

# Computation of the Solid Catalyzed Gas Phase Reactions with a Simultaneous Choice of the Scheme of the Reactions for Different Composition of the Initial Reaction Mixture

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One of the features of the industrial heterogeneous catalytic reactions is an influence of qualitative and quantitative composition of the initial reaction mixture on the reactions proceeded. At the stage of the laboratory experiments it is possible to find the stoichiometry, kinetic equations and reaction constants for different components of the initial flow of the raw materials. It is important also to take into account multivariant composition of the initial flows. For these purposes we developed and realized an algorithm for using the model with a simultaneous choice of model equations depending on the composition of the initial reaction mixture. The algorithm was checked on the basis of an example of the aromatization of light alkanes with the different composition of the initial mixture.

## 1. Introduction

Solving of the problems of investigation, optimization and design of the catalytic reactors is based on developing of the models of the chemical transformations and determination of the rate constants of the corresponding reactions. One of the characteristics of the process of developing of the models of the industrial reactors is the need for taking into account a variation of the composition, pressure and temperature of the raw materials in the reactor input (Chistyakov et al., 2013). Variation of these parameters of the initial flow gives different quality and quantity composition of the reaction products (House, 2007). These features are necessary to take into account both in the laboratory investigations and in the process of design of the mathematical model (Gartman and Klushin, 2008). For this reason, it is desirable to carry out experiments in the wide range of parameters of the raw materials and to take into account a variation of the composition of the initial mixture in the mathematical models (Dobrynkin et al., 2012).

There is important in this case to develop an algorithm for solving identification task for a wide range of experimental data which includes various input parameters for reactors and allow to determine simultaneously one set of model parameters for using by simulation pilot and industrial reactor processes. Finally the mathematical model should have a complex structure with different equation systems depending on the parameters the raw's streams of reactors (temperature, pressure and composition). This model allowed to make automatically choice between different equation systems which describes processes for inlet streams with different parameters of raw to the reactor (Gartman et al., 2014).

The procedure of the mathematical model design was investigated by treatment of experimental data of processing of light alkanes into aromatics (Gartman et al., 2009). The significance of the investigated process derives from necessity of an expansion of the source of raw materials, especially cheap ones, for aromatics production. Such a source is light alkanes (for example associated gas).

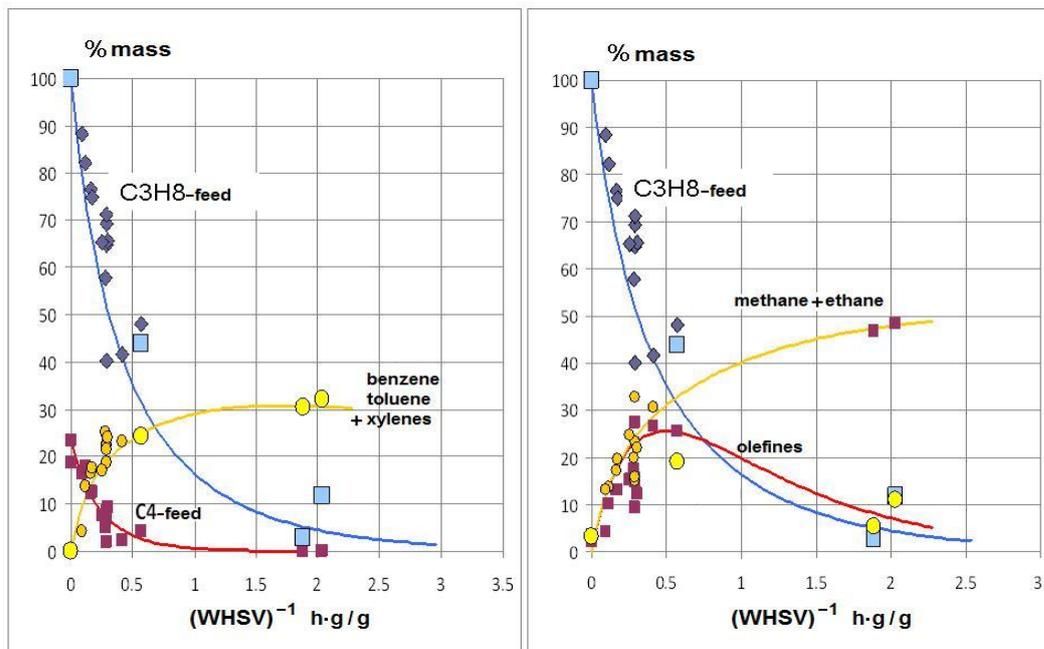


Figure 1: The kinetic data of consumption of initial reagents and formation of products (sorted by type of hydrocarbons): symbols – experimental, lines – calculated

## 2. Experimental section

The experiments were carried out in a laboratory tube flow isothermal reactor with a fixed-bed of the catalyst. The length of the reactor was 450 mm and diameter 10 mm. Promoted ZSM-5 was used as a catalyst. Particle size of the catalyst was 0.5 - 1 mm. Catalyst loading was 1 – 2 g. The mixture of propane (81 %) and butane (19 %), and the mixture of propane (14.8 %), butane (10.2 %), i-butane (37.2 %) and butane (36.8 %) were used as a raw material. The range of conditions were: temperature 520 – 650 °C, pressure 0.1 MPa, WHSV 0.5 – 15 g/(g·h). The composition of the inlet and outlet mixtures was determined by GC.

The experimental data on changing of reaction mixture composition in dependence of WHSV showed that the main products were: alkanes C1-C2, light olefins C3-C4 and aromatics C6-C9. The preliminary kinetic treatment of the whole array of the experimental data (46 experiments) showed that consumption of initial reagents was well described by first-order kinetics, and the products were formed by parallel-consecutive reactions (Figure 1).

## 3. Mathematical model of the chemical transformations

On the base of the obtained data the minimal system of reactions (27 reactions) describing these transformations was proposed:

1.  $C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6$
2.  $2C_4H_{10} + 2H_2 \rightarrow 2CH_4 + C_2H_6$
3.  $4C_3H_8 \rightarrow 3C_2H_4 + 2C_3H_6 + 4H_2$
4.  $4C_4H_{10} \rightarrow 3C_2H_4 + 2C_3H_6 + C_4H_8 + 4H_2$
5.  $C_2H_4 + H_2 \rightarrow C_2H_6$
6.  $2C_3H_6 + 3H_2 \rightarrow 3C_2H_6$
7.  $3C_2H_4 \rightarrow C_6H_6 + 3H_2$
8.  $2C_3H_6 \rightarrow C_6H_6 + 3H_2$
9.  $3C_4H_8 \rightarrow 2C_6H_6 + 6H_2$
10.  $7C_2H_4 \rightarrow 2C_6H_5CH_3 + 6H_2$
11.  $7C_3H_6 \rightarrow 3C_6H_5CH_3 + 9H_2$
12.  $7C_4H_8 \rightarrow 4C_6H_5CH_3 + 12H_2$
13.  $4C_2H_4 \rightarrow p-C_6H_4(CH_3)_2 + 3H_2$
14.  $8C_3H_6 \rightarrow 3p-C_6H_4(CH_3)_2 + 9H_2$
15.  $2C_4H_8 \rightarrow p-C_6H_4(CH_3)_2 + 3H_2$
16.  $2C_3H_8 \rightarrow C_6H_6 + 5H_2$
17.  $7C_3H_8 \rightarrow 3C_6H_5CH_3 + 16H_2$
18.  $8C_3H_6 \rightarrow 3p-C_6H_4(CH_3)_2 + 9H_2$
19.  $3C_3H_{10} \rightarrow 2C_6H_6 + 9H_2$
20.  $7C_4H_{10} \rightarrow 4C_6H_5CH_3 + 19H_2$
21.  $2C_4H_{10} \rightarrow p-C_6H_4(CH_3)_2 + 5H_2$
22.  $5C_6H_6 \rightarrow 3C_{10}H_8 + 3H_2$
23.  $10C_6H_5CH_3 \rightarrow 7C_{10}H_8 + 12H_2$
24.  $5p-C_6H_4(CH_3)_2 \rightarrow 4C_{10}H_8 + 9H_2$
25.  $C_2H_6 + H_2 \rightarrow 2CH_4$
26.  $C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$
27.  $C_2H_6 + CH_4 \rightarrow C_3H_8 + H_2$

Mathematical model of the chemical transformations was developed using the following assumptions: isothermal conditions, quasi-homogeneous kinetics and ideal gas phase.

On the basis of the above scheme of the reactions the following system of twelve differential equations were used for description of all the chemical transformations including experiments with and without butane in the starting mixture:

$$\frac{d\bar{n}}{dm_k} = \bar{g} \quad (1)$$

where  $\bar{n}$  – is the vector of mole of twelve key components,  $m_k$  – is current mass of catalyst,  $\bar{g}$  – is the vector of rates of formation (consumption) of the components which are determined by means of matrix equation:

$$\bar{g} = \alpha \bar{r}, \text{ where } \alpha - \text{ given by the matrix of stoichiometric coefficients; } \bar{r} - \text{ are rates of the reactions.}$$

Values of  $\bar{r}$  are based on the analysis of experimental data and calculated as follows:

$$\begin{aligned} r_1 &= k_1 c_{C_3H_8} K_{C_3H_8}; r_2 = k_2 c_{C_4H_{10}} K_{C_4H_{10}}; r_3 = k_3 c_{C_3H_8} K_{C_3H_8}; r_4 = k_4 c_{C_4H_{10}} K_{C_4H_{10}}; \\ r_5 &= k_5 c_{C_2H_4} K_{C_2H_4}; r_6 = k_6 c_{C_3H_6} K_{C_3H_6}; r_7 = k_7 c_{C_2H_4} K_{C_2H_4}; r_8 = k_8 c_{C_3H_6} K_{C_3H_6}; \\ r_9 &= k_9 c_{C_4H_8} K_{C_4H_8}; r_{10} = k_{10} c_{C_2H_4} K_{C_2H_4}; r_{11} = k_{11} c_{C_3H_6} K_{C_3H_6}; r_{12} = k_{12} c_{C_4H_8} K_{C_4H_8}; \\ r_{13} &= k_{13} c_{C_2H_4} K_{C_2H_4}; r_{14} = k_{14} c_{C_3H_6} K_{C_3H_6}; r_{15} = k_{15} c_{C_4H_8} K_{C_4H_8}; r_{16} = k_{16} c_{C_3H_8}^2 K_{C_3H_8}; \\ r_{17} &= k_{17} c_{C_3H_8}^2 K_{C_3H_8}; r_{18} = k_{18} c_{C_3H_8}^2 K_{C_3H_8}; r_{19} = k_{19} c_{C_4H_{10}}^2 K_{C_4H_{10}}; r_{20} = k_{20} c_{C_4H_{10}}^2 K_{C_4H_{10}}; \\ r_{21} &= k_{21} c_{C_4H_{10}}^2 K_{C_4H_{10}}; r_{22} = k_{22} c_{C_6H_6} K_{C_6H_6}; r_{23} = k_{23} c_{C_7H_8} K_{C_7H_8}; r_{24} = k_{24} c_{C_8H_{10}} K_{C_8H_{10}} \\ r_{25} &= k_{25} c_{C_2H_6} K_{C_2H_6}; r_{26} = k_{26} c_{C_4H_{10}} K_{C_4H_{10}}; r_{27} = k_{27} c_{C_2H_6} K_{C_2H_6}; \end{aligned}$$

Where:

$c_i$  – is the concentration of i-component [mass % relative to the mass of propane];

$K_i$  – is the conversion factor for the rate of the reaction to [mol/(g(cat) h)]

$$K_i = \frac{m_{C_3H_8}^{(0)}}{100M_i} \quad (i = 1, 2, \dots, m) \quad (2)$$

$M_i$  – is the molar mass of i-component [g/mol].

The following equation was used for conversion of any of 27 rate constants to any other temperature:

$$\bar{k} = \frac{\bar{k}^{(0)}}{\gamma}, \text{ where } \gamma - \text{ is factor taking account the dependence of the rate constants on the temperature:}$$

$$\gamma = e^{-B\left(\frac{1}{T_0} - \frac{1}{T}\right)}, \text{ where } T_0 = 813 \text{ K (540 } ^\circ\text{C)}, B - \text{ is a determined coefficient [K].}$$

As a result, 28 coefficients  $\bar{k}^{(0)}$  and coefficient B of the system of differential Eq(1) were the fit parameters.

Calculations were made by means of the fourth-order algorithm of Runge-Kutta and the procedure used makes it possible automatically to choose the system of the differential equation for each composition of the starting material.

#### 4. Determination of kinetic parameters of the chemical transformations

The task of parametric identification of the model (system of Eq(1)) was solved simultaneously for all the three sets of experimental data with and without butene and *i*-butane in the starting material with the general criteria for minimization of the target function:

$$S = \sum_{u=1}^f \sum_{i=1}^m [\alpha_i (\omega_i^{calc} - \omega_i^{exp})^2] \quad (3)$$

where:

$\omega_i$  – is mass. % of the components (starting materials and products), “calc” – calculated by model, “exp” – experimental data;

$m$  – is the number of the components (starting materials and products);

$f$  – is the number of the experimental points;

$\alpha_1, \alpha_2, \dots, \alpha_m$  – are weight coefficients.

After the procedure of minimization of mismatch criterion was reduced from 261,125 to 17,900 with using Generalized Least Squares methods, adequate description of experimental data was received and 28 parameters of the kinetic equations were determined:

$$k_1^{(0)} = 0.02 \frac{1}{h}; \quad k_2^{(0)} = 0.05 \frac{1}{h}; \quad k_3^{(0)} = 0.04 \frac{1}{h}; \quad k_4^{(0)} = 0.01 \frac{1}{h}; \quad k_5^{(0)} = 0.04 \frac{1}{h}; \quad k_6^{(0)} = 0.09 \frac{1}{h};$$

$$k_7^{(0)} = 0.05 \frac{1}{h}; \quad k_8^{(0)} = 0.05 \frac{1}{h}; \quad k_9^{(0)} = 0.11 \frac{1}{h}; \quad k_{10}^{(0)} = 0.03 \frac{1}{h}; \quad k_{11}^{(0)} = 0.02 \frac{1}{h}; \quad k_{12}^{(0)} = 0.05 \frac{1}{h};$$

$$k_{13}^{(0)} = 0.005 \frac{1}{h}; \quad k_{14}^{(0)} = 0.004 \frac{1}{h}; \quad k_{15}^{(0)} = 0.09 \frac{1}{h};$$

$$k_{16}^{(0)} = 5.75 \cdot 10^{-7} \frac{1}{\% \text{ mass} \cdot h};$$

$$k_{17}^{(0)} = 1.25 \cdot 10^{-5} \frac{1}{\% \text{ mass} \cdot h}; \quad k_{18}^{(0)} = 4.75 \cdot 10^{-7} \frac{1}{\% \text{ mass} \cdot h};$$

$$k_{19}^{(0)} = 2.95 \cdot 10^{-6} \frac{1}{\% \text{ mass} \cdot h}; \quad k_{20}^{(0)} = 9 \cdot 10^{-5} \frac{1}{\% \text{ mass} \cdot h}; \quad k_{21}^{(0)} = 1.95 \cdot 10^{-5} \frac{1}{\% \text{ mass} \cdot h};$$

$$k_{22}^{(0)} = 0.003 \frac{1}{h}; \quad k_{23}^{(0)} = 0.003 \frac{1}{h}; \quad k_{24}^{(0)} = 0.004 \frac{1}{h}; \quad k_{25}^{(0)} = 0.32 \frac{1}{h}; \quad k_{26}^{(0)} = 1.28 \frac{1}{h}; \quad k_{27}^{(0)} = 0.8 \frac{1}{h};$$

$$k_{28}^{(0)} \equiv B = 6000 \text{ K}^{-1}$$

Partly the results of the kinetic model reconciliation for one of the experimental point (Number 11 from the all number of 46 experimental points) listed in Table 1.

Table 1: Results of the kinetic model reconciliation. Comparison of the calculated and experimental data for one of the experiments

Parameter of the flows			
P; KPa	WHSW; g/(g·h)	G; g/h	t; °C
100	5.52	11.04	575
Components	Input composition	Output composition	Experimental Data
	% mass	in % mass	
		Calculated Data with above defined parameter set	
<b>CH<sub>4</sub></b>	0.63	4.87	5.46
<b>C<sub>2</sub>H<sub>6</sub></b>	1.99	8.01	3.7
<b>C<sub>3</sub>H<sub>8</sub></b>	76.55	43.82	42.03
<b>C<sub>4</sub>H<sub>10</sub></b>	18.03	13.63	6.78
<b>C<sub>2</sub>H<sub>4</sub></b>	0	7.63	7.4

Table 1 (Continued): Results of the kinetic model reconciliation. Comparison of the calculated and experimental data for one of the experiments

<b>C<sub>3</sub>H<sub>6</sub></b>	2.26	7.83	6.52
<b>H<sub>2</sub></b>	0	1.57	1.23
<b>C<sub>6</sub>H<sub>6</sub></b>	0	3.92	4.97
<b>C<sub>7</sub>H<sub>8</sub></b>	0	7	9.38
<b>C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub></b>	0	1.12	2.65
<b>C<sub>10</sub>H<sub>8</sub></b>	0	0.44	0.46

In Figure 1 below the composition of the reaction mixture is presented for one of the experiment where synthesis of the aromatic compounds is proved (lines 9–12).

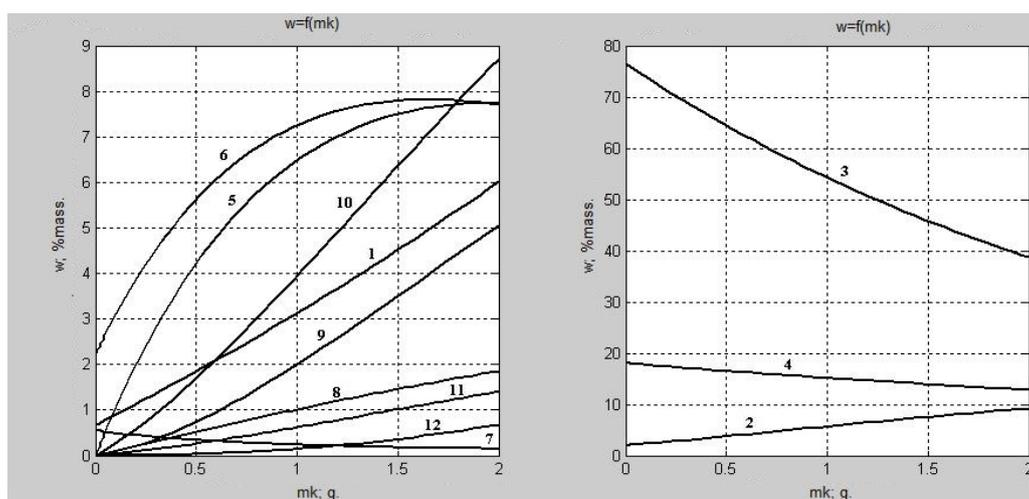


Figure 1: The composition of the reaction mixture along the tube of the reactor in experiment from set No 1. 1 – methane, 2 – ethane, 3 – propane, 4 – butane, 5 – ethylene, 6 – propene, 7 – butene, 8 – hydrogen, 9 – benzene, 10 – toluene, 11- p-xylene, 12 – naphthalene Computer modelling of polytrophic reactor of catalytic process of aromatization of light alkanes

The pilot reactor for modeling was a tube with a fixed-bed of catalyst (mass of the catalyst was 1,000 g) with a jacket heated by furnace gas.

Computer model of polytrophic reactor was developed on the basis of Eq(1) by adding the equation of the heat balance:

$$\frac{dT}{dm_k} = \frac{1}{C_p N} \Delta q^R + \frac{F^T}{M_k C_p N} \Delta q^T + \frac{T}{N} \frac{dN}{dm_k} \quad (4)$$

Where:

$$\Delta q^R = \sum_{j=1}^{27} \Delta H_j^R r_j; \quad \Delta q^T = k^T (T_T - T); \quad \Delta q^R - \text{is the rate of heat [J/g]; } \Delta q^T - \text{is the rate of heat allocation$$

[J/m<sup>2</sup>];  $\Delta H^R$  - is the enthalpy of reaction [J/mol];  $F^T$  - is the area of heat exchange [m<sup>2</sup>];  $k^T$  - is the heat-exchanger coefficient [W/(K·m<sup>2</sup>)];  $T_T$  - is the temperature in the shell of tube reactor;  $C_p$  - is the heat capacity [J/(mol·K)];  $N$  - is the total number of moles in the mixture.

The developed model makes it possible to take into account variation of mathematical model which depends on the composition of the initial mixture and to vary in the wide range parameters of the starting flow: feed rate in the range of 0.6 – 12 g/(g·h), temperature in the input of the reactor in the range of 550 – 645 °C, temperature of the furnace gas in the jacket in the range of 675 – 725 °C. As it follows from the above, an increase in the temperature in the input of the reactor and in the jacket caused an increase in the aromatics content but an increase in the feed rate worked in the reverse direction. The highest overall

yield of aromatics was about 40 %. It was received with the parameters of the process listed in Tables 2 & 3.

Table 2: Compositions (% mass) of feed and output at  $WHSV = 0.6 \text{ g/(g}\cdot\text{h)}$ ,  $G = 600 \text{ g/h}$ ,  $P = 0.1 \text{ MPa}$ ,  $t(\text{input}) = 600 \text{ }^\circ\text{C}$

Components	Input	Output
$CH_4$	0	18.78
$C_2H_6$	1.74	5.70
$C_3H_8$	80.64	16.95
$C_4H_{10}$	14.96	6.81
$C_2H_4$	0	5.09
$C_3H_6$	2.36	4.43
$C_4H_8$	0.31	0.07
$H_2$	0	2.58
$C_6H_6$	0	13.59
$C_7H_8$	0	16.94
$p\text{-}C_6H_4(CH_3)_2$	0	5.36
$C_{10}H_8$	0	3.62

Final parameters of the process modelling in the pilot reactors are given in Table 3.

Table 3: Final parameters of the process modelling

Conversion of the starting material; %	71.21
Selectivity of aromatics formation; %	56.49
Yield of aromatics; %	40.22
Average heat load; MJ/h	2.08
Average temperature; $^\circ\text{C}$	598

## 5. Conclusion

The mathematical model of important industrial process of transformation of light alkanes into aromatics was designed. The model is applicable for calculating of the composition of products mixture in processing paraffines to aromatics considering 27 reactions, which were choose on the base of analysis of experimental data. Algorithm of calculation included a choose of mathematical model equation depending on the composition of the initial reaction mixture.

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