SENSITIVITY ANALYSIS OF THE KINETIC MODEL OF GASEOUS AUTOCATALYTIC PROPANE PYROLYSIS

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XXIV International Conference on Chemical Reactors CHEMREACTOR-24
September 12 - 17, 2021

Introduction

Creation of reduced schemes for pyrolysis of hydrocarbons is an important problem:

•In the gas-phase kinetic experiments, propane pyrolysis was carried out in laboratory reactors with the reaction mixture heated by CO_2 laser irradiation.

• Due to a large number of parameters affecting the yield of products, investigation of this process is based not only on experiments but also on numerical modeling of the dynamics of chemically active gas in a laboratory reactor by means of the Ansys Fluent software.

•The reduced (compact) kinetic schemes describing the most essential aspects of the mechanism of a chemical process are needed for such simulations.

This work objectives

•Development of a procedure for analysing sensitivity of mathematical models aimed at reducing the kinetic reaction scheme.

•Construction of a compact kinetic model of gas-phase propane pyrolysis using the developed procedure that adequately describes the experimental data on low-temperature propane pyrolysis (820-980 K).

•Numerical modeling of three-dimensional dynamics of a gas flow in a reactor in the ANSYS Fluent software package using a compact kinetic model.

Mathematical model

The equation describing the reaction of decomposition/ formation of intermediate and final products of the reaction:

$$u\frac{dc_i}{dl}=\sum_{j=1}^{N}P_{ij}w_j,\ i=1..M.$$

The u is inferred from the mass flow rate of the mixture:

$$u=\frac{m}{\rho S}=\frac{m}{\rho\pi D^2/4}.$$

Equations for chemical reactions are presented as:

$$w_j=k_j\prod_{i=1}^{M}(c_i)^{|\alpha_{ij}|}-k_{-j}\prod_{i=1}^{M}(c_i)^{\beta_{ij}}$$

The rate constants for reactions were calculated from the Arrhenius equation:

$$k_i=A_i\cdot(T/298)^{m_i}\cdot\exp(-E_i/RT)$$

Here c_i are concentrations of the substances, M is the number of substances, N is the number of steps, B_{ij} are stoichiometric coefficients, α_{ij} are negative elements of B_{ij}, β_{ij} are positive elements of B_{ij}, w_j is the rate at the j step, k_j, k_{-j} are the rate constants for the forward and reverse reaction, respectively, t is time, u is the speed of the mixture, L is the distance from the entrance of the rector to the current point, E_i is the activation energy, A_i is kinetic parameter, R is the universal gas constant, T is temperature.

Sensitivity analysis

$$\begin{cases}\dfrac{dx}{dt}=f(x,k),\ t\in[0,t_k]\\ \dfrac{d}{dt}\left(\dfrac{\partial x_i}{\partial k_j}\right)=\dfrac{\partial f_i}{\partial k_j}+\sum_{l=1}^{n}\dfrac{\partial f_i}{\partial x_l}\dfrac{\partial x_l}{\partial k_j}\\ x_i(0)=x_i^0,\\ \dfrac{\partial x_i(0,k)}{\partial k_j}=0\end{cases}$$

$$S_{ijt}^{loc}=\frac{k_j}{x_i(t,k)}\frac{\partial x_i(t,k)}{\partial k_j}$$

Local sensitivity coefficients

It is proposed to analyses the sensitivity of the functional model to variations of the rate constants, where the functional determines how close the values calculated using the existing reaction scheme are to those calculated using the scheme obtained by perturbation of its parameters at various time points and/or for various temperatures:

$$F_{obj}=\sum_{i=1}^{M}\sum_{j=1}^{N}\sum_{k=1}^{R}w_i\left(c_{ijk}^{sh1}-c_{ijk}^{sh2}\right)^2$$

Where $c^{sh1}{}_{ijk}$ are the concentrations calculated using the initial scheme; $c^{sh2}{}_{ijk}$ are concentrations calculated after variation (perturbation) of parameters of the scheme.

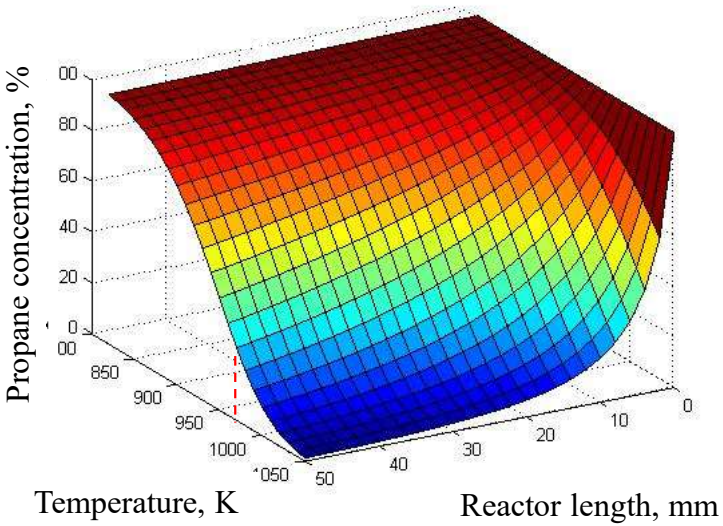
Kinetic scheme

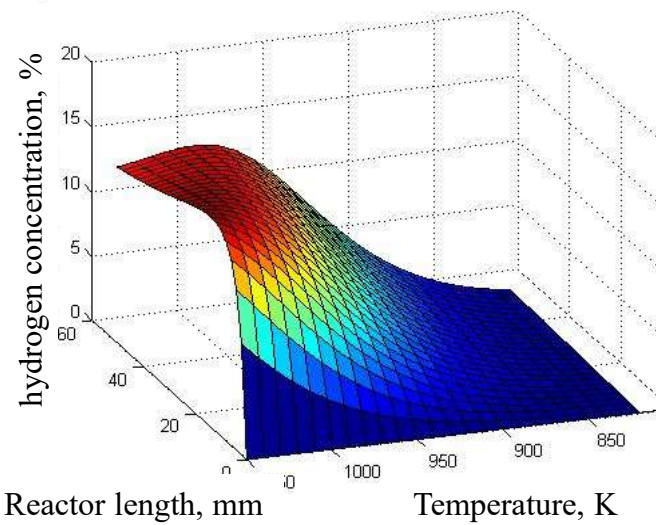
№	стадия	A	E	m	№	стадия	A	E	m
1	$C_3H_8 \rightarrow C_2H_5\bullet + CH_3\bullet$	2,78E+18	376,00	-1,80	16	$H_2 + C_3H_5\bullet \rightarrow C_3H_6 + H\bullet$	8,37E+07	79,49	2,38
2	$C_2H_5\bullet \rightarrow C_2H_4 + H\bullet$	4,31E+12	155,00	1,19	17	$C_3H_6 + H\bullet \rightarrow H_2 + C_3H_5\bullet$	2,61E+08	10,39	2,50
3	$C_2H_4 + H\bullet \rightarrow C_2H_5\bullet$	4,09E+09	4,15	1,49	18	$C_2H_6 + H\bullet \rightarrow H_2 + C_2H_5\bullet$	2,48E+09	35,34	1,50
4	$C_3H_8 + CH_3\bullet \rightarrow CH_4 + n\text{-}C_3H_7\bullet$	2,98E+05	29,93	3,65	19	$n\text{-}C_3H_7\bullet \rightarrow C_3H_6 + H\bullet$	1,09E+13	149,00	0,17
5	$C_3H_8 + CH_3\bullet \rightarrow CH_4 + iso\text{-}C_3H_7\bullet$	5,48E+05	22,95	3,46	20	$C_3H_6 + H\bullet \rightarrow n\text{-}C_3H_7\bullet$	1,30E+10	13,64	0,00
6	$C_3H_8 + H\bullet \rightarrow H_2 + n\text{-}C_3H_7\bullet$	2,55E+09	28,27	2,54	21	$H_2 + CH_3\bullet \rightarrow CH_4 + H\bullet$	1,52E+07	36,42	3,12
7	$C_3H_8 + H\bullet \rightarrow H_2 + iso\text{-}C_3H_7\bullet$	1,13E+09	18,71	2,40	22	$C_2H_4 + C_2H_3\bullet \rightarrow C_4H_7$	9,21E+08	19,00	0,00
8	$n\text{-}C_3H_7\bullet \rightarrow C_2H_4 + CH_3\bullet$	1,20E+13	126,00	0,00	23	$C_4H_7 \rightarrow C_4H_6 + H\bullet$	6,40E+12	144,20	0,00
9	$iso\text{-}C_3H_7\bullet \rightarrow C_3H_6 + H\bullet$	1,60E+13	150,00	0,00	24	$C_4H_7 \rightarrow C_2H_4 + C_2H_3\bullet$	2,10E+13	149,20	0,00
10	$C_2H_4 + CH_3\bullet \rightarrow CH_4 + C_2H_3\bullet$	9,45E+06	39,74	3,70	25	$C_3H_5\bullet \rightarrow C_2H_2 + CH_3\bullet$	3,00E+13	151,00	0,00
11	$CH_4 + C_2H_3\bullet \rightarrow C_2H_4 + CH_3\bullet$	1,28E+07	22,86	4,02	26	$C_4H_8 \rightarrow C_3H_5\bullet + CH_3\bullet$	1,00E+16	305,00	0,00
12	$C_3H_8 + C_2H_5\bullet \rightarrow C_2H_6 + n\text{-}C_3H_7\bullet$	9,70E+05	38,25	3,65	27	$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$	2,64E+10	0,00	0,00
13	$C_3H_8 + C_2H_3\bullet \rightarrow C_2H_4 + iso\text{-}C_3H_7\bullet$	4,79E+07	36,92	3,10	28	$C_3H_5\bullet + CH_3\bullet \rightarrow C_4H_8$	1,64E+10	-0,55	-0,32
14	$C_3H_6 + C_2H_5\bullet \rightarrow C_2H_6 + C_3H_5\bullet$	1,02E+06	27,77	3,50	29	$C_2H_3\bullet + CH_3\bullet \rightarrow C_3H_6$	9,56E+11	0,57	-0,54
15	$C_3H_8 + C_3H_5\bullet \rightarrow C_3H_6 + n\text{-}C_3H_7\bullet$	3,44E+07	83,06	3,30	30	$C_2H_5\bullet + CH_3\bullet \rightarrow C_3H_8$	2,83E+10	0,00	-0,50

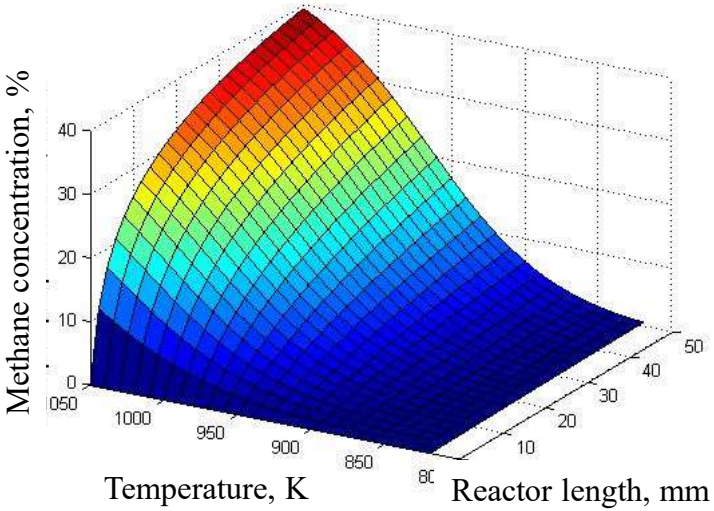
Sensitivity analysis

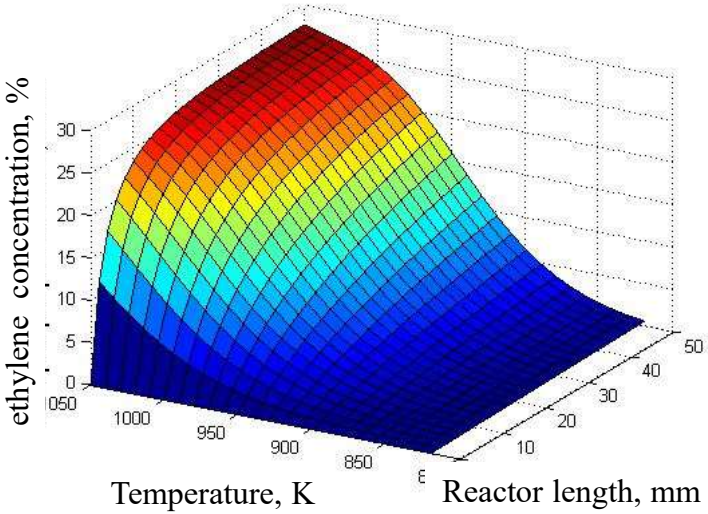
Decomposition C_3H_8	S_i %	formation CH_4	S_i %
$C_3H_8 \rightarrow C_2H_5\bullet + CH_3\bullet$	48,52	$C_3H_8+CH_3\bullet \rightarrow CH_4 + n\text{-}C_3H_7\bullet$	97,08
$C_3H_8+CH_3\bullet \rightarrow CH_4 + n\text{-}C_3H_7\bullet$	27,00	formation C_4H_6	
$C_3H_8+CH_3\bullet \rightarrow CH_4 + iso\text{-}C_3H_7\bullet$	13,50	$C_4H_7 \rightarrow C_4H_6 + H\bullet$	100,00
$C_3H_8 +H\bullet \rightarrow H_2 + iso\text{-}C_3H_7\bullet$	9,56	formation C_4H_8	
		$C_3H_5\bullet + CH_3\bullet \rightarrow C_4H_8$	100,00
formation C_2H_4		decompositionC_2H_4	
$C_2H_5\bullet \rightarrow C_2H_4 + H\bullet$	63,80	$C_2H_4 + H\bullet \rightarrow C_2H_5\bullet$	55,52
$n\text{-}C_3H_7\bullet \rightarrow C_2H_4 +CH_3\bullet$	13,70	$C_2H_4+CH_3\bullet \rightarrow CH_4 + C_2H_3\bullet$	37,81
$CH_4 + C_2H_3\bullet \rightarrow C_2H_4+CH_3\bullet$	13,20	$C_2H_4+ C_2H_3\bullet \rightarrow C_4H_7$	6,67
formation C_3H_6		Decomposition C_3H_6	
$n\text{-}C_3H_7\bullet \rightarrow C_3H_6 + H\bullet$	86,48	$C_3H_6 + H\bullet \rightarrow n\text{-}C_3H_7\bullet$	83,80
$C_3H_8 + C_3H_5\bullet \rightarrow C_3H_6 + n\text{-}C_3H_7\bullet$	7,67	$C_3H_6 + H\bullet \rightarrow H_2 +C_3H_5\bullet$	11,07
$C_2H_3\bullet + CH_3\bullet \rightarrow C_3H_6$	3,60	$C_3H_6 + C_2H_5\bullet \rightarrow C_2H_6 + C_3H_5\bullet$	5,13
formation H_2		Decomposition H_2	
$C_3H_8 +H\bullet \rightarrow H_2 + n\text{-}C_3H_7\bullet$	91,97	$H_2 +C_3H_5\bullet \rightarrow C_3H_6 + H\bullet$	56,09
$C_3H_8 +H\bullet \rightarrow H_2 + iso\text{-}C_3H_7\bullet$	7,88	$H_2+CH_3\bullet \rightarrow CH_4 + H\bullet$	43,91
formation C_2H_6		Decomposition C_2H_6	
$C_3H_8 + C_2H_5\bullet \rightarrow C_2H_6 + n\text{-}C_3H_7\bullet$	53,29	$C_2H_6 + H\bullet \rightarrow H_2 +C_2H_5\bullet$	100,00
$C_3H_6 + C_2H_5\bullet \rightarrow C_2H_6 + C_3H_5\bullet$	28,59	formation C_2H_2	
$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$	18,12	$C_3H_5\bullet \rightarrow C_2H_2 + CH_3\bullet$	100,00

Influence of temperature on food composition









Gas flow dynamics

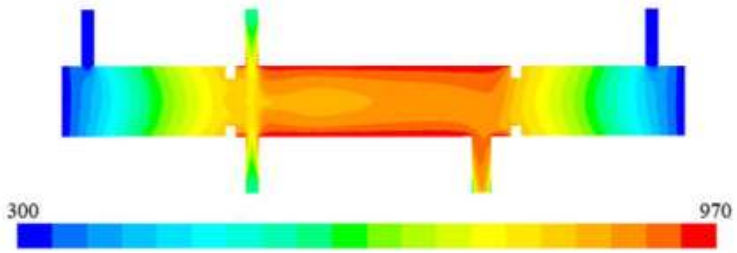


Figure 2 The temperature distribution in the longitudinal section in the reactor (see online version for colours)

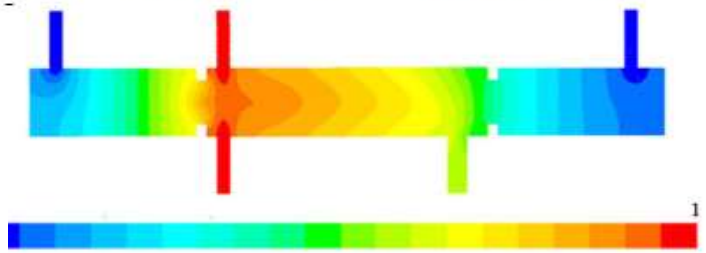


Figure 3 The propane mole fraction distribution in the longitudinal section (see online version for colours)

ure 4 The methane mole fraction distribution in the longitudinal section (see online version for colours)

Conclusions

We have developed a procedure for constructing reduced schemes of chemical reactions predicting the concentrations and the major yields of reactions with the desired accuracy and requiring moderate computing resources. The efficiency of using this procedure was demonstrated for modelling propane pyrolysis using detailed and reduced schemes. The reduction of the 157 reactions in the detailed propane pyrolysis scheme to the 30 reaction scheme was carried out using this procedure. The reduced kinetic model of low-temperature pyrolysis of propane is proposed. This model adequately describes the yield of the reaction products in the temperature range 820–980 K at atmospheric pressure. The dynamics of the propane pyrolysis gas flow was calculated for the laboratory reactor and taking into account the diffusion processes, thermal effects of the reaction and other thermal processes in the reactor using ANSYS Fluent software package including the newly developed kinetic model.

References

1. Nurislamova, L.F. and Gubaydullin, I.M. (2017)'Mechanism reduction of chemical reaction based on sensitivity analysis: development and testing of some new procedure', *Journal of Mathematical Chemistry*, Vol. 55, No. 9, pp.1779–1792.
2. Nurislamova, L.F., Stoyanovskaya, O.P., Stadnichenko, O.A., Gubaidullin, I.M., Snytnikov, V.N. and Novichkova, A.V. (2014) 'Few-step kinetic model of gaseous autocatalytic ethane pyrolysis and its evaluation by means of uncertainty and sensitivity analysis', *Chemical Product and Process Modeling*, Vol. 9, No. 2, pp.143–154
3. Stadnichenko, O.A., Nurislamova, L.F., Masyuk, N.V., Snytnikov, V.N. and Snytnikov, V.N. (2018) 'Radical mechanism for the gas-phase thermal decomposition of propane', *Reaction Kinetics, Mechanisms and Catalysis*, Vol. 123, No. 2, pp.607–624.
4. Safiullina L. F., Gubaydullin I. M., Uzyanbaev R. M., Musina A. E. Computational aspects of Simplification of Mathematical Models of Chemical Reaction Systems // Journal of Physics: Conference Series. — 2019. — Vol. 1368, №. 4. — P. 042022.
5. Safiullina L.F., Gubaydullin I.M. Numerical analysis of parameter identifiability for a mathematical model of a chemical reaction // Int. J. Engineering Systems Modelling and Simulation. — 2020. — Vol. 11, №. 4. — P. 207–213.