SIMULATION OF PRIMARY SELECTIVITY OF HYDROCARBON PYROLYSIS

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The mathematical model is described for the determination of primary selectivity of hydrocarbon pyrolysis, i.e., the determination of proportion of single components in the first generation of products of pyrolysis. The model stems from the radical reaction mechanism. It is assumed that the main influence on the product composition has the chain propagation involving the hydrogen atom transfer, isomerization and breaking the hydrocarbon radical. To determine the rate constants, the kinetic data published in the literature and the data on bond enthalpies in hydrocarbon molecules were employed. The simulation results were compared with the experimental data taken from the literature and with the results of measurements obtained in pyrolysis of two types of naphthas in a pilot-plant reactor.

On modelling the hydrocarbon pyrolysis, the primary and secondary reactions are distinguished as a rule. The primary reactions describe the formation of the first generation of molecular products from hydrocarbons of the raw material pyrolysed, the secondary reactions include the subsequent changes of the products. Since hydrocarbons may react in more ways, the primary reactions are, from the kinetic point of view, a set of parallel reactions which result in a spectrum of products:

$$\text{raw material} \rightarrow \nu_1 H_2 + \nu_2 CH_4 + \nu_3 C_2H_6 + \ldots + \nu_n C_x H_y \ , \qquad (A)$$

where ν denotes the empirical stoichiometric coefficient. The distribution of products of the primary reactions will be henceforth designated as the primary selectivity of pyrolysis. The primary selectivity is experimentally determined by analysing the products of pyrolysis at low conversion of reaction mixture and/or by extrapolating the experimental data to a low extent of conversion. The data on the primary step of pyrolysis form the starting point of a number of kinetic models of hydrocarbon pyrolysis.

The aim of this work has consisted in exploiting the hitherto concepts of the pyrolysis mechanism to establish the primary selectivity of pyrolysis of hydrocarbons constituting the main portion of the naphtha raw materials. The source of information were the data on the behaviour of molecules and radicals[1-6], on bond enthalpies[7] and

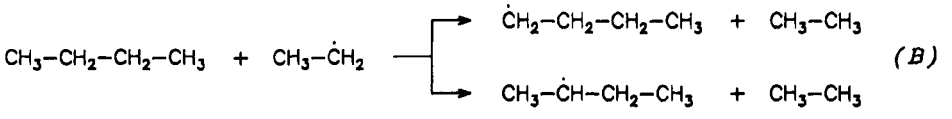
the published results of the experimentally determined primary selectivities of hydrocarbons[1,3,8 - 10].

THEORETICAL

Reaction Mechanism

When making up the model, it was assumed that the primary reactions take place via a radical chain mechanism. To describe the primary selectivity of pyrolysis, the most important phase is the chain propagation in which the substitution, isomerization, breaking and addition reactions are cyclically repeated. If the reaction chain is sufficiently long, even a relatively small number of radicals is able to bring about the conversion of a great number of molecules owing to their repeated regeneration. Since the initiation and termination concern only comparatively very small portion of molecules, the description of primary selectivity was limited to the four types of the most important reactions: hydrogen transfer including the hydrogen atom abstraction and, at the same time, its absorption, further intramolecular isomerization and radical breaking.

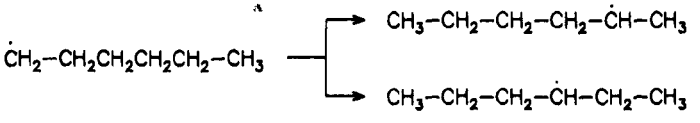
Hydrogen transfer. Hydrogen molecules enter the reaction chain by the reaction with a radical in which hydrogen atom is abstracted out of the molecule, e.g.,



(B)

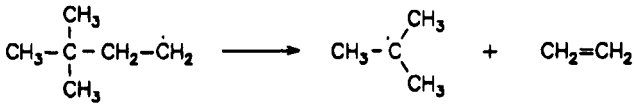
Since the higher radicals are unstable, practically only lower radicals – hydrogen, methyl, ethyl, propyl, and butyl – abstract hydrogen. For these radicals, the term active radicals is used in further text. Considering that the hydrogen molecules contain hydrogen atom bound to different carbon atoms, a wide spectrum of radicals is formed by abstracting hydrogen.

Radical isomerization. The intramolecular isomerization is characteristic of higher radicals consisting in the hydrogen atom transfer in the framework of the only radical. The reaction takes place through a cyclic transition state of five or six members (four of five carbon atoms and one hydrogen atom). A radical is formed by isomerization which differs from the original one by the position of unpaired hydrogen, e.g.,



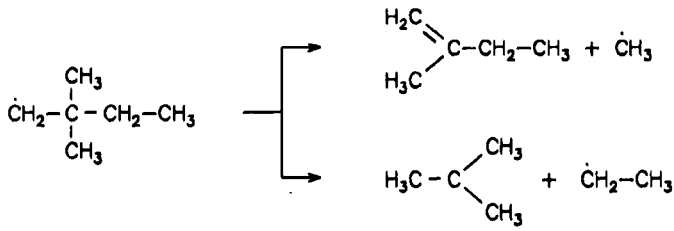
(C)

Radical scission. A so-called β-scission (β-transformation) is typical of hydrocarbon radicals, i.e., bond breaking in β-position to the carbon carrying unpaired hydrogen. Mostly the carbon–carbon (C–C) bond is broken, less often the carbon–hydrogen (C–H) bond. A stable molecule, which is one of products of the primary pyrolysis reactions, and a secondary radical result from the scission, e.g.,



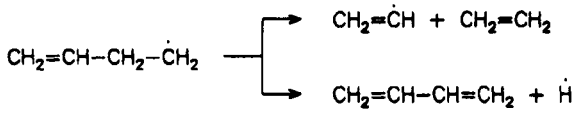
(D)

As to the saturated radicals, it is assumed that, with respect to the considerable difference in the C–C and C–H bond energies, only the C–C bond splitting takes place. If there is more C–C bonds in β-position to unpair electron, different types of product species result, e.g.,



(E)

In case of the unsaturated radicals, the C–C bond in α-position to the multiple bond is strengthened and, on the contrary, the C–H bond in β-position to the multiple bond is weakened owing to the presence of unsaturated bonds. Consequently, splitting the weakened C–H bond is considered as well with unsaturated radicals, e.g.,



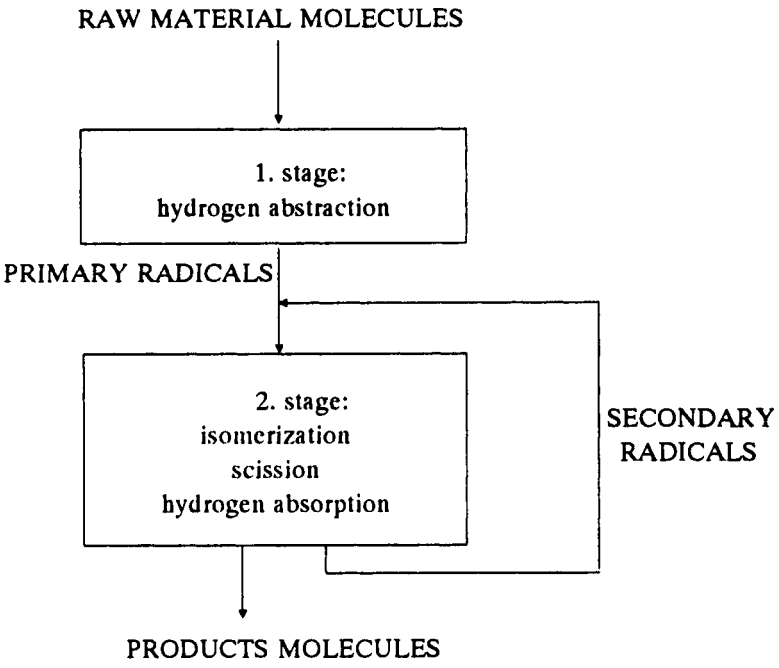
(F)

As for the multiple bonds in β-position to unpair electron, it is assumed that under usual conditions of pyrolysis, they are not split.

Description of Reaction Kinetics

On describing the kinetics of primary reactions, it is assumed that the rate-controlling step of hydrocarbon pyrolysis is the formation of primary radicals by hydrogen abstraction from hydrocarbon molecules. The other reactions in chain take place practically instantaneously. The determination of primary selectivity can therefore be divided

into two basic phases, viz., the reaction of molecules and the stabilization of radicals (see Scheme 1).



SCHEME 1

Reaction of molecules. The starting relation for the description of reactions of hydrocarbon molecules were the rate equations of changes of hydrocarbons by hydrogen abstraction

$$\boldsymbol{r}_m' = -\boldsymbol{K}_m' \, c_a \, \boldsymbol{c}_m , \qquad (1)$$

where $\boldsymbol{r}_m'$ is the vector of hydrocarbon changes, $\boldsymbol{K}_m'$ matrix of rate constants, c_a the concentration of active radical (short-chain radical, e.g., hydrogen, methyl, ethyl), and $\boldsymbol{c}_m$ the vector of hydrocarbon concentrations. For the determination of primary selectivity, the absolute reaction rates are not decisive but only the relative rates are sufficient. On the assumption of an approximately constant concentration of active radicals, the relative rate of removing the hydrocarbons by abstracting hydrogen was determined from the relation

$$\boldsymbol{r}_m = -\boldsymbol{K}_m \, \boldsymbol{c}_m , \qquad (2)$$

where $\boldsymbol{r}_m$ is the vector of relative rates and $\boldsymbol{K}_m$ the diagonal matrix of relative rate constants. The relative rate constants, $K_{m(j,j)}$, i.e., the elements of matrix $\boldsymbol{K}_m$ were assessed from the equation

$$K_{m(j,j)} = \sum_i (\alpha_i k_i) , \tag{3}$$

where k_i stands for the relative rate constant of hydrogen abstraction corresponding to splitting the different carbon–hydrogen bonds of the given type and α_i the number of single types of carbon–hydrogen bonds in hydrocarbon molecule. Constants k_i were determined from the relation

$$k_i = \frac{A_i \exp(-E_i/RT)}{A_0 \exp(-E_0/RT)} , \tag{4}$$

where A_i and E_i are the frequency factors and activation energies of the absolute rate constants, A_0 and E_0 the frequency factor and activation energy of the standard rate constant, respectively, R the gas constant and T temperature. On the assumption that the values of frequency factors are approximately identical[1], Eq. (4) can be simplified to the form

$$k_i = \exp[(-E_i + E_0)/RT] . \tag{5}$$

When deriving the relative rate constants, the data on bond enthalpies were employed. As the standard bond, the bond of hydrogen on primary carbon (C–H bond in CH_3 group) was chosen. The difference of activation energies in Eq. (5) was replaced by the difference of bond enthalpies:

$$k_i = \exp[(-D_i + D_0)/RT] , \tag{6}$$

where D_i are enthalpies of certain bonds of hydrogen on carbon and D_0 the enthalpy of standard C–H bond. The parameters of Eq. (6) were derived or, if need be, modified

TABLE I
Relative rate constants of hydrogen abstraction for the carbon–hydrogen bonds

Subscript *i*	Type of hydrogen abstracted	k_i
1	hydrogen on carbon of multiple or aromatic bond	0
2	primary hydrogen	1
3	secondary hydrogen	exp (10/*RT*)
4	tertiary hydrogen	exp (19/*RT*)
5	primary hydrogen, multiple or aromatic bond in β-position	exp (20/*RT*)
6	secondary hydrogen, multiple or aromatic bond in β-position	exp (39/*RT*)
7	tertiary hydrogen, multiple or aromatic bond in β-position	exp (40/*RT*)

according to literature[1 - 7] and are given in Table I. For instance, the rate constant of decrease of pentane by hydrogen abstraction can be determined from the equation

$$K_{m(\text{pentane})} = 6\,k_2 + 6\,k_3\,. \tag{7}$$

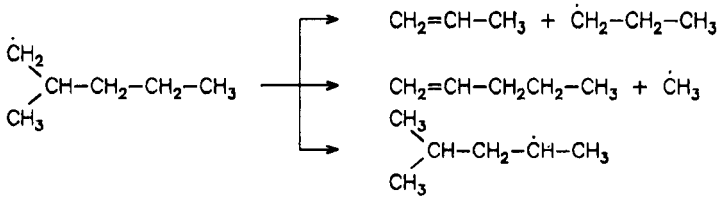
Reaction of radicals. The description of the radical reaction stems from the assumption of direct transformation of primarily formed radicals to molecular products. For the radical transformations, the selectivity coefficients were used expressing the proportion of the rate of formation of the given product from the total rate of change of initial radical. The quantity of the product formed in the radical reaction was determined as the product of selectivity coefficient and the quantity of initial radical.

The higher radicals with five and more carbon atoms are stabilized above all by isomerization and β-scission and under the usual conditions of pyrolysis, their hydrogen absorption may be neglected. The selectivity coefficients of isomerization and/or scission were determined according to the relations

$$s^{I}_{i,j,k\ldots} = k^{I}_i/(k^{I}_i + k^{I}_j + k^{D}_k + \ldots)\,, \tag{8}$$

$$s^{D}_{k,i,j\ldots} = k^{D}_k/(k^{I}_i + k^{I}_j + k^{D}_k + \ldots)\,, \tag{9}$$

where $s^{I}_{i,j,k}$ is the selectivity coefficient of isomerization of type (i) with which compete isomerization (j) and scission (k), $s^{D}_{k,i,j}$ is the selectivity coefficient of scission of type (k) with which competes isomerization (i) and (j), k^{I}_i, k^{I}_j and k^{D}_k are the rate constants of isomerizations and scission of radicals. The values of the constants were taken over or



(G)

derived from the data in works[1 - 7] and are given in Tables II and III.

For instance, the conversion of 1-radical of 2-methylpentane through three parallel reactions can be described, according to Tables II and III, by the selectivity coefficients

$$s^{D}_{6,1,5} = k^{D}_6/(k^{I}_1 + k^{D}_5 + k^{D}_6)\,, \tag{10}$$

$$s^{D}_{5,1,6} = k^{D}_5/(k^{I}_1 + k^{D}_5 + k^{D}_6)\,, \tag{11}$$

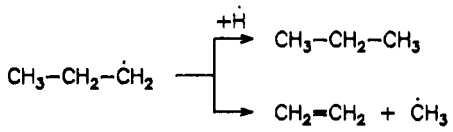
$$s^{I}_{1,5,6} = k^{I}_1/(k^{I}_1 + k^{D}_5 + k^{D}_6)\,. \tag{12}$$

Unlike the higher radicals, the radicals with four and less carbon atoms are stabilized through two competitive reactions – β-scission and hydrogen absorption. An exception are methyl and hydrogen radicals which are stabilized by hydrogen absorption only. The selectivity coefficients of hydrogen absorption and competitive scission were determined according to the relations

$$s^{D}_{i,j} = k^{D}_{i}/(k^{A}_{j} H + k^{D}_{i}) \ , \tag{13}$$

$$s^{A}_{j,i} = k^{A}_{j} H/(k^{A}_{j} H + k^{D}_{i}), \tag{14}$$

where $s^{D}_{i,j}$ is the selectivity coefficient of scission of type (i) with which hydrogen absorption (j) competes, $s^{A}_{j,i}$ is the selectivity coefficient of hydrogen absorption of type (j) with which scission (i) competes, H is the hydrocarbon concentration in reaction mixture transformed into the number of standard C–H bonds, and k^{A}_{j} the rate constant of hydrogen absorption. The values of rate constants of scission and hydrogen



(H)

absorption were taken from literature[1,2] and are given in Tables IV and V. For instance, the stabilization of 1-propyl through the reactions can be described, according to Tables IV and V, by the selectivity coefficients

$$s^{D}_{12,1} = k^{D}_{12}/(k^{A}_{1} H + k^{D}_{12}) \ , \tag{15}$$

$$s^{A}_{1,12} = k^{A}_{1} H/(k^{A}_{1} H + k^{D}_{12}) . \tag{16}$$

TABLE II

Rate constants of isomerization of 1-radicals. TS – transfer between primary and secondary hydrogen atom, TT – transfer between primary and tertiary hydrogen atom

Subscript i	Size of transition ring	k^{I}_{i}, s^{-1}
1	five-membered ring TS	6.7E10 exp (–88/RT)
2	six-membered ring TS	1.1E10 exp (–59/RT)
3	five-membered ring TT	3.3E10 exp (–88/RT)
4	six-membered ring TT	5.3E09 exp (–59/RT)

Concentration H was determined from the equation

$$H = \frac{P_c}{RT}\,\beta\,, \tag{17}$$

where P_c is the partial pressure of hydrocarbons and β the average number of standard C–H bonds in one hydrocarbon molecule. Quantity β was established from the relation

$$\beta = \gamma_1 + \gamma_1' k_5 + \gamma_2 k_3 + \gamma_2' k_6 + \gamma_3 k_4 + \gamma_3' k_7\,, \tag{18}$$

where γ_1 to γ_3 are the average numbers of bonds between carbon and primary, secondary and tertiary hydrogen atom, respectively, in one hydrogen molecule, γ_1' to γ_3' express the analogous number of C–H bonds neighbouring in β-position with multiple or aromatic bond. Coefficients k_i in Eq. (*18*) express the reduced bond strength in units of the standard bond. Their value was adjusted according to Table I.

Principle of Mathematical Model

The proposed model works with direct composition of raw material. To describe the pyrolysed naphthas, 34 hydrocarbons was chosen which represent the most important identified components of industrially processed naphtha raw materials. The simulation takes place in a sufficiently short dimensionless time interval, Δt, which corresponds to a small change of conversion. The calculation can be divided into two phases:

TABLE III
Rate constants of breaking C–C and C–H bonds of radicals with more than four carbon atoms

Subscript i	Type of β-bond	k_i^D, s^{-1}
1	CH_2=CH – CH–	2.0E14 exp (–155/*RT*)
2	CH_2=CH–CH – H	1.0E13 exp (–132/*RT*)
3	CH_3 – CH_2–	1.0E14 exp (–132/*RT*)
4	–CH_2 – CH_2–	1.0E14 exp (–126/*RT*)
5	CH_3 – CH<	1.0E14 exp (–126/*RT*)
6	–CH_2 – CH<	1.0E14 exp (–116/*RT*)
7	CH_3 – C(–)(–)–	1.0E14 exp (–116/*RT*)
8	–CH_2 – C(–)(–)–	1.0E14 exp (–106/*RT*)
9	>CH – CH<	1.0E14 exp (–106/*RT*)
10	>CH – C(–)(–)–	1.0E14 exp (–96/*RT*)

1. The formation of the first generation of radicals through the hydrogen abstraction from hydrocarbon molecules. The result of calculation is a set of radicals with concentration given by the relation

$$\boldsymbol{c}_r = \boldsymbol{K}_r \boldsymbol{c}_m \Delta t \,, \tag{19}$$

where $\boldsymbol{c}_r$ is the vector of concentrations of the first generation of radicals, $\boldsymbol{K}_r$ the matrix of products of relative rate constants for hydrogen abstraction and number of H atoms whose abstraction leads to the formation of the given radical type, and $\boldsymbol{c}_m$ the vector of concentrations of molecules of pyrolysed material. In this phase, the decrease in hydrocarbon concentrations by hydrogen abstraction corresponding to the chosen time interval Δt are determined for all hydrocarbons in reaction mixture:

$$\Delta \boldsymbol{c}_m = -\boldsymbol{K}_m \boldsymbol{c}_m \Delta t \,. \tag{20}$$

The determined changes of concentrations of hydrocarbons are employed in calculating the selectivities of reaction products.

2. Stabilization of radicals. In this phase, the set of radicals is gradually transfered to stable products by the simulation of isomerization, scission and hydrogen absorption. For instance, the conversion of 1-hexyl can be described by Scheme 2.

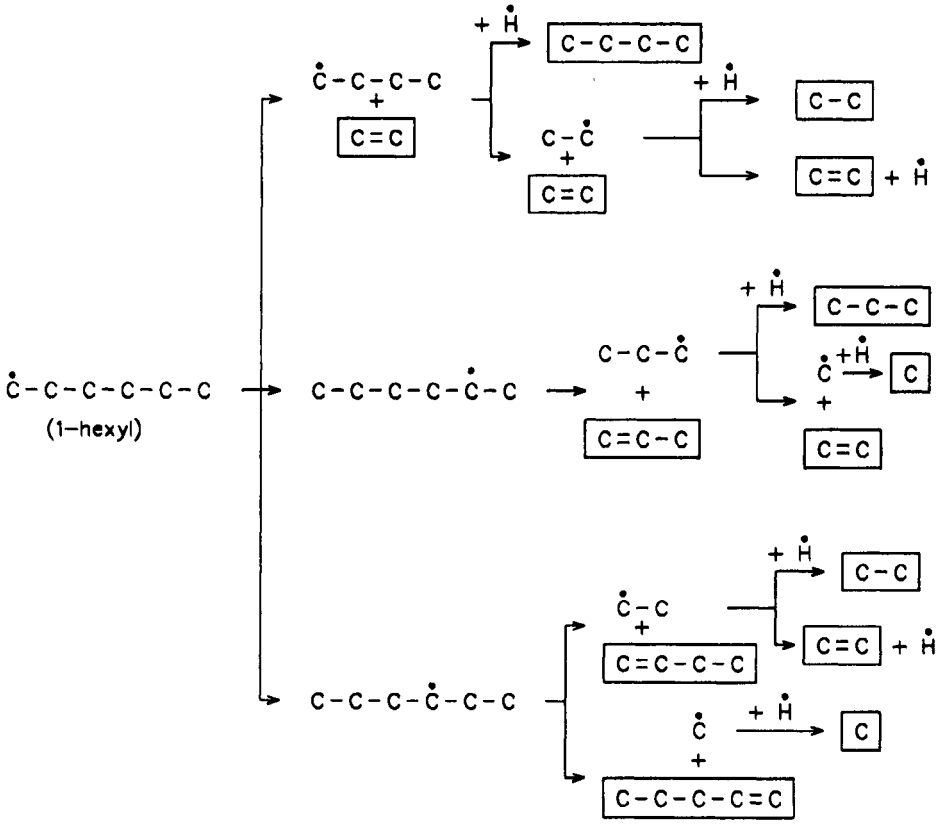
The mechanism of radical transformation is based on consecutive stabilization in the direction from higher to lower radicals. The molecular products can be written as

$$\boldsymbol{c}_p = \boldsymbol{S}_m [\boldsymbol{I} + \boldsymbol{S}_r + \boldsymbol{S}_r^2 + \ldots + \boldsymbol{S}_r^n] \boldsymbol{c}_r \,, \tag{21}$$

TABLE IV
Rate constants of breaking C–C and C–H bonds of radicals with at most four carbon atoms

Subscript *i*	Type of radical	k_i^D, s^{-1}
11	ethyl	3.2E13 exp (−170/*RT*)
12	1-propyl	5.0E13 exp (−134/*RT*) + 7.9E13 exp (−159/*RT*)
13	2-propyl	2.0E14 exp (−176/*RT*)
14	1-butyl	4.0E13 exp (−121/*RT*) + 1.3E14 exp (−163/*RT*)
15	2-butyl	1.0E14 exp (−138/*RT*) + 1.6E14 exp (−172/*RT*)
16	p-isobutyl	2.0E14 exp (−142/*RT*) + 1.0E14 exp (−159/*RT*)
17	t-isobutyl	2.0E14 exp (−176/*RT*)
18	3-butenyl	1.0E14 exp (−205/*RT*)
19	4-butenyl	2.0E14 exp (−165/*RT*) + 1.0E13 exp (−142/*RT*)
20	isobutenyl	1.0E14 exp (−196/*RT*)

where c_p is the vector of concentrations of molecular products, S_m the matrix of selectivity coefficients for the formation of molecular products, I udentity matrix, S_r the matrix of selectivity coefficients for the formation of radical intermediates and n total number of radical intermediates generations. According to Eq. (*21*), at first is solved the decomposition of the first generation of radicals. By their breaking, a spectrum of the second generation radicals and, simultaneously, the molecular reaction products are formed. In the next step, the decomposition of the third generation of



SCHEME 2

radicals is solved etc. During the consecutive decomposition of radical generations, the generated molecular products are recorded.

The simulation model was developed in Turbo Pascal computer language. The program of about 100 kB extent is divided into 7 modules for practical reasons.

EXPERIMENTAL

The primary selectivity of both the naphtha samples was determined experimentally in Research Institute of Chemical Equipments, Brno. The pyrolysis was studied in a pilot-plant reactor placed in electric furnace. The tubular reactor of length 22 m and inside diameter 10 mm was made of stainless steel. The flow rate was set at 5 to 8 kg h^{-1}. The experiments take place at the temperature of 680 to 820 °C at approximately unit steam/oil ratio (kg kg^{-1}). The reaction mixture was, after cooling, separated to the liquid and gaseous part, the composition of both parts was analysed separately by gas chromatography. The yields of single products were determined from the overall balance of mixture. The type composition of petrol samples is given in Table VI. The composition of outlet mixture at different reactor loadings was determined for each raw material. The primary selectivity of pyrolysis was obtained by extrapolating the selectivities of the components chosen to the zero conversion.

RESULTS AND DISCUSSION

Simulation of Pure Hydrocarbon Pyrolysis

On testing the model, the pyrolysis of pure hydrocarbons was simulated. A comparatively wide spectrum of primary selectivities of linear and non-linear alkanes is published in the literature, however, the data on cyclic hydrocarbons are missing. The

TABLE V
Rate constants of hydrogen absorption

Subscript i	Type of radical	k_i^A, m^3 mol^{-1} s^{-1}
1	$\dot{C}H_2-$	2.0E8 exp (−59/*RT*)
2	$-\dot{C}H-$	2.0E8 exp (−67/*RT*)
3	$-\dot{C}-$	1.0E8 exp (−71/*RT*)

Table VI
Characteristic of naphtha raw materials

Characteristic	Naphtha A	Naphtha B
Density ρ_{20}, kg m^{-3}	717	717
Group analysis, wt.%:		
n-alkanes	57	31
iso-alkanes	18	33
naphthenes	18	28
aromates	7	8
Average molar mass, kg $kmol^{-1}$	107	98

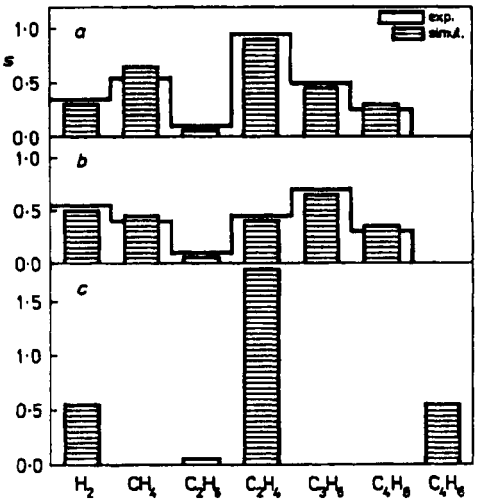


FIG. 1

Simulated and experimentally found primary selectivities, *S*, of hydrocarbons with six carbon atoms in molecule. Temperature 700 °C, partial pressure 10 kPa. *a* n-Hexane, *b* methylpentane, *c* cyclohexane

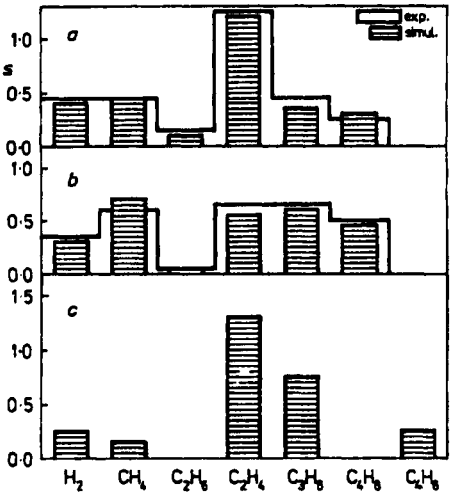


FIG. 2

Simulated and experimentally found primary selectivities, *S*, of hydrocarbons with seven carbon atoms in molecule. Temperature 700 °C, partial pressure 10 kPa. *a* n-Heptane, *b* methylhexane, *c* methylcyclohexane

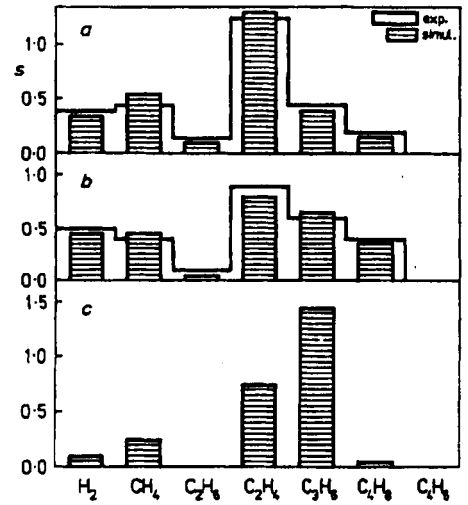


FIG. 3

Simulated and experimentally found primary selectivities, *S*, of hydrocarbons with eight carbon atoms in molecule. Temperature 700 °C, partial pressure 10 kPa. *a* n-Octane, *b* methylheptane, *c* 1,3-dimethylcyclohexane

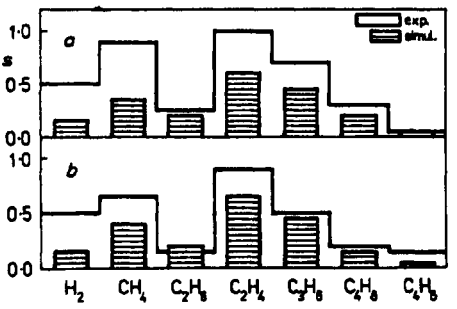


FIG. 4

Comparison of experimental and simulated primary selectivity *S* of naphthas A and B. Naphtha A: temperature 670 °C, pressure 240 kPa, steam/petrol ratio 0.6 kg kg^{-1}. Naphtha B: temperature 650 °C, pressure 270 kPa, steam/oil ratio 0.8 kg kg^{-1}. *a* Naphtha A, *b* naphtha B

simulated and experimentally determined primary selectivities are illustrated in Figs 1, 2 and 3 for linear, non-linear and cyclic hydrocarbons with six, seven and eight carbon atoms in molecule. For cycloalkanes, only simulated data are given because the experiments on pyrolysis of individual hydrocarbons lead to the quite different results from those of cycloalkane pyrolysis in mixtures with other hydrocarbons[8,10].

The diagram plotted support a good agreement of the simulated and experimental data, comparable to the accuracy of simulations reported in the literature. For a more detailed analysis of the model reliability, however, the information is missing on the reliability of experimental data. In case of the primary selectivity of cycloalkanes, rather a hypothetical selectivity is concerned, nevertheless the differences in the cycloalkane primary selectivities reveal the considerable effect of methyl substituents.

Simulation of Naphtha Pyrolysis

The comparison of compositions of the naphthas used as a raw material with representative components in mathematical model showed that 34 hydrocarbons with which the model works, covers approximately 80 mass% and/or 90 mole% of hydrocarbons present in the material used. The remainder is formed by a great number of heavier components with comparatively low mole fraction. In one series of simulations, this remainder was neglected, in the second one, the missing hydrocarbons in the model mixture were replaced by intuitively chosen model compounds. The evaluation of simulations led to the conclusion that both the ways yield practically equivalent results, thus, it is more advantageous to employ the simpler method.

The comparison of the experimental and simulated data is illustrated in Fig. 4. It is evident that the results of comparison are conspicuously worse than for pure hydrocarbons. The disagreement cannot be uniquely interpreted as a drawback of the model. Similar disagreement was observed also by other authors[9,11] . Its main reason is probably the effect of secondary reactions whose influence cannot be eliminated in pilot-plant or bench-scale reactors especially at higher reaction temperatures. In case of the pilot-plant or bench-scale measurements, the result may be mainly influenced by the methods of selectivity calculations and also by an error in balance calculations which influence the accuracy of extrapolating the results to the zero conversion.

CONCLUSION

The model developed is able to describe the relation between the raw material composition, temperature, pressure, steam dilution, and primary products of raw material splitting. It may be exploited as a constituent part of a complex pyrolysis model whose second part is the description of secondary reactions. It will be possible to analyse the reliability of the model only after setting-up the complex model on the basis of compa-

rison of the experimentally determined and simulated selectivities at high conversions of different raw materials.

SYMBOLS

A_i	frequency factors, $m^3\ mol^{-1}\ s^{-1}$
A_0	standard frequency factor, $m^3\ mol^{-1}\ s^{-1}$
c_a	active radical concentration, mol m^{-3}
$\boldsymbol{c}_m$	vector of hydrocarbon concentrations
$\boldsymbol{c}_p$	vector of concentrations of molecular products
$\boldsymbol{c}_r$	vector of concentrations of first generation of radicals
D_i	bond enthalpies, kJ mol^{-1}
D_0	standard bond enthalpy, kJ mol^{-1}
E_i	activation energies, kJ mol^{-1}
E_0	standard activation energy, kJ mol^{-1}
H	concentration of hydrocarbons in reaction mixture, transformed to number of standard C–H bonds, mol m^{-3}
$\boldsymbol{I}$	udentity matrix
k_i^A	rate constants of hydrogen absorption, $m^3\ mol^{-1}\ s^{-1}$
k_i^D	rate constants of radical scission, s^{-1}
k_i^J	rate constants of radical isomerization, s^{-1}
k_i	relative rate constants of hydrogen abstraction
$\boldsymbol{K}_m$	matrix of relative rate constants of hydrocarbon changes by hydrogen abstraction
$\boldsymbol{K}'_m$	matrix of absolute rate constants of hydrocarbon changes by hydrogen abstraction
$K_{m(j,j)}$	relative rate constants of hydrocarbon conversions by hydrogen abstraction
$\boldsymbol{K}_r$	matrix of products of relative rate constants of hydrogen abstraction and number of H atoms whose abstracting gives rise to radical of given type
P_c	partial pressure of hydrocarbons, kPa
$\boldsymbol{r}_m$	vector of relative rates of hydrocarbon conversions by hydrogen abstraction
$\boldsymbol{r}'_m$	vector of rates of hydrocarbon conversions by hydrogen abstraction
R	gas constant, kJ $mol^{-1}\ K^{-1}$
S	primary selectivity
$\boldsymbol{S}_m$	matrix of selectivity coefficients of molecular product formation
$\boldsymbol{S}_r$	matrix of selectivity coefficients of radical product formation
s^A	selectivity coefficients of hydrogen absorption
s^I	selectivity coefficients of isomerization
s^D	selectivity coefficients of breaking
t	dimensionless time
T	reaction mixture temperature, K
α_i	numbers of carbon–hydrogen bonds of certain type in hydrocarbon molecule
β	average number of standard carbon–hydrogen bonds in hydrocarbon molecule
γ_i	average numbers of carbon–hydrogen bonds of certain type in one hydrogen molecule
ν_i	stoichiometric coefficients

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