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# EFFECT OF ENERGY RELEASE
# AND DETAILED SURFACE MECHANISMS ON
# MULTICOMPONENT CATALYTIC COMBUSTION

The effect of combustion energy release and detailed surface mechanisms on multicomponent catalytic combustion process intensification is presented. It was found that in a recuperative converter the combustion of species of decreased reactivity ($CH_4$) resulted in an increased heat recirculation and a higher temperature and consequently in higher $CH_4$ conversion compared to more reactive $C_3H_8$. Further it was also found that catalytic combustion could be enhanced by the addition of other flammable gases even under isothermal conditions. The effect of $H_2$ addition on combustibles conversion was more pronounced than that after CO addition because of the higher $H_2$ adsorption rate that resulted in the consumption of $O_2$ near and on the surface and consequently in an increased free sites availability for adsorption of other reactants.

## NOMENCLATURE

$A$ – the pre-exponential factor, (mol, m, s),
$C$ – the concentration of gaseous phase species, (mol m$^{-3}$, ppmv, %v),
$Cs$ – the concentration of surface species, (mol m$^{-2}$),
$D$ – the bulk molecular diffusivity in the gaseous phase, (m$^2$ s$^{-1}$),
$d_h$ – the hydraulic diameter in the catalytic zone, (m),
$E$ – the activation energy, (J mol$^{-1}$),
$k$ – the reaction rate coefficient, units vary,
$L_C$ – the catalytic layer thickness, (m),
$L_{CONV}$, $L_{NC}$, $L_{RCC}$ – the length of the catalytic zone, non-catalytic zone, recuperative zone, (m),
$M$ – the molecular mass of species, (kg mol$^{-1}$)
$mf$ – the mass flow rate, (kg s$^{-1}$),
$R$ – the combustion reaction rate, (mol m$^{-2}$ s$^{-1}$),

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$R_g$    – the universal gas constant, (J mol$^{-1}$ K$^{-1}$),
$T$      – the temperature, K,
$x$      – the radial distance within a diffusion layer of the thickness $\delta$, (m) or (-).

## GREEK SYMBOLS

$\Gamma$    – the surface site density, (mol m$^{-2}$),
$\gamma$    – the adsorption sticking coefficient, (-)
$\Delta T_{ad}^{comb}$ – the adiabatic temperature rise in complete combustion, (K),
$\eta,\ \eta^{\Sigma}$ – the conversion and global conversion, respectively, (-),
$\theta$    – the surface species coverage, (-),
$v$         – the stoichiometric coefficient, (-),
$\psi$      – the relative mole content in the mixture of methane and propane, (-).

## SUBSCRIPTS AND SUPERSCRIPTS

ads, pure surf, des – the adsorption, pure surface, desorption reaction, respectively,
free   – the free, uncovered sites,
$i$      – the gaseous phase species,
$j, k$   – the surfaces of the species,
$m, n$   – the reaction order of a component in a reaction,
$r$      – the reaction.

# 1. INTRODUCTION

Multicomponent catalytic combustion of diluted flammable gases is an attractive process of the effective removal of volatile organic compounds (VOCs) [1]. Such multicomponent mixtures often consists of species that exhibit different reactivities. A decreased reactivity of flammable gases in catalytic incineration processes is linked with reaction chemistry, i.e. high-energy barrier required for breaking bonds (methane), the limited rate of gas surface adsorption and low sticking coefficients, the limited desorption rate of combustion products or the presence of other surface species that occupy active sites (inhibitors). The combustion of multicomponent mixtures is often characterised by interactions between reactants. Those interactions can be described at least in two ways, i.e. as linked either with combustion energy release or with surface mechanisms. The combustion energy released by one reactant can lead to an increase in reactor temperature and hence the reaction rates of other reactants can be increased. The effect of energy release depends on the geometry of the reactor used. Surface processes may also affect the multicomponent catalytic combustion of gases. As the number of surface active sites is limited and some reactants or products are in a large excess or exhibit different physical properties, it is very likely that the reaction rate of one reactant will affect the reaction rate of other reactants. This paper is aimed at revealing, explaining, discussing and mathematically describing two phenomena that accompany the multicomponent catalytic combustion, i.e. the effect of energy release and detailed surface mechanisms.

## 2. EXPERIMENTAL METHODS

### 2.1. ENERGY RELEASE

The energy released at the catalytic surface is a product of the heat of combustion reaction and catalytic reaction rate described by intrinsic kinetics, i.e. all transport-related phenomena should be excluded from a kinetic equation. We use intrinsic catalytic oxidation rates of propane and methane over PdO catalyst at the atmospheric pressure when oxygen is in large excess [2]–[4]. The methane catalytic oxidation is characterised by a much higher activation energy compared to the oxidation of propane which is attributed to a high energy barrier required for breaking C–H bonds in a methane molecule, thus higher temperature needs to be applied in its combustion. In the present case study, it is assumed that a model mixture contains two flammable components, i.e. propane and methane and air which is in a large excess. The process is carried out in an adiabatic, cylindrical single-channelled catalytic converter and in a recuperative combustor. The description and detailed 2D model of the latter can be found in [3].

### 2.2. DETAILED SURFACE MECHANISMS

In order to examine the effect of detailed surface mechanisms on catalytic combustion of multicomponent mixtures, a simple isothermal analysis is performed. For this purpose a new mathematical 1D model is utilised which takes into account species balance both in the gaseous phase and on the catalyst surface. A multicomponent mixture examined here contains $CH_4$, $C_3H_8$, $CO$, $H_2$, $O_2$, and $Ar$. It is assumed that a reduced system contains 8 gaseous species, 6 surface species and 21 surface reactions (table) [5].

The reactions orders of $R_1$, $R_2$, $R_3$ and $R_6$ with respect to $Pt(s)$ are 2.3, 2.5, 1 and 2, respectively. The reaction orders of $R_6$ and $R_{16}$ with respect to $O(s)$ are 0 and 1, respectively. Reactions 4 and 5 are the same. $R_6$ is an adsorption reaction that concerns $CO$ and pure surface reaction that concerns $O(s)$ and $CO_2(s)$, but its rate in all cases is calculated as for the adsorption reactions. The rates of reactions $R_{11}$, $R_{13}$, $R_{15}$ are calculated using the forward rate coefficients and surface thermochemical data [6]. $\Gamma$ equals $2.7 \cdot 10^{-5}$ m$^2 \cdot$mol$^{-1}$.

The adsorption (calculated based on the kinetic theory of gases), pure surface and desorption reaction rate constants are as follows:

$$k_r^{\text{ads}} = \gamma_i \sqrt{\frac{R_g T}{2\pi M_i}}, \quad k_r^{\text{puresurf}} = k_r^{\text{des}} = \Gamma^{1-m} A_r \exp\left(\frac{-E_r}{R_g T}\right). \tag{1}$$

Table

Reduced heterogeneous scheme of $CH_4$, $C_3H_8$, CO, $H_2$, $O_2$ and Ar catalytic combustion

| Number | Reaction | $A$ (m, mol, s) or $\gamma$ (–) | $E$ (J mol$^{-1}$) |
|---|---|---|---|
| | Adsorption reactions | | |
| 1 | $CH_4 + 5Pt(s) \rightarrow C(s) + 4H(s)$ | 0.01 | 0 |
| 2 | $C_3H_8 + 11Pt(s) \rightarrow 3C(s) + 8H(s)$ | 0.06 | 0 |
| 3 | $H_2 + 2Pt(s) \rightarrow 2H(s)$ | 0.046 | 0 |
| 4 | $O_2 + 2Pt(s) \rightarrow 2O(s)$ | 0.023 | 0 |
| 5 | $O_2 + 2Pt(s) \rightarrow 2O(s)$ | $4.9 \cdot 10^6$ | 0 |
| 6 | $CO + O(s) + Pt(s) \rightarrow CO2(s) + Pt(s)$ | 0.84 | 0 |
| 7 | $CO_2 + Pt(s) \rightarrow CO_2(s)$ | $10^{-5}$ | 0 |
| 8 | $H_2O + Pt(s) \rightarrow H_2O(s)$ | 0.75 | 0 |
| 9 | $OH + Pt(s) \rightarrow OH(s)$ | 1 | 0 |
| | Pure surface reactions | | |
| 10 | $H(s) + O(s) \rightarrow OH(s) + Pt(s)$ | $10^{13}$ | 11 500 |
| 11 | $OH(s) + Pt(s) \rightarrow H(s) + O(s)$ | reverse reaction of R10 | |
| 12 | $H(s) + OH(s) \rightarrow H_2O(s) + Pt(s)$ | $10^{13}$ | 17 400 |
| 13 | $H_2O(s) + Pt(s) \rightarrow H(s) + OH(s)$ | reverse reaction of R12 | |
| 14 | $2OH(s) \rightarrow H_2O(s) + O(s)$ | $10^{13}$ | 48 200 |
| 15 | $H_2O(s) + O(s) \rightarrow 2OH(s)$ | reverse reaction of R14 | |
| 16 | $C(s) + 2O(s) \rightarrow CO_2(s) + 2Pt(s)$ | $10^{13}$ | 62 800 |
| | Desorption reactions | | |
| 17 | $2H(s) \rightarrow H_2 + 2Pt(s)$ | $10^{13}$ | 67 400–6 000 $\theta_H$ |
| 18 | $2O(s) \rightarrow O_2 + 2Pt(s)$ | $10^{13}$ | 213 200–60 000$\theta_O$ |
| 19 | $CO_2(s) \rightarrow CO2 + Pt(s)$ | $10^{13}$ | 125 500 |
| 20 | $H_2O(s) \rightarrow H_2O + Pt(s)$ | $10^{13}$ | 40 300 |
| 21 | $OH(s) \rightarrow OH + Pt(s)$ | $10^{13}$ | 192 800 |

To each reaction of table 1 the appropriate reaction rate formula is ascribed:

$$R_r^{\text{ads}} = k_r^{\text{ads}} C_i \theta_{\text{free}}^m , \quad R_r^{\text{puresurf}} = -k_r^{\text{pure surf}} Cs_j^m Cs_k^n , \quad R_r^{\text{des}} = -k_r^{\text{des}} Cs_j^m . \quad (2)$$

As this paper is aimed at examining only the surface phenomena in the multicomponent combustion, a full 3D or 2D reactor model can be reduced to a simple 1D process model (figure 1). The model consists of:

• The balance of gaseous phase species

$$\nabla(-D_i \nabla C_i) = 0 . \quad (3)$$

• Boundary conditions

$$x = 0, \quad C_i = C_i^{\text{bulk}} , \quad x = \delta \ - D_i \nabla C_i = -(v_{ir} R_r^{\text{ads}} + v_{ir} R_r^{\text{des}}) . \quad (4a)$$

• The balance of surface species

$$v_{jr} R_r^{\text{ads}} + v_{jr} R_r^{\text{puresurf}} + v_{jr} R_r^{\text{des}} = 0 . \quad (4b)$$

$C_i^{bulk}$

$C_i(x)$

$C_i(\delta)$

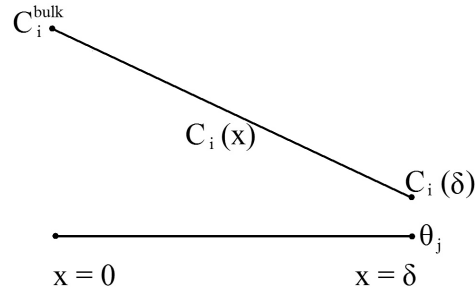$\theta_j$

x = 0          x = δ

Fig. 1. Scheme of 1D model of catalytic combustion for the analysis of detailed surface mechanisms

1D models can predict only a radial distribution of gaseous phase species and surface species coverages of active sites. 2D model can additionally predict an axial distribution of gaseous phase species, whereas 3D model enables also determination of angular distribution. However, based on such models less reactions can be analysed with computational effort comparable to that of a simpler 1D model. Whereas appropriate gaseous phase reactions can easily be included into consideration by means of a reaction term on the right-hand side of equation (3).

## 3. RESULTS AND DISCUSSION

### 3.1. ENERGY RELEASE

The ignition curves in figure 2a enable a comparison of the catalytic combustion of propane and methane. The adiabatic cylindrical single-channelled converter used closely approximates monolithic-type converters. Two extreme mixture compositions are utilised. From figure 2a it is seen that the temperatures of propane combustion are lower than those of methane. Its ignition curves overlap each other, thus the propane combustion is almost independent of a relative mixture composition. Only the upper part of the curve representing the propane combustion in figure 2a is slightly improved if the mixture is richer in propane. This is attributed to the fact that in the converter examined, the complete combustion of propane proceeds at temperatures at which methane conversion only starts. At low propane conversion the combustion heat effect is small, thus the propane conversion is independent of the propane content. On the other hand, at the higher propane conversion the combustion heat effect is quite considerable ($\Delta T_{ad}^{comb} = 10.3$ K), therefore the propane conversion is slightly higher when the mixture is richer in propane. In turn methane oxidises slightly better when its content is lower as it benefits from the propane combustion heat effect. The main cause of the differences in the curves representing methane and propane com-

bustion is the activation energy of reaction which is higher for the methane oxidation. Hence for similar conversion of methane, as compared to propane, higher reactor temperature is required. In figure 2a, it approaches 60 K. The effect of the relative mixture content $\psi$ on the ignition curves is reduced for extremely low calorific values, when the combustion heat effect does not affect the combustor temperature, i.e. when the temperature distribution in the combustor is independent of $\Delta T_{ad}^{comb}$ and $\psi$.
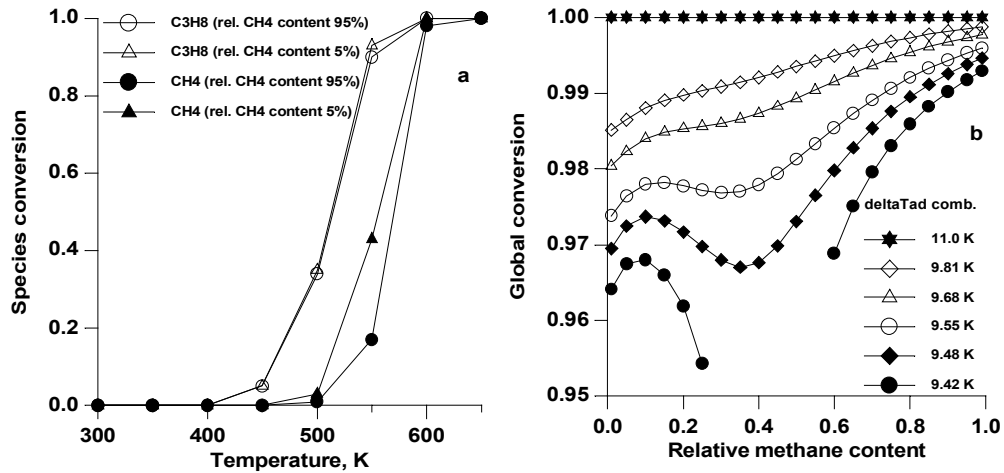


Fig. 2. Ignition curves of propane and methane in two multicomponent mixtures
of high and low methane content and constant calorific value of propane–methane–air mixture supplied.
The adiabatic cylindrical single-channelled catalytic combustor. Parameters: $\psi_{CH_4}$ = 0.05 and 0.95,
$\Delta T_{ad}^{comb}$ = 10.3 K, $L_{CONV}$ = 1.0 m, $d_h$ = 2.0 mm, $L_C$ = 30 μm, $mf_{in}$ = 2.0·10$^{-6}$ kg s$^{-1}$(a).
Dependence of global conversion of methane and propane $\eta^{\Sigma}$ on relative composition of purified
gas $\psi_{CH_4}$ at different fuel calorific values. The recuperative catalytic combustor.
Parameters: $\Delta T_{ad}^{comb}$ = 11.0, 9.81, 9.68, 9.55, 9.48, 9.42 K, $L_{CONV}$ = 0.5 m, $d_h$ = 1.28 mm,
$L_C$ = 30 μm, $L_{NC}$ = 0.4 m, $L_{RCC}$ = 0.5 m, $mf_{in}$ = 2.0·10$^{-6}$ kg s$^{-1}$, $T_{in}$ = 300 K (b)

It can be inferred that a complete methane conversion requires higher temperatures of a purified gas or the supply of an auxiliary heat or auxiliary fuel to the converter. To avoid those expensive procedures it is proposed to recirculate combustion energy in the recuperative combustor [3] in order to increase the temperature in its catalytic zone, i.e. to produce a superadiabatic effect. Under the superadiabatic conditions, it is most convenient to supply cold purified gases of certain minimal calorific value of combustibles since then there exists a large difference in the temperatures of exhaust gas and feed, i.e. a considerable driving force appears which intensifies the heat transfer. The combustion of the methane–propane–air mixture in the recuperative converter differs from the combustion of such a mixture in the monolithic converter. As it is seen in figure 2b, the complete conversion of com-

bustibles occurs at above $\Delta T_{ad}^{comb} > \approx 11$ K. At $\Delta T_{ad}^{comb} < \approx 11$ K the highest conversion occurs for the mixtures that contain higher concentration of low-reactive methane. This advantageous phenomenon results from the fact that less reactive mixtures react farther in the catalytic zone and hence the recirculation of combustion heat is more effective, leading to higher temperatures. This mixture displays an inverse behaviour compared to that in the monolithic converter in which the methane conversion is always lower than propane conversion (see figure 2a). Another interesting feature of recuperative oxidation of the mixture examined is the characteristic minimum at $\psi_{CH_4} \approx 0.35$. This minimum on the global conversion curve has smaller value when $\Delta T_{ad}^{comb}$ becomes lower, finally leading to the extinction for mixtures whose composition corresponds to this minimum. This complex phenomenon can be ascribed to two competitive phenomena. When $\psi_{CH_4} \to 0$ (propane in excess) the mixture is very reactive, hence reaction heat is released at the inlet of the catalytic zone. When $\psi_{CH_4} \to 1$ (methane in excess) the mixture is less reactive, hence reaction heat is released farther in the catalytic zone, leading to the intensified recirculation of the combustion energy and the higher autothermal temperature. As a result both the reaction rates and the species conversions are much increased.

### 3.2. DETAILED SURFACE MECHANISMS

According to the kinetic theory of gases the frequency of collisions of gaseous molecules with a surface is slightly higher for the species with a lower molecular weight (equation (1)). Thus the highest frequency of the molecular collisions with the surface is ascribed to $H_2$, and the lowest – to $C_3H_8$. The probability of a successful collision of gaseous molecules with active sites depends on the molecule and catalyst type and is characterised by a sticking coefficient. Its very low value on Pt–$Al_2O_3$ is characteristic of $CO_2$ ($10^{-5}$) and $CH_4$ ($10^{-2}$). Adsorption reactions take place at extremely low activation energies, surface reactions occur at low or medium activation energy, whereas desorption reactions – at very high energies. O(s), OH(s) and $CO_2$(s) are very actively desorbed, which leads to the relatively large component coverages of active sites of those surface species, especially at low temperatures. As the adsorption rate depends on $T^{0.5}$, whereas the desorption rate is an exponential function of $T$, at higher temperatures the desorption of oxygen and other species dominates and hence the availability of free sites increases. Under such conditions, the incorporation of surface site balance into the process model is less pronounced. However, as oxygen is in a large excess, its surface coverage is large even at relatively high temperatures. It is found that the oxygen coverage is so high here that it limits combustion of diluted VOC gases, i.e. the process proceeds faster when oxygen is partly replaced by argonium. The model may also predict the site coverages of species that are not combusted, e.g. chlorine, which is known for its role in the catalyst deactivation process.

To investigate the effect of the detailed surface mechanisms on the multicomponent catalytic combustion, the effect of hydrogen and carbon monoxide addition is analysed. The dependence of conversion of combustibles and the free sites coverage on the bulk hydrogen content and on the bulk carbon monoxide content is presented in figure 3a and figure 3b, respectively.
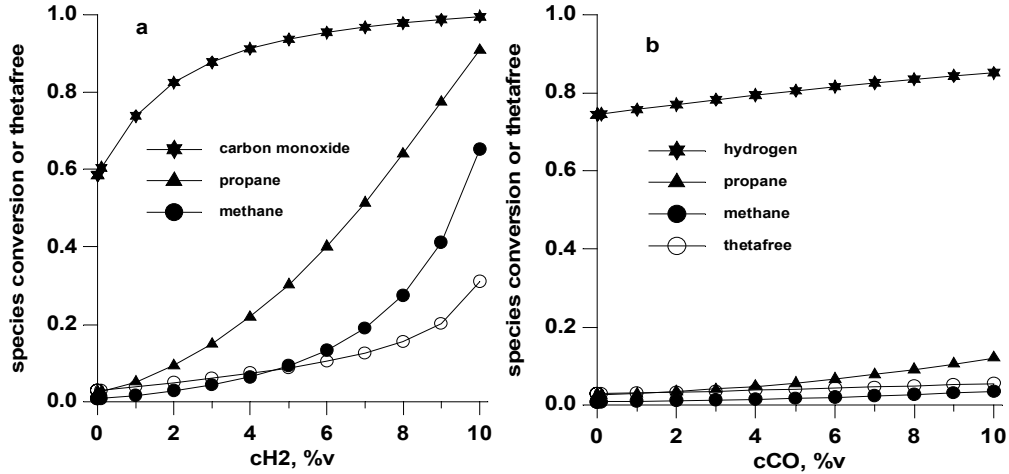


Fig. 3. The effect of hydrogen (a) and CO (b) addition on the species conversion and the free sites coverage. Parameters: 1D model, $T = 800$ K, bulk gas composition $C_{CH_4} = 1\ 000$ ppmv, $C_{C_3H_8} = 1\ 000$ ppmv, $C_{O_2} = 20\%$v; a) $C_{CO} = 1\ 000$ ppmv, $C_{H_2} = 0$–$10\%$v; b) $C_{CO} = 0$–$10\%$v, $C_{H_2} = 1\ 000$ ppmv; Ar balance

From figure 3a it is seen that the hydrogen added affects the conversion of all combustibles. However, the effect is pronounced when the hydrogen bulk content is approximately higher than 1%v. The enhanced species conversion is attributed to the surface consumption of oxygen by highly concentrated hydrogen gas, since oxygen concentration near the surface drops considerably. As a result, at above 1%v bulk $cH_2$, the free sites coverage starts to increase and the rates of adsorption reactions of methane, propane and CO substantially increase. Thus hydrogen must be added in large quantities to rise significantly the consumption of oxygen on the surface. As a result, the resistance to the oxygen transport develops, its concentration drops near the surface and finally the availability of free sites increases. In figure 3b, it is clearly seen that the effect of adding the same amount of CO on the species conversion is less pronounced than in the case of $H_2$ addition, though the stoichiometry of the reaction with oxygen is the same. This is attributed to the lower $D_{CO}$, higher $M_{CO}$ and higher $m_{CO}$, with respect to $\theta_{free}$, of CO compared to $H_2$ which are not compensated for higher $\gamma_{CO}$. Hence the adsorption rate of CO on the surface and consequently the oxygen consumption are lower. Thus the oxygen concentration drop near the surface is less pronounced and hence (see figure 3b) $\theta_{free}$

is not high enough to enhance the adsorption reactions of other combustibles. Finally, it is found that as oxygen occupies active sites, it inhibits the adsorption of the combustibles and the combustion is favoured when the bulk concentration of oxygen is decreased to the nearly stoichiometric composition. The surface reactions from the table are relatively simple as most of them are independent of the others. It is expected that the approach proposed here can be utilised when the efficiencies of complicated reactions [1] or catalyst modifications [7] are to be predicted.

## 4. CONCLUSIONS

The catalytic combustion of species in the multicomponent mixtures is affected by at least two phenomena, i.e. the combustion energy release and detailed surface mechanisms. In the recuperative converter, the combustion of species with the decreased reactivity (methane) resulted in the increased heat recirculation and higher temperature and consequently in the higher conversion of methane compared with that of more reactive propane. The 1D model presented enabled the efficient analysis of the effect of the detailed surface mechanisms on the process intensification. It was found that the catalytic combustion could be enhanced by the addition of the other flammable gases, even under the isothermal conditions, as oxygen being in excess inhibited reactions. The effect of the hydrogen addition on the conversion of combustible species was more pronounced than that produced by the carbon monoxide addition as a result of the higher rate of hydrogen adsorption that resulted in the consumption of oxygen near and on the surface and consequently in the increased free sites' availability for adsorption of the other reactants.

LITERATURE

[1] MUSIALIK-PIOTROWSKA A., *Destruction of trichloroethylene (TCE) and trichloromethane (TCM) in the presence of selected VOCs over Pt-Pd-based catalyst*, Catalysis Today, 2007, 119, 301–304.
[2] HAYES R.E., KOLACZKOWSKI S.T., *Introduction to catalytic combustion*, Gordon and Breach Science Publishers, Amsterdam, 1997.
[3] BUDZIANOWSKI W.M., MILLER R., *Auto-thermal combustion of lean gaseous fuels utilizing a recuperative annular double-layer catalytic converter*, Can. J. Chem. Eng., 2008, 86, 4.
[4] BUDZIANOWSKI W.M., MILLER R., *Intensyfikacja procesu dopalania gazów o niskiej reaktywności*, [in:] *Aktualne problemy w ochronie powietrza atmosferycznego*, edited by A. Musialik-Piotrowska, J.D. Rutkowski, PZITS Sekcja Główna Inżynierii Ochrony Atmosfery, Wrocław, 2008.
[5] REINKE M., MANTZARAS J., SCHAEREN R., BOMBACH R., INAUEN A., SCHENKER S., *High-pressure catalytic combustion of methane over platinum: in situ experiments and detailed numerical predictions*, Combust. Flame, 2004, 136, 217–240.
[6] WARNATZ J., ALLENDORF M.D., KEE R.J., COLTRIN M.E., *A model of elementary chemistry and fluid mechanics in the combustion of hydrogen on platinum surfaces*, Combust. Flame, 1994, 96, 393–406.

[7] KUCHARCZYK B., TYLUS W., *Partial substitution of lanthanum with silver in the LaMnO₃ perovskite: effect of the modification on the activity of monolithic catalysts in the reactions of methane and carbon oxide oxidation*, Applied Catalysis A: General, 2008, 335, 28–36.

WIELOSKŁADNIKOWE SPALANIE KATALITYCZNE: WPŁYW UWALNIANIA ENERGII
I SZCZEGÓŁOWYCH MECHANIZMÓW POWIERZCHNIOWYCH

Pokazano, jak uwalnianie energii spalania i szczegółowe mechanizmy powierzchniowe wpływają na intensyfikację procesu katalitycznego spalania mieszanin wieloskładnikowych. Stwierdzono, że w konwertorze rekuperacyjnym [3] spalanie składników o obniżonej reaktywności ($CH_4$) skutkowało zwiększoną recyrkulacją ciepła i podwyższoną temperaturą, a w efekcie wyższą konwersją $CH_4$ w porównaniu z konwersją bardziej reaktywnego $C_3H_8$. Stwierdzono również, że katalityczne spalanie można zintensyfikować, dodając do mieszanki, nawet w warunkach izotermicznych, inne gazy palne. Dodany $H_2$ bardziej wpływał na konwersję składników niż dodany CO, gdyż większa szybkość adsorpcji $H_2$ powodowała zużycie $O_2$ nad powierzchnią i na niej, a w konsekwencji zwiększoną dostępność wolnych centrów aktywnych dla adsorpcji pozostałych reagentów.