Computer Generation of Reaction Schemes and Rate Equations for Thermal Cracking

Reaction schemes for the thermal cracking of paraffins, naphthenes, olefins, and aromatics, and the associated rate equations, are generated by an algorithm based upon Boolean relation matrices. In order to reduce calculation times for the heavier components, a self-learning system is introduced. This self-learning system avoids repetition of identical calculations by recognizing intermediate species, for which the reaction schemes have already been generated. The software includes routines for standardizing the representation of the species, an information retrieval system, and libraries containing the necessary information for recognition of the species and the reaction schemes for these species.

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Introduction

Although the production of light olefins and aromatics by thermal cracking is mainly based upon light hydrocarbons such as ethane and propane, or light petroleum fractions such as naphtha, a few plants operate on gas oil, vacuum gas oil, or partially hydrogenated vacuum gas oil.

The kinetics of the thermal cracking of such complex mixtures have either been bypassed by the use of yield predictions, that is, correlations of product yields as a function of feedstock properties and operating conditions (Green et al., 1975; Lohr and Dittmann, 1977; Rennard and Swift, 1984; Zimmermann et al., 1984), or were based upon lumped-reaction models (Dente et al., 1986). Yet, the optimal operation of thermal cracking units in today's competitive market requires simulation models that accurately predict the product distribution as a function of feedstock properties and operating conditions. The present paper develops a simulation model based upon the radical reactions occurring in the complex reaction mixture. True, models of this type contain a large number of kinetic parameters, but their fundamental nature provides them with general validity, whereas the parameters of the lumped models used so far have to be redetermined on the basis of extensive experimentation for each type of feedstock. Also, an important fraction of the fundamental parameters can be taken from the wealth of information available on the cracking of light hydrocarbons or light petroleum fractions. Allara and Shaw (1980), have reviewed the subject.

Yet, the extraction of fundamental kinetic parameters from experimental data on the thermal cracking of heavy feedstocks requires in the first place the reaction paths followed by feedstock components and reaction intermediates. For complex feedstocks, containing large molecules, this in itself is a formidable task. The present paper deals with the computer generation of such networks and of the rate equations for the production of primary products. Most of these are relatively light hydrocarbons, also encountered in the cracking of light hydrocarbons. Their reactions, which form a network of so-called secondary reactions, and are well documented already.

Primary Reaction Paths for Pyrolysis of Hydrocarbons

An example of a primary reaction scheme for hydrogen abstraction on a typical molecule of a (vacuum) gas oil feedstock is given in Figure 1. It concerns the disappearance of isohexylbenzene and the formation of so-called primary products. The latter are radicals and olefins with four or less carbon atoms, or heavier radicals without further possibilities for decomposition, or heavier olefins with no further possibilities for hydrogen abstraction.

In thermal cracking, by far the major fraction of the feedstock molecules is transformed through hydrogen abstraction by means of radicals produced by initiations. Abstractions are then followed by radical isomerization and by radical decomposition. Extremely reactive intermediates such as radicals and some olefins are present only in very small quantities. Their concentrations can be eliminated by means of Bodenstein and Lutkemeyer's (1924) steady state approximation, so that for the purpose of kinetics, the reaction scheme is reduced to a simpli-

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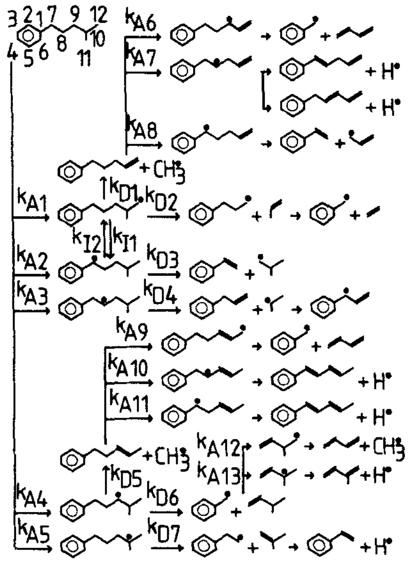

Figure 1. Primary reaction scheme for hydrogen abstraction on isohexylbenzene.

fied one containing only the feed component, isohexylbenzene, and its primary products. The reaction rate coefficients in the latter reaction scheme are functions of the rate coefficients of the individual reactions appearing in Figure 1. The procedure for the elimination of intermediate radicals and olefins is illustrated by means of the following example.

The net rates of formation of the 12- and the 7-isohexylbenzyl radical can be written:

$$\begin{aligned} r(\text{12-isohexylbenzyl}) &= k_{A1}[\text{isohexylbenzene}][R_\beta] \\ &\quad + k_{I2}[\text{7-isohexylbenzyl}] \\ &\quad - (k_{D1} + k_{D2} + k_{I1}) \cdot [\text{12-isohexylbenzyl}] \end{aligned} \quad (1)$$

$$\begin{aligned} r(\text{7-isohexylbenzyl}) &= k_{A2}[\text{isohexylbenzene}][R_\beta] \\ &\quad + k_{I1}[\text{12-isohexylbenzyl}] \\ &\quad - (k_{D3} + k_{I2})[\text{7-isohexylbenzyl}] \end{aligned} \quad (2)$$

The R_β radicals in Eqs. 1 and 2 are radicals that mainly disappear by bimolecular chain propagating mechanisms, such as addition on olefins or hydrogen abstraction. 12-isohexylbenzyl and 7-isohexylbenzyl are R_μ radicals, which mainly disappear by unimolecular isomerization and decomposition. In the steady state, their net rates of formation are zero:

$$r(\text{12-isohexylbenzyl}) = 0 = r(\text{7-isohexylbenzyl}) \quad (3)$$

This system can be solved for the concentrations of the R_μ radicals:

$$[\text{12-isohexylbenzyl}] = \frac{(k_{D3} + k_{I2})k_{A1} + k_{I2} \cdot k_{A2}}{(k_{D3} + k_{I2})(k_{D1} + k_{D2} + k_{I1}) - k_{I2} \cdot k_{I1}} \cdot [\text{isohexylbenzene}][R_\beta] \quad (4)$$

$$[\text{7-isohexylbenzyl}] = \frac{(k_{D1} + k_{D2} + k_{I1})k_{A2} + k_{I1} \cdot k_{A1}}{(k_{D1} + k_{D2} + k_{I1})(k_{D3} + k_{I2}) - k_{I1} \cdot k_{I2}} \cdot [\text{isohexylbenzene}][R_\beta] \quad (5)$$

The 12-isohexylbenzyl radical decomposes, for instance, into 5-phenyl-1-pentene and methyl, which is an R_β radical. The rate of formation of the methyl radical can be written:

$$r(\text{12-isohexylbenzyl} \rightarrow \text{methyl}) = k_{D1} \cdot [\text{12-isohexylbenzyl}] \quad (6)$$

Eliminating the concentration of the 12-isohexylbenzyl radical by means of Eq. 4 leads to:

$$r(\text{12-isohexylbenzyl} \rightarrow \text{methyl}) = k_{D1} \cdot \frac{(k_{D3} + k_{I2})k_{A1} + k_{I2} \cdot k_{A2}}{(k_{D3} + k_{I2})(k_{D1} + k_{D2} + k_{I1}) - k_{I2} \cdot k_{I1}} \cdot [\text{isohexylbenzene}][R_\beta] \quad (7)$$

The olefin, formed by the same decomposition, can also be eliminated, assuming steady state for its concentration. Only terms representing hydrogen abstractions are written in the continuity equations of intermediate olefins to account for their disappearance. Considering alternative mechanisms of disappearance, such as initiation or radical addition, would lead to a continuity equation from which the concentrations of the R_β radicals cannot be eliminated. Consequently, the steady state concentration of the intermediate olefin would be a function of the concentrations of the R_β radicals, which are not known until the reaction network is actually being used in a reactor simulation. So, the olefin should either not be eliminated at all or should be eliminated assuming that only one mechanism is important for its disappearance, namely hydrogen abstraction. For olefins with relatively high concentrations, this approximation is not justified. The additions of hydrogen and methyl radicals on straight chain 1-, 2-, or diolefins, for instance, cannot be neglected. These olefins are considered final products in the primary reaction schemes of feed components. Their continuity equations are appended to the other model equations, and their reaction schemes for hydrogen abstraction and radical addition are constructed as outlined above, as if they were feed components. 5-phenyl-1-pentene, the olefin originated along with the methyl radical from the decomposition of 12-isohexylbenzyl, is not likely to attain a high concentration level at any point in the reactor. Its concentration can be eliminated:

$$\begin{aligned} r(\text{5-phenyl-1-pentene}) &= k_{D1}[\text{12-isohexylbenzyl}] \\ &\quad - (k_{A6} + k_{A7} + k_{A8})[\text{5-phenyl-1-pentene}][R_\beta] = 0 \end{aligned} \quad (8)$$

$$\begin{aligned} [\text{5-phenyl-1-pentene}] &= \frac{k_{D1}}{k_{A6} + k_{A7} + k_{A8}} \frac{[\text{12-isohexylbenzyl}]}{[R_\beta]} \\ &= \frac{k_{D1}}{k_{A6} + k_{A7} + k_{A8}} \frac{(k_{D3} + k_{I2})k_{A1} + k_{I2} \cdot k_{A2}}{(k_{D3} + k_{I2})(k_{D1} + k_{D2} + k_{I1}) - k_{I2} \cdot k_{I1}} \cdot [\text{isohexylbenzene}] \end{aligned} \quad (9)$$

The concentration of 5-phenyl-1-pentene can be substituted into the rates of formation of the primary products:

$$r(\text{5-phenyl-1-pentene} \longrightarrow \text{benzyl}) = r(\text{5-phenyl-1-pentene} \longrightarrow C_4H_6) = k_{A6}[\text{5-phenyl-1-pentene}]$$

$$= \frac{k_{A6} \cdot k_{D1}[(k_{D3} + k_{I2})k_{A1} + k_{I2} \cdot k_{A2}]}{[(k_{D3} + k_{I2})(k_{D1} + k_{D2} + k_{I1}) - k_{I2} \cdot k_{I1}]} \cdot \frac{[\text{isohexylbenzene}][R_{\dot{\beta}}]}{(k_{A6} + k_{A7} + k_{A8})} \tag{10}$$

Primary products are radicals and olefins with four or less carbon atoms, or heavier radicals without further possibilities for decomposition, or heavier olefins with no further possibilities for hydrogen abstraction. Reactions between primary products are common to all feed components and, to a certain extent, are independent of the feed composition. A standard set of these so-called secondary reactions is appended to the primary reaction network for reactor simulation.

The rates of formation of primary products along different branches of the primary reaction network of a feed component are pooled for every primary product. The resulting reaction rates, the rate of disappearance of the feedstock component, and the rate of disappearance of the $R_{\dot{\beta}}$ radicals can be written as:

$$r(\text{component}) = k_A \cdot \text{PRC(component)} \cdot [\text{feed component}] \cdot [R_{\dot{\beta}}] \tag{11}$$

Table 1. Reaction Rate Coefficients for Formation of Primary Products*

	Reac. Rate Coeff. × 10^9** $m^3/kmol \cdot s$
For disappearance of	
Isohexylbenzene	0.9589
Abstracting radicals†	1.386
For formation of	
$H^\bullet$	0.4816
$CH_3^\bullet$	0.0316
$C_3H_5^\bullet$	0.0004
2-$C_3H_7^\bullet$	0.2022
i-$C_4H_9^\bullet$	0.0548
$C_7H_7^\bullet$	0.4131
$C_9H_9^\bullet$	0.2022
C_2H_4	0.1904
C_3H_6	0.1904
1,3-C_4H_6	0.0295
i-C_4H_8	0.2867
i-C_5H_8	0.1932
C_8H_8	0.3419
$C_{11}H_{12}$	0.0017
Calculation time, 7 s per temp.	

*Product formation through hydrogen abstraction on isohexylbenzene, after elimination of intermediate radicals and olefins. Feed component, isohexylbenzene; temp. 1,073.15 K.

**Reaction rate coefficients obtained from PRC's after multiplication by reference value, which is the reaction rate constant for abstraction of a single primary hydrogen atom by a hydrogen radical; i.e., 0.34085 × 10^8 $m^3/kmol \cdot s$ at 1,073.15 K.

†Abstracting radicals disappear by hydrogen abstraction on both feed components and intermediate olefins.

The k_{Ai} in the denominator have been replaced by $k_A \cdot \varphi_{Ai} \cdot k_A$ is the reaction rate constant for abstraction of a single primary hydrogen atom by a hydrogen radical. φ_{Ai} is the relative reactivity of the hydrogen atoms involved in hydrogen abstraction i. It is the product of the number of hydrogen atoms involved in reaction i and an Arrhenius-type expression for the relative reactivity of these atoms. For abstracting radicals other than the hydrogen radical, the righthand side of Eq. 11 can be multiplied by the relative reactivity of the abstracting radical. PRC is the "pseudo rate coefficient" for the formation of a primary product from a feedstock molecule. It is a function of rate coefficients and relative reactivities, and consequently of temperature. The influence of temperature is small, however, because most of the temperature dependency of the reaction rate coefficients is comprised in k_A. A set of pseudo rate coefficients calculated for a temperature T is sufficiently accurate for reactor simulation in a temperature range of some 20 K around T. Thus, the introduction of PRC's substantially reduces the number of temperature points to be considered.

For a given temperature, the calculation of PRC's is straightforward, provided that values for the reaction rate constants in Figure 1 are known. These reaction rate constants were determined by regression from our own experimental work and from literature data, as published by Tsang (1972) and Kopinke et al. (1985). An example of a set of reaction rate coefficients, obtained from pseudo rate coefficients after multiplication by the appropriate value of the reference rate constant, is given in Table 1.

The construction of the complete reaction network and the calculation of the associated PRC's are very time consuming, especially for the heavy molecules that occur in vacuum gas oil. Clymans and Froment (1984) developed a computer program that can generate the reaction networks and the associated rate equations for the thermal cracking of relatively light paraffins and naphthenes. The present paper deals with an extended version that can handle heavier paraffins and naphthenes, as well as aromatics and olefins. In this program, chemical structures are represented by the binary relation matrix (Himmelblau and Bischoff, 1968) or adjacency matrix (Marshall, 1971). Reactions are simulated by mathematical operations on the relation matrix, as outlined in the example below.

Computer Generation of Primary Reaction Network

A hydrocarbon is represented by a binary matrix $\boldsymbol{M}$. A carbon-carbon bond between atoms i and j is indicated by a 1 on the intersection of the ith row and the jth column. A vector $\boldsymbol{A}$ contains a 1 in every position that corresponds to the location of an aromatic carbon atom. The positions of the free electron and of double-bonded carbon atoms are stored in separate variables. For isohexylbenzene, only the matrix $\boldsymbol{M}$ and the vector $\boldsymbol{A}$ are

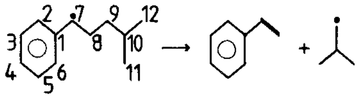

Figure 2. Decomposition of 7-isohexylbenzyl radical into styrene and isobutyl radical.

relevant:

$$M = \begin{array}{r|cccccccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ \hline 1 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 2 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 3 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 6 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 7 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 8 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 9 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 10 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 11 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 12 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{array} \qquad A = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

The carbon atoms can be numbered in an arbitrary way. The computer program, however, contains subroutines that renumber any species in a standard way. The reason for this will be explained below.

From the matrix M, the order of the carbon atoms can be determined by counting the relations on a row or column. The tenth row contains three relations, which indicates that carbon atom 10 is tertiary. The possibilities for β-scission of radicals can be determined from M^2, the Boolean square of matrix M. The definition of the Boolean square of matrix M indicates that this operation is equivalent to looking for the 1–3 relations between carbon atoms, or the possibilities for β-scission. In the actual F77 program, M and A are logical variables, and the calculations are executed by logical operators.

$$M^2 = \begin{array}{r|cccccccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ \hline 1 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 2 & 0 & 1 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 3 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 4 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 5 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 6 & 0 & 1 & 0 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 7 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 8 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 9 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 1 \\ 10 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 11 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 12 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \end{array}$$

The diagonal elements in this matrix are *1* because every carbon atom is connected to itself by two bonds via a neighboring carbon atom. Since these elements do not represent a true β position, they are set to zero. Thus, a *1* on row *i* of matrix $M^2 - I$ represents a carbon atom in β position with respect to carbon atom *i*. The minus sign is an arithmetic matrix subtraction.

Furthermore, no aromatic carbon atoms can be involved in a β-scission, because of the mesomeric stabilization of the aromatic ring. Therefore, all elements in columns 1 to 6 and rows 1 to 6 are set to zero. This operation also excludes the rupture of bonds in α position with respect to the aromatic ring. The resulting matrix $(M^2 - I)'$ gives the possibilities for β-scission:

$$(M^2 - I)' = \begin{array}{r|cccccccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ \hline 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 6 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 7 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 9 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 \\ 10 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 11 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 12 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \end{array}$$

The possibilities for β-scission are then (7, 9), (8, 10), etc. The first possibility corresponds to the decomposition of the 7-isohexylbenzyl radical into styrene and the isobutyl radical, as shown in Figure 2.

Each of the products of this reaction is represented by its own relation matrix M, a vector A labeling the aromatic carbon atoms, a vector D labeling the double-bonded carbon atoms in the olefin, and an integer variable R, containing the location of the free electron in the radical.

For the olefin, styrene, these variables are assigned a sub-

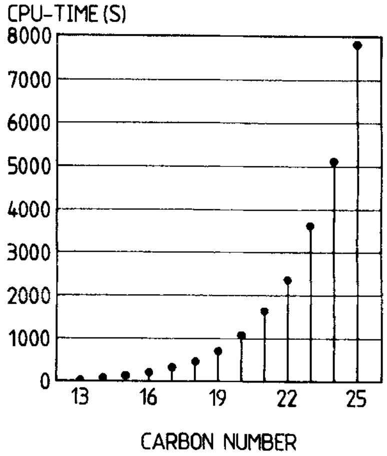

Figure 3. Required calculation time vs. carbon no. for homologous series of 2-methylparaffins.

script O:

$$M_O = \begin{array}{c|cccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ \hline 1 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 \\ 2 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 3 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 4 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 6 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 7 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 8 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{array} \qquad A_O = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} \qquad D_O = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \end{bmatrix}$$

$$R_O = 0$$

The variables describing the isobutyl radical are distinguished by the subscript R:

$$M_R = \begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 1 & 0 & 1 & 0 & 0 \\ 2 & 1 & 0 & 1 & 1 \\ 3 & 0 & 1 & 0 & 0 \\ 4 & 0 & 1 & 0 & 0 \end{array} \qquad A_R = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad D_R = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad R_R = 1$$

From A, M, and $M^2 - I$, the program deduces that the reagent for the above β-scission is a secondary radical in the allylic position with respect to the aromatic nucleus. The products are a primary radical and a primary olefin. The appropriate reaction rate constant is selected from the database and compared to the rates of alternative reaction paths for the disappearance of the 7-isohexylbenzyl radical, if there are any. The relation matrices and other variables representing the products of the β-scission can be derived from M and A, as outlined by Clymans and Froment (1984). By an analogous approach, the possibilities for 1,5-isomerization can be determined from the matrix $[(M^2 - I)^2 - (M^2 - I) - I]'$.

For small chain molecules, the computer program generates the primary reaction network within a few seconds. With growing chain length, however, the required calculation time increases dramatically. Figure 3 shows the influence of the chain length on the required calculation time for the homologous series of the 2-methylparaffins. For 2-methyldodecane, 41 CPU-seconds are needed, for 2-methylhexadecane 310 s, and for 2-methyleicosane 1,617 s. For naphthenes, which are important feedstock components in hydrotreated vacuum gas oil, the CPU times are even higher.

Self-learning System for Generation of Primary Reaction Schemes

From Figure 3, it may seem impossible to generate the primary reaction schemes for vacuum gas oil components using the described algorithm. The calculation time would become prohibitive, if the efficiency of the program would not be increased. A detailed inspection of the primary reaction schemes of homologous components indicates how a higher efficiency can be achieved.

Figures 4 and 5 show the formation of first-generation descendants through hydrogen abstraction on n-decane and n-undecane. First-generation descendants are products formed after one initiation, hydrogen abstraction, or radical addition, followed by isomerization and β-scission. Most of the first-generation descendants of n-undecane also appear in the network for n-decane. Only R_9 and O_9, the largest radical and olefin, are new. Repetitive calculations can be avoided if intermediate results from the reaction scheme of n-decane can be copied during the generation of the network for n-decane. The reaction scheme will have to be calculated only for R_9 and O_9.

Figure 6 shows the reaction scheme for the disappearance of R_8. The rate coefficients for the formation of primary products of n-decane through the radical R_8 are divided by the rate coefficient for the formation of R_8 from n-decane, and stored in a data file.

When R_8 is met again during the generation of the reaction scheme for n-undecane cracking, the coefficients for the formation of primary products from R_8 can be read from the data file, and multiplied by the current rate of formation of R_8. This operation is equivalent to generating the reaction scheme for R_8 again, but it saves the time required for the generation of the reaction scheme, at the cost of a library search and the input of the rate coefficients associated with the network for R_8.

This approach has been implemented in the computer program as shown in Figure 7. Whenever a descendant is being formed from a feed component, it is searched for in the library. If it is not found, its reaction scheme is generated and stored. If the descendant is present in the library, however, its reaction scheme is read from the library, instead of being generated again.

When a species is being formed from different radicals or feed components, the relation between the carbon atoms and the numbers of the rows and columns in the relation matrix may be different. In order to make sure that a species will always be recognized, it is renumbered in a standard way before being stored, or searched for, in the library. Since the number of structural elements that can occur in a species is relatively small, a unique

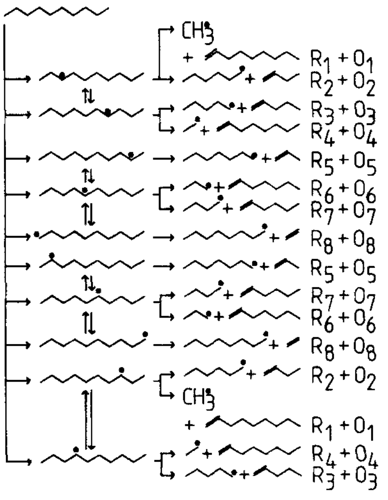

Figure 4. Formation of first-generation descendants through hydrogen abstraction on normal decane.

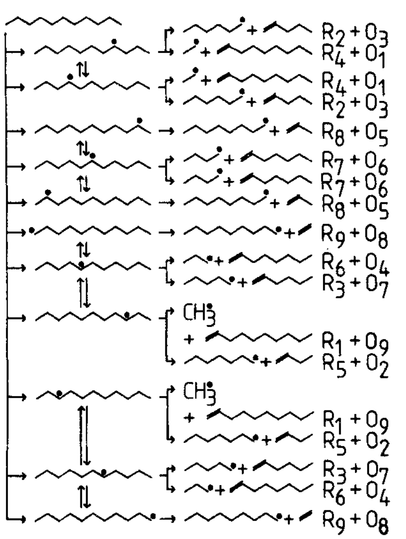

Figure 5. Formation of first-generation descendants through hydrogen abstraction on normal undecane.

numbering is possible for each species. Consequently, only one possible candidate must be compared with the specimen in the library, and not the minimum set of isomorphic representations that is usually left by the more general algorithms reviewed by Calusaru and Volanschi (1986). Moreover, another application can be envisaged for short chain molecules: intermediate species need not be eliminated under the hypothesis of a steady state, since they can be identified.

In order to reduce the calculation time to a minimum, the primary reaction schemes for a group of homologous components are generated with increasing chain length. For more efficiency in the library search, libraries can be dumped on tape. Later on, a library can be loaded from tape to replace a current one that contains superfluous components. For instance, after generation of the reaction schemes for 2-methylparaffins, a library containing only unbranched species will be more efficient than the existing one for the calculations concerning the 3-methylparaffins, or the aromatics.

The above modifications have turned the computer program into a self-learning system. Whenever a primary reaction scheme is generated for a feedstock molecule, intermediate radicals and olefins that are not present in the library are stored. As more networks are generated, the library becomes larger and larger, thus increasing the probability for recognition of olefins and radicals, and in principle reducing the CPU time required for the generation of a primary reaction network.

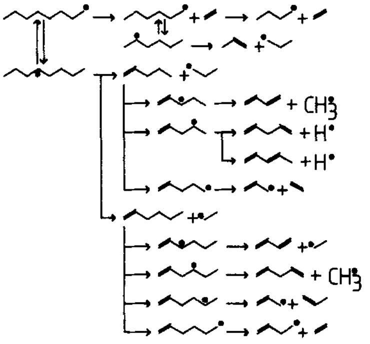

Figure 6. Reaction scheme for disappearance of straight chain 1-octyl radical.

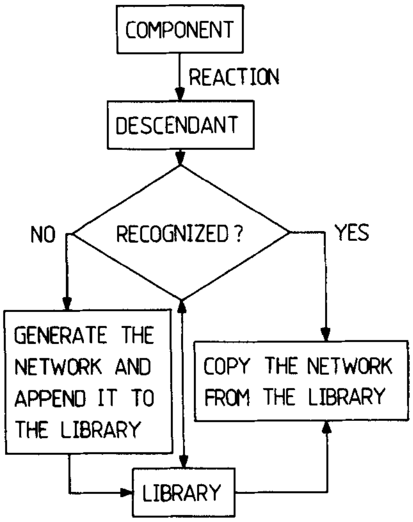

Figure 7. Implementation of self-learning system in computer program.

Organization of Library Containing Reaction Networks for Radicals and Olefins

A library must be well structured to reduce the time needed to search for a certain radical or olefin. When a species, encountered while generating a primary reaction path is not found in the library, its carbon number and, for radicals, the position of the free electron, are determined. Consider a radical containing 11 carbon atoms, with the free electron on the atom carrying number 1. The information needed to recognize this radical is stored in file 1101.DA, together with the name of another data file that contains the pseudo rate coefficients associated with the reaction scheme for the disappearance of this radical. In file 1101.DA, this information is listed for all radicals containing 11 carbon atoms, and a free electron in position 01.

The information necessary for recognition of the radical consists of two rows of numbers. For the straight chain 1-undecyl radical, these rows would look like this:

122222222210000000000000000000000

111111111110000000000000000000000

The first row indicates whether the carbon atoms are primary, secondary, tertiary, or quaternary. The second row gives more information on the nature of the carbon atom. The digits in this row can have the following values:

2	naphthenic carbon atoms
3	acyclic carbon atoms that are part of a double bond
4	aromatic carbon atoms
6	naphthenic carbon atoms that are part of a double bond
1	all other carbon atoms
0	if the digit's sequence number is higher than the carbon number of the species

Table 2. CPU Times With and Without Self-learning System (SLS)

Carbon No. of 2-Methylparaffin	Time, s	
	With SLS	W/out SLS
13	41	35
14	81	62
15	127	80
16	191	96
17	310	120
18	464	144
19	707	176
20	1,068	207
21	1,617	250
22	2,340	302
23	3,592	357
24	5,127	417
25	7,831	497

The rate coefficients associated with the disappearance of the radical are stored in, for instance, file 11010105004.DA, with:

11	carbon number
01	position of the free electron, 00 for olefins
0105	sequence number of the feedstock component from which the radical is formed
004	sequence number of the descendant of the feed molecule; this number is incremented for each new initiation, radical addition or abstraction, and for each radical and olefin formed by β-scission.

Grouping all radicals and olefins with the same carbon number and the same position of the free electron in one file reduces the search time to a minimum. If all radicals and olefins were stored in a single file, more CPU time would be needed to search for a specific radical or olefin.

Effect of Introduction of Self-Learning System on Required Calculation Time

Table 2 gives the the calculation times needed to generate the reaction schemes for the series of the 2-methylparaffins, with and without the self-learning system. Introduction of the self-learning system reduces the total CPU time required to generate the primary reaction schemes for the series 2-methyldodecane--2-methyltetracosane to 11.7% of the time that would be needed without it. For the generation of the primary reaction schemes of the 2-methylparaffins with carbon numbers from 13 up to 33, the self-learning system reduces the CPU time to 2.2% of what would be needed without it.

Conclusions

The thermal cracking of complex mixtures of heavy hydrocarbons is described in terms of the cracking of their components. The complex reaction networks for each of these are generated by a computer program using graph theory.

The kinetic equations can be generated automatically because the reaction paths are followed step by step and the reaction products are identified by the computer program. The elimination of intermediates that are present in low concentrations by means of the steady state approximation reduces the reaction scheme to a set of so-called pseudo rate coefficients, which are functions of reaction rate constants only.

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Notation

A = vector that labels the aromatic carbon atoms in a hydrocarbon
[component] = concentration of component in [ ], kmol/m^3
D = vector that labels the double-bonded carbon atoms in a hydrocarbon
I = unity matrix
k_A = reaction rate constant of reference hydrogen abstraction reaction, m^3/kmol · s
k_{Ai} = reaction rate constant of hydrogen abstraction reaction i, m^3/kmol · s
k_{Di} = reaction rate constant of radical decomposition reaction i, 1/s
k_{Ii} = reaction rate constant of radical isomerization reaction i, 1/s
M = relation matrix
O_i = an olefin of identity i
PRC(comp) = pseudo rate coefficient for formation of component in ( ); ratio of reaction rate coefficient for formation of a product to reference reaction rate constant for reaction responsible for disappearance of the feedstock
r(comp) = rate of formation of component in ( ), kmol/m3 · s
r(reac) = rate of reaction in ( ), kmol/m^3 · s
R = integer variable containing location of the free electron in a radical
R_i = a radical of identity i
T = temperature

Greek letters

α = first bond along a carbon chain
β = second bond along a carbon chain
φ_{Ai} = relative reactivity of hydrogen atoms involved in hydrogen abstraction reaction i

Subscripts

i = arbitrary integer identifying an olefin or reaction
O = olefin
R = radical
β = a radical that mainly disappears by bimolecular reactions
μ = a radical that mainly disappears by unimolecular reactions

Superscript

2 = Boolean square of a matrix

Literature Cited

Allara, D. L., and R. Shaw, "A Compilation of Kinetic Parameters for the Thermal Degradation of *n*-Alkane Molecules," *J. Phys. Chem. Ref. Data*, **9**(3), 523 (1980).

Bodenstein, M., and H. Lütkemeyer, "Die photochemische Bildung von Bromwasserstoff und die Bildungsgeschwindigkeit der Brommolekel aus den Atomen," *Z. Physik. Chem.*, **114**(3), 208 (1924).

Calusaru, A., and C. Volanschi, "The Nonnumerical, Mathematical Expression of Chemical Structures and Reactions. I: The Representation of Chemical Structures and Computer Algorithms by Matrices," *Int. Chem. Eng.*, **26**(3), 428 (1986).

Clymans, P. J., and G. F. Froment, "Computer Generation of Reaction Paths and Rate Equations in the Thermal Cracking of Normal and Branched Paraffins," *Comput. Chem. Eng.*, **8**(2), 137 (1984).

Dente, M., E. Ranzi, S. Barendregt, and P. G. Cronin, "Steam Cracking of Heavy Liquid Feedstocks—Cracking Yields Rigorously Predicted," Paper D, AIChE Spring Nat. Meet., Sess. 48, "Olefins Production: Fundamentals and Technological Aspects, I," New Orleans (1986).

Green, E. J., S. B. Zdonik, and L. P. Hallee, "Olefins Production by Gas Oil Cracking," *Hydrocarbon Process.*, **54**(9), 164 (1975).

Himmelblau, D. M., and K. B. Bischoff, *Process Analysis and Simulation. Deterministic Systems,* Wiley, New York (1968).

Kopinke, F.-D., G. Bach, B. Ondruschka, and G. Zimmermann, "Relative Reaktivitäten von C-H-Bindungen bei der thermischen Spaltung Gesättigter Kohlenwasserstoffe," *Z. Physik. Chem.*, **266**(3), 610 (1985).

Lohr, B., and H. Ditmann, "New Gas-Oil Model Calculates Ethylene Yield," *Oil Gas J.*, **75**(27), 53 (1977).

Marshall, C. W., *Applied Graph Theory,* Wiley-Interscience, New York, 15 (1971).

Rennard, R. J., and H. E. Swift, "Pyrolysis Feedstock Studies: Correlation and Modeling of Hydrogenated Distillates," *Ind. Eng. Chem. Prod. Res. Dev.*, **23**(1), 106 (1984).

Tsang, W., "Thermal Decomposition of 3,4-Dimethylhexane, 2,2,3-Trimethylpentane, tert-Butylcyclohexane, and Related Hydrocarbons," *J. Phys. Chem.*, **76**(2), 143 (1972).

Zimmermann, G., H. Günschel, S. Nowak, and W. Nette, "Vergleichende Untersuchungen zur Pyrolyse von Höhersiedenden Kohlenwasserstoff-Fraktionen," *Erdoel Kohle, Erdgas, Petrochem. Brennst.-Chem.*, **37**(9), 411 (1984).

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