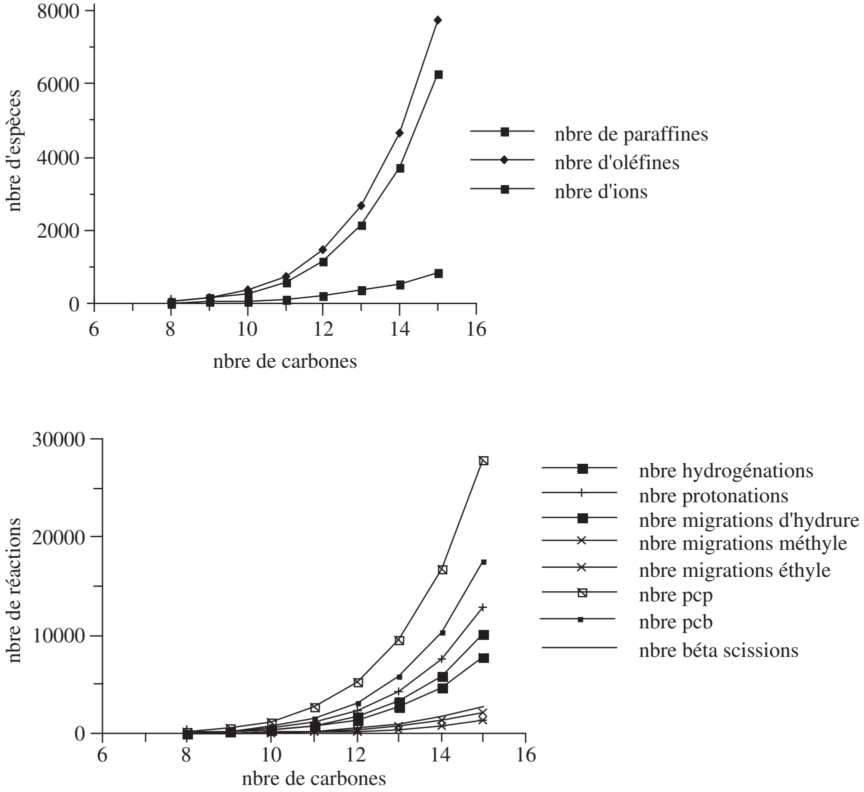


FIG. 15. Results of networks generation.

The following figure shows an isomerisation equilibrium by MS between two secondary ions. Two methyls can shift in the direction A→B,[8] but only one in the direction B→A. The example of Fig. 16[9] illustrates the importance of symmetries in the reaction rates.

We are now at the root of the principles on which the single-events method is based. The rate constant of an elementary step depends on two classes of factor (Van Raemdonck and Froment, 1989):

- The specific reactivity of the active centre (more precisely, of the activated complex). This reactivity is defined by the reaction type (in our example, an MS) and by the type of reactant and product ions (in our example, secondary ions).
- The multiplicity of structural elements involved in the elementary step. In our example, this is the number of methyl groups likely to shift (two for A and one for B).

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[8] A = the methyl_2 hexyl_3 ion and B = the methyl_3 hexyl_2 ion.

[9] "Branchement(s)" means "Branching(s)" and "Migration(s)" means "Shift(s)".

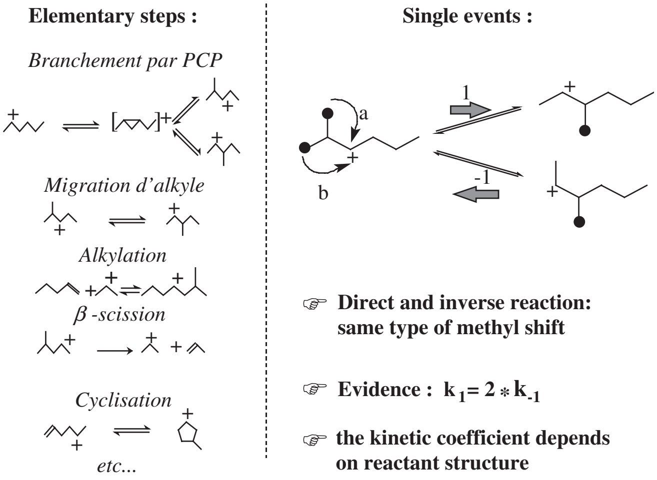

FIG. 16. Elementary steps/Single-events.

The kinetic constant of each elementary step will therefore be the product of a single-events number n_e and an intrinsic constant k_{reac} which depends on the reaction type and on the types (*m,u*) of the reactant and product ions:

$$K = n_e * k_{reac}(m, u)$$

The following paragraph shows how to calculate the single-events number n_e from the symmetries of the reactant and of the activated complex.[10]

B. SEPARATION OF CHEMICAL AND STRUCTURAL CONTRIBUTIONS

In Fig. 17, we will start from the activated complex theory and the Eyring law and decompose the free enthalpy into its *intrinsic* and *symmetry components*.

The standard entropy S° is the sum of several contributions, translation, internal rotation, external rotation and vibration. Each rotational contribution can be broken down into an intrinsic term S°_{int} and a logarithmic term taking into account the symmetry number σ of the compound (if the molecule is optically active, the standard entropy must also be corrected by adding an asymmetry term related to the chirality: 2^n).[11] We can therefore express above

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[10] Remark: The number of single-events could also be calculated using the notion of statistical factors (Bishop and Laidler, 1965, 1969). The statistical factor of a reaction is equal to the number of products that a reaction can form if a distinction is made between the atoms of each reactant. In our example, two methyl groups can shift in one direction and only one in the other direction: $k_1 = 2 * k_{-1}$.

[11] n = number of chiral carbon atoms.

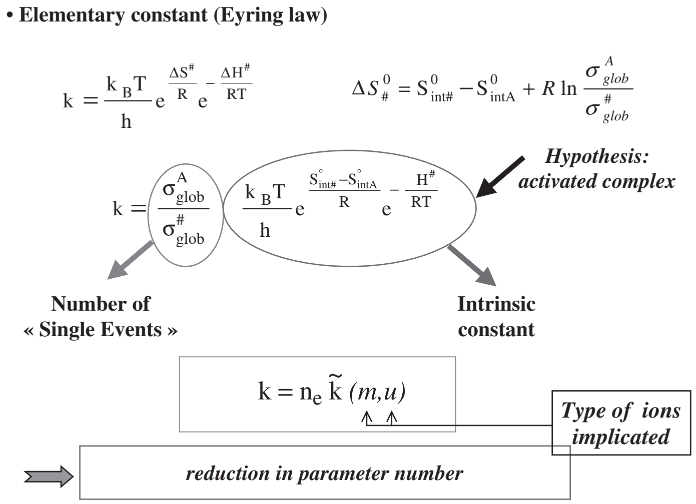

FIG. 17. Single-events.

the activation entropy $\Delta S^\circ_\#$ which is equal to the entropy difference between the activated complex and the reactant.

> The elementary kinetic constant k is therefore the product of a term calculated from a difference of intrinsic free enthalpies [12] and a ratio of symmetry numbers, which we will call: single-events number: $n_e = \sigma^A_{glob}/\sigma^\#_{glob}$.[13]

Since the Eyring relation can be used to link a free activation enthalpy to a kinetic constant, the single-events method can be described in two different ways:

- Either as a model composed of single-events number and intrinsic kinetic constants (see above).
- Or as an "energy" model[14] for the reactants and activated complexes composed of intrinsic free enthalpy components and symmetry number (see below).

C. FREE ENTHALPIES OF REACTANTS AND ACTIVATED COMPLEXES

The single-events theory, in its "energy form" is therefore an alternative to the molecular modelling approach. Instead of using *ab initio* calculations, the

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[12] The intrinsic free enthalpy is the free enthalpy minus the symmetry entropic contributions.

[13] $\sigma_{glob} = \sigma_{int} * \sigma_{ext}/2^n$

[14] The free enthalpy is homogeneous with an energy.

single-events method proposes a model of free enthalpy levels for ions and activated complexes, which involves few parameters. The idea remains the same: calculate the free activation enthalpy to calculate the kinetic constant of each elementary step.

1. *Paraffins and Olefins*

The free enthalpy of a paraffin or an olefin is determined by the Benson group contribution method (Benson, 1976). This method is traditionally used to calculate the formation enthalpies in gaseous phase at a given temperature of a molecule by describing it as structural atomic groups. Amongst other things, this provides a way of calculating the equilibrium constant of the hydrogenation/dehydrogenation reactions between the paraffins and olefins of the model.

2. *Ions*

To calculate the free enthalpy of an ion, we need to know its symmetry number and its intrinsic free enthalpy. The symmetry number can be calculated methodically and algorithmically. The intrinsic free enthalpy is obtained from the assumptions of the single-events theory. For an ion, the intrinsic free enthalpy calculations involve two parameters:

- The ion type (secondary or tertiary).
- The number of carbon atoms.

a. Intrinsic free enthalpy and ion type. Several formation enthalpies were determined further to studies conducted by (Brouwer, 1980) in superacid media and confirmed by *ab initio* calculations (Lenoir and Siehl, 1990).

The ions shown on the Fig. 18 all have seven carbon atoms. We observe that the formation enthalpy depends neither on the position of the charge nor on the neighbouring groups, but only on the primary,[15] secondary or tertiary character of the ion. The single-events theory accepts that observations made for formation enthalpy are also true for the intrinsic free enthalpy of formation.

Assumption 1. For a given number of carbon atoms, the intrinsic free enthalpy of formation of an ion depends only on its type (secondary or tertiary).

It means the stability of an ion depends only on the degree of substitution of the carbon atom carrying the charge.

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[15] 181.8 kcal/mol for a primary ion. This higher value corresponds to greater instability and explains why the formation of primary ions is generally neglected compared with that of secondary- and *a fortiori* tertiary-ions.

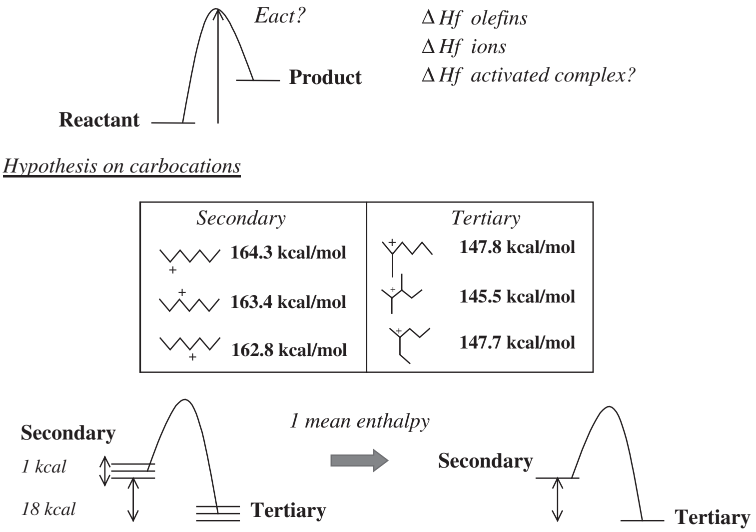


FIG. 18. Hypothesis 1 on carbocations enthalpy.

b. Intrinsic free enthalpy and number of carbon atoms. The single-events theory is also based on the assumption that only the nature of the reaction centre and its immediate environment will have an impact on the rate:

Assumption 2. The intrinsic free enthalpy of activation of an event depends only on the nature of the event and the type of ion(s) involved (Van Raemdonck and Froment, 1989; Vynckier and Froment, 1991).

The number and position of the carbon atoms surrounding the active centre have only a minor influence, since the stability of a double bond, a carbocation or an activated complex is primarily modified by the inductive effect, Fig. 19.

D. THERMOCHEMICAL RESTRICTIONS AND CONSTRAINTS

In addition to the first assumptions of the single-events theory, we must also include the various thermodynamic relations linking in particular the direct and inverse elementary constants through the thermochemical equilibrium constants. This is detailed in all the studies, and more completely by (Verstraete, 1997, Chapter 11).

These assumptions and thermodynamic constraints considerably reduce the number of kinetic parameters to be estimated; this is one of the main advantages of this theory compared with the representation and modelling of complex feedstocks.

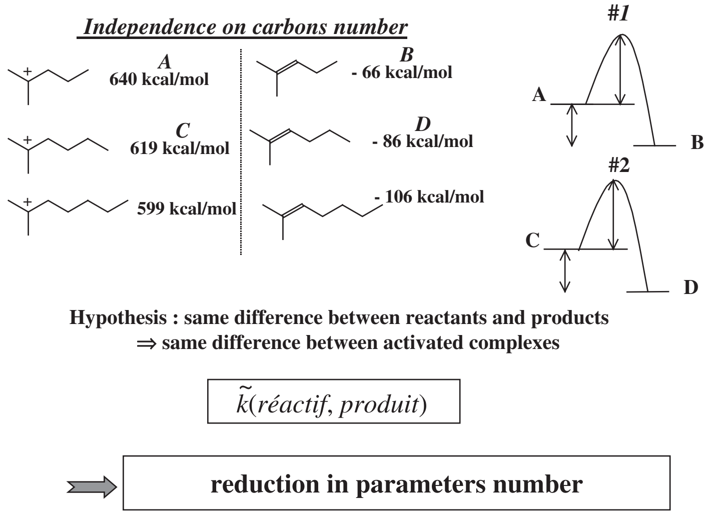


FIG. 19. Hypothesis 2 on activated complexes enthalpy.

- **Required S. E. constants** (acidic phase)
  - ◆ Protonation: $k_{Pr}(s)$ $k_{Pr}(t)$
  - ◆ Deprotonation: $k_{De}(s;O_i)$ $k_{De}(t;O_i)$
  - ◆ Isomerisation : $k_{iso}(s;s)$ $k_{iso}(s;t)$ $k_{iso}(t;s)$ $k_{iso}(t;t)$
  - ◆ Cyclisation: $k_{Cyc}(s;s)$ $k_{Cyc}(s;t)$ $k_{Cyc}(t;s)$ $k_{Cyc}(t;t)$
  - ◆ Cracking: $k_{Cr}(s;s,O_i)$ $k_{Cr}(s;t,O_i)$ $k_{Cr}(t;s,O_i)$ $k_{Cr}(t;t,O_i)$
- **Total : 57559 kinetics constants** (C_{11} network)

FIG. 20. Reduction in number of parameters.

In the example given on Fig. 20, only 16 intrinsic parameters are required to define all the kinetic constants regarding the 57,559 constitutive pathways of a catalytic reforming reaction network, including molecules with up to 11 carbon atoms.

V. Late Lumping Kinetic Model

Another—important—advantage of the single-events method is that it allows *rigorous* lumping by chemical families, using a few simple additional assumptions.

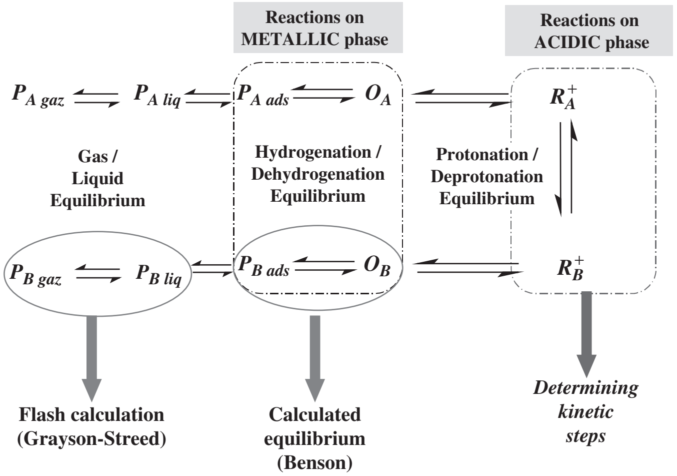


FIG. 21. Reaction model.

Although the single-events theory defines a kinetic model of elementary reactions occurring on the acid phase, this model must be included in a more general framework in order to model access to this acid phase. We will therefore consider the reaction path of a paraffin in Fig. 21:

A. THREE-PHASE MODEL

The three-phase model takes into account the possible appearance of a liquid phase in the reactor.

Assumption 3. The associated gas–liquid equilibrium is generally achieved.

Under these conditions—the solid is considered as being completely wetted (by capillary action)—the activity of a compound will be considered as equal to its liquid concentration. The gas–liquid partition of the compounds is expressed using Henry coefficients He[16] whose values are obtained by a standard Flash calculation (Grayson–Streed method if hydrogen is present).

B. CATALYTIC ACT

All reactions on the acid phase are preceded by a series of input/output steps: possible physisorption, hydrogenation/dehydrogenation and protonation/

---

[16] $\mathrm{He}_{\mathrm{Pi}} = \mathrm{P}_{\mathrm{Pi}}/[\mathrm{P_i}]$; $\mathrm{He}_{\mathrm{Oij}} = \mathrm{P}_{\mathrm{Oij}}/[\mathrm{O_{ij}}]$; $\mathrm{He}_{\mathrm{H_2}} = \mathrm{P}_{\mathrm{H_2}}/[\mathrm{H_2}]$; the non-idealities, concerning hydrogen in particular, were not taken into account here, considering the lower activity of the sulphide catalysts.

deprotonation. These steps are considered as being fast enough to be in equilibrium (Vynckier and Froment, 1991).

Assumption 4. The possible steps of physisorption, hydrogenation/dehydrogenation, shift between the metallic and acid sites, and protonation/deprotonation, are in equilibrium.

C. Composition of the Reaction Intermediates

The free enthalpies of formation and therefore the equilibrium constants between paraffins, olefins and ions are known: we can therefore calculate the olefin and ion concentrations. Given the operating conditions (high temperature and high hydrogen pressures), the quantities of olefins and ions are always negligible compared with those of paraffins.[17]

Assumption 5. In addition to the steady state—the quasi-steady state approximation (QSSA) applies locally to ions and olefins.

Consequently, the rates of appearance of these reaction intermediates are zero and those of paraffins take the following form, Fig. 22:

$r_{reac}(\{m\} \rightarrow \{p\})$ = double summation of the reaction rates "reac" where m and p are reactant and product carbocations (summation indices m and p)

$\{m\}$ = summation set counted on the reaction network generated.

D. Lumping by Families

Various experimental observations (Svoboda *et al.*, 1995; Weitkamp, 1982) demonstrated that the reaction rates of methyl (Me) or ethyl (Et) group shifts are much faster than those of PCP and PCB isomerisation reactions and cracking reactions. Consequently, when a compound is formed, all its isomers with the same number of branches are instantaneously formed by shift reactions. All compounds with the same number of carbon atoms and the same number of branches are therefore in thermodynamic equilibrium, Fig. 23.

For example, a given paraffin will not react alone, as would be expected due to its specific structure; the reactivity observed will be that of the family of paraffins with the same numbers of carbon atoms and branches. The notion of reactive paraffin is therefore replaced by the notion of reactive paraffin family. Figure 24 summarizes the above.

---

[17] Remark: The single-events theory itself does not make any presumptions regarding the nature of the elementary steps which could be kinetically determining for the rate(s) on the acid phase. Only the introduction of Assumption 4 leads to a certain number of restrictions, by excluding the protonation/deprotonation steps.

- **Formation rate of paraffins**

$$\begin{aligned} R(Pi) = {} & r_{cr}(\{s\} \rightarrow \{j\}) - r_{alk}(\{j\} \rightarrow \{t\}) \\ & + r_{isom}(\{o\} \rightarrow \{m\}) - r_{isom}(\{m\} \rightarrow \{o\}) \\ & + r_{cr}(\{p\} \rightarrow \{m\}) - r_{cr}(\{m\} \rightarrow \{p\}) \\ & + r_{alk}(\{q\} \rightarrow \{m\}) - r_{alk}(\{m\} \rightarrow \{q\}) \\ & + r_{end}(\{r\} \rightarrow \{n\}) - r_{cyc}(\{n\} \rightarrow \{r\}) \end{aligned}$$

- **Intermediaries concentrations**

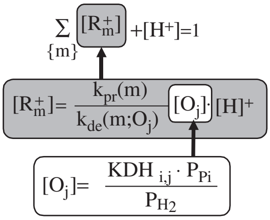
* **Q.S.S.A.**

\+ site balance

$R(R^{+}_{m}) = 0$

$R(Oj) = 0$

* **Equilibria**



$$\sum_{\{m\}} \boxed{[R^{+}_{m}]} + [H^{+}] = 1$$

$$[R^{+}_{m}] = \frac{k_{pr}(m)}{k_{de}(m;O_j)} \boxed{[O_j]} \cdot [H]^{+}$$

$$[O_j] = \frac{KDH_{i,j} \cdot P_{Pi}}{P_{H2}}$$

FIG. 22. Kinetic equations.

Assumption 6. Compounds[18] with the same number of carbon atoms and the same number of branches are lumped in the same-reactivity-family.

The Fig. 25 shows a simple example of lumpings used in the case of isomerisation of molecules with seven carbon atoms:

E. LUMPED KINETICS

Based on the previous assumptions, we can *rigorously and explicitly* determine an analytical expression of the apparent kinetic constants, between all the lumped families ($F_x \rightarrow F_y$) according to intrinsic elementary kinetic constants as specified in the "Single-Events" theory (Cochegrue, 2001; Schweitzer, 1998; Valery, 2002). The same applies for the denominator DEN (see next Fig. 26), in which the sum of the terms expresses the competitive chemisorption of all secondary and tertiary carbocations on the acid sites. The apparent kinetics so obtained formally return Langmuir–Hinshelwood expressions, traditional

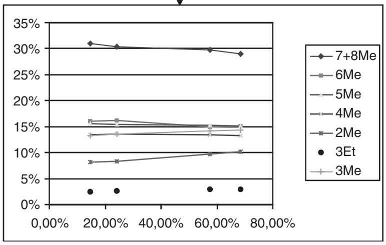
---

[18] This means that a paraffin, an olefin and an ion with the same numbers of carbon atoms and branches belong to the same family. We have seen however (see Assumption 4) that thermodynamically the paraffins are the most stable compounds, to such an extent that all compounds in a family are mixed with all the paraffins in this family.

MB = MonoBranched; DB = DiBranched; TB = TriBranched and over

Composition of C16 monobranched lump

Quasi-invariant composition with conversion



	Benson	Expérience
(7+8)MeC15	22.4%	28.8%
5MeC15	14.9%	15.1%
6MeC15	14.9%	14.7%
3MeC15	14.9%	14.2%
4MeC15	14.9%	13.9%
2MeC15	13.9%	10.3%
3EtC14	4.0%	3.1%

Theoretical and experimental compositions

FIG. 23. Consistency from experiment and hypothesis.

Hypothesis that lead to Lumping

Equilibria
Hydrogenation/dehydrogenation
Protonation/deprotonation

Quick shifts (H, Me, Et)

Compounds
by the same carbon atoms number
and the same branches number
are in equilibrium

Lumping type

$$\begin{tikzcd}
n-P \arrow[r, leftrightharpoons] & MB \arrow[r, leftrightharpoons] \arrow[dr] & DB \arrow[r, leftrightharpoons] \arrow[d] & TB \arrow[dl] \\
 & & \textit{Cracking Products} &
\end{tikzcd}$$

↳ ***Lumping by families in thermodynamic equilibrium***

FIG. 24. Lumping.

in catalytic heterogeneous kinetics, but in this case generalised to the case of chemical families lumped by number of carbon atoms, by number of branches, and therefore having reached their equilibrium composition.

Written in this way, each global kinetic constant can be broken down into a sum of generally four terms. Each term is itself the product of intrinsic elementary constants—in common factor—and a (double) sum of contributions usually known as "Lumping Coefficient"—in white in Fig. 26—see also Section VI.B.1. There are as many lumping coefficients as there are different

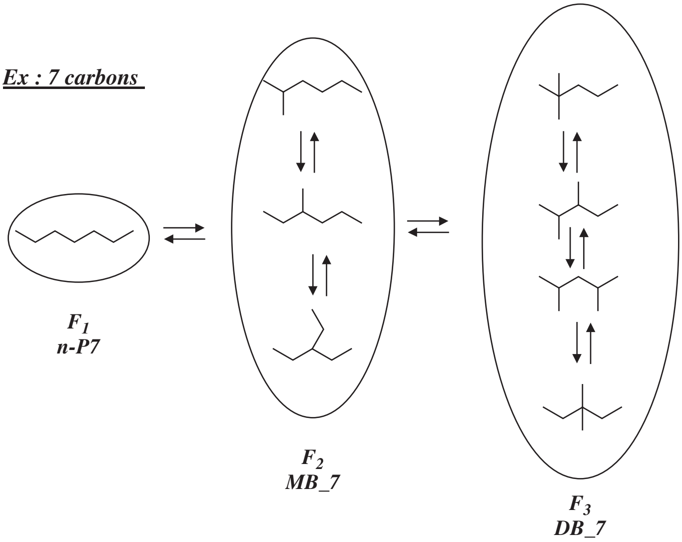


FIG. 25. Lumping by families in equilibrium.

reactions and reaction types (s,s), (s,t), (t,s), (t,t),[19] involved in the transformation of chemical families F_1 into F_2.

These "lumping coefficients" contain no kinetic parameters and can be calculated *independently* using:

the knowledge, through its *a priori* generation, of the complete reaction network, in order to enumerate the set $\{S_1\}$ of elementary steps involved in the transformation $F_1 \rightarrow F_2$.

the calculation of the single-events numbers n_e associated with all these steps; note that this initial calculation (see Section IV.B) involves determining the symmetry numbers σ of the ions, and activated complexes, derived from all the constituents of the lumpings F_1 and F_2.

the prior calculation of thermochemical equilibria (Benson group contribution method) to determine the molar fractions y_i of the lumped families—see Fig. 25, as well as the hydrogenation/dehydrogenation equilibrium constants between paraffins and olefins forming the lumpings F_1 and F_2—for given operating conditions (P,T).

Today, these calculations are easily carried out on modern workstations with no CPU limits through the use of a suitable computer architecture.

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[19] (s,s) = secondary–secondary
(s,t) = secondary–tertiary
(t,s) = tertiary–secondary
(t,t) = tertiary–tertiary

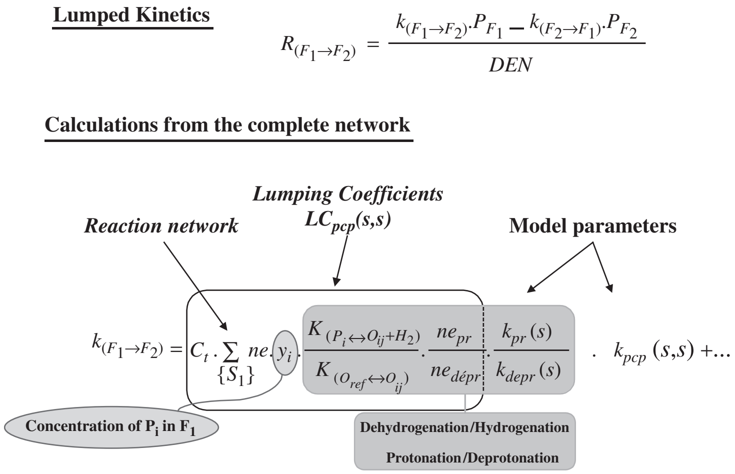

FIG. 26. Regrouped kinetics.

Paraffins	nP	11
	moP	8
	diP	7
	triP	5
Naphtènes	N	2
	SN	6
	DN	5
	TN	4
	TeN	3
Dinaphtènes	DiN	3
	SDiN	3
	DDiN	2
	TDiN	1
Aromatiques	A	1
	SA	5
	DA	4
	TA	3
	TeA	2
Naphténo-aromatiques	NA	2
	SNA	2
	DNA	1
Diaromatiques	DA	1
	SDA	1
		82

- **Constituents:**
  - **22 for the C7 network**
  - **82 for the C11 network**
- **Reactions:**
  - **59 for the C7 network**
  - **483 for the C11 network**
- **Parameters:**
  - **20 kinetic constants, 3 adsorption constants for the C7 network**
  - **23 kinetic constants, 6 adsorption constants for the C11 network**

FIG. 27. Lumped reforming network.

F. SUMMING UP

To conclude, we will give the example of a lumped network, built as part of the thesis of (Cochegrue, 2001) and including cyclic and acyclic molecules up to C11, to represent a complex reaction network of catalytic reforming, Fig. 27.

This example demonstrates the benefit of using the single-events theory in the *reduction of kinetic networks*.

We can also appreciate the utility of this method in *reducing the number of kinetic parameters*, not only in terms of their number but also in terms of their meaning;

Remember that we are concerned here with parameters that are intrinsic by construction and independent of the nature and composition of the feedstock; as a result, they will be easier to determine from simple model molecules; this last point will be demonstrated in all the following sections.

VI. Extrapolation to Heavy Cuts

By construction, the single-events theory introduces kinetic parameters which are not only intrinsic but, above all, independent of the feedstock. This first property offers a twofold advantage:

Firstly, these fundamental parameters can be determined from measurements taken on model molecules, often simpler to implement experimentally and analyse.

Secondly, using the estimations of the kinetic parameters obtained, we can predict—directly—the behaviour of heavy feedstocks, which are much more complex in terms of the number of carbon atoms and the number of branches.

In this chapter, we will illustrate this double extrapolation capacity of the single-events theory, using the example of hydrocracking[20]/hydroisomerisation of paraffinic cuts, Fig. 28.

A. Estimation of Kinetic Parameters

1. *Hydrocracking of n-Hexadecane (nC16 = Model Molecule)*

n-Hexadecane was chosen as model molecule since it is relatively easy to implement and obtain as a pure body. Its reaction network—non-exhaustive on Fig. 29—is representative since it includes all the elementary steps involved in the hydrocracking/hydroisomerisation of heavy paraffinic cuts. After reduction, just six kinetic parameters (two for isomerisation, four for cracking) are required to represent this type of network.

The model derived from the single-events theory is generally more detailed than that which can be really obtained by analysing recipes: with *n*C16 for example, the single-events theory—generalised up to six branches—will use seven

---

[20] Remark: The objective here is simply to represent the chemical transformations occurring in the 2nd reactor.

Catalytic Cracking Process under Hydrogen

Aim: Conversion of heavy cuts to fuels (gas oil)

Operating Conditions

- High Pressure (100-150 bar)
- Temperature from 350 to 400°C
- Excess of hydrogen (H_2/oil from 1000 to 2000 Nl_{H2}/l_{feed})

Advantages	**Drawbacks**
High quality products	Investments
Low deactivation	Operating Costs

FIG. 28. Hydrocracking processes.

5 isothermal mass balances
from 5 to12 days per m.balance

For 1 balance, 32 concentrations

⇨ **C16 families**:
nC16
monobranched
multibranched

⇨ **Cracking products:**
n-paraffins (C3-C13)
monobranched (C4-C13)
multibranched (C6-C13)

[Valery,2002]

6 kinetic parameters
PCP isomerisations:2
β cracking:4

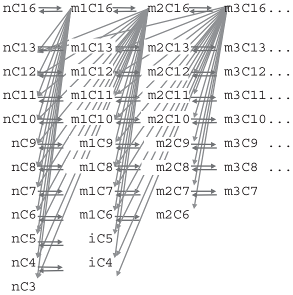

FIG. 29. Hydrocracking of *n*C16—experiment and model.

families per number of carbon atoms, whereas analytically, only three families can be measured (*n*-alkane, monobranched isomers and multibranched isomers). Cracking by β-scission forms alkanes with 3 to 13 carbon atoms. The analyses can be used to determine a total of 32 independent observables in each recipe of the five isothermal balances carried out on a pilot unit in continuous operation.[21]

a. Model vs. experiment comparison

(1) Yields and C16 fraction
There is good agreement between the conversion, isomerisation and cracking yield calculations (full lines) and the experimental data (dots), Fig. 30.

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[21] Remark: Allow 5 to 12 days per balance.

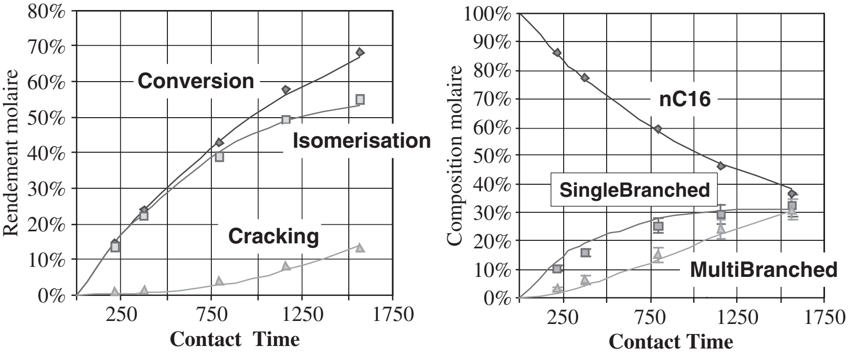
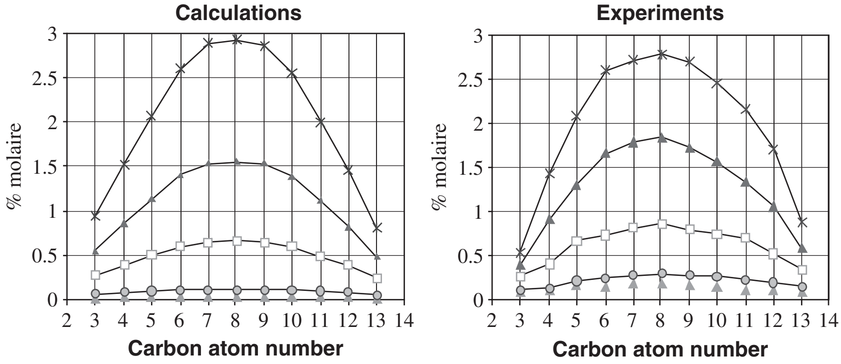


FIG. 30. Parameters estimation—yields and C16 fractions.



[Valery, 2002]

FIG. 31. Parameters estimation—cracking products distribution.

Describing the composition of the C16 fraction in terms of its linear, monobranched and multibranched paraffins provides an understanding into the evolution of the isomerisation. We also observe the appearance of monobranched compounds as primary products and multibranched compounds as secondary products.

(2) Cracking products
The calculated composition of cracking products depends not only on the model parameters, but also on the reactants, i.e. the variation in composition of the C16 fraction throughout the reactor.

The Fig. 31 shows the experiment—calculation comparisons for the sum—by number of carbon atoms from C3 to C13—of all the paraffins produced during cracking, for five increasing contact times.

B. Extension to Heavy Paraffins

The single-events theory uses computer algorithms to generate the exhaustive network of reactions and species involved (see Section III). The number of molecules and reactions in the generation process increases with the number of carbon atoms of the molecules considered.

When implementing this methodology, however, current storage capacities and the CPU time required to generate the networks quickly become limiting factors for large molecules (number of carbon atoms greater than or equal to 20).

For the hydrocracking process, we must therefore find a way of directly calculating the lumping coefficients between chemical families (see Section V), without having to generate the reaction network (no storage of molecules and reactions), Fig. 32.

The methodology applied is based on *factorisation of lumping coefficients* into several elements which can be calculated independently:

- A first Section (VI.B.1) describes the factorisation of the equation giving the expression of lumping coefficients,
- The second Section (VI.B.2) will describe how each element of this reformulation is calculated.

1. *Simplified Equation of Lumping Coefficients*

The equation of lumping coefficients is the product of a sum of inverse symmetry numbers and an entire series of thermodynamic terms (see Section V.E). This complex sum is generally calculated by adding its component terms after generating a reaction network. If we examine the problem which led to this complex sum from a different angle, we can determine another equation which is as rigorous but formally simpler.

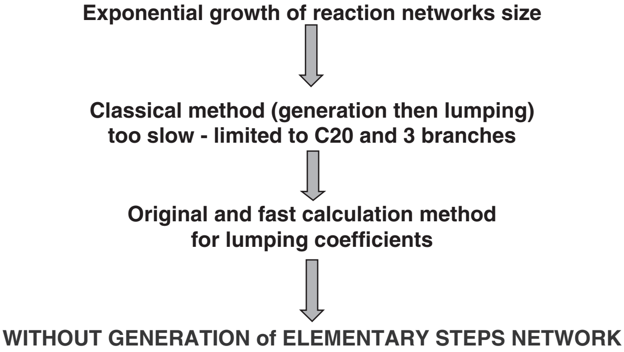
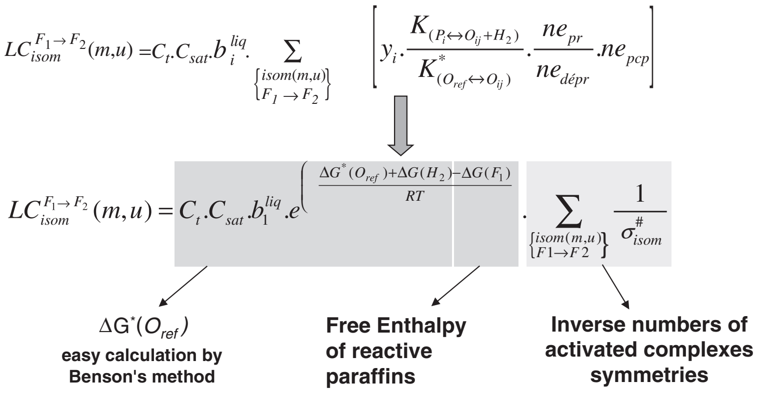


FIG. 32. Extrapolation to heavy reactants “the Real Problem”.



[Valery, 2002]

FIG. 33. Extrapolation of calculations—factorised equation.

On the basis of the simplified (in the mathematical meaning) equation of Fig. 33, we can identify a calculation logic; all lumping coefficients can be broken down into a product of two terms describing the respective free enthalpies of the reactive paraffins and activated complexes involved.[22] These two terms are calculated irrespective of the number of carbon atoms and the number of branches. The calculation is performed using recursive series and is therefore extremely fast (approximately two minutes for a C30 network limited to eight branches); this is discussed in Paragraph VI.B.2 below.

At this stage, it is important to understand that the summations no longer concern the elementary reactions but the activated reaction intermediates; *consequently, there is no need to generate the elementary step network* (Martens, 2000; Schweitzer, 1998; Thybaut, 2002; Valery, 2002; Vynckier, 1994).

2. *Calculation of the Activated Complex Component*

We now need to calculate the sum of the reciprocals of the symmetry numbers of the activated complexes for all reactions included within a given lumping coefficient. This calculation requires two calculation principles:

> First principle: rather than generating and counting the reactions, simply generate the activated complexes involved and calculate the symmetry numbers.
>
> Second principle: find how many reactions are likely to correspond to each complex generated.

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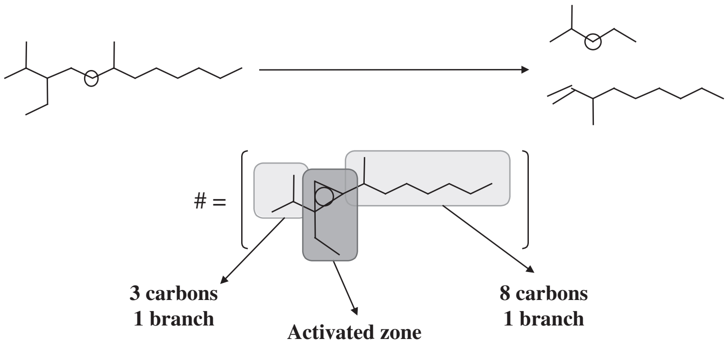
[22] After mathematical simplification, we are only left—*in fine*—with the reciprocals of the symmetry numbers of the activated complexes (see Fig. 33).



[Valery, 2002]

FIG. 34. Structure of an activated complex.

a. Description of an activated complex. In this section, we will take the simplest example: cracking by β-scission.

The first point to note is that cracking a compound with *nc* carbon atoms and *nb* branches by β-scission involves an activated complex with *nc* carbon atoms and *nb* branches, as shown on the following Fig. 34.

All activated complexes—written #—will be broken down into three parts:

a "*left*" side chain, written A;
an activated zone, written ZA;
a "*right*" side chain, written B.

The associated global symmetry number is equal to: $\sigma_{\#} = \sigma_A \sigma_{ZA} \sigma_B \, \sigma_{\mathrm{ext}(A,ZA,B)}$[23]

b. Sets of reactions and complexes.

$\left\{ \begin{matrix} react(m,u) \\ F_o \rightarrow F_p \end{matrix} \right\}$	Set of reactions react(m,u) leading from reactive family F_o to family F_p.
$\mathrm{R} = {}^{\#}\left\langle \begin{matrix} react(m,u) \\ F_o \rightarrow F_p \end{matrix} \right\rangle$	Set of activated complexes of reactions react(m,u) leading from reactive family F_o to family F_p.
$CA(\mathrm{R})$	Set of all triplets $A-ZA-B$ forming an activated complex of the set R.

---

[23] With cracking, the active zone is, by definition, asymmetric. Consequently, the possibilities of external symmetries are eliminated. In addition, in this case each activated complex corresponds to one and only one reaction type—in our example, secondary–secondary. The same is not true for PCP isomerisation, whose activated complexes include *nc* carbon atoms and *nb*–1 branches, and which requires some additional developments (external symmetries, etc. Valery, 2002).

$n_{\mathrm{corr}(A,ZA,B)}$ Number of times where an activated complex $A{-}ZA{-}B$ appears in the set R.

The sum to be calculated concerns the set of reactions and we will replace it by a sum over the set of activated complexes in Eq. (1). We therefore need to introduce $n_{\mathrm{corr}(A,ZA,B)}$ to count the activated complexes as many times as required.

We then obtain:

$$\sum_{ikl\in\left\{\begin{array}{c} react(m,u) \\ F_o \rightarrow F_p \end{array}\right\}} \frac{1}{\sigma_{\#}} = \sum_{\#\in \mathrm{R}} \frac{1}{\sigma_{\#}} = \sum_{(A,ZA,B)\in CA(\mathrm{R})} \frac{n_{\mathrm{corr}(A,ZA,B)}}{\sigma_A.\sigma_{ZA}.\sigma_B.\sigma_{\mathrm{ext}(A,ZA,B)}} \qquad (1)$$

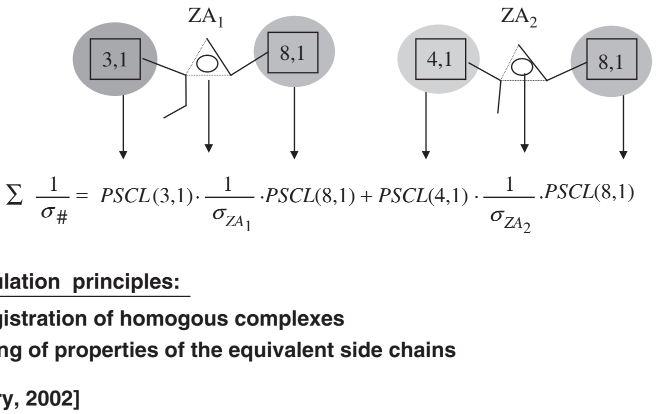
The problem of calculating the symmetry properties of the activated complexes is therefore uncoupled and reduced to calculating these properties for the equivalent side chains.

1. Activated zones. An activated complex has a limited number of carbon atoms involved in the activated zones of the molecules; the other carbon atoms form the side chains.

Taking the special case above: secondary–secondary cracking by β-scission of ions from a family of tribranched paraffins with 16 carbon atoms, into monobranched olefins with five carbon atoms and into monobranched ions with 11 carbon atoms. Two types of complex are involved in this type of elementary reaction (see Fig. 35):

1st type ZA_1: the activated zone carries an ethyl group; the side chains then share 16–5 = 11 carbons and 3–1 = 2 branches

2nd type ZA_2: the activated zone carries a methyl group; the side chains then share 16–4 = 12 carbons and 3–1 = 2 branches



$$\sum \frac{1}{\sigma_{\#}} = PSCL(3,1)\cdot\frac{1}{\sigma_{ZA_1}}\cdot PSCL(8,1) + PSCL(4,1)\cdot\frac{1}{\sigma_{ZA_2}}.PSCL(8,1)$$

Calculation principles:

1. Registration of homogous complexes

2. Using of properties of the equivalent side chains

[Valery, 2002]

FIG. 35. Cracking (s,s) $C16,3 \rightarrow C5,1 + C11,1$—homologous activated complexes.

2. Side chains. The speed of the hydride, methyl and ethyl shift reactions is the basis of the lumping by number of carbon atoms and by number of branches. Consequently, as soon as a compound with a given number of branches is formed, the other isomers with the same number of branches are formed immediately. This is also true for the side chains of an activated complex, enabling us to define the notion of equivalent side chains.

> *Side chains* with the same number of carbon atoms and the same number of branches are said to be *equivalent*.

Using recursive series, the symmetry properties of the side chains can be calculated step by step (Valery, 2002). These series $U(np,nc,nb)$ are used to obtain the sum of the reciprocals of the symmetry numbers of the side chains with *nc* carbon atoms and *nb* branches $PSCL(nc,nb)$.[24]

3. Homologous activated complexes

> *Activated complexes* with the same 'activated zone' and two 'equivalent side chains' two-by-two are said to be *homologous*.

By definition, homologous activated complexes have the same number of carbon atoms and the same number of branches. They are therefore involved in the same lumping coefficient. Consequently, each lumping coefficient has a sum of sums of the reciprocals of the symmetry numbers of each class of homologous activated complexes as a factor—Fig. 35 as cracking example.

3. Summary of the Method[25]

The objective is to calculate, in the reformulated lumping coefficient (of Section VI.B.1), the sum of the reciprocals of the symmetry numbers of the activated complexes: $\sum_{ikl\in\left\{\substack{\text{réact}(m,u)\\ F\to G}\right\}} 1/\sigma_{\#_{ikl}}$ according to the breakdown of Eq. (1) (see Section VI.B.2).

After listing the activated zones and "homologous complexes" involved in a given reaction type, the method is based on a threefold observation, see Fig. 36:

The previous problem of calculating a sum on the activated complexes is therefore "*replaced*" by the problem of calculating sums on the equivalent side chains. The PSCL series can then be defined and calculated by:

$$PSCL(nc,nb) = \sum_{A\in\left\{\substack{nc\ \text{carbones}\\ nb\ \text{branchements}}\right\}} \frac{1}{\sigma_A} = \sum_{np=1}^{nc} U(np,nc,nb)$$

A summary of the applied methodology is given in Fig. 37.

---

[24] $\boldsymbol{PSCL}(nc,nb)$ = side chain symmetry properties (**P**ropriétés de **S**ymétries des **C**haînes **L**atérales). $PSCL(nc,nb) = \sum_{A\in\left\{\substack{nc\ \text{carbones}\\ nb\ \text{branchements}}\right\}} 1/\sigma_A = \sum_{np=1}^{nc} U(np,nc,nb)$ where np = main chain length.

[25] An alternative method was developed at Ghent University (Martens, 2000; Martens and Marin, 2001).

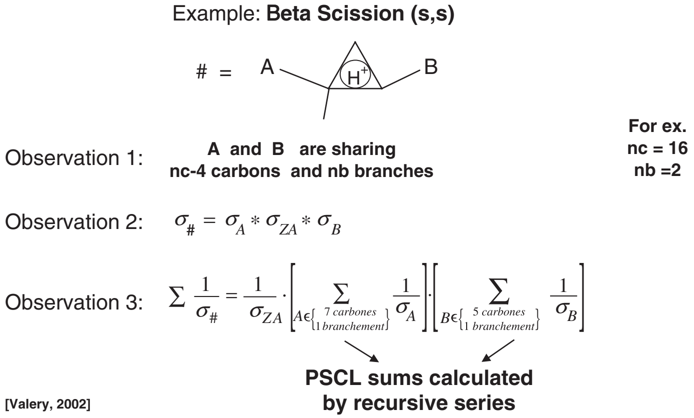


FIG. 36. Extrapolation of calculations—activated complexes.

C. EXTRAPOLATION CAPACITIES IN NUMBER OF CARBON ATOMS: HEAVY PARAFFINIC WAXES

Paraffinic waxes are a mixture of linear and branched paraffins.

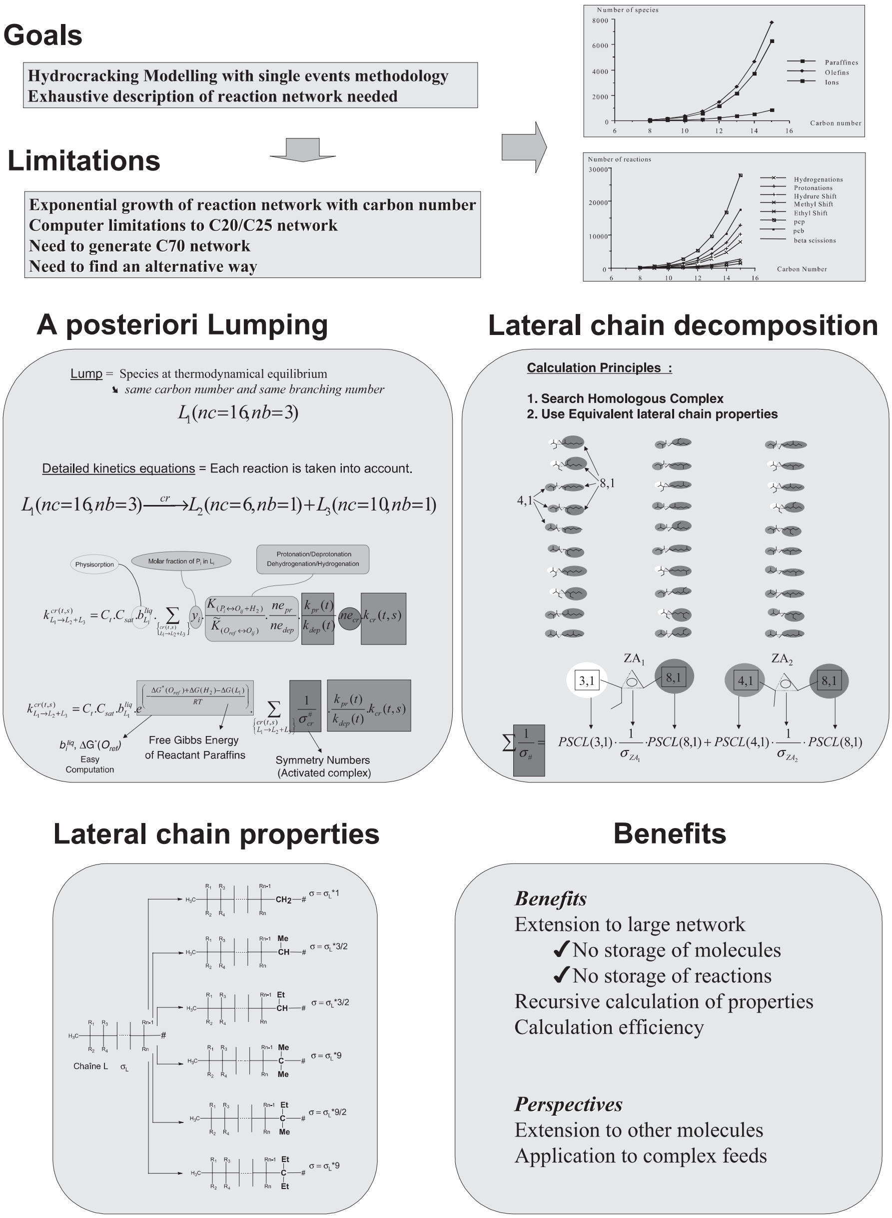
Apart from the very large number of elementary steps it contains, the reaction network of heavy paraffins is the same as that of *n*-hexadecane. The apparent kinetic network is unchanged: the linear paraffins are isomerised, and then cracked.

A set of kinetic parameters was produced using the experimental data obtained on *n*-hexadecane. The reaction rates of all the acyclic paraffins can therefore be calculated. This Section VI.C will compare the calculation results with the experimental data obtained on heavy feedstocks. The experiments conducted on heavy paraffinic waxes can be used to test the extrapolation capacities with respect to the number of carbon atoms (from *n*C16 to *n*C20–*n*C33).

1. Hydrocracking of n-Paraffin Mixtures Composed of 20–30 Carbon Atoms

This feedstock, supplied by the company Schuman Sasol, is a cut of a Fischer–Tropsch effluent. NMR and infrared spectroscopy analyses revealed no traces of olefins or alcohols. The impurities (13% of the total) were therefore interpreted as being monobranched isomers.

Some of this feedstock was fractionated on a vacuum distillation unit at IFP into four other narrower cuts, centred on an increasing number of carbon atoms from C24 to C27/C28. These cuts cannot be used to accurately determine the reaction kinetics of a given linear paraffin, but may reveal possible mixture effects or steric hindrance.



Goals

Hydrocracking Modelling with single events methodology
Exhaustive description of reaction network needed

Limitations

Exponential growth of reaction network with carbon number
Computer limitations to C20/C25 network
Need to generate C70 network
Need to find an alternative way

A posteriori Lumping

Lump = Species at thermodynamical equilibrium
↘ *same carbon number and same branching number*

$$L_1(nc=16,nb=3)$$

Detailed kinetics equations = Each reaction is taken into account.

$$L_1(nc=16,nb=3)\xrightarrow{cr}L_2(nc=6,nb=1)+L_3(nc=10,nb=1)$$

$$k^{cr(t,s)}_{L_1\to L_2+L_3}=C_t.C_{sat}.b^{liq}_{L_1}.\sum_{\left\{\substack{cr(t,s)\\ L_1\to L_2+L_3}\right\}}y_i.\frac{K_{(P_i\leftrightarrow O_{ij}+H_2)}}{\widetilde{K}_{(O_{ref}\leftrightarrow O_{ij})}}.\frac{ne_{pr}}{ne_{dep}}.\frac{k_{pr}(t)}{k_{dep}(t)}.ne_{cr}.k_{cr}(t,s)$$

$$k^{cr(t,s)}_{L_1\to L_2+L_3}=C_t.C_{sat}.b^{liq}_{L_1}.e^{\left(-\frac{\Delta G^*(O_{ref})+\Delta G(H_2)-\Delta G(L_1)}{RT}\right)}.\sum_{\left\{\substack{cr(t,s)\\ L_1\to L_2+L_3}\right\}}\frac{1}{\sigma^{\#}_{cr}}.\frac{k_{pr}(t)}{k_{dep}(t)}.k_{cr}(t,s)$$

Lateral chain decomposition

Calculation Principles :

1. Search Homologous Complex
2. Use Equivalent lateral chain properties

$$\sum\frac{1}{\sigma_{\#}}=PSCL(3,1)\cdot\frac{1}{\sigma_{ZA_1}}\cdot PSCL(8,1)+PSCL(4,1)\cdot\frac{1}{\sigma_{ZA_2}}\cdot PSCL(8,1)$$

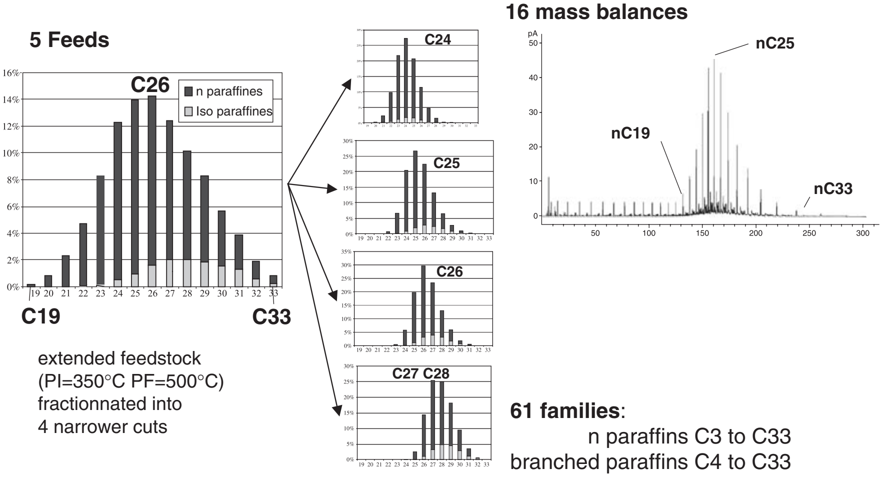
Lateral chain properties

Benefits

Benefits
Extension to large network
✓No storage of molecules
✓No storage of reactions
Recursive calculation of properties
Calculation efficiency

Perspectives
Extension to other molecules
Application to complex feeds

FIG. 37. Single-events modelling—extension to large networks (Please see Color Plate Section in the back of this book).



[Valery, 2002]

FIG. 38. Hydrocracking of paraffinic waxes—feeds and analysis.

For the paraffinic wax recipes, 61 observables can be deduced from the chromatograms, Fig. 38.

The molar composition in linear paraffins with 3 to 33 carbon atoms, i.e. 31 observables.[26]

The molar composition in isomers with 4 to 33 carbon atoms, i.e. 30 observables.[27]

a. Experimental results. Considering all the paraffinic feedstocks, 16 isothermal balances have been produced for increasing contact times:

The Fig. 39—evolution of molar concentrations (in %) of recipes resulting from the hydrocracking of C20–C30 waxes—illustrates the reactivity of paraffinic waxes:

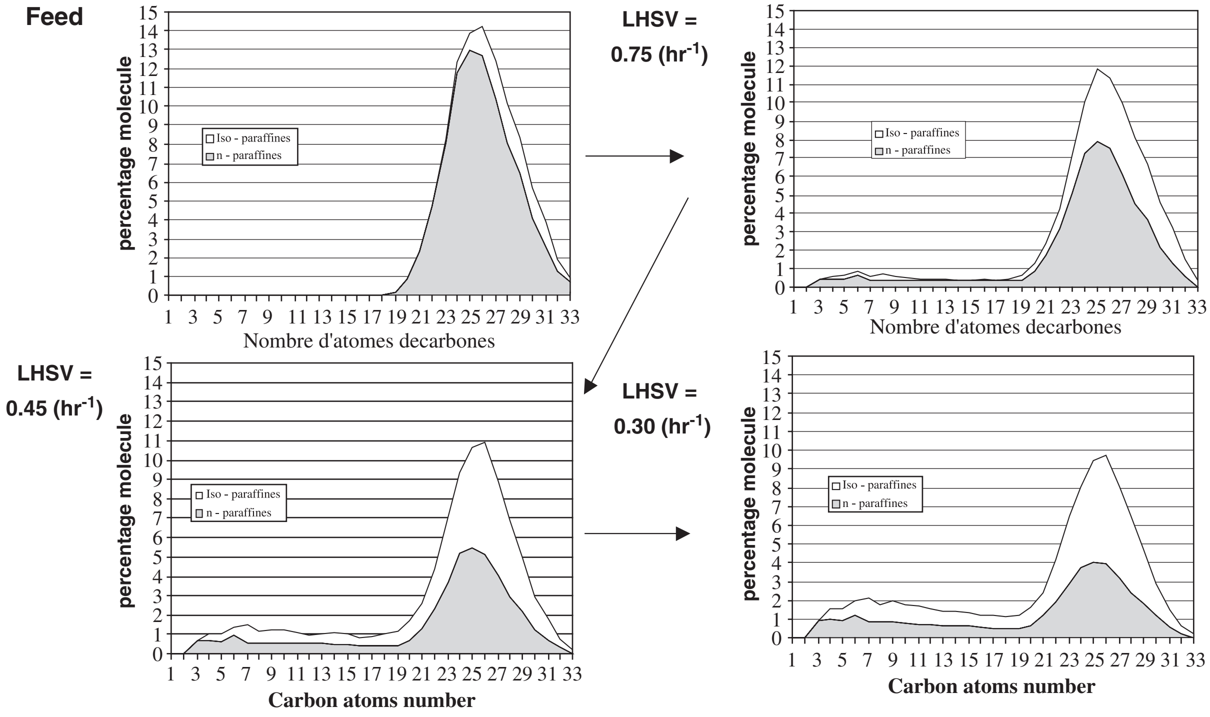
At low contact time, the concentration in heavy isomers increases (larger white area) and the cracking products are distributed uniformly between the C3 and C19 hydrocarbons.

At high contact time, the heavy paraffins disappear (smaller blue area) and the distribution of cracking products is deformed by overcracking.

---

[26] In these recipes, it is no longer possible to measure a conversion since it is impossible to distinguish between the linear paraffins produced by cracking and those which have not been converted.

[27] It is no longer possible to distinguish between monobranched–multibranched compounds by analysing the heavy paraffin mixtures.



[Valery, 2002]

FIG. 39. Hydrocracking of paraffinic waxes—experimental results.

b. Extrapolation vs. experiment comparisons

(1) Comparisons of Global Quantities

On Fig. 40, the global quantities used to compare experiments (dots) and extrapolated calculations (full lines) are:

Weight of linear paraffins with 20 or more carbon atoms (written %*n*C20+)

Weight of isomerised paraffins with 20 or more carbon atoms (written %iC20+)—approaching an isomerisation yield

Weight of paraffins with less than 20 carbon atoms—approaching a cracking yield.

The fact that there is good agreement between experiments and extrapolated calculations obtained on the evolution of the percentages by weight of heavy linear paraffins, irrespective of the initial mixture, indicates:

that for up to 30 carbon atoms there is no steric limitation in the catalyst.
that the physisorption and gas–liquid equilibria used clearly represent the activities of the paraffins in various mixtures.

We will now examine the details of the point circled on Fig. 40.

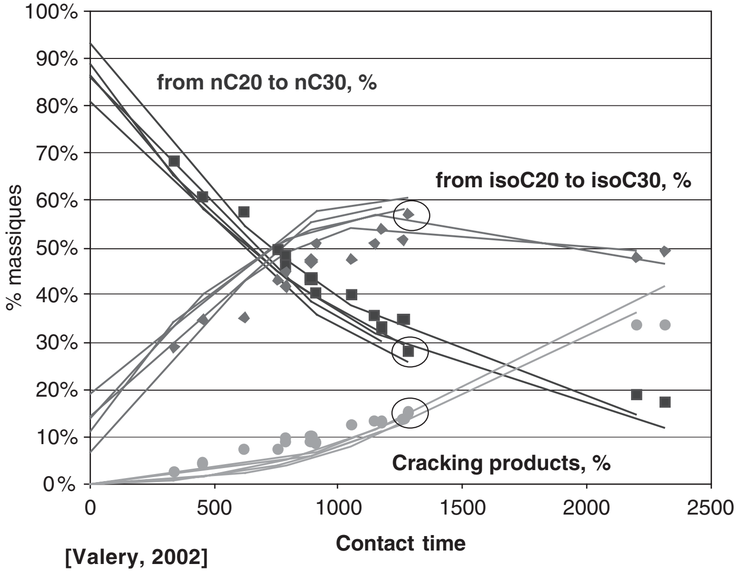


FIG. 40. Experimental—extrapolation: global comparison.

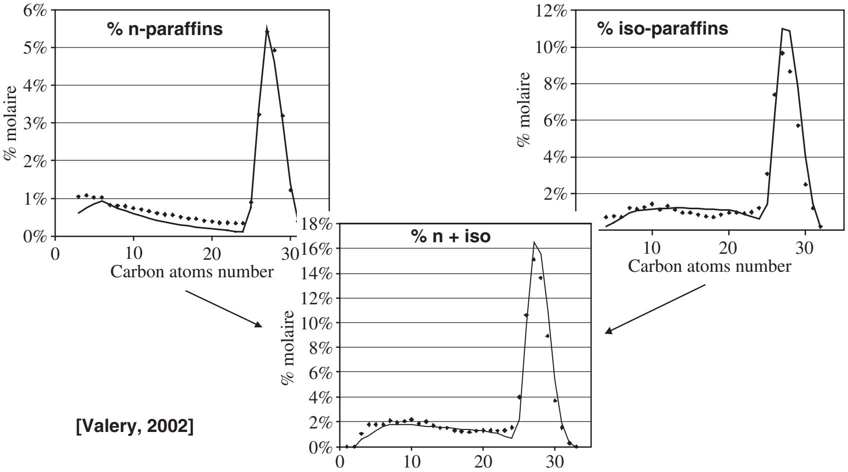


FIG. 41. Experimental—extrapolation: detailed comparison.

(2) Detailed Comparisons

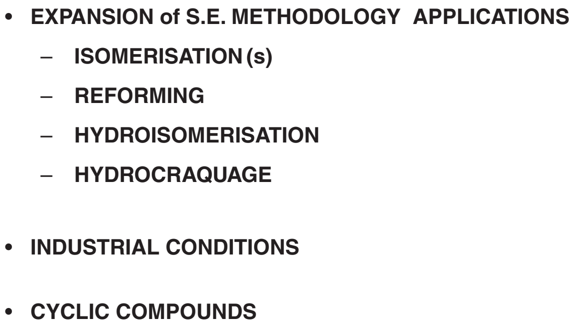
On Fig. 41, we can observe the marked absence of a maximum at C13 (rupture in the middle of the reactive paraffin chain), unlike the cracking of C16s which displays a maximum at C8. These characteristic phenomena are therefore perfectly predicted and taken into account by the single-events theory calculations.

VII. Perspectives

The principles of the single-events methodology, then of its extrapolation to heavy cuts, have already been summarised in Paragraphs V.F and VI.B.3. The method provides a detailed and rigorous kinetic model, regarding the elementary steps, from which we must draw all the consequences.

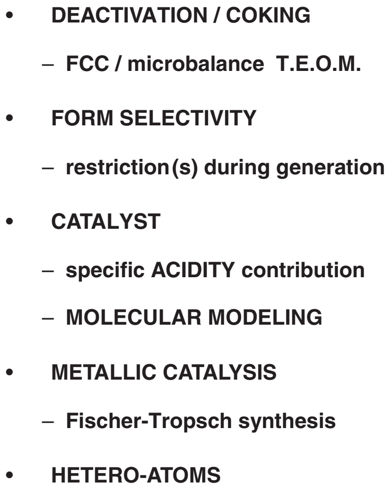
Considering the potential interest of this method and its generic character, the IFP decided to apply it and validate it for nearly all the major refining processes involving acid catalysis, alone and/or bifunctional. Examples are given in Fig. 42. Specific adaptations are required each time to take into account the characteristics of the transformations but also of the complex hydrocarbon feedstocks involved for each of these processes.

In line with the IFP's vocation, we kept in mind that these validations should only be carried out under *conditions* truly representative of *industrial* operations, both as regards the operating conditions (temperature, partial pressures, contact times, etc.) and the actual reaction media (number of phases, real feedstocks,



- **EXPANSION of S.E. METHODOLOGY APPLICATIONS**
  - **ISOMERISATION (s)**
  - **REFORMING**
  - **HYDROISOMERISATION**
  - **HYDROCRAQUAGE**
- **INDUSTRIAL CONDITIONS**
- **CYCLIC COMPOUNDS**

FIG. 42. Perspectives.



- **DEACTIVATION / COKING**
  - **FCC / microbalance T.E.O.M.**
- **FORM SELECTIVITY**
  - **restriction (s) during generation**
- **CATALYST**
  - **specific ACIDITY contribution**
  - **MOLECULAR MODELING**
- **METALLIC CATALYSIS**
  - **Fischer-Tropsch synthesis**
- **HETERO-ATOMS**

FIG. 43. Extensions.

impurities, deactivation, etc.). In this respect, we benefit from the know-how of the IFP "processes" teams.

The next important development concerns *cyclic compounds*; for these compounds, the choice of model molecules and their availability will be determining. Amongst other things, the existing rules and calculation codes will have to be adapted and possibly new ones created.

The longer term objective is to extend the scope of the single-events method, in particular to improve the way that the *nature and structure of the catalyst* are taken into account.

These items on Fig. 43 represent *research directions* to continue developing and extending the scope of the single-events theory.

(1) The first extension to be considered concerns *catalyst deactivation and coke formation*. This is studied in two cases:

- Firstly, for the FCC reaction, in which the coke formation kinetics is the same order of magnitude as the kinetics of the main reactions,
- Secondly, for the regenerative catalytic reforming reaction (with Pt–Sn/Al_2O_3 catalyst), and, in this case, prediction of coke formation is essential for the design and dimensioning of the reactors at the centre of the process.

For this approach, the use of a novel experimental tool, the TEOM (Tapered Element Oscillating Microbalance) inertial microbalance, for continuous recording of weight increases in a catalytic (micro)-bed, opens new perspectives regarding the problem of determining deactivation functions. In collaboration with Ghent University, our aim is therefore to produce a detailed and not simply cursory description of the kinetics of coke formation, according to a methodology derived from the single-events approach.

(2) One limitation of the single-events theory consists in considering the surface intermediates, carbocations and/or activated compounds, as if they were free species or radicals. In the important case of small-pore zeolitic catalysts, this limited representation of the catalytic act is no longer valid since the *shape selectivity* problems, introduced by the geometry and confinement of zeolitic cages, are ignored.

This type of restricted, steric selectivity must therefore be introduced into the "single-events" methodology. Fortunately, a certain number of exclusion rules can be introduced at the reaction network generation step, to take into account this type of restriction.

(3) Apart from taking into account these possible steric limitations, the chronic weakness of kinetic modelling in heterogeneous catalysis lies in the absence of a direct relation between the catalyst type (composition, structure, morphology, etc.) and its reactivity. In practice, the *nature and structure of the catalyst* are only involved through the values of kinetic constants. These values vary from one catalyst to another and, in principle, must be re-estimated whenever the catalyst is changed.

- An initial step was carried out by taking into account the *catalyst acidity*. A recent study (Thybaut, 2002; Thybaut *et al.*, 2001) demonstrated how microkinetics considerations (Dumesic *et al.*, 1993) can be used to restrict the specific contribution of the acid strength of the catalytic sites to the stability of adsorbed carbocations. The standard protonation enthalpy term varies with the number of carbon atoms and the strength of the acid sites.
- In the longer term, we must be able to predict the values of the kinetic constants *ab initio* according to the type and morphology of the catalyst. It is now possible to determine these structure/reactivity relations thanks to the rapid development of *molecular modelling* techniques, which will become an essential tool in the near future.

(4) Although currently limited to acid and/or bifunctional catalysis, the approach most frequently applied in the refining and petrochemistry processes

is the "single-events" approach. The main reason behind this suitability is based on the chemistry of carbocations, whose reaction mechanisms are relatively well known and described. Our goal is to extend the scope of this "single-events" method to the no less important case of *metal catalysis.* In this case there is much less agreement regarding the chemical mechanisms; one of the obstacles to be crossed concerns the adsorption mode of the molecules which, for a metal, may be multi-site. This partly explains why we chose a monometallic catalyst and the Fisher–Tropsch synthesis reaction to tackle this study (thesis in progress).

(5) Lastly, the "single-events" theory, which was historically designed for the activation of carbon–carbon bonds, does not currently cover the reactivity of C–S and C–N bonds. Some computer models have been produced to represent the possible presence of *hetero atoms* in hydrocarbon structures. Avenues are therefore open for a very wide field of application, that of HDT reactions and sulphide catalysis. They must nevertheless be based on an in-depth, improved description of the heterolytic mechanisms, also studied (Blanchin *et al.*, 2001) under IFP supervision.

These outlines demonstrate—if need be—that much research work is still essential before kinetic modelling using the "single-events" methodology can become a fully predictive tool. Nevertheless, this theory already represents a significant breakthrough and now provides the solution to several industrial problems.

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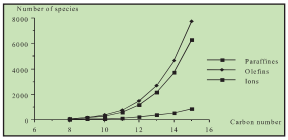
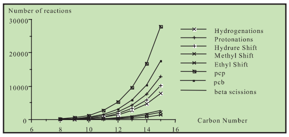




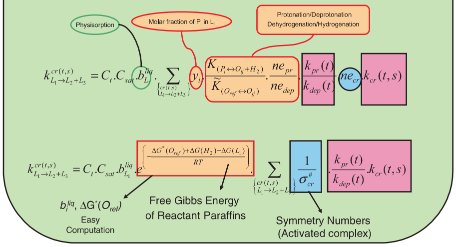
A posteriori Lumping

Lump = Species at thermodynamical equilibrium
↘ *same carbon number and same branching number*

$$L_1(nc=16,nb=3)$$

Detailed kinetics equations = Each reaction is taken into account.

$$L_1(nc=16,nb=3)\xrightarrow{cr}L_2(nc=6,nb=1)+L_3(nc=10,nb=1)$$



$$k^{cr(t,s)}_{L_1\rightarrow L_2+L_3}=C_t.C_{sat}.b^{liq}_{L_i}.\sum_{\left\{\begin{smallmatrix}cr(t,s)\\ L_1\rightarrow L_2+L_3\end{smallmatrix}\right\}} y_i.\frac{K_{(P_i\leftrightarrow O_{ij}+H_2)}}{\tilde{K}_{(O_{ref}\leftrightarrow O_{ij})}}.\frac{ne_{pr}}{ne_{dep}}.\frac{k_{pr}(t)}{k_{dep}(t)}.ne_{cr}.k_{cr}(t,s)$$

$$k^{cr(t,s)}_{L_1\rightarrow L_2+L_3}=C_t.C_{sat}.b^{liq}_{L_1}.e^{\left(-\frac{\Delta G^*(O_{ref})+\Delta G(H_2)-\Delta G(L_1)}{RT}\right)}.\sum_{\left\{\begin{smallmatrix}cr(t,s)\\ L_1\rightarrow L_2+L_3\end{smallmatrix}\right\}}\frac{1}{\sigma^{\#}_{cr}}.\frac{k_{pr}(t)}{k_{dep}(t)}.k_{cr}(t,s)$$

b_i^{liq}, $\Delta G^*(O_{ref})$
Easy
Computation

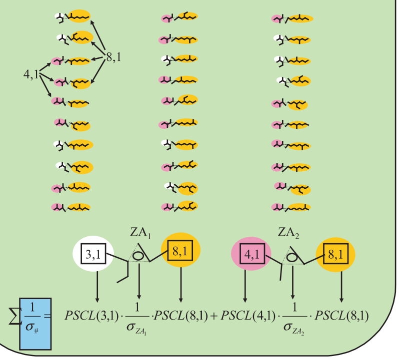
Free Gibbs Energy
of Reactant Paraffins

Symmetry Numbers
(Activated complex)

Lateral chain decomposition

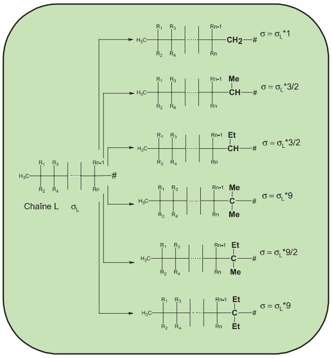
Calculation Principles :

1. Search Homologous Complex
2. Use Equivalent lateral chain properties



$$\sum\frac{1}{\sigma_{\#}}=PSCL(3,1)\cdot\frac{1}{\sigma_{ZA_1}}\cdot PSCL(8,1)+PSCL(4,1)\cdot\frac{1}{\sigma_{ZA_2}}\cdot PSCL(8,1)$$

Lateral chain properties



Benefits

Benefits

Extension to large network
- ✓No storage of molecules
- ✓No storage of reactions

Recursive calculation of properties
Calculation efficiency

Perspectives

Extension to other molecules
Application to complex feeds

PLATE 3. Single-events modelling—extension to large networks (For Black and White version, see page 295).