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Determination and Application of Improved Kinetic Parameters for Simulation of Maleic Anhydride Synthesis in Industrial Fixed-Bed Reactor

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Abstract
The aims of this study were to determine improved kinetic parameters in five kinetic models for oxidation of n-butane into maleic anhydride in an industrial fixed-bed reactor, and to simulate the reactor performance. On the basis of the measured process parameters, inlet and outlet concentrations of n-butane were calculated and then used to fit the kinetic models. The industrial fixed-bed reactor was approximated by 10 continuous stirred tank reactors (CSTR) connected in series. Based on the calculated outlet concentration of n-butane from the industrial reactor, the outlet concentration of n-butane from the penultimate reactor was calculated. Then the concentrations of n-butane were calculated until the inlet concentration of n-butane in the first reactor was obtained. Kinetic parameters were determined by comparing the inlet concentrations of n-butane in the first reactor with the inlet concentration of n-butane obtained on the basis of the measured process parameters in the industrial fixed-bed reactor. Kinetic models with improved kinetic parameters showed better simulation results compared to kinetic models with the existing kinetic parameters. The best agreement of simulation results and measured values was achieved with application of the kinetic model 2 (Equations (2a-c)). The smallest deviations of numerical simulation in comparison with measured values of the outlet pressure of reaction mixture were 0.45, 0.75 and 0.75% for application of the kinetic model 3 (Equations (3a-c)). The percentage deviations of numerical simulation with improved kinetic parameters and the existing kinetic parameters in comparison with measured values of inside reactor temperature were in the range 0.90-5.36% and in the range 4.17-9.78% (kinetic model 2, Equations (2a-c)), respectively.

1. INTRODUCTION

Maleic anhydride (MA) is an important intermediate in the chemical industry. It is produced by selective catalytic oxidation of *n*-butane with air over vanadium phosphorus oxide (VPO) catalyst. More than 50% of maleic anhydride global production is used to produce unsaturated polyester resins, which are used in a lot of applications such as boat hulls, bathroom fixtures, car parts, furniture, tanks and pipes. MA is also used to produce copolymers (such as maleic anhydride-styrene, maleic anhydride acrylic acid), paints, lubricants, pesticides, and other organic compounds (Caldarelli, 2012). The selective oxidation of *n*-butane to maleic anhydride is a complex reaction from the mechanistic and modeling point of view. Besides the main reaction of selective formation of maleic anhydride from *n*-butane, two other side reactions, namely the complete oxidation of *n*-butane and of maleic anhydride to oxides of carbon, take place simultaneously (Bey and Rao, 1991). The ability of a mathematical model to simulate the reactor behavior is highly dependent on kinetics (Petric and Husanović, 2015). Morais et al. (2007) presented a robust procedure to estimate the parameters set of the kinetic model, as the activation energy and the pre-exponential factor, used in the calculation of the constant of Arrhenius for the partial oxidation of benzene to maleic anhydride. This estimate is carried through Genetic Algorithms (*GAs*) with the purpose to minimize an objective function that considers the error between real values operation supplied by literature, industrial units or laboratory scale reactors and the simulated theoretical values from the used model. Rodionova and Pomerantsev (2005) estimated the parameters of the Arrhenius Equation and suggested simple expedients for model modification that reduce multicollinearity, thus allowing the parameters to be determined. Romano et al. (2016) obtained the pre-exponential factor and activation energy for a turbulent catalytic bed reactor. Petric and Karić (2016) developed a mathematical model for numerical simulation of partial oxidation of *n*-butane to maleic anhydride in a fixed-bed reactor, and then they validated the model with real process data from the industrial reactor located in the Global Ispat Coke Industry Lukavac. The aims of this study are to determine improved kinetic parameters in five kinetic models for oxidation of *n*-butane into maleic anhydride in industrial fixed-bed reactor, and to simulate the reactor performance.

2. MATERIAL AND METHODS

2.1. Process parameters and industrial reactor

In this study, process data from the industrial fixed-bed reactor (located in the Global Ispat Coke Industry Lukavac) was used. Maleic anhydride is produced with an annual output of 10,000 tons. The synthesis is carried out in a fixed-bed reactor consisted of 11,600 tubes in a parallel arrangement with length (height) of 3.7 m, outside diameter of 25 mm and wall thickness of 2 mm. The reactor tubes are filled up to height of 3.25 m with total mass of 11.2 tons of catalyst based on vanadium-phosphorus oxide. The measured inlet process parameters are temperature, pressure and flow rates of reactants. The measured process parameter within the reactor is temperature. The measured outlet process parameters are temperature and pressure.

2.2. Kinetic models

The investigated kinetic models (model 1, Equations (1a-c), Buchanan and Sundaresan (1986), model 2, Equations (2a-c), Buchanan and Sundaresan (1986); model 3, Equations (3a-c), Marin et al. (2010); model 4, Equations (4a-c), Lorences et al. (2003); model 5, Equations (5a-c), Centi et al. (1985)) are given by the following equations:

$$r_1' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{1a}$$

$$r_2' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{1b}$$

$$r_3' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{1c}$$

$$r_1' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{2a}$$

$$r_2' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{2b}$$

$$r_3' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{2c}$$

$$r_1' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{3a}$$

$$r_2' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{3b}$$

$$r_3' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{3c}$$

$$r_1' = \left[k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \right] \cdot \frac{C_A}{\left[1 + \frac{K_1 \cdot C_A}{C_B} + \frac{K_2 \cdot C_C}{C_B} \right]} \tag{4a}$$

$$r_2' = \left[k_0 \cdot e^{-\frac{E_a}{R\cdot T}}\right]\cdot \frac{C_A}{\left[1+\frac{K_1\cdot C_A}{C_B}+\frac{K_2\cdot C_C}{C_B}\right]} \tag{4b}$$

$$r_3' = \left[k_0 \cdot e^{-\frac{E_a}{R\cdot T}}\right]\cdot \frac{C_A}{\left[1+\frac{K_1\cdot C_A}{C_B}+\frac{K_2\cdot C_C}{C_B}\right]} \tag{4c}$$

$$r_1' = \frac{k_1 \cdot K_B \cdot C_A \cdot {C_B}^{\alpha}}{1+K_B\cdot C_A} \tag{5a}$$

$$r_2' = k_2 \cdot {C_B}^{\beta} \tag{5b}$$

$$r_3' = k_3 \cdot C_C \cdot \left(\frac{{C_B}^{\gamma}}{{C_A}^{\delta}}\right) \tag{5c}$$

where: r_1', r_2', r_3' – reaction rates (kmol/(kg$_{cat}$ ·s)), R – gas constant (= 8.314 J/(mol·K)), T - temperature of reaction mixture in a reactor (K), C_A, C_B, C_C – concentrations of *n*-butane, oxygen, and maleic anhydride (kmol/m^3), p_A, p_B, p_C – partial pressures of *n*-butane, oxygen, and maleic anhydride (atm), E_a – activation energy (kJ/kmol), k_0 – pre-exponential factor (various units), K_1 – inhibition factor (–), K_2 – inhibition factor (-), k_1 – rate constant in the equations (5a) (mol·L/(g$_{cat}$ ·h)), K_B – adsorption equilibrium constant for *n*-butane (L/mol), k_2 – rate constant in equations (5b) (mol·L/(g$_{cat}$ ·h)), k_3 – rate constant in equations (5c) (mol·L/(g$_{cat}$ ·h)), α – exponent in the equation 5a (–), β - exponent in the equation (5b) (–), γ – exponent in the equation 5c (–), δ – exponent in the equation (5c) (–). The industrial fixed-bed reactor is approximated by 10 continuous stirred tank reactors (CSTR) connected in series. Based on the calculated outlet concentration of *n*-butane from industrial reactor, the outlet concentration of *n*-butane from the penultimate reactor is calculated. Equation (6) is used to calculate the outlet concentration from each reactor:

$$Q\cdot C_{A,j-1} - Q\cdot C_{A,j} = (-r_{Aj})\cdot V_j \tag{6}$$

where: Q – volumetric rate (m^3/s), j – number of CSTR (–), $-r_{Aj}$ – rate of disappearance of A in in j-CSTR (kmol/(m$^3_{cat}$ ·s)), V_j – volume of CSTR (m^3).

In the first step, the industrial fixed-bed reactor is divided into 10 CSTRs. The outlet concentration of *n*-butane of the 9-*th* CSTR is calculated from equation (7):

$$C_{A,9} = C_{A,10} + (-r_{A9})\cdot V_j / Q \tag{7}$$

where: $C_{A,9}$ – outlet concentration of *n*-butane from 9-*th* CSTR (kmol/m^3), $C_{A,10}$ – outlet concentration from reactor (kmol/m^3), $-r_{A9}$ – rate of disappearance of A in 9-th CSTR (kmol/(m$^3_{cat}$ ·s)).

After that, the concentrations of *n*-butane of all the remaining CSTRs are calculated. SOLVER routine in the software program Microsoft Excel is used to fit kinetic models and estimate the kinetic parameters by comparing the inlet concentrations of *n*-butane at the first reactor with the inlet concentration of *n*-butane obtained on the basis of the measured process parameters in the industrial fixed-bed reactor.

The inlet concentration of *n*-butane to 1-st CSTR is compared with inlet concentration of *n*-butane calculated from the following equation:

$$C_{A0} = \frac{y_{A0}\cdot P_0}{R\cdot T_0} \tag{8}$$

where: C_{A0} – inlet concentration of *n*-butane in industrial fixed-bed reactor (kmol/m^3), y_{A0} – inlet molar fraction of *n*-butane in industrial fixed-bed reactor (-), P_0 – inlet pressure of reaction mixture (Pa), T_0 – inlet temperature of reaction mixture (K).

The outlet concentration of *n*-butane from industrial fixed-bed reactor is given by the equation:

$$C_{A,10} = C_{T0}\cdot\left(\frac{F_A}{F_T}\right)\cdot\left(\frac{T_0}{T}\right)\cdot\left(\frac{P}{P_0}\right) \tag{9}$$

where: C_{T0} – total inlet concentration of reaction mixture (kmol/m^3), F_T – total molar flow of reaction mixture (kmol/h), F_A – molar flow of *n*-butane (kmol/h), T – temperature of reaction mixture in reactor (K), P – pressure of reaction mixture (Pa).

The mechanism of reaction set I has the following main reaction (Equation (10)) and side reactions (Equations (11) and (12)):

$$n-C_4H_{10} + 3.5O_2 \rightarrow C_4H_2O_3 + 4H_2O \tag{10}$$

$$n-C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O \tag{11}$$

$$C_4H_2O_3 + 3O_2 \rightarrow 4CO_2 + H_2O \tag{12}$$

The mechanism of reaction set II has the following main reaction (Equation (13)) and side reactions (Equations (14) and (15)):

$$n-C_4H_{10} + 3.5O_2 \rightarrow C_4H_2O_3 + 4H_2O \tag{13}$$

$$n-C_4H_{10} + 4.5O_2 \rightarrow 4CO + 5H_2O \tag{14}$$

$$n-C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O \tag{15}$$

The equations (10-12) are used in the case of application of the kinetic model (Equations (3a-c)). The equations (13-15) are used in the case of application of the kinetics models (Equations (1a-c), (2a-c), (4a-c) and (5a-c)).

2.3. Reactor model

Equations for reactor model (molar balances of components, energy balance, pressure drop), other necessary equations (heats of reactions, specific heat capacities, concentrations of components, density of catalyst bed, density of catalyst particle, cross section of reactor tube, effective diameter of particle, superficial mass velocity, viscosity of gas mixture, viscosity of each components in the gas mixture, density of reaction mixture at reactor inlet, molar mass of mixture) and input data (inlet temperature of reaction mixture, molar flow rates of reactants, temperature of cooling fluid, volume of reactor, mass of catalyst, overall heat transfer coefficient, etc.) for the mathematical model were taken from Petric and Karić (2019). Numerical software package Polymath with Runge-Kutta-Fehlberg method was used for a numerical solution of set of differential equations.

3. RESULTS AND DISCUSSION

Existing and improved kinetic parameters in the kinetic models 1-5 (Equation (1a-1c), (2a-2c), (3a-3c), (4a-4c) (5a-5c)) are presented in Table 1 and Table 2. Kinetic models 1 and 2 (Equations (1a-c) and (2a-c)) showed slight deviations for kinetic parameters K_1 and K_2 in comparison with the results of Buchanan and Sundaresan (1986). Buchanan and Sundaresan (1986) used data obtained from a reactor whose dimensions significantly differ from those of the fixed-bed reactor located in the Global Ispat Coke Industry Lukavac, which may be one of the reasons for poor agreement of some kinetic parameters. However, the values of k_0 and E_a deviate significantly in comparison with the values in the study of Buchanan and Sundaresan (1986). Kinetic model 3 (Equations (3a-c)) showed good agreement for K_2

Table 1. Existing kinetic parameters and improved kinetic parameters in the kinetic models 1-4 (Equations (1a-c), (2a-c), Buchanan and Sundaresan (1986); Equations (3a-c), Marin et al. (2010); Equations (4a-c), Lorences et al. (2003))

	Buchanan and Sundaresan (1986)				**Present study**			
Kinetic model	**E_a (kJ/kmol)**	**k_0 (various units)**	**K_1 (-)**	**K_2 (-)**	**E_a (kJ/kmol)**	**k_0 (various units)**	**K_1 (-)**	**K_2 (-)**
1a	125,000	$1.96\cdot10^{10}$ $(cm^3/(s\cdot g_{cat}))$	59	26	23,784.53	10,171.41 $(cm^3/(s\cdot g_{cat}))$	55.91	30.76
1b	145,000	$3.40\cdot10^{11}$ $(cm^3/(s\cdot g_{cat}))$	59	26	32,320.17	18,442.90 $(cm^3/(s\cdot g_{cat}))$	55.91	30.76
1c	180,000	$1.7\cdot10^{13}$ $(cm^3/(s\cdot g_{cat}))$	59	26	40,220.90	10,626.90 $(cm^3/(s\cdot g_{cat}))$	55.91	30.76
2a	116,000	$1.16\cdot10^{9}$ $(cm^3/(s\cdot g_{cat})$	20	12	22,599.12	15,209.24 $(cm^3/(s\cdot g_{cat}))$	19.24	13.17
2b	130,000	$7.50\cdot10^{9}$ $(cm^3/(s\cdot g_{cat}))$	20	12	99,623.40	41,760.05 $(cm^3/(s\cdot g_{cat}))$	19.24	13.17
2c	138,000	$4.80\cdot10^{9}$ $(cm^3/(s\cdot g_{cat}))$	20	12	39,492.00	20,012.00 $(cm^3/(s\cdot g_{cat}))$	19.24	13.17
	Marin et al. (2010)				**Present study**			
3a	86,515.5	$8.82\cdot10^{3}$ $(m^3/(kg\cdot s))$	0.08	124.24	23,855.78	9,868.65 $(m^3/(kg\cdot s))$	0.022	124.34
3b	103,293.1	$5.55\cdot10^{4}$ $(m^3/(kg\cdot s))$	0.08	124.24	147,997.90	15,817.70 $(m^3/(kg\cdot s))$	0.022	124.34
3c	146,052	$4.61\cdot10^{8}$ $(m^3/(kg\cdot s))$	0.08	124.24	40,264.40	10,941.20 $(m^3/(kg\cdot s))$	0.022	124.34
	Lorences et al. (2003)				**Present study**			
4a	54,418	$4.89\cdot10^{4}$ (s^{-1})	14	208	24,603.94	6,685.99 (s^{-1})	14.33	207.50
4b	104,650	$3.15\cdot10^{8}$ (s^{-1})	14	208	153,002.00	44,161.32 (s^{-1})	14.33	207.50
4c	66,976	$4.33\cdot10^{4}$ (s^{-1})	14	208	40,723.30	14,233.80 (s^{-1})	14.33	207.50

while values of k_0, E_a and K_1 showed poor agreement with the results of Marin et al. (2010). Marin et al. (2010) used laboratory fluidized-bed membrane reactor which may be one of the reasons for poor agreement of some kinetic parameters. Kinetic model 3 (Equations (3a-c)) showed poor agreement of improved kinetic parameters with the existing kinetic parameters. Lorences et al. (2003) used different inlet volume percentages of *n*-butane in comparison with the industrial reactor located in Global Ispat Coke Industry Lukavac and it is probably the main reason for poor agreement of kinetic parameters. The reason for poor agreement between the kinetic parameters also may be the fact that the kinetic parameters in this study are obtained with application of measured process parameters from an industrial fixed-bed reactor. Activation energies and pre-exponential factors found mainly depend on the range of experimental conditions (Romano et al., 2016). Romano et al. (2016) estimated the values of activation energies, 60,000 kJ/kmol for the first reaction, 45,000 kJ/kmol for the second reaction and 190,000 kJ/kmol for the third reaction. Varma and Saraf (1978) estimated the following values of activation energies, 92,520 kJ/kmol for the first reaction, 72,100 kJ/kmol for the second reaction and 84,990 kJ/kmol for the third reaction. Depending on the model, there are smaller or greater deviations in the values of the activation energies compared to Romano et al. (2016) and Varma and Saraf (1978). Shekari and Patience (2013) estimated the values of activation energies at 100 and 410 kPa. At 100 kPa the values of activation energies were 199,200 kJ/kmol for the first reaction, 135,600 kJ/kmol for the second reaction and 154,400 kJ/kmol for the third reaction, while at the 410 kPa the values of activation energies were 240,600 kJ/kmol for the first reaction, 149,000 kJ/kmol for the second reaction and 157,300 kJ/kmol for the third reaction. In this study, the values obtained for the activation energies deviate from the results in the study of Shekari and Patience (2013). Kinetic model 5 (Equations (5a-c)) showed good agreement for improved kinetic parameters K_B, α, β, γ and δ in comparison with existing kinetic parameters, due to use of the similar type of reactor and the same type of catalyst. Centi et al. (1985) used a fixed-bed reactor based on a vanadium-phosphorus. On the other side, the kinetic model 5 (Equations (5a-c)) showed poor agreement for the improved kinetic parameters k_1, k_2 and k_3 in comparison with the existing kinetic parameters. Table 3 shows comparisons of simulation results with the existing kinetic parameters (Petric and Karić, 2016) and the improved kinetic parameters (present study) from the measured values of outlet process parameters.

Table 2. Existing kinetic parameters and improved kinetic parameters in kinetic model 5 (Equations (5a-5c), Centi et al. (1985))

			Centi et al. (1985)					
Kinetic model	**k_1 (mol·L/(g_{cat}·h))**	**k_2 (mol·L/(g_{cat}·h))**	**k_3 (mol·L/(g_{cat}·h))**	**K_B (L/mol)**	**α (-)**	**β (-)**	**γ (-)**	**δ (-)**
5a	$2.191\cdot10^{-4}$	-	-	2,616	0.2298	-	-	-
5b	-	$7.028\cdot10^{-5}$	-	-	-	0.2298	-	
5c	-	-	$4.989\cdot10^{-6}$	-	-	-	0.6345	1.151
			Present study					
5a	$6.07\cdot10^{-5}$	-	-	2,514.2	0.3012	-	-	-
5b	-	0.00343	-	-	-	0.3012	-	
5c	-	-	0.006089	-	-	-	0.6612	1.241

Table 3. Comparison of simulation results with existing kinetic parameters and improved kinetic parameters from measured values of outlet process parameters

Kinetic model	T_{out} (K)	P_{out} (bar)	Reference
A	682.74	0.664	
B	678.90	0.672	
C	683.15	0.662	
(1a)-(1c)	650.32	0.644	Petric and Karić (2016)
(2a)-(2c)	651.97	0.642	Petric and Karić (2016)
(3a)-(3c)	673.03	0.615	Petric and Karić (2016)
(4a)-(4c)	628.99	0.689	Petric and Karić (2016)
(5c)-(5c)	674.01	0.610	Petric and Karić (2016)
(1a)-(1c)	673.04	0.672	Present study
(2a)-(2c)	673.08	0.669	Present study
(3a)-(3c)	672.60	0.667	Present study
(4a)-(4c)	672.45	0.675	Present study
(5a)-(5c)	607.58	0.614	Present study

A - average measured values from December 2015, B - average measured values from January 2016, C - average measured values from February 2016, T_{out} – outlet temperature of reaction mixture (K), P_{out} – outlet pressure of reaction mixture (bar).

The measured outlet process parameters are the outlet temperature and pressure of the reaction mixture.

Table 4. Percentage deviations of simulation results with existing kinetic parameters and improved kinetic parameters from measured values of outlet process parameters

Kinetic model	T_{out} (%)	P_{out} (%)	Reference
(1a)-(1c)	4.75	3.01	Petric and Karić (2016)
	4.21	4.17	
	4.8	2.72	
(2a)-(2c)	4.51	3.43	Petric and Karić (2016)
	3.97	4.67	
	4.56	3.12	
(3a)-(3c)	1.42	7.38	Petric and Karić (2016)
	0.86	8.48	
	1.48	7.10	
(4a)-(4c)	7.87	3.63	Petric and Karić (2016)
	7.35	2.47	
	7.93	3.92	
(5a)-(5c)	1.30	8.85	Petric and Karić (2016)
	0.73	10.16	
	1.36	8.52	
(1a)-(1c)	1.44	1.19	Present study
	0.87	0.00	
	1.50	1.49	
(2a)-(2c)	1.43	0.75	Present study
	0.86	0.45	
	1.50	1.05	
(3a)-(3c)	1.51	0.45	Present study
	0.94	0.75	
	1.57	0.75	
(4a)-(4c)	1.53	1.63	Present study
	0.96	0.44	
	1.59	1.93	
(5a)-(5c)	12.37	6.75	Present study
	11.74	8.04	
	12.44	6.43	

Table 4 shows percentage deviations of simulation results for the existing kinetic parameters and the improved kinetic parameters from the measured values of outlet process parameters. The best agreement of simulation results and measured values with application of improved kinetic parameters was achieved with the application of the kinetic model 2 (Equations (2a-c)). The simulation results of the kinetic models 1, 3 and 4 (Equations (1a-c), (3a-c) and (4a-4c)) also showed a good agreement with the measured values. The use of the measured values from Global Ispat Coke Industry Lukavac for the determination of kinetic parameters is the main reason for good agreement of simulated and measured values. The kinetic model 5 (Equation (5a-5c)) showed poor agreement of simulation results and measured values. The smallest deviations for the outlet temperature of reaction mixture were observed with the application of the kinetic model 2 (Equations (2a-c)), while the largest deviations for the outlet temperature of reaction mixture were observed with the application of the kinetic model 5 (Equations (5a-c)). The smallest deviations for the outlet pressure of reaction mixture were observed with application of the kinetic model 3 (Equations (3a-c)), while the largest deviations for the outlet pressure of reaction mixture were observed with the kinetic model 5 (Equations (5ac)). The smallest deviations of numerical simulations in comparison with the measured values of the outlet temperature of reaction mixture were 1.43, 0.86 and 1.50% for the kinetic model 2 (Equations (2a-c)). The smallest deviations of numerical simulation in comparison with the measured values of the outlet pressure of reaction mixture were 0.45, 0.75 and 0.75% for the kinetic model 3 (Equations (3a-c). Table 5 shows comparisons of simulation results with the existing kinetic parameters (Petric and Karić, 2016) and the improved kinetic parameters (present study) from the measured values of temperatures of the reaction mixture along the reactor length. The best agreement of simulation results for temperatures of the reaction mixture along the reactor length was achieved with the kinetic model 2 (Equations (2a-c)). Kinetic models with improved kinetic parameters 1-4 (Equations (1a-c), (2a-c), (3a-c) and (4a-c) showed better agreement with the measured values, while the kinetic model 5 (Equation (5a-c)) showed poorer agreement with the measured values compared to the kinetic models from the study of Petric and Karić (2016).

Table 6 shows the percentage deviation of simulation results with the existing kinetic parameters (Petric and Karić, 2016) and the improved kinetic parameters from the measured values of temperatures of the reaction mixture along the reactor length. The percentage deviations of numerical simulation with improved kinetic parameters and existing kinetic parameters in comparison with measured values of inside reactor temperature were in the range 0.90-5.36% and in the range 4.17-9.78% (kinetic model 2, Equations (2a-c)), respectively.

Table 5. Comparisons of simulation results with existing kinetic parameters and improved kinetic parameters from measured values of inside reactor temperatures

L (m)	T (K)	Petric and Karić (2016)					Present study				
		(1a)-(1c)	(2a)-(2c)	(3a)-(3c)	(4a)-(4c)	(5a)-(5c)	(1a)-(1c)	(2a)-(2c)	(3a)-(3c)	(4a)-(4c)	(5a)-(5c)
0.0	431.15	431.15	431.15	431.15	431.15	431.15	431.15	431.15	431.15	431.15	431.15
0.5	696.15	642.07	646.00	666.03	596.50	675.01	672.89	673.07	672.67	671.60	637.16
0.6	683.15	642.30	645.98	666.56	599.07	674.95	672.88	673.06	672.76	671.73	636.55
0.7	705.15	642.49	645.98	666.86	600.97	674.85	672.87	673.06	672.80	671.80	636.03
0.8	709.15	642.68	645.99	667.18	602.68	674.77	672.86	673.06	672.84	671.86	635.47
0.9	700.15	642.88	646.02	667.49	604.23	674.66	672.86	673.06	672.87	671.92	634.88
1.0	701.15	643.03	646.06	667.79	605.32	674.56	672.86	673.06	672.89	671.97	634.41
1.1	694.15	643.23	646.12	668.01	606.68	674.46	672.85	673.06	672.91	672.02	633.75
1.2	699.15	643.44	646.20	668.29	607.95	674.38	672.85	673.06	672.93	672.06	633.04
1.3	703.15	643.66	646.26	668.56	609.17	674.29	672.85	673.06	672.95	672.10	632.30
1.4	687.15	643.94	646.40	668.89	610.61	674.19	672.85	673.06	672.96	672.14	631.31
1.5	691.15	644.12	646.52	669.14	611.44	674.11	672.86	673.06	672.98	672.17	630.68
1.6	692.15	644.36	646.66	669.32	612.52	674.03	672.86	673.06	672.99	672.21	629.79
1.7	684.15	644.61	646.82	669.57	613.58	673.98	672.86	673.06	672.99	672.23	628.85
1.8	690.15	644.87	646.95	669.80	614.61	673.92	672.87	673.06	673.00	672.26	627.86
1.9	684.15	645.07	647.14	670.04	615.37	673.86	672.87	673.06	673.01	672.29	627.07
2.0	681.15	645.42	647.41	670.33	616.62	673.80	672.88	673.06	673.02	672.32	625.70
2.1	684.15	645.72	647.65	670.50	617.62	673.77	672.88	673.06	673.03	672.35	624.52
2.2	683.15	646.03	647.90	670.72	618.61	673.74	672.89	673.06	673.03	672.37	623.28
2.3	682.15	646.19	648.04	670.89	619.11	673.73	672.89	673.06	673.03	672.39	622.63
2.4	683.15	646.62	648.42	671.18	620.36	673.71	672.90	673.06	673.04	672.42	620.94
2.5	684.15	646.98	648.75	671.35	621.38	673.71	672.91	673.07	673.05	672.44	619.50
2.6	684.15	647.37	649.11	671.58	622.41	673.72	672.91	673.07	673.05	672.46	617.99
2.8	680.15	648.12	649.83	672.05	624.27	673.78	672.92	673.07	673.06	672.50	615.15
3.0	683.15	649.24	650.94	672.54	626.81	673.92	672.94	673.07	673.07	672.54	611.11
3.2	679.15	650.32	651.97	673.03	628.99	674.10	672.95	673.08	673.07	672.58	607.58

Table 6. Percentage deviation of simulation results with existing kinetic parameters and improved kinetic parameters from measured values of inside reactor temperatures

L (m)	**Petric and Karić (2016)**					**Present study**				
	(1a)-(1c)	(2a)-(2c)	(3a)-(3c)	(4a)-(4c)	(5a)-(5c)	(1a)-(1c)	(2a)-(2c)	(3a)-(3c)	(4a)-(4c)	(5a)-(5c)
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	8.42	7.76	4.52	16.71	3.13	3.46	3.43	3.49	3.66	9.26
0.6	6.36	5.75	2.49	14.04	1.21	1.53	1.50	1.54	1.70	7.32
0.7	9.75	9.16	5.74	17.34	4.49	4.80	4.77	4.81	4.96	10.87
0.8	10.34	9.78	6.29	17.67	5.10	5.39	5.36	5.40	5.55	11.59
0.9	8.91	8.38	4.89	15.87	3.78	4.06	4.02	4.05	4.20	10.28
1.0	9.04	8.53	5.00	15.83	3.94	4.20	4.17	4.20	4.34	10.52
1.1	7.92	7.43	3.91	14.42	2.92	3.17	3.13	3.16	3.29	9.53
1.2	8.66	8.19	4.62	15.00	3.67	3.91	3.88	3.90	4.03	10.44
1.3	9.24	8.80	5.17	15.43	4.28	4.50	4.47	4.49	4.62	11.21
1.4	6.71	6.30	2.73	12.54	1.92	2.13	2.09	2.11	2.23	8.85
1.5	7.30	6.90	3.29	13.04	2.53	2.72	2.69	2.70	2.82	9.59
1.6	7.42	7.03	3.41	13.00	2.69	2.87	2.84	2.85	2.97	9.90
1.7	6.13	5.77	2.18	11.50	1.51	1.68	1.65	1.66	1.77	8.79
1.8	7.02	6.68	3.04	12.29	2.41	2.57	2.54	2.55	2.66	9.92
1.9	6.06	5.72	2.11	11.18	1.53	1.68	1.65	1.66	1.76	9.10
2.0	5.54	5.21	1.61	10.47	1.09	1.23	1.20	1.21	1.31	8.86
2.1	5.95	5.64	2.04	10.77	1.54	1.67	1.65	1.65	1.76	9.55
2.2	5.75	5.44	1.85	10.43	1.40	1.52	1.50	1.50	1.60	9.61
2.3	5.56	5.26	1.68	10.18	1.25	1.38	1.35	1.36	1.45	9.56
2.4	5.65	5.36	1.78	10.12	1.40	1.52	1.50	1.50	1.60	10.02
2.5	5.75	5.46	1.91	10.10	1.55	1.67	1.65	1.65	1.74	10.44
2.6	5.68	5.40	1.87	9.92	1.55	1.67	1.65	1.65	1.74	10.71
2.8	4.94	4.67	1.21	8.95	0.95	1.07	1.05	1.05	1.14	10.57
3.0	5.22	4.95	1.58	8.99	1.37	1.52	1.50	1.50	1.58	11.79
3.2	4.43	4.17	0.91	7.97	0.75	0.92	0.90	0.90	0.98	11.78

Figures 1-5 show comparisons of simulated (with improved kinetic parameters) and measured values for temperatures of the reaction mixture along the reactor length for different kinetic models that were used in simulation. Kinetic models 1-4 with improved kinetic parameters (Equations (1a-1c), (2a-3c), (3a-3c) and (4a-4c)) showed very good agreement between simulated and measured values for temperatures of the reaction mixture along the reactor length.

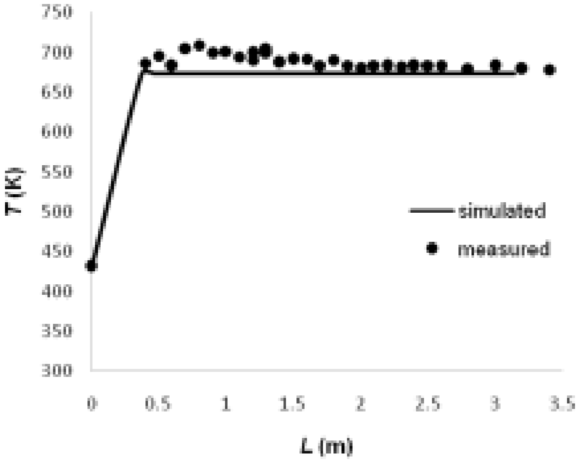

Figure 1. Comparison of simulated (Equations (1a-1c)), with improved kinetic parameters and measured values for temperature of reaction mixture along the reactor length.

Based on the comparison of the simulated and measured values for the temperatures of the reaction mixture along the reactor length, it can be concluded that the improved kinetic parameters in four kinetic models can be used to adequately simulate temperature profile in an industrial fixed-bed reactor.

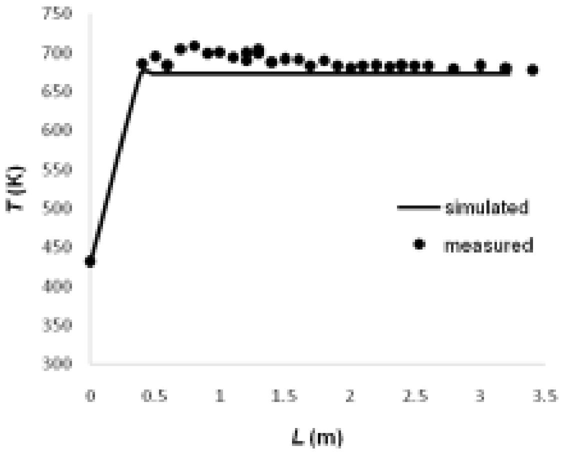

Figure 2. Comparison of simulated (Equations (2a-2c)), with improved kinetic parameters) and measured values for temperature of reaction mixture along the reactor length.

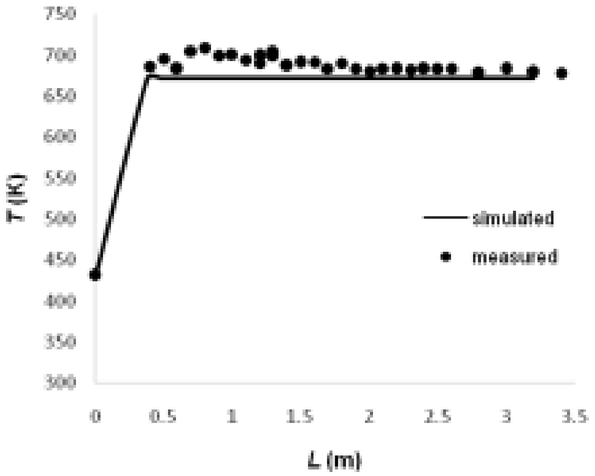

Figure 3. Comparison of simulated (Equations (3a-3c)), with improved kinetic parameters and measured values for temperature of reaction mixture along the reactor length.

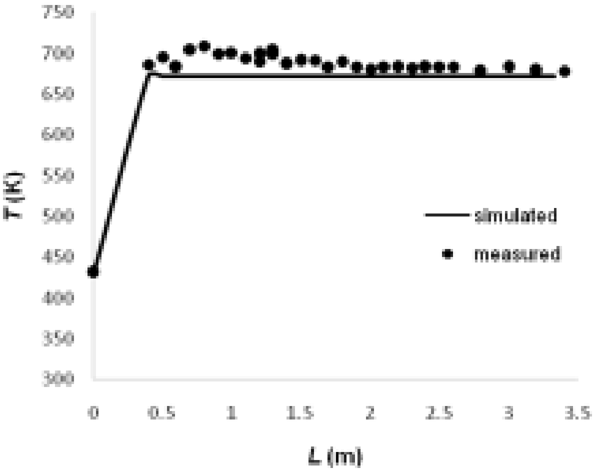

Figure 4. Comparison of simulated (Equations (4a-4c)), with improved kinetic parameters and measured values for temperature of reaction mixture along the reactor length.

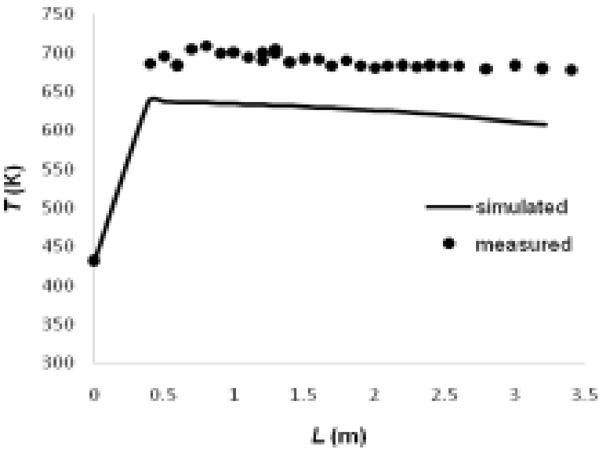

Figure 5. Comparison of simulated (Equations (5a-5c)), with improved kinetic parameters and measured values

Only the kinetic model 5 (Equations (5a-5c)) with improved kinetic parameters showed poor agreement between simulated and measured values for the temperatures of the reaction mixture along the reactor length. This finding can be explained by the fact that the temperature dependence is not included in kinetic model 5 (Equations (5a-5c)).

4. CONCLUSIONS

Kinetic models with improved kinetic parameters showed better simulation results compared to kinetic models with the existing kinetic parameters. Parameters used for comparison were temperature inside the reactor, outlet temperature and outlet pressure. The best agreement of simulation results and measured values was achieved with application of the kinetic model 2 (Equations (2a-c)).

The simulations results of the kinetic models 1, 3 and 4 (Equations (1a-c), (3a-c) and (4a-4c)) also showed a good agreement with measured values. The smallest deviations of numerical simulations in comparison with the measured values of the outlet temperature of reaction mixture were 1.43, 0.86 and 1.50% for kinetic model 2 (Equations (2a-c)). The smallest deviations of numerical simulation in comparison with the measured values of the outlet pressure of the reaction mixture were 0.45, 0.75 and 0.75% for kinetic model 3 (Equations (3a-c)). The percentage deviations of numerical simulation with improved kinetic parameters and existing kinetic parameters in comparison with measured values of inside reactor temperature were in the range 0.90-5.36% and in the range 4.17-9.78% (kinetic model 2, Equations (2a-c)), respectively.

Future work should be directed to the development of a rigorous model by introducing mass and heat transfer in a two-dimensional reactor model and other phenomena, as well as to the simultaneous optimization of the inlet process parameters for an industrial fixed-bed reactor.

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