THE MATHEMATICAL MODEL OF NAPHTHA STEAM CRACKING

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The mathematical model of naphtha steam cracking has been developed to predict products yields. The feedstock composition, feedstock rate, steam-oil ratio, inlet temperature, outlet temperature and outlet pressure are introduced as inputs. The reaction model consists of two parts: the radical reactions of higher alkanes, higher alkenes, naphthenes and alkylaromatics and the formal molecular reactions of lower alkanes and lower alkenes. The model was identified using a series of large-scale experiments including four naphtha raw materials. Eight experiments were carried out for each naphtha kind at two levels of the temperature profile, feed rate and steam-oil ratio.

Prediction of valuable products yields in thermal cracking of hydrocarbon feedstocks can be a very attractive tool in selecting feedstock blends to produce ethylene, propylene, benzene and other important products. The traditional kinetic approach based on a detailed description of all reactions is not applicable because the pyrolysis process presents an extensive reaction complex. As a consequence, individual chemical reactions cannot be investigated isolated. Kinetic data on the steam cracking of individual hydrocarbons measured in laboratory reactors cannot be utilized to construct a large-scale model because reaction conditions in a laboratory reactor are different from those in large-scale reactors. To develop a model based on the representation of reaction mechanisms, many simplifications must be introduced to reduce the number of adjustable parameters (rate constants, activation energies).

Several principles are used to develop predictive models for industrial steam cracking. Dante and Ranzi[1,2] developed a model which is based on the representation of reaction mechanisms. In its final version the model involves about 500 reactions. To obtain a model applicable in practice, the assumption of pseudostationary state of radicals and other simplifications were introduced. This model is perhaps the most sophisticated model described in chemical engineering literature.

Other types of models are based on formal molecular reactions[3,4] which do not reflect the real reaction mechanisms. These models may be effective in describing the thermal cracking of lower hydrocarbons.

Another practical approach proceeds from the so called initial selectivities[5]

$$\text{raw material} \rightarrow \nu_1H_2 + \nu_2CH_4 + \nu_3C_2H_6 + \ldots + \nu_nC_xH_y , \qquad (1)$$

where ν_i are stoichiometric coefficients which can be evaluated from laboratory experiments. Reliability of this approach is reduced due to differences between industrial-, pilot-, and bench-scale units.

Empirical statistical correlations are utilized to predict yields in production plants. These models are based on long-term experimental experience. Yields are described as empirical functions of reaction conditions and feedstock characteristics. The basic disadvantage of these models is the impossibility of application to reactors with different constructions.

The mathematical model described in this paper represents an interconnection of radical reactions and formal molecular reactions. In contrast to physico-mathematical models which connect two separate steps – experimentally evaluated primary selectivities followed by secondary molecular reactions, this pure mathematical model solves simultaneously both steps in every computation step. The model was developed in cooperation with the Research Institute for the Chemical Utilization of Hydrocarbons, Litvínov.

THEORETICAL

Mathematical model. A simplified approach was applied to simulate the behaviour of the reactor. The inputs into the mathematical model are summarized in Table I.

The axial temperature profile was calculated from the inlet and exit temperatures introduced as inputs. An empirical formula was used to describe the profile

$$T = \theta_1 z + \theta_2 z^2 + \theta_3 z^3 + \theta_4 z^4 + \theta_5 z^5 + T_{in}(1 - z) + T_{out} z , \qquad (2)$$

TABLE I
Mathematical model inputs

Input	Unit
Feedstock composition (Table II)	wt.%
Inlet reaction temperature	°C
Outlet reaction temperature	°C
Outlet reaction pressure	kPa
Feed rate of feedstock	$kg\ h^{-1}$
Dilution ratio (steam/hydrocarbons)	$kg\ kg^{-1}$

where z represents the dimensionless length of the reactor tube, T_{in} inlet temperature, T_{out} outlet temperature and $\theta_1 - \theta_5$ empirical constants which were evaluated from temperatures measured along the industrial reactor.

The pressure profile is established by using the preliminary estimate of inlet pressure and iterative solution of reactor model. The pressure drop along the tube reactor was calculated from

$$\frac{\mathrm{d}P}{\mathrm{d}z} = -\frac{\lambda}{d}\frac{\rho w^2}{2} = -\theta_6\frac{\dot{m}^2 T}{PM}, \tag{3}$$

where ρ is the density of reaction mixture, w flow velocity, $\dot{m}$ mass feed rate, P pressure, M mean molecular weight of reaction mixture, T reaction temperature, and θ_6 an empirical constant. Since the reactor diameter, d, and friction factor, λ, where considered as approximately constant, an empirical parameter θ_6 was introduced. The value of this parameter was evaluated from pressure measurements in the industrial reactor.

The feedstock is represented by a mixture of individual hydrocarbons. The hydrocarbons included in the mathematical model are listed in Table II. The kinetic computations include three subsystems: radical formation, radical decomposition and molecular reactions (Scheme 1). A simple example of model mechanism for pentane pyrolysis is presented in Scheme 2. The radical reactions include reactions of higher

TABLE II
Basic hydrocarbons included in the mathematical model

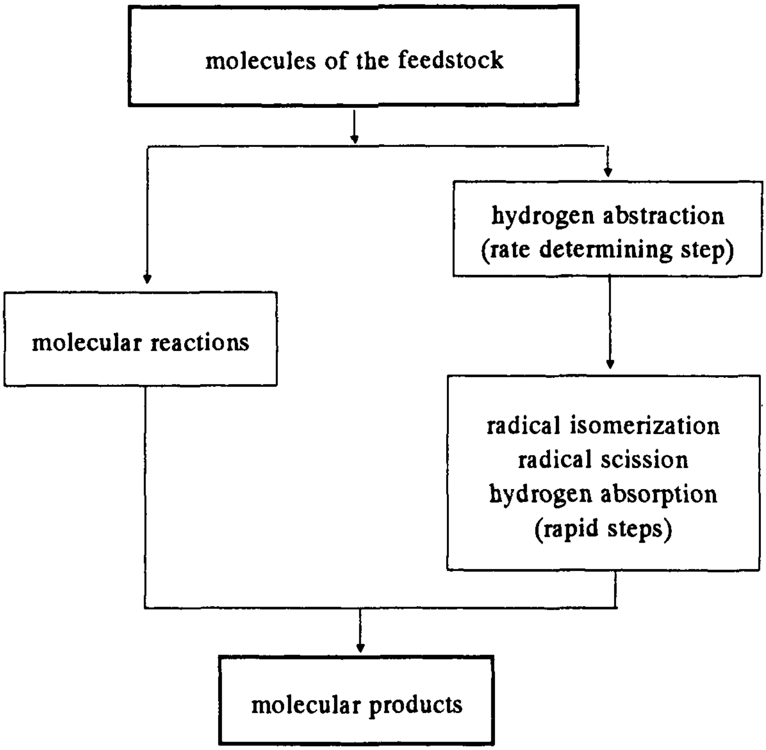
No.	Compound	No.	Compound
1	Ethane	18	1,3-Dimethylcyclopentane
2	Propane	19	3-Ethylpentane
3	Isobutane	20	Heptane
4	Butane	21	1,2-Dimethylcyclopentane
5	Isopentane	22	Methylcyclohexane
6	Pentane	23	Toluene
7	2,2-Dimethylbutane	24	2-Methylheptane
8	Cyclopentane	25	3-Methylheptane
9	2-Methylpentane	26	2,2,4-Trimethylpentane
10	3-Methylpentane	27	1,3-Dimethylcyclohexane
11	Hexane	28	Octane
12	Methylcyclopentane	29	Ethylbenzene
13	2,4-Dimethylpentane	30	Nonane
14	Benzene	31	Propylbenzene
15	Cyclohexane	32	Isopropylbenzene
16	2-Methylhexane	33	Trimethylbenzenes
17	3-Methylhexane	34	Decane

alkanes, higher alkenes, naphthenes and some alkylaromatics, i.e. reactions of hydrocarbon molecules, the radicals of which can easily degrade by the β-scission of weak C–C bond or C–H bonds. The molecular reactions correspond to the formal reaction set, in literature usually denoted as secondary reactions. They consist of reactions of lower alkanes and lower alkenes.

I. Radicals formation. Transformations of hydrocarbon molecules are initiated by the hydrogen abstraction which is supposed to be a first order reaction. Assuming plug flow, the radicals formed due to hydrogen abstraction from hydrocarbon molecules can be calculated from the equation

$$\frac{\mathrm{d}\mathbf{c}_\mathrm{r}}{\mathrm{d}z} = \mathbf{K}_\mathrm{r}\mathbf{c}_\mathrm{m}\frac{PVM}{RT\dot{m}}, \qquad (4)$$

where $\mathbf{c}_\mathrm{r}$ represents the vector of radicals concentrations, $\mathbf{K}_\mathrm{r}$ matrix of rate constants for radicals formation[6], $\mathbf{c}_\mathrm{m}$ vector of molecular species concentrations, V reactor volume and R gas constant. Hydrogen abstraction is supposed to be rate controlling in primary



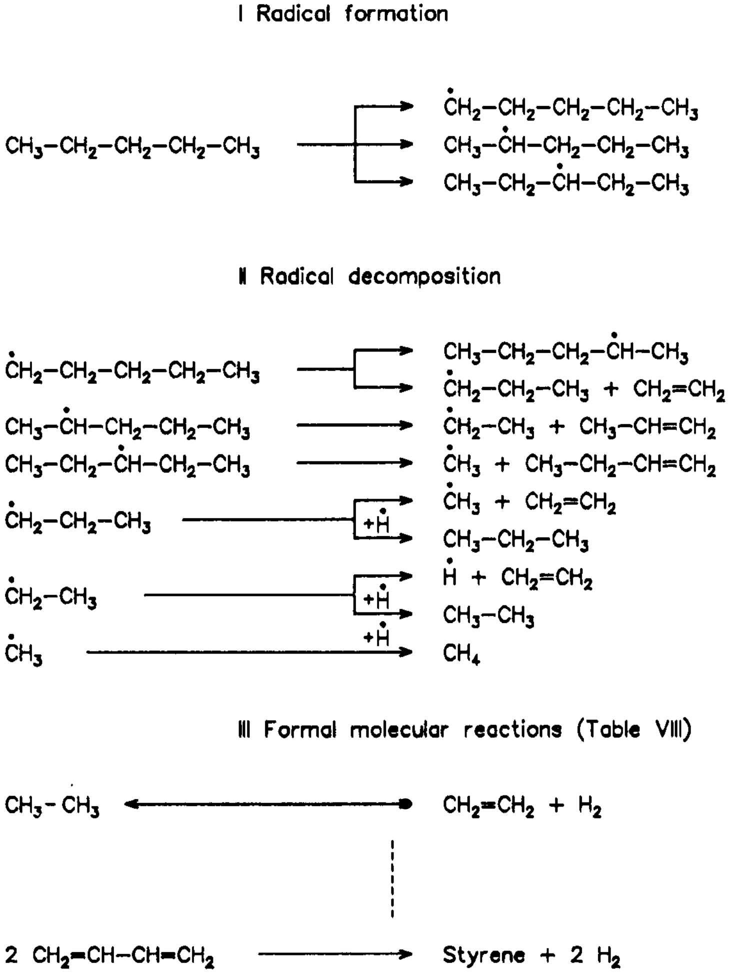
SCHEME 1

reactions[7]. To calculate the abstraction rates of different hydrogen atoms, the rate constants were derived from data published in literature and from identification of the model (Table III).

The corresponding losses in concentrations of molecules can be written as

$$\frac{\mathrm{d}\, c_m}{\mathrm{d}\, z} = -K_m\, c_m \frac{P V M}{R T \dot{m}}, \tag{5}$$

where K_m is the matrix of rate constants for transformation of molecules to radicals.



SCHEME 2

II. Radical decomposition. The radicals formed in the previous step are transferred to the stable molecular products by isomerization, β-scission and hydrogen absorption. The mechanism is based on consecutive radical stabilization in the direction from higher to lower radicals. The molecular products gaines can be written as

$$\frac{\mathrm{d}\,\boldsymbol{c}_\mathrm{m}}{\mathrm{d}\,z} = \boldsymbol{S}_\mathrm{m}\,[\boldsymbol{I} + \boldsymbol{S}_\mathrm{r} + \boldsymbol{S}_\mathrm{r}^2 + \ldots + \boldsymbol{S}_\mathrm{r}^n\,]\,\boldsymbol{c}_\mathrm{r}\,, \qquad (6)$$

where $\boldsymbol{S}_\mathrm{m}$ is the matrix of selectivity coefficients for the formation of molecular products, $\boldsymbol{I}$ udentity matrix, $\boldsymbol{S}_\mathrm{r}$ the matrix of selectivity coefficients for the formation of radical intermediates and n total number of radical intermediates generations (Scheme 2, $n = 3$). The selectivity coefficients express a ratio of the formation rate of a given product to the total rate of the radical transformation[6]. For example, the selectivity coefficient of formation of ethylene from 1-pentyl radical (Scheme 2) is expressed as the ratio of scission rate to sum of isomerization and scission rate.

III. Molecular reactions. In order to explain the reactions of lower alkanes and lower alkenes, a formal molecular mechanism was used. Material balances for reaction components can be written in the form

$$\frac{\mathrm{d}\,c_{\mathrm{m(i)}}}{\mathrm{d}\,z} = \sum \nu_{\mathrm{ij}}\, r_\mathrm{j}\, \frac{P V M}{R T \dot{m}}\,, \qquad (7)$$

where $c_{\mathrm{m(i)}}$ is the concentration of reaction component (*i*) and r_j rate of reaction (*j*). Equations (*4*), (*5*) and (*7*) were solved using a fourth-order Runge–Kutta method. The molecular reactions are supposed to be first order to reactants. The system of equations published in literature[5,8] was used as the basis to develop the system. The equilibrium constants for reversible reactions were calculated by standard procedures and checked with published values.

TABLE III
Rate constants for abstraction of different hydrogen atoms

Subscript *i*	Type of hydrogen abstracted	k_i, s^{-1}
1	hydrogen on C atoms with multiple or aromatic bonds	0
2	primary hydrogen	$7.2\,.\,10^{10}\exp(-225/RT)$
3	secondary hydrogen	$7.2\,.\,10^{10}\exp(-215/RT)$
4	tertiary hydrogen	$7.2\,.\,10^{10}\exp(-206/RT)$
5	primary hydrogen, multiple or aromatic bond in β-position	$7.2\,.\,10^{10}\exp(-205/RT)$
6	secondary hydrogen, multiple or aromatic bond in β-position	$7.2\,.\,10^{10}\exp(-186/RT)$
7	tertiary hydrogen, multiple or aromatic bond in β-position	$7.2\,.\,10^{10}\exp(-185/RT)$

Simulation model. The software was programmed in the Turbo Pascal language. The programme extent is about 150 kB and includes seven units:

- Input data according to Table I
- Calculations of reaction parameters
- Radical formation (hydrogen abstraction)
- Radical stabilization (radical isomerization and scission, hydrogen absorption)
- Formal molecular reactions
- Economic evaluation (calculation of product prices obtained from 1 ton of raw material)
- Output of data according to Table IV.

The program allows to input higher number of raw material streams and to carry out simulation experiments with different naphtha mixtures.

TABLE IV
Mathematical model outputs

Outputs	Unit
Current reactor length	dimensionless
Current reaction temperature	°C
Current reaction pressure	kPa
Propylene/methane ratio	dimensionless
Degree of conversion	%
Selectivities:	wt.%
hydrogen	
methane	
ethane	
ethylene	
propane	
propylene	
butane + isobutane	
1-butene	
2-butene	
isobutene	
butadiene	
benzene	
toluene	
ethylbenzene	
styrene	

EXPERIMENTAL

Large-scale experiments. The experimental research was carried out in the Chemical Works in Litvínov, by the staff of the production unit in co-operation with specialists from the Chemopetrol, Research Institute for the Chemical Utilization of Hydrocarbons. The steam cracking furnace of type SRT3 (Short Residence Time Reactor) was used in experiments. A full factor plan of experiments of dimension 2^3 (three factors at two levels) was carried out. The factors can be seen in Table V. Four naphthas were tested and their basic characteristics are summarized in Table VI.

RESULTS AND DISCUSSION

Reliability analysis of experimental data. In the model development, the simulated yields were compared with those obtained in experiments and the differences were evaluated. Therefore, the significant magnitudes of these differences had to be defined. No objective statistical method could be used to evaluate the significance of the differences because the experimental runs could not be repeated several times to obtain

TABLE V
Reaction conditions selected as factors in large-scale experiments

Factor	Unit	First level	Second level
Feed rate	kg h^{-1}	20 000	25 000
Temperature interval	°C	600 – 810	630 – 840
Dilution ratio	kg kg^{-1}	0.5	0.7

TABLE VI
Characteristics of naphthas investigated in large-scale experiments

Characteristic	Naphtha code			
	A	B	C	D
Density ρ_{20}, kg m^{-3}	706	717	721	750
Type analysis, wt.%:				
total paraffins	68.1	64.5	62.3	61.2
normal paraffins	30.5	29.6	29.1	25.4
naphthenes	25.3	25.8	29.6	21.4
aromates	6.6	9.7	8.1	17.4
Average molar mass, kg kmol^{-1}	91.1	97.6	98.5	103.7

information on the measurement reproducibility and the number of experimental points was too small to apply any statistical method. An intuitive method was used: The experimental evaluated yields for each naphtha blend were described by an empirical function and the trends of yields were observed and compared for different feedstocks, i.e. the effects of temperature, load and steam-oil ratio were compared and analyzed.

The analysis proved that the relative errors in yields depend on the content of the particular product in the exit reaction mixture and on its molar mass. The highest accuracy can be expected for the basic low molar mass products (ethylene, propylene, ethane, methane) present in high concentrations. The error increases with increasing molar mass. It seems that errors of the mass balances increase with increasing mean molar mass of the naphtha blend. Estimates of errors in evaluation of the concentrations of products are given in Table VII.

Agreement between simulated and measured values. Longitudinal temperature and pressure profiles and longitudinal changes of the reaction mixture composition were obtained as results of each simulation run. An example of temperature and pressure profiles is shown in Fig. 1 and the corresponding changes of products composition are illustrated in Fig. 2. The end points of the profiles represent the exit compositions.

During the model development the equations system of formal molecular reactions and their parameters were changed to obtain agreement between the simulated and measured exit compositions. No sophisticated method could be applied to find the best combination of equations and their parameters. An empirical procedure based on "trial and error" was used. It was found in the model identification step that the equation system published in literature[5,8] does not fit satisfactory the experimental results, espe-

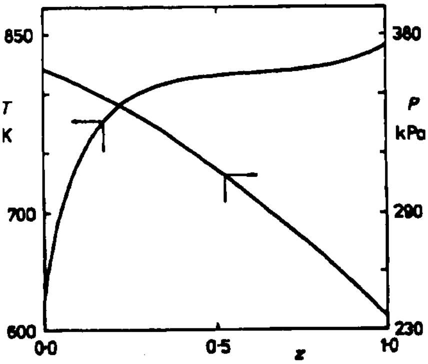


FIG. 1

Examples of longitudinal profiles resulting from simulation with naphtha A. Regime characteristics are given in Fig. 3

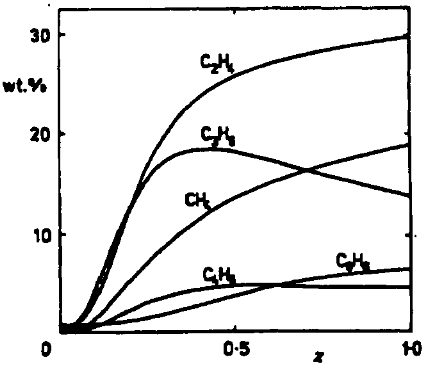


FIG. 2

Examples of longitudinal product yields resulting from simulation with naphtha A. Regime characteristics are given in Fig. 3

cially for the methane and propylene yields. Therefore, a modified reaction set was taken to get acceptable agreement between the experimental and simulated data. The resulting system of molecular reactions is shown in Table VIII.

The simulation model is able to reflect the typical features of the steam cracking behaviour. Examples of model ability to describe experimental yields are given in Figs 3 and 4. It can be concluded that differences between simulated and experimental yields are approximately of the same order of magnitude as the uncertainty of the experimental data. That could be taken as a proof that the model can describe the steam cracking with the accuracy necessary for technical application.

However, the ability of the model to fit the experimental data set cannot prove its general validity. A long-term verification in a production plant would be necessary for

TABLE VII
Estimates of relative errors of products yields

Range of error, rel%	Product
0 – 5	ethylene, propylene, butenes
5 – 10	methane, ethane, butadiene
> 10	aromatics

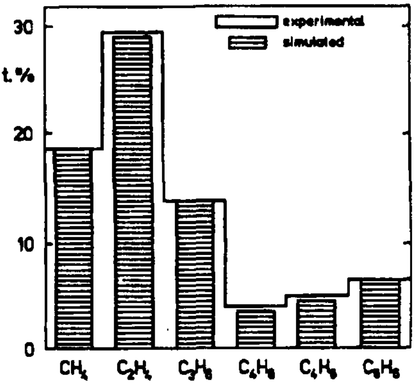


FIG. 3
Example of comparison of simulated and experimental yields for naphtha A. Feed rate $\dot{m}$ = 25 000 kg h^{-1}, steam-oil ratio SO = 0.5 kg kg^{-1}, inlet temperature T_{in} = 630 °C, outlet temperature T_{out} = 840 °C, outlet pressure P_{out} = 240 kPa

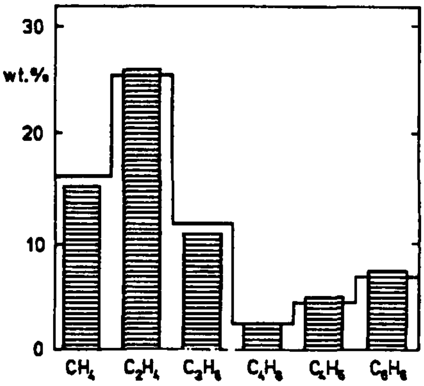


FIG. 4
Example of comparison of simulated and experimental yields for naphtha D. Regime characteristics are given in Fig. 3

TABLE VIII

List of formal molecular reactions. B benzene, T toluene, EB ethylbenzene, ST styrene, C_6^+ aromatics-free product boiling above the end point of the feed

Reaction No.	Stoichiometric equation	Frequency factor		Activation energy kJ mol^{-1}
		s^{-1}	m^3 mol^{-1} s^{-1}	
1	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	$4.65 . 10^{13}$		272.6
2	$C_3H_6 \leftrightarrow C_2H_2 + CH_4$	$7.28 . 10^{12}$		273.1
3	$C_2H_2 + C_2H_4 \rightarrow C_4H_6$		$1.03 . 10^{9}$	172.5
4	$2\ C_2H_6 \rightarrow C_3H_8 + CH_4$	$3.75 . 10^{12}$		272.8
5	$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$		$7.08 . 10^{10}$	252.6
6	$C_3H_8 \leftrightarrow C_3H_6 + H_2$	$1.30 . 10^{10}$		214.4
7	$C_3H_8 \rightarrow C_2H_4 + CH_4$	$4.69 . 10^{10}$		211.5
8	$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$		$2.54 . 10^{10}$	246.9
9	$2\ C_3H_6 \rightarrow 2.5\ CH_4 + 1.3\ C_2H_4 + 1.5\ C_6^+$	$4.65 . 10^{6}$		130.0
10	$C_3H_6 + C_2H_6 \rightarrow 1\text{-}C_4H_8 + CH_4$		$1.00 . 10^{11}$	250.8
11	$C_4H_{10} \rightarrow C_3H_6 + CH_4$	$7.00 . 10^{12}$		249.3
12	$C_4H_{10} \rightarrow 2\ C_2H_4 + H_2$	$7.00 . 10^{14}$		295.4
13	$C_4H_{10} \rightarrow C_2H_4 + C_2H_6$	$4.10 . 10^{12}$		256.3
14	$C_4H_{10} \leftrightarrow 1\text{-}C_4H_8 + H_2$	$1.64 . 10^{12}$		260.7
15	$1\text{-}C_4H_8 \rightarrow 2\ C_2H_4$	$1.09 . 10^{11}$		212.1
16	$1\text{-}C_4H_8 \leftrightarrow C_4H_6 + H_2$	$6.40 . 10^{10}$		209.0
17	$2\text{-}C_4H_8 \rightarrow C_3H_6 + CH_4 - H_2$	$2.80 . 10^{7}$		136.3
18	$i\text{-}C_4H_8 \rightarrow C_3H_6 + CH_4 - H_2$	$1.10 . 10^{11}$		210.0
19	$C_4H_6 + C_2H_4 \rightarrow B + 2\ H_2$		$8.00 . 10^{6}$	144.5
20	$C_4H_6 + C_3H_6 \rightarrow T + 2\ H_2$		$9.74 . 10^{5}$	149.0
21	$C_4H_6 + 1\text{-}C_4H_8 \rightarrow EB + 2\ H_2$		$6.40 . 10^{11}$	242.3
22	$C_4H_6 + C_4H_6 \rightarrow ST + 2\ H_2$		$1.51 . 10^{6}$	124.4

that. For a more precise description of different naphthas behaviour in the industrial reactor, the more detailed energy and momentum balances and the thorough characterization of naphthas composition are inevitable.

SYMBOLS

$c_{m(i)}$	concentration of molecular reaction component, mol/kg of reaction mixture
c_r	vector of radical concentrations
$\mathbf{c}_m$	vector of molecular species concentrations
d	internal reactor diameter, m
k_i	rate constant for abstraction of hydrogen atom, s^{-1}
$\mathbf{I}$	udentity matrix
$\mathbf{K}_m$	matrix of rate constants of molecules transformations
$\mathbf{K}_r$	matrix of rate constants of radicals formation
$\dot{m}$	mass feed rate, kg s^{-1}
M	mean molecular weight of reaction mixture, kg mol^{-1}
n	total number of radical intermediates generations
P	total pressure, Pa
P_{out}	outlet total pressure, Pa
r_j	rate of formal molecular reaction, mol kg^{-1} s^{-1}
R	gas constant, J mol^{-1} K^{-1}
$\mathbf{S}_m$	matrix of selectivity coefficients for the formation of molecular products
$\mathbf{S}_r$	matrix of selectivity coefficients for the formation of radical intermediates
T	reaction temperature, K
T_{in}	inlet reaction temperature, K
T_{out}	outlet reaction temperature, K
V	reactor volume, m^3
w	flow velocity, m s^{-1}
z	dimensionless axial reactor coordinate
λ	friction factor
ν_i	stoichiometric coefficient
θ_i	empirical constant
ρ	density of reaction mixture, kg m^{-3}

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