

Kinetics of catalytic combustion processes of air admixtures

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Abstract: A catalytic combustion of organic admixtures of air belongs to the basic technologies of gas purification. A macrokinetics of admixtures combustion over the porous catalysts was described. The theoretical approach is in agreement with standard description of macrokinetics of the catalytic processes. The relationship between the fundamental magnitudes: observed process rate r^* , reaction rate r in the kinetic zone, and a coefficient of the surface utilization η in the form $r^* = r \cdot \eta$ have been described. These magnitudes combines the Thiele module ϕ . A kinetics equation for the isothermal and non-isothermal conditions was provided. The influence of mass and heat transfer in the catalyst grain on the course of the process was described by means of the surface utilization coefficient η . An equation describing this coefficient for both isothermal and non-isothermal conditions was given. The second part of this work concerns the application of theory. When the composition of purified gas is continuously varied, a quantitative approach is rather impossible. The theory was used for the qualitative analysis of process on the basis of the experimental results. A fulfillment of the first-order kinetics means that the degree of admixtures conversion does not depend on their initial concentrations. A non-isothermicity of the catalyst grain is expressed in such a way that the process rate observed over the large porous grains of the catalyst can be higher than the reaction rate in the kinetic zone. A temperature deference between the catalyst grains and flowing gas causes that the reactor can be stably operated at varied concentrations of admixtures and temperature over a relatively wide range. It was also demonstrated that the flammable admixtures may advantageously influence the conversion of hardly combustible admixtures.

Introduction

A catalytic combustion of air admixtures is a commonly used method of gas purification (Koniecznyński 1993). The porous catalysts are usually used in this process, including noble metals mainly supported platinum and palladium (Avgourpoulos 2006, Tsou et al. 2005, Ordóñez et al. 2007, Pecchi et al. 2006, Osaki et al. 2007, Okumura et al. 2003, Takeguchi et al. 2003, Verykios et al. 1997, Shim et al. 2008) as well as the transition metals oxides such as CuO, Mn₂O₃, MnO₂, Fe₂O₃, Co₂O₃, V₂O₅ and MoO₃ or their mixtures (Spivey 1987, Wang 2004, Drago et al. 1995, Kennedy et al. 1984, Everaert et al. 2004, Łojewska et al. 2005, Morales et al. 2006, Trawczyński et al. 2005, Yang et al. 2006, Delimaris et al. 2008, Choudhary et al. 2004, Carpentier et al. 2002, Li et al. 2009, Parus et al. 2009, Parus et al. 2011). They are prepared both as the pelleted catalysts, and supported catalysts, mostly on Al₂O₃. The course of contact combustion process of admixtures on an isotropic porous grain of the catalyst has been considered. It was assumed that the heat transfer in the catalyst grain can be described by the Fourier equation, whereas the mass transfer by the Fick's equation (Satterfield et al. 1963, Satterfield 1970).

It was assumed that the process proceeds under the stationary conditions. The process rate was related to a unitary internal surface, unitary catalyst volume or to unitary catalyst mass. The first step in the construction of a mathematical model is the derivation of the Prater equation (Petersen 1965, Prater 1958, Straszko et al. 1978). This equation determines the interdependence between a local temperature in the grain and the local concentration of balanced component, what allows to use only one balance equation (mass or heat) during a process description. The mass balance equation is usually used. This equation is written for the differential element of grain which is determined for the grain with spherical geometry by a change of radius in the range $R, R+dR$.

The Prater equation

The Prater equation is obtained basing on the heat balance equation and mass balance equation

$$\lambda \nabla^2 T = r_i (-\Delta H)_i \quad (1)$$

and

$$D_i \nabla^2 c_i = r_i \quad (2)$$

In the case of isotropic grain, the parameters D_i , λ and $(-\Delta H)_i$ are constant.

By using the substitution

$$\alpha = (-\Delta H)_i \frac{D_i}{\lambda} \quad (3)$$

the magnitude of which is also independent on the coordinate R , the heat balance equation and mass balance equation were written as follows

$$\nabla^2 T = r_i (-\Delta H)_i / \lambda \quad (4)$$

$$\alpha \nabla^2 c_i = r_i (-\Delta H)_i / \lambda \quad (5)$$

By subtracting from both sides it was obtained

$$\nabla^2 (\alpha c_i - T) = 0 \quad (6)$$

The Laplace equation was derived for the function $f_i = \alpha c_i - T$

$$\nabla^2 f_i = 0 \quad (7)$$

For $R = R_0$; $T_s = \text{const.}$ and $c_i = c_{i,s} = \text{const.}$, hence $f_{i,s} = \text{const.}$

From a uniqueness proof (the second boundary value problem) we have

$$f_i = f_{i,s} = f_{i,o} \quad (8)$$

The notation $f_{i,o}$ indicates the function value f_i related to the flowing gas stream.

On the basis of these assumptions we derive the Prater equation which determines the interdependence between the temperature distribution and concentration distribution of the balanced component in the catalyst grain.

This equation has the form

$$T = T_0 + \frac{(-\Delta H)_i D_i}{\lambda} (c_{0i} - c_i) \quad (9)$$

For $c_i = 0$ (balanced component reacts completely) the temperature will reach maximum, equal to

$$T_{\max} = \frac{(-\Delta H)_i D_i}{\lambda} c_{0i} \quad (10)$$

After the introduction of the Prater number into equation (9)

$$\beta_i = \frac{(-\Delta H)_i D_i}{\lambda} c_{0i} \quad (11)$$

we obtain

$$T = T_0 + \beta_i \left(1 - \frac{c_i}{c_{0i}} \right) = T_0 + \beta_i (1 - \psi_i) \quad (12)$$

Kinetic equation for nonisothermal conditions

A kinetic equation is used for the description of the course of contact process, in the form

$$r_i = k(T) \varphi(c_i) \quad (13)$$

In general, the n-th order equation $\varphi(c_i) = (c_{0i} \psi_i)^n$ is assumed.

The function $k(T)$ is described by the Arrhenius equation

$$k(T) = A e^{-\frac{E}{RT}} \quad (14)$$

The equation (14) should be adopted to the nonisothermal conditions (temperature changing along the radius of the catalyst grain). The Weisz method was applied (Weisz et al. 1962). A temperature of the flowing gas stream (T_0) was assumed as the reference temperature. A variable Θ was introduced

$$\Theta = \frac{T - T_0}{T_0} \quad (15)$$

The factor $e^{-\frac{E}{RT}}$ can be now written as follows

$$e^{-\frac{E}{RT}} = e^{-\frac{E}{RT_0(1+\Theta)}} \approx e^{-\frac{E}{RT_0}(1-\Theta)} \approx e^{-\frac{E}{RT_0}} e^{\frac{E}{RT_0}\Theta} \quad (16)$$

Using the Prater equation (12), the variable Θ was described by equation

$$\Theta = \frac{\beta_i (1 - \psi_i)}{T_0} \quad (17)$$

The substitution $\gamma_i = \frac{E_i}{RT_0^2}$ was also used. These magnitudes were inserted to equation (13) and

$$r_i = A_i e^{-\frac{E}{RT_0}} e^{\gamma_i \beta_i (1 - \psi_i)} (c_{0i} \psi_i)^n = k_i(T_0) e^{\gamma_i \beta_i (1 - \psi_i)} (c_{0i} \psi_i)^n \quad (18)$$

was obtained.

The notation $k_i(T_0)$ indicates the reaction rate constant related to a temperature of the flowing gas stream.

Combustion of hazardous air admixtures most often proceeds as the first – order reaction (Straszko, 1979).

Then

$$r_i = k_i(T_0) e^{\gamma_i \beta_i (1 - \psi_i)} (c_{0i} \psi_i) \quad (19)$$

The application of two parameters $\gamma_i = \frac{E_i}{RT_0^2}$ and $\beta_i = \frac{(-\Delta H)_i D_i}{\lambda} c_{0i}$ facilitates an analysis of the influence of flammable admixtures on the conversion of hardly combustible admixtures.

In such a case $\gamma_i = \frac{E_i}{RT_0^2} = \text{const.}$ Therefore, instead of the parameter β_i , one should use the parameter β_i^* described by equation

$$\beta_i^* = \beta_1 + \beta_i = \frac{(-\Delta H)_1 D_1}{\lambda} c_{01} + \frac{(-\Delta H)_i D_i}{\lambda} c_{0i} \quad (20)$$

The symbol 1 concerns a readily flammable admixture.

Coefficient of the surface utilization η

The temperature distributions and the concentration distribution of balanced component in the catalyst grain are not considered in the applications, but the influence of heat transfer and mass transfer in the catalyst grain on the process rate is evaluated. The coefficient η of the surface utilization is used. This coefficient depends on the grain symmetry, effective heat transfer coefficients and the effective diffusion coefficients as well as on the form of a kinetic equation (Petersen, 1965, Prater, 1958, Satterfield et al. 1963, Satterfield, 1970, Straszko et al. 1978).

Determination of coefficient η

The concentration \hat{c}_i and temperature \hat{T} at the point P of the catalyst grain surface depend on the location of this point in the space $\{\hat{c}_i(P); \hat{T}(P)\}$. A detailed form of the kinetic equation is achieved as a result of solution of the partial differential equations with boundary conditions c_i, T . The integration is carried out over the entire volume of grain. As a result, the following general relationship is obtained for the observed process rate:

$$\hat{r}^* = \frac{1}{V_p} \iiint \hat{r}[c_i(P), T(P)] dV_p \quad (21)$$

It should be added that the process rate \hat{r}^* relates to the unitary surface of grain. Whereas during the applications the rate r^* related to the unitary volume of grain is used, hence $r^* = \rho_K S_K \hat{r}^*$.

Equation (21) determinates the average process rate for the volume of grain. A coefficient of utilization of the catalyst surface is defined as follows

$$\eta = \frac{r^*}{r} \quad (22)$$

Equation (22) expresses the interdependence among the observed process rate r^* and the reaction rate r in the kinetic region. The observed rate is equal to the diffusion rate of balanced component into the reaction zone.

Accordingly, for the first-order reaction and a spherical geometry, equation (22) takes the form

$$\begin{aligned} \eta_{K,1} &= \frac{-4\pi R_0^2 \left(\frac{dc_i}{dR} \right)_{R=R_0}}{\frac{4}{3} \pi R_0^3 k_v c_{0i}} = -\frac{3D_i}{R_0 k_v c_{0i}} \left(\frac{dc_i}{dR} \right)_{R=R_0} = \\ &= -\frac{3D_i}{R_0 k_v} \left(\frac{d\psi_i}{dR} \right)_{R=R_0} \end{aligned} \quad (23)$$

In order to calculate the effectiveness factor $\eta_{K,1}$ one should know a value of derivative $-\left(\frac{dc_i}{dR} \right)_{R=R_0}$, or a derivative $\left(\frac{d\psi_i}{dR} \right)_{R=R_0}$. The values of these derivatives are calculated by solving the balance equations (1) and (2).

Quantitative presentation, the isothermal conditions

The Prater equation is satisfied for the catalyst grains with arbitrary geometry and for the reaction of arbitrary order provided that the heat transfer in the catalyst grain can be described by the Fourier equation, whereas the mass transfer by the Fick's equation.

The Prater equation allows to eliminate one variable, usually temperature, from this system of partial differential equations (1, 2).

The mass balance equation for a stationary process and a grain with spherical symmetry has the form:

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 D_i \frac{dc_i}{dR} \right) = \rho_K S_K r'(c_i) \quad (24)$$

By solving equation (24), the following boundary conditions are assumed: $R = R_0, c_i = c_{0i}, R = 0, dc_i/dR = 0$. The first boundary condition means that the external diffusion is not taken into account (the Dirichlet model), the second condition results from the symmetrical distribution of balanced component in the grain.

The external diffusion is taken into account by changing the first boundary condition (Straszko 1979). It should be mentioned that the combustion of admixtures is carried out at the gas flow rates larger than 0.2 m/s. The external diffusion can be omitted at these flow rates of gas (Szarawara et al. 1980).

Equation (24) is appropriate for both isothermal and nonisothermal conditions. For description of these processes, the different kinetic equations (equation (13) in the case of the isothermal process, whereas equation (18) for nonisothermal process) are used.

A solution method of equation (24) is similar in both cases. For the isothermal conditions and the first-order reaction, equation (24) has the form

$$\frac{d^2 c_i}{dR^2} + \frac{2}{R} \frac{dc_i}{dR} = \frac{\phi_{K,1}}{R_0^2} c_i \quad (25)$$

Equation (25) has an analytical solution (Straszko et al. 1978, Straszko 1979). By using this solution, the following equation is obtained for a derivative $-\left(\frac{dc_i}{dR}\right)_{R=R_0}$,

$$-\left(\frac{dc_i}{dR}\right)_{R=R_0} = \frac{\phi_{K,1} c_{oi}}{R_0} \left[\frac{1}{\tanh \phi_{K,1}} - \frac{1}{\phi_{K,1}} \right] \quad (26)$$

Substitution of (26) into (23) leads to:

$$\eta_{K,1} = \frac{3}{\phi_{K,1}} \left[\frac{1}{\tanh \phi_{K,1}} - \frac{1}{\phi_{K,1}} \right] \quad (27)$$

Equation (27) concerns an arbitrary reaction of the first-order, hence it also concerns various admixtures. First, the graphs of function $\eta_{K,1} = f(\phi)_{K,1}$ are plotted using this equation,

then, $\phi_{K,1} = R_0 \sqrt{\frac{k_v}{D_{ef}}}$ is calculated for a considered case and

a value $\eta_{K,1}$ is read out from the graph. However, there exist no analytical solutions for the reaction of higher orders and for the nonisothermal processes. In these cases asymptotic equations are used.

Asymptotic equations

The dimensionless magnitudes

$$\psi_i = \frac{c_i}{c_{oi}}; \zeta = \frac{3(R_0 - R)}{R_0}; r''(\psi_i) = \frac{r'(c_i)}{r'(c_{oi})}$$

and the Thiele module

$$\phi_{k,n} = \frac{R_0}{3} \sqrt{\frac{\rho_K S_K r'(c_{oi})}{D_i c_{oi}}} \quad (28)$$

are substituted into equation (24).

After the substitutions we obtain:

$$\frac{d^2 \psi_i}{d\zeta^2} - \frac{2}{\left(1 - \frac{\zeta}{3}\right)} \frac{d\psi_i}{d\zeta} = \phi_{k,n}^2 r''(\psi_i) \quad (29)$$

If we also apply the substitution, $\zeta = \phi_{k,n} \tilde{\zeta}$, then we obtain equation in the form

$$\frac{d^2 \psi_i}{d\tilde{\zeta}^2} = \frac{2}{\Phi_{K,n} \left(1 - \frac{\tilde{\zeta}}{3}\right)} \frac{d\psi_i}{d\tilde{\zeta}} = r''(\psi_i) \quad (30)$$

There exists no analytical solution for equation (30).

The second term of equation (30) can be omitted for large values of $\phi_{K,n}$. Thus the asymptotic equation in the form

$$\frac{d^2 \psi_i}{d\tilde{\zeta}^2} = r''(\psi_i) \quad (31)$$

will be obtained.

We can assume the following boundary conditions

$$\zeta = 1, \psi_i = 1; \zeta = 0, \psi_i = 0 \text{ and } \frac{d\psi_i}{d\tilde{\zeta}} = 0. \text{ Integrating equation (31) we use the substitution } p = \frac{d\psi_i}{d\tilde{\zeta}}, \text{ then } p \frac{dp}{d\psi_i} = \frac{d^2 \psi_i}{d\tilde{\zeta}^2}.$$

For the first-order reaction we have

$$\frac{d^2 \psi_i}{d\tilde{\zeta}^2} = \psi_i \quad (32)$$

Thus

$$p = \frac{d\psi_i}{d\tilde{\zeta}} = \psi_i \quad (33)$$

For $\zeta = 0, \psi_i = 1$, hence

$$\left(\frac{d\psi_i}{d\tilde{\zeta}}\right)_{\tilde{\zeta}=0} = 1 \quad (34)$$

Using equation (34) a derivative $\left(\frac{d\psi_i}{dR}\right)_{R=R_0}$ is calculated

$$\left(\frac{d\psi_i}{dR}\right)_{R=R_0} = \left(\frac{d\psi_i}{d\tilde{\zeta}}\right)_{\tilde{\zeta}=0} \frac{d\tilde{\zeta}}{dR} = -\frac{3\phi_{K,1}}{R_0} \left(\frac{d\psi_i}{dR}\right)_{R=R_0} \quad (35)$$

By transforming (23) and taking into account the equation (35) we obtained

$$\eta_{K,1} = \frac{1}{\phi_{K,1}} \quad (36)$$

This formula is correct for $\phi_{K,1} > 1$. The calculations are performed in the same manner for the reactions described by various kinetic equations.

Quantitative presentation, nonisothermal conditions

In this case the kinetic equation describing the rate of nonisothermal process (equation (18)) was substituted into equation (31) and

$$\frac{d^2 \psi_i}{d\tilde{\zeta}^2} = k_i(T_0) e^{\gamma_i \beta_i (1 - \psi_i)} (c_{oi} \psi_i)^n \quad (37)$$

was obtained.

The combustion of admixtures in air usually proceeds as a first-order reaction. Thus for nonisothermal conditions we obtain

$$\frac{d^2 \psi_i}{d\tilde{\zeta}^2} = k_i(T_0) c_{oi} e^{\gamma_i \beta_i (1 - \psi_i)} \psi_i \quad (38)$$

Since

$$\zeta = \phi_{K,1} \tilde{\zeta} \text{ and } \phi_{K,1} = \frac{R_0}{3} \sqrt{\frac{\rho_K S_K k_i(T_0)}{D_i}} = \frac{R_0}{3} \sqrt{\frac{k_v}{D_i}} \text{ then we}$$

obtain

$$\frac{d^2\psi_i}{d\xi^2} = k_i(T_0)c_{oi}e^{\gamma_i\beta_i(1-\psi_i)}\psi_i \quad (39)$$

$$\beta_i^* = \beta_1 + \beta_i = \frac{(-\Delta H)_1 D_1}{\lambda} c_{o1} + \frac{(-\Delta H)_i D_i}{\lambda} c_{oi} \quad (46)$$

We assume the following boundary conditions $\zeta = 0$,

$$\psi_i = 1; \zeta \rightarrow \infty, \psi_i = 0 \text{ and } \frac{d\psi_i}{d\xi} = 0.$$

After the integration of equation (39) we obtain

$$\frac{d\psi_i}{d\xi} = \pm \sqrt{2} e^{\frac{\gamma_i\beta_i}{2}} \left\{ \int_0^{\psi_i} e^{-\gamma_i\beta_i\psi_i} \psi_i d\psi_i \right\}^{\frac{1}{2}} \quad (40)$$

$$\text{Because } \int x e^{-ax} dx = \frac{e^{-ax}}{a^2} (1 + ax)$$

Thus

$$\int_0^{\psi_i} \psi_i e^{-\gamma_i\beta_i\psi_i} d\psi_i = \frac{1}{(\gamma_i\beta_i)^2} \left\{ 1 - e^{-\gamma_i\beta_i\psi_i} (1 + \gamma_i\beta_i\psi_i) \right\} \quad (41)$$

After substituting (41) into (40) we obtain

$$\frac{d\psi_i}{d\xi} = \pm \frac{\sqrt{2}}{\gamma_i\beta_i} e^{\frac{\gamma_i\beta_i}{2}} \left\{ 1 - e^{-\gamma_i\beta_i\psi_i} (1 + \gamma_i\beta_i\psi_i) \right\}^{\frac{1}{2}} \quad (42)$$

For $\zeta = 0$, $\psi_i = 0$, thus we have

$$\left(\frac{d\psi_i}{d\xi} \right)_{\zeta=0} = \pm \frac{\sqrt{2}}{\gamma_i\beta_i} \phi_{K,1} e^{\frac{\gamma_i\beta_i}{2}} \left\{ 1 - e^{-\gamma_i\beta_i} (1 + \gamma_i\beta_i) \right\} \quad (43)$$

Substituting (43) into (23) we obtain

$$\eta_{K,1} = \frac{\sqrt{2}}{\phi_{K,1}} e^{\frac{\gamma_i\beta_i}{2}} \left\{ 1 - e^{-\gamma_i\beta_i} (1 + \gamma_i\beta_i) \right\}^{\frac{1}{2}} \quad (44)$$

The graphs $\eta_{K,1}$ as a function of $\phi_{K,1}$ for different values of $\gamma_i \cdot \beta_i$ are plotted using equation (44). Then, for a considered case, the parameter $\phi_{K,1}$ and the value of expression $\gamma_i \cdot \beta_i$ ($\gamma_i = \frac{E_i}{RT_0^2}$, $\beta_i = \frac{(-\Delta H)_i D_i}{\lambda} c_{oi}$) are calculated and the value $\eta_{K,1}$ (Petersen, 1965, Straszko et al. 1978) is read out from the graph.

The observed process rate is calculated from equation

$$r_i^* = \eta_{K,1} \cdot r_i \quad (45)$$

The influence of flammable admixtures on the conversion of slow-burning admixtures is described in a similar way as in the case of the process rate. For slow-burning admixture, the parameter $\gamma_i = \frac{E}{RT_0^2}$ does not undergo change. However, in this case one should use β_i^* described according to expressions

The presented approach is in agreement with the standard description of macrokinetics of the catalytic processes. Nowadays, there is no need to justify the validity of the theory in such approach. Only its application is important. In the case of traditional catalytic processes, the application of theory relies on a quantitative description of the process. The combustion of admixtures should be treated differently. During the operation of installation, the qualitative and quantitative composition of purified gases is varied. A quantitative description of such processes is not always possible. Therefore, the application of theory during the qualitative analysis of the course of the process, carried out based on the experimental data, has been presented. They concerned the determination of the form of kinetic equation describing the course of admixture combustion, the influence of temperature difference between the catalyst grains and flowing gas on the process effectiveness and the effect of flammable admixtures on the transformation of hardly combustible admixtures.

Experimental section

Methods of catalysts preparation

The catalysts were prepared by a co-precipitation method. As the precursors the following nitrates were used: $\text{Mn}(\text{NO}_3) \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ purchased from Chempur. The hydroxides were precipitated by a 10 wt % solution of NaOH. At the final stage, a small amount of 20 wt % solution of Na_2CO_3 was added in order to adjust the pH of solution equal to 9. The salts were dissolved in deionized water. A solution was heated to 80°C. At this temperature, the hydroxides were precipitated. A solution of NaOH was added in small portions from dropping funnel. The precipitation was performed for about 2 h. After precipitation, the precipitate was stabilized for 2 h at 80°C. The system was then cooled down to a room temperature, the precipitate was first rinsed several times by decantation, subsequently, the precipitated oxides were separated on a filter paper. A mass was dried at 110°C. A dried material was subjected to calcination at 400°C for 2 h.

Methodology

The measurements were carried out using the experimental set-up shown in Fig 1.

A part of the air stream from a gas cylinder, controlled by a valve (18) was directed to a column packed with glass rings (3) and sprinkled with organic compound. In the column, the air was saturated with the vapour of this compound. After the saturation, the air was introduced into a mixer (4). The second part of the air stream was directed directly to the mixer (4). The total volume flow rate of the air was measured by a venturi flow-meter (14). The flow was readout from the calibration curve $\dot{V}_{0v} = f(\Delta p)$, where Δp corresponds to a pressure decline on the Venturi tube measuring device located in the air stream which was registered by U – type manometer. The obtained mixture was introduced into the tubular microreactor (1) heated by a tube furnace (5). The temperature was measured by a thermocouple (15) placed in the catalyst bed. The amount of used catalyst was (approximately) 0.5 g. The grain size of

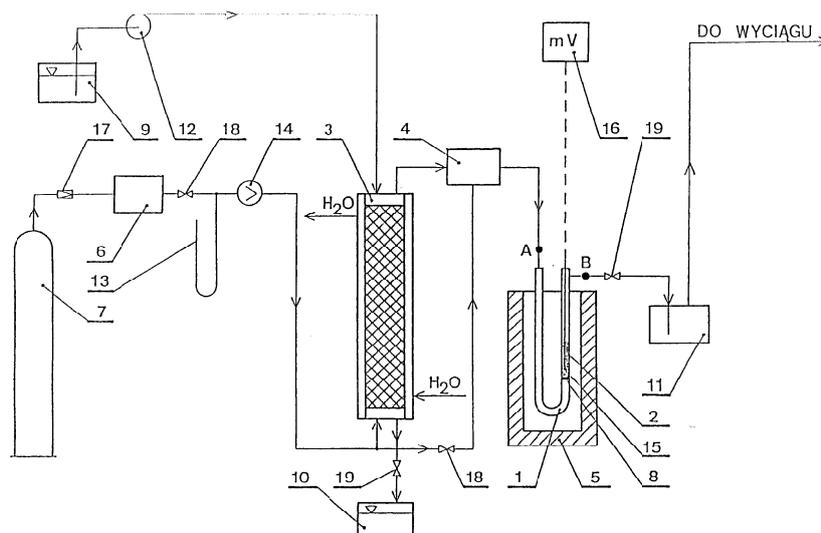


Fig. 1. The experimental set-up: 1 – tubular reactor, 2 – catalyst bed, 3 – packed column (saturator), 4 – mixer of the gases, 5 – electric furnace, 6 – air purification system, 7 – high-pressure air cylinder, 8 – grate from quartz wool, 9 – tank of liquid organic compound or mixture of liquid organic compounds, 10 – tank of the liquid from column, 11 – surge tank, 12 – peristaltic feed pump, 13 – mercury gauge, 14 – venturi flow-meter, 15 – thermocouple, 16 – milli-voltmeter, 17 – reducing valve, 18 – needle valves, 19 – control valve, A, B – sampling ports

the catalyst (dimensions of grain equal to 0.102–0.12 mm.) was selected according to the rules described in works (Parus et al. 2009, Parus et al. 2011, Straszko, 1979). The powder fractions were separated on the sieves. The air flow amounted to $20 \text{ dm}_n^3/\text{h}$, what gives the loading of $40 \text{ dm}_n^3/\text{g}_k \cdot \text{h}$ after the recalculation per 1 g of the catalyst.

The samples for analysis were collected at the inlet and outlet of the reactor. The determination was performed using a gas chromatograph CHROM 5 (Czech Republic). On the basis of the obtained results the degree of conversion was calculated using the formula

$$\alpha_i = 1 - (c_i / c_{0i}) \quad (47)$$

A change of volumetric flow rate of gas caused by the combustion of admixtures to the gaseous products, amounted to maximum 0.4 vol % (Parus et al. 2009). This allowed to assume $\dot{F}_{0v} = \dot{F}_v = \text{const}$ and justified the application of equation (47).

It is worthy to notice that in the case of kinetic studies, the higher concentrations of admixtures were used than those usually occurring in the purified gases. In the kinetic equations, in the case of the described processes, an adsorption term is likely to occur. Then, the kinetics is no longer linear. The adsorption term occurs at higher concentrations of admixtures. This means that if the first – order kinetic equation is achieved at these concentrations, this equation can be also used in the case of real mixtures, also at lower concentrations.

In the theoretical section a dimensionless concentration ψ_i was used with regard to a simplified notification. In this part the degree of conversion was used because it describes the course of the process. Moreover, this parameter is commonly used for the evaluation of catalysts activity. The experimental section concerns the fundamental issues: the form of kinetic equations, the influence of nonisothermality of the catalyst grain on the stability of the reactor process and the effect of

combustible admixtures on the conversion of slow burning admixtures.

Equations and kinetic parameters

The kinetic equations comprise a basis for the design of chemical reactors (Szarawara et al. 1980). When they are formulated, the form of function $\varphi(c_i)$ (kinetic model) is determined on the basis of the experimental data and the parameters A and E of the Arrhenius equation are then determined.

Numerous works have demonstrated that the rate of combustion of air admixtures on the porous catalysts can be described by the first-order equation

$$r_i = \frac{d\alpha_i}{d\tau} = k_v(1 - \alpha_i) \quad (48)$$

A tubular flow reactor was used during the measurements. A design equation of the ideal tubular reactor which is appropriate for the first-order reaction, and when a balanced reactor element is related to the catalyst mass, has the form

$$\frac{dm_K}{\dot{F}_{0v}} = \frac{d\alpha_i}{k(1 - \alpha_i)} \quad (49)$$

After the integration (48) and transformations we obtain

$$k = \frac{\dot{F}_{0v}}{m_K} [-\ln(1 - \alpha_i)] \quad (50)$$

Hence, the experimentally determined relationships of the degree of admixture conversion as a function of temperature $\alpha_i(T)$ comprise a basis of the calculations.

The measurements were carried out using the experimental set-up shown in Fig. 1. The amount of catalyst

was 0.5 g. A loading of the catalyst with gas was constant and amounted to $40 \text{ dm}_n^3/\text{g}_k \cdot \text{h}$.

The combustion of acetone was carried out over different catalysts whereas several admixtures were combusted over the catalyst with the composition of 60 wt % MnO_2 + 40 wt % CuO . In order to compare the activity of this catalyst with the activity of industrial catalysts the measurements were performed over the Pt-p catalyst by the combustion of m-xylene. It should be noticed that during the studies the low-temperature catalysts prepared in our laboratory were used (Straszko et al. 2012).

For the case of acetone combustion over different catalysts the plots of $\alpha(T)$ are presented in Fig. 2a, whereas the plots in the coordinate system $\ln k + \frac{1000}{T}$ obtained on this basis are presented in Fig 2b.

The plots $\alpha(T)$ for the combustion processes of various admixtures over the catalyst 60 wt % MnO_2 + 40 wt % CuO and for the combustion process of m-xylene over the Pt-p catalyst are presented in Fig 3a, whereas the plots $\ln k + \frac{1000}{T}$ are shown in Fig 3b.

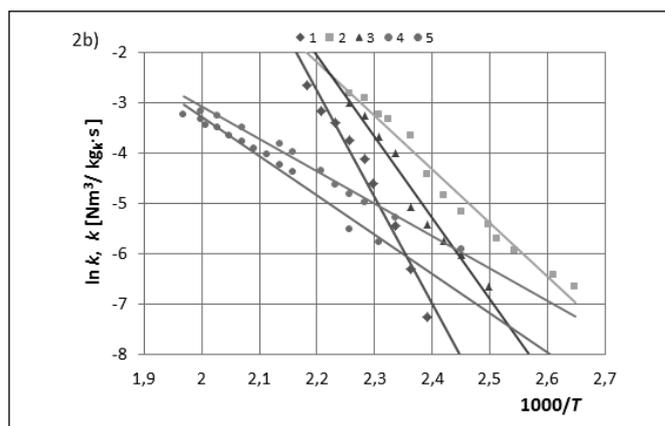
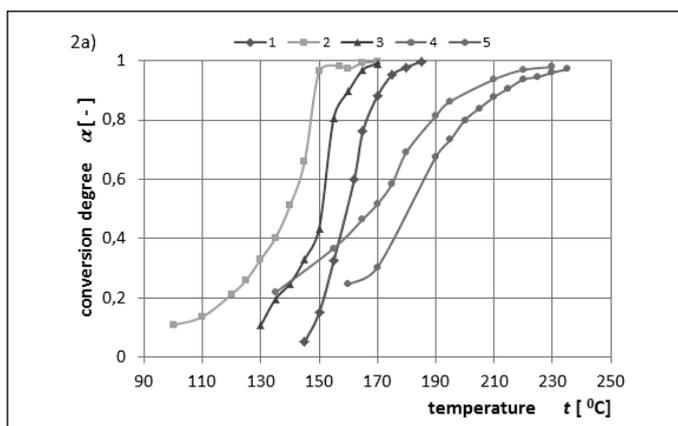


Fig. 2. The dependence of the degree of conversion on temperature (2a) and the plots $\ln k + \frac{1000}{T}$ (2b). Combustion of acetone over the catalysts: 1. 55 wt % MnO_2 + 45 wt % CuO , 2. 65 wt % MnO_2 + 35 wt % CuO , 3. 45 wt % MnO_2 + 55 wt % CuO , 4. 55 wt % MnO_2 + 45 wt % Fe_2O_3 , 5. 55 wt % MnO_2 + 45 wt % Fe_2O_3

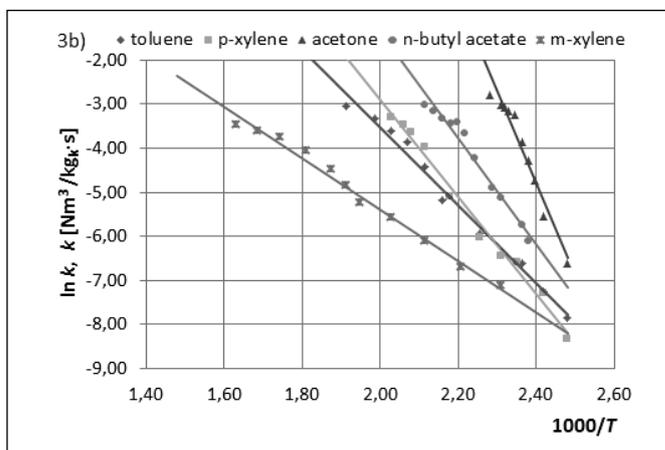
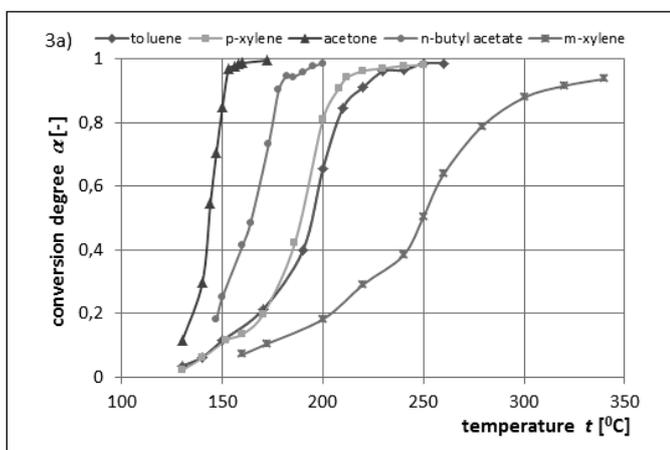


Fig. 3. The dependence of the conversion degree on temperature (3a) and the plots $\ln k + \frac{1000}{T}$ (3b). Combustion of toluene, p-xylene, acetone and n-butyl acetate over the catalyst 60 wt % MnO_2 + 40 wt % CuO , whereas the combustion of m-xylene over the Pt-p catalyst

The straight lines were obtained in the coordinate system $\ln k + \frac{1000}{T}$. The calculated parameters A and E of the Arrhenius equation are compiled in Table 1. A computer software statistic 6 was used.

The statistical evaluations indicate that a good accuracy was obtained. On the basis of the results of measurements it was determined that the first-order kinetic equation can be used for the description of the course of combustion of admixtures in air over different catalysts.

Stability of the reactor process

This issue concerns the influence of the temperature difference between the catalyst grains and flowing gas. This difference depends on the admixture concentration. It should be mentioned that in the case of strongly exothermic processes, which are involved in our study, this difference can also occur in the case of fine catalyst grains. Such a case was described.

The measurements were carried out using the experimental set-up shown in Fig 1. The combustion of acetone was performed using the 45 wt % MnO_2 + 30 wt % Fe_2O_3 + 25 wt % CuO catalyst in the amount of 0.5 g with the

Table 1. The Arrhenius equation coefficients. The catalytic combustion of admixtures in air

Admixture	A $m_n^3/kg_k \cdot s$	E kJ/mol	R^2
toluene	$1.47 \cdot 10^6$	73.66	0.989
acetone	$5.58 \cdot 10^{13}$	174.18	0.959
n-butyl acetate	$8.15 \cdot 10^9$	100.47	0.970
m-xylene	$5.34 \cdot 10^2$	48.49	0.987
p-xylene	$2.14 \cdot 10^8$	91.79	0.988

dimensions of the catalyst grain equal to 0.102–0.12 mm. The gas loading amounted to $40 \text{ dm}_n^3/g_k \cdot h$, and the initial concentration of acetone was equal to 23.3 g/m^3 . A high concentration of acetone was used in order to make the discussed effect visible.

The relationship between the conversion degree and temperature, during heating the reactor was first-order determined over the entire range and then during cooling the reactor until quenching. The results are presented in Fig 4.

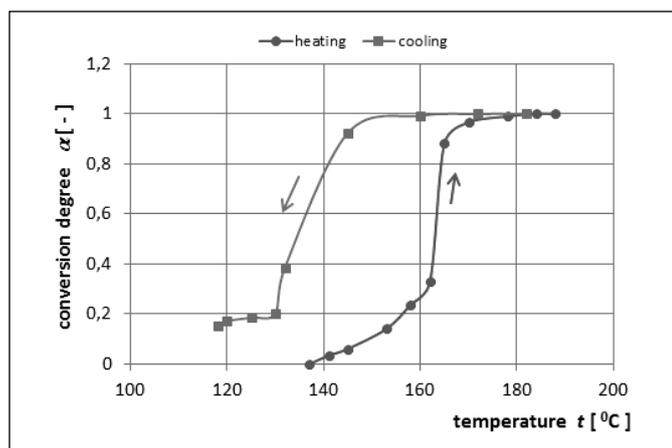


Fig. 4. The relationship between the conversion degree of acetone and temperature, 1 – heating of reactor, 2 – cooling of reactor

The curve 2 is shifted to a range of lower temperature, while the high degree of acetone conversion was maintained. In such case the reactor can be operated in a stable manner when the temperature is varied over a relatively wide range.

In the case of highly exothermic processes, the temperature of the catalyst grain is significantly higher than the temperature of gas flowing through the catalyst bed. During heating of the reactor, the gas temperature and the grain temperature are initially the same. After starting the combustion process of admixture, the temperature of the catalyst grain is rapidly increased.

The temperature reaches a maximum value at the complete conversion of admixture. When we start to cool down the reactor from this moment, then the temperature of the flowing gas will quickly decline, and the temperature of the catalyst grain will still be high until the moment when at temperature t^* , the amount of heat removal from the catalyst grain will be higher than the amount of heat released during

the combustion of admixture. It should be noticed that during cooling the reactor down to a temperature slightly higher than t^* , the reactor returns to a high temperature regime, whereas during cooling the reactor down to a temperature lower than t^* , quenching of the reactor takes place and it must be heated again. This issue should be considered in details a category of the multiple stationary states (Szarawara et al. 1980).

The effect of combustible admixtures on the conversion of hardly combustible admixtures

In this case the measurements were also carried out using the experimental set-up shown in Fig. 1. The 45 wt % MnO_2 + 30 wt % Fe_2O_3 + 25 wt % CuO catalyst with the dimensions of grain within 0.102–0.12 mm was used in the amount of 0.5 g. The catalyst loading with gas amount to $40 \text{ dm}_n^3/g_k \cdot h$. The combustion of pure acetone and pure toluene (initial concentration 5.826 g/m^3) and the mixture containing 5.739 g/m^3 of acetone and 6.239 g/m^3 of toluene was performed. The results are presented in Fig. 5. The curve 1 relates to the combustion of pure acetone, the curve 2 – combustion of acetone in the mixture, the curve 3 – combustion of toluene in the mixture and the curve 4 – combustion of pure toluene.

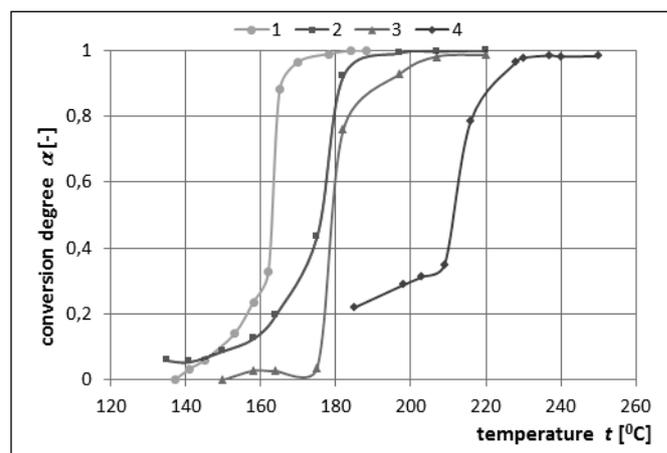


Fig. 5. The relationship between the conversion degrees and temperature. The combustion of admixtures over 45 wt % MnO_2 + 30 wt % Fe_2O_3 + 25 wt % CuO catalyst. 1 – combustion of pure acetone, 2 – combustion of acetone in the mixture, 3 – combustion of toluene in the mixture, 4 – combustion of pure toluene

It can be seen that acetone in the mixture undergoes the combustion at a slightly higher temperature than that of pure acetone, whereas toluene in the mixture undergoes the

combustion at a significantly lower temperature than that of pure toluene. The obtained result is in accordance with the theoretical description of such case presented in this work.

Conclusions

The kinetic combustion of organic admixtures of air over the porous catalysts belongs to the basic technologies of gases purification. This work concerns a macrokinetics of these processes. The theoretical approach was presented, which is in agreement with standard description of macrokinetics of the catalytic processes over the porous grains of the catalysts. This approach describes a relationship between the fundamental magnitudes: observed process rate r^* , reaction rate r in the kinetic zone and the surface utilization coefficient η in the form $r^* = r \cdot \eta$. These magnitudes are combined by the Thiele module ϕ .

A kinetic equation for the isothermal and non-isothermal conditions was given. The observed process rate r^* was determined as the average magnitude, after taking into account the distribution of the admixture concentration and the temperature distribution in the catalyst grain. By using the differential equations of the mass and heat balance, the influence of the mass and heat transfer on the process rate in a spherical grain of the catalyst was considered. This influence was described by means of a coefficient of the surface utilization η . In the case of isothermal conditions this coefficient is dependent on the grain geometry, effective diffusion coefficient of admixture in the catalyst grain and the form of kinetic equation. In the case of grain with spherical geometry and the first-order reaction, the equation describing η has the form

$$\eta_{K,1} = \frac{3}{\phi_{K,1}} \left[\frac{1}{\tanh \phi_{K,1}} - \frac{1}{\phi_{K,1}} \right]$$

where: $\phi_{K,1} = R_0 \sqrt{\frac{k_v}{D_{ef}}}$ – the Thiele module

In the case of non-isothermal process, η also depends on the effective coefficients of thermal conduction in the catalyst grain and on the concentration and enthalpy of admixture combustion. In the case of the first-order reaction, this coefficient is described according to:

$$\eta_{K,1} = \frac{\sqrt{2}}{\phi_{K,1}} \frac{e^{\frac{\gamma_i \beta_i}{2}}}{\gamma_i \beta_i} \left[1 - e^{-\gamma_i \beta_i} (1 + \gamma_i \beta_i) \right]^{\frac{1}{2}}$$

where: $\gamma_i = \frac{E_i}{RT_0^2}$, $\beta_i = \frac{(-\Delta H)_i D_i}{\lambda} c_{0i}$.

The methods of η calculations with the application of these equations have been presented.

Nowadays, the demonstration of validity of the theory in a standard approach is not necessary. The nature relies on its application. In the case of traditional catalytic processes, the application of theory relies on a quantitative description of the process. Combustion of admixtures should be treated differently. During the installation operation, a qualitative and quantitative composition of purified gases is usually varied. The quantitative description of such processes is rather impossible. In the case of important meaning it has the application of theory to a qualitative analysis of the course of process. The results of such analysis have been presented. A fulfillment of the first-order kinetic equation for used catalysts means that the degree of admixtures conversion does not depend on their initial concentration. A non-isothermicity of the catalyst grain is expressed in such a way that observed process rate over the large porous grains of the catalysts can be higher than that in the kinetic zone. A temperature difference between the catalyst grains and flowing gas causes that the reactor may be operated stably at varied concentrations of admixtures and temperature over relatively wide ranges. The influence of the flammable admixture on the conversion of hardly combustible admixtures was also considered. It was established that the presence of flammable admixtures in the gases can advantageously influence the conversion of hardly combustible admixtures.

Abbreviations

A	– pre-exponential coefficient in the Arrhenius equation	
c_{0i}	– admixture concentration in the gas stream or at the inlet of the reactor	mole/m ³ , g/m ³
c_i	– local concentration of admixture	mole/m ³ , g/m ³
\hat{c}_i	– local concentration of component on the internal surface of the catalyst grain	mole/m ³ , g/m ³
D_i	– effective coefficient of diffusion	m ² /h, m ² /s
E_i	– activation energy	kJ/mole
\dot{F}_{0v}	– initial volume flow rate of gas through the reactor	Nm ³ /h, Nm ³ /s
F_v	– volume flow rate of gas through the reactor	Nm ³ /h, Nm ³ /s
$\varphi(c_i)$	– kinetic model of reaction	
$(-\Delta H)_i$	– enthalpy reaction for mole of reagent i	kJ/mole
k_v	– rate constant of the reactor related to the constant of the catalyst grain	1/s
k	– rate constant of the reaction related to the unit mass of the catalyst grain	Nm ³ /kg
$k(T)$	– reaction rate constant	
$k_i(T_0)$	– reaction rate constant related to the temperature of flowing gas	
m	– mass of the catalyst during measurements	kg, g
$r_i(c_i)$	– reaction rate in the catalyst grain	mole/m ³ ·s
$r_i^*(c_i)$	– observed process rate related to the unit volume of the catalyst grain	mole/m ³ ·s
$\hat{r}^*(c_i)$	– the process rate related to the surface area of the catalyst,	mole/m ² ·s
$r_i(c_i)$	– reaction rate in the kinetic region	mole/m ³ ·s

R_0	– gas constant	kJ/mole·K
R	– radius of the catalyst grain	m, cm
S_K	– the specific surface area of catalyst	m ² /g
t	– temperature	°C
T	– temperature	K
T_0	– temperature of gas stream	K
T_S	– temperature of the external surface of the catalyst grain	K
V_p	– volume of the catalyst grain	m ³ , cm ³
τ	– time	h, s
α_i	– conversion degree of admixtures	
β_i	– the Prater number	
∇	– the Laplace operator	
$\gamma_i = \frac{E_i}{RT_0^2}$	– parameter	
η	– coefficient of the utilization of catalyst surface	
$\eta_{K,n}$	– coefficient of utilization of the catalyst surface for grain with spherical symmetry and n-th order reaction	
$\eta_{K,1}$	– coefficient of utilization of the catalyst surface for grain with spherical symmetry and first order reaction	
λ	– effective coefficient of thermal conductivity	
$\phi_{K,n}$	– the Thiele's modular for the spherical symmetry of the catalyst grain and the n-th order reaction	
$\phi_{K,1}$	– the Thiele's modular for the spherical symmetry of the catalyst grain and the first-order reaction	
ρ_K	– specific density of the catalyst grain	g/cm ³
$\zeta = \varphi_{K,n} \zeta$	– dimensionless coordinate concerning a radius of the catalyst grain	
$\psi_i = \frac{c_i}{c_{oi}}$	– dimensionless concentration	
$\zeta = \frac{3(R_0 - R)}{R_0}$	– dimensionless coordinate concerning a radius of the catalyst grain	

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Aspekty kinetyczne procesów katalitycznego spalania domieszek powietrza

Katalityczne spalanie domieszek organicznych powietrza należy do podstawowych technologii oczyszczania gazów. Opisano makrokinetykę spalania domieszek na katalizatorach porowatych. Ujęcie teoretyczne jest zgodne ze standardowym opisem makrokinetyki procesów katalitycznych. Opisano relacje pomiędzy podstawowymi wielkościami: obserwowaną szybkością procesu r^* , szybkością reakcji w obszarze kinetycznym r i współczynnikiem wykorzystania powierzchni η , w formie $r^* = r \cdot \eta$. Łączy je moduł Thielego ϕ . Podano równanie kinetyczne dla warunków izotermicznych i warunków nieizotermicznych. Wpływ transportu masy i transportu ciepła w ziarnie katalizatora na przebieg procesu opisano za pomocą współczynnika wykorzystania powierzchni η . Podano równanie opisujące ten współczynnik dla warunków izotermicznych i nieizotermicznych.

Druga część pracy dotyczy zastosowania teorii. Przy ciągłej zmianie składu oczyszczanego gazu ujęcie ilościowe nie bardzo jest możliwe. Teorię zastosowano do jakościowej analizy procesu na podstawie wyników doświadczalnych. Spełnienie kinetyki I-rzędu oznacza, że stopień przemiany domieszek nie zależy od ich stężenia początkowego. Nieizotermiczność ziarna katalizatora przejawia się w ten sposób, że obserwowana szybkość procesu na dużych ziarnach porowatych katalizatorów może być wyższa niż szybkość reakcji w obszarze kinetycznym. Różnica temperatury pomiędzy ziarnami katalizatora i przepływającym gazem powoduje, że reaktor może pracować stabilnie przy zmiennych stężeniach domieszek i temperatury w dosyć szerokich zakresach. Wykazano też, że domieszki spalające się łatwo mogą korzystnie wpływać na przemianę domieszek spalających się trudno.