Analysis of species diffusion and methanol decomposition source in thermocatalytic reactor based on the intermetallic phase of Ni₃Al for low Reynolds numbers

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Abstract. In this paper, the numerical modelling of hydrogen production by methanol decomposition in the thermocatalytic reactor based on the intermetallic phase of Ni₃Al has been presented. The experimental results of flowing mixtures containing helium and methanol in a thermocatalytic reactor incorporating microchannels were used for the preliminary calibration of the Computational Fluid Dynamics “CFD” calculations. The thermocatalytic decomposition reaction of methanol has been modelled by employing experimental data related to the active surface area. It should be understood that a decrease of methanol concentration at inlet into package, mainly, ten millimetres before the thermocatalytic area, is connected with the diffusion fluxes of the other components, mainly hydrogen and carbon monoxide. The commercial CFD code has been expanded by User Defined Functions “UDFs” to include surface chemical reaction rates on the interphase between fluid and solid. The data extrapolated via the implemented numerical model have made it possible to assess the minimal length of the micro-reactor channels which predicts an optimal dimension at the system outlet. Results obtained through numerical calculations were calibrated and compared with experimental data to receive satisfactory agreement.

1. Introduction

Ni-based catalysts exhibit extremely high catalytic activity in methanol decomposition and other gasses synthesis and promote the production of carbon nanostructures (mainly carbon nanotubes) [1,2]. One of the Ni-based, solid-state catalysts is the Ni₃Al intermetallic phase and its alloys [3], which belongs to a sort of multunctional materials, combining properties of both the structural and functional materials. According to the literature, Ni₃Al intermetallic thin foils exhibit extremely high catalytic properties in hydrocarbon decomposition reactions [4]. On the other hand, also based on the literature, the relatively high temperature of maximal hydrocarbon conversion is the main disadvantage of this material [1,5]. Nevertheless, the high temperature of the process can be utilized by placing a regenerative heat exchanger downstream of the reactor [3]. Therefore, the thermocatalytic reactor with thin strips or thin foils based on the Ni₃Al intermetallic phase produced according to technology presented by Jóźwik et al. in works [1,3] appears as an innovative and extremely promising technology in the making. One
example of an alloy foil package based on the intermetallic phase Ni$_3$Al, constructed as a rolled up honeycomb structure, is shown in Fig.1a). The micro-reactor generally consists of microchannels which are separated by a thin solid wall, as is highlighted schematically in Fig.1b). The cross section of the micro-channels with characteristics dimensions in the honeycomb set is presented in Fig. 1 c).

![Figure 1. a) The alloy foil package based on the Ni$_3$Al intermetallic phase rolled into a honeycomb; b) the eight single microchannels beginning at inlet into the package and terminating at the outlet from the package taken to numerical simulation; c) the characteristic dimensions of reactor.](image)

1.1. Motivation
The appropriate selection of the dimensions of the device, in such way that the contact time of the flow across the catalytically active surface of the substrate providing the reaction of the target product, is very important. In addition to experimental studies, work focused on the modelling of thermocatalytic processes is becoming increasingly interesting. Besides these works, that describe in general the processes of chemical reactions [6-8] there are articles concerning models of reactors and catalytic micro-reactors [9,10].

This paper is a continuation of the analysis of the presented geometry of a single microchannel [9]. However, different issues have been considered, namely the catalytic surface reactions of the decomposition of methanol and the volume reaction of shifting or methanation inside a microchannel. Generally, it is widely known that the catalytic surface reactions, in the direct vicinity of walls coated with active layers, are very often present in technical situations [11,12]. For thermal decomposition reactions, these active layers are often built on the base of Ni alloys [2,13,14]. As previously mentioned in this paper, one of the most promising potential applications of the thin alloy foils, based on the intermetallic phase Ni$_3$Al with high thermocatalytic activity, is within the field of air purification and removal of harmful substances and the controlled decomposition of hydrocarbons, and extended consideration is given here. In this study, the thermocatalytic reactor with microchannels has, with respect to the production of hydrogen, been numerically considered. The main focus of the this paper is to describe the mathematical modelling the chemical surface reactions of the flow of a helium and methanol mixture. The model has been verified and the performance of the thermocatalytic reactor with microchannels within the hydrogen production regime has been investigated.

2. Model description
A mathematical model of the thermocatalytic micro-reactor is based on the elementary balance equations solved for fluids to include continuity, momentum, energy, evolution of kinetic energy of turbulence, evolution of dissipation of kinetic energy of turbulence and species transport in the frame of finite volume method (FVM). The governing equations for the whole device model can be given in the following compact with CFD form:
Boundary layer transport Eq. (1). At this point it should be emphasized that numerous problems of the gas-dynamic boundary layer increase as a result of combination with the chemical phenomena that are taking place.

In the above $\rho = \rho(x, t)$ is the mixture density that depends, in general, on gas component $m$, time $t$ and location $x$, $v = v_i e_i$ - velocity vector, $e_i$ - versor in direction $i$, $v_i$ - value of vector. Next, in the second row $\rho v$, are the bulk momentum density vectors, $p$ is thermodynamic pressure, $I = \delta_{ij} e_i \otimes e_j$ defines unit tensor, $\delta_{ij}$ is Kronecker's delta. $t^t = t^{\text{am}} + t^{\text{tur}}$ takes into account total diffusive momentum flux (flux components of viscous stress, namely, laminar and turbulent, respectively), $\rho S_v$ includes all momentum sources. Additionally, the total specific energy $e = u + \frac{1}{2} v^2$ is a sum of specific kinetic energy $\frac{1}{2} v^2$, $q^t$ represents the total diffusive heat flux, and $S_e$ are the energy sources. Furthermore, in the evolution part of kinetic energy of turbulence $k$ and dissipation of the kinetic energy of turbulence $\varepsilon$, occur diffusive fluxes of $k$ and diffusive flux of $\varepsilon$, i.e. $J_k$, $J_e$, respectively, and sources, namely, the source of the kinetic energy of turbulence $S_k$ together with the source of the dissipation of the kinetic energy of turbulence $S_\varepsilon$. Finally, $Y_m$ is mass fraction of gas component $m = \text{He}; \text{CH}_3\text{OH}; \text{CO}; \text{H}_2; \text{CH}_4; \text{H}_2\text{O}; \text{CO}_2$, $S_m$ is creation/destruction sources of species $m$ and $J_m$ define flux of $m$ components of mixture. More detailed description of Eq. (1) is presented in [6].

### 2.1. Chemical reactions

The main products of the methanol decomposition reaction over the Ni$_3$Al foils are the hydrogen, carbon monoxide and solid carbon deposits. The by-products are carbon dioxide, methane and water [5,13,14]. In the simplest case, methanol decomposition may be described by the following equation [14]:

$$\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \quad (2)$$

If we consider the thermocatalytic microreactor fed by methanol via the decomposition reaction, it should be noticed that carbon monoxide and hydrogen, which are the products, can be consumed in the reacting flow via the following methanation reaction:

$$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (3)$$

The carbon monoxide component is converted into carbon dioxide via shift reaction. We decided to employ a simplified single-step non-reversible reaction in the form of:

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4)$$

Carbon deposition can be considered through the Boudouard reaction:

$$2\text{CO} \rightarrow \text{C} + \text{CO}_2 \quad (5)$$

It should be mentioned that some of the by-products, especially water, can oxidize the Ni$_3$Al catalyst surface. Based on the paper [5], where H$_2$O is the by-product of methanol decomposition and can be used to create the metallic Ni and also can be converted into aluminium hydroxide. It is worth noting that the appearing Ni nanoparticles can be oxidized by H$_2$O according to the reaction, and it can then also take part in the subsequent reaction of spinel formation.

### 2.2. Methanol decomposition source

As has been already mentioned, changes of gas component, $m$, concentration in the mixture due to chemical reactions can be implemented via a volumetric or surface source term, $S_m$, in the species transport Eq. (1). At this point it should be emphasized that numerous problems of the gas-dynamic boundary layer increase as a result of combination with the chemical phenomena that are taking place.
in the vicinity of solids. The flow model of chemical reactions, discussed in many works [6-8] refers to mechanical, thermal and chemical issues of the phenomena occurring in volume. Phenomena occurring on the surface of the thermocatalytic reactor (or the combustion chamber) are characterized by complete anisotropy. Apart from the volume production of component, $S_m$, the reaction of the surface absorption also describes chemical kinetics, and therefore they should be treated as some surface source (or discounts) for the gas component [15,16].

It is assumed in the numerical case that there is no coke creation during micro-reactor operation and the products of thermocatalytic oxidation are not deposited on the catalyst surface. Hence, to provide a complete CFD model of the catalytic micro-reactor, it will be necessary to consider the coke deposition phenomena. In the future, the wall boundary conditions (temperature and emissivity) should be corrected to account for the effects of this deposit accumulation under the conditions of this reaction. Examples of publications that consider ash deposition and temperature fields, may be found as [17-19], and could be helpful in the future works including the growth of carbon nanotubes. In this paper, it is also assumed that there are no site species involved in the surface reactions and hence only gas phase species are modeled. For modelling purposes only the methanol decomposition reaction is catalytic so it is assumed that the source term, $S_{CH_3OH}$, for methanol can be formulated in finite volumes strictly adjacent to the micro-reactor wall. The source of the decomposition of methanol ($S_{CH_3OH}$) depends on the catalytic properties of the intermetallic phase of the Ni$_3$Al, and can be expressed via the following equation:

$$S_{CH_3OH} = W_{CH_3OH} v_{CH_3OH} (k_{Ni_3Al}[X_{CH_3OH}] A_{Ni_3Al})$$  \hspace{1cm} (6)

where, $v_{CH_3OH}(\alpha)$ - the molar stoichiometric coefficient for CH$_3$OH and $\alpha$-th non-reversible reaction and $W_{CH_3OH}$ molecular mass of methanol, kg/kmol. To obtain the volumetric source term, $S_{CH_3OH}$, the surface reaction rate should be divided by the height of the computational cell adjacent to the microreactor wall $(A_{cat}/V_{cell})$. It should be added that the source of methanol decomposition $S_{CH_3OH}$ is then usually given as a function of methanol molar concentration $[X_{CH_3OH}]$ and the forward catalytic rate constant $k_{cat}$. There exist no proper data for a full model validation. Partially, it can be done through the methanol conversion to reaction time characteristics diagram that is often available for a particular thermocatalytic micro-reactor. Kinetic mechanism was simplified by introducing one step reaction.

2.3. The diffusion of mixture components
For methanol and others component concentrations, it is necessary to consider the effect of diffusive fluxes, such as ordinary molecular diffusion, in gas channels as well as Knudsen diffusion. As was presented in the work [10,20], for the considered geometry of the thermocatalytic microreactor, Knudsen diffusion is neglected. In general, diffusion flux $J_m$ depends on the diffusion velocity $V_m$ in the following way:

$$J_m = \rho V_m v_m$$  \hspace{1cm} (7)

The best proven closure on $V_m$ is Dixon-Lewis’ formula [6]:

$$V_m = \frac{1}{X_m W} \sum_{m'=m}^{NS} \begin{cases} W_{m'}, & m'=m \ 
D_{mm'} \nabla X_{m'} - \frac{D_{m'm}}{\rho \gamma_m} \frac{V_{m'} - V_m}{T} \end{cases}$$  \hspace{1cm} (8)

where: $D_{mm'}$ and $D_{m'm}$ are coefficients of respectively: multi-components and temperature diffusion, $W_{m'}$, molecular mass of component $m' \neq m$, the average molecular mass of components, $\bar{W}$, while $T$ is the temperature in the reactor.

3. Analysis
3.1. Experiment and constant to calibration
In the examinations the thin Ni$_3$Al foils with thickness about 50µm and average grain size about 15µm were taken. The stability test for Ni$_3$Al catalyst in methanol decomposition to hydrogen has been carried
out in the flow reactor, under atmospheric pressure, at 500 °C. In this case, Ni₃Al foil was placed in the reactor and vapour mixture containing 40 %vol. of methanol was introduced into reactor (W/F = 1.5 (g cat s ) / cm³). The desired methanol concentration in the gas phase was obtained by bubbling helium through methanol saturator held at 43 °C. The reaction mixture was analysed on-line on TCD-GC (HP 5890 Series II) equipped with Porapak Q packed column. Helium was used as carrier gas in GC. All lines were heated above 100 °C in order to prevent water and methanol from condensation. The thermocatalytic decomposition rate of methanol $q_{\text{CH}_3\text{OH}}$ presented in Table 1 has been employed for validation purposes. Others parameters have been treated as boundary conditions for CFD calculations.

| Parameter                          | Unit           | Value     |
|------------------------------------|----------------|-----------|
| Total mass of catalytic specimens  | g              | 0.777     |
| W/F (weight / flow)                | (g cat s) / cm³| 1.48      |
| Conversion of methanol             | %              | 100       |
| Experimental reaction rate of methanol | g / (g cat s ) | 1.39      |

### 3.2. Numerical boundary condition
The recalculation of the experimental reaction rate and diffusion flux were performed under the following assumptions: 1) constant temperature of the process; 2) monolithic structure of the reactor; 3) conversion parameters as in table 1; 4) geometric dimensions as were presented in Fig. 1 c). Therefore, temperature diffusion part is neglected and only $D_{mm\text{r}}$ is considered in numerical way.

Microchannels coupled at the inlet and outlet are shown in Fig. 1 b). The velocity was assumed at the level $v = 1$ cm/s. It is also known that the lowest possible temperature of the catalysis process which is sufficient to obtain a full conversion from the initial mole fraction i.e. $X_{\text{CH}_3\text{OH}} = 0.4$.

The grid used in the numerical calculations presented here consist of 1 600 000 finite volumes. This enables the model to maintain a high accuracy of the results, without consuming unnecessary computing power. The channels beginning at inlet into the package and terminating at the outlet from the package has been divided into some blocks that have been discretized by means of a structured numerical grid, steeply refined in the normal wall direction. Initial tests allowed to use the numerical grid to ensure that further refinement did not influence the computational results. In the microreactor, a $k - \varepsilon$ turbulent approach was applied due to necessity of utilizing the Eddy-Dissipation model which was considered as the simplest one to work through using UDF. Regarding the fact that Reynold’s numbers are very small we assumed that turbulence model does not affect results in significant way. Therefore, the $k - \varepsilon$ model was chosen as the most wide applied one. It was also assumed that the surface structure of the micro-reactor can be treated as homogeneous.

The standard SIMPLE (semi-implicit method for pressure-linked equations) method has been used for pressure-velocity coupling. The second order upwind schemes have been employed for the solution of the convection term in the governing equations. The diffusion terms have been central-differenced with second order accuracy as well.
4. Results and discussion
Thermocatalytic decomposition of methanol in a single package micro-reactor is considered as a complicated phenomenon where the main products of the reaction are hydrogen and CO (see Eq. (2)). Considering obtained experimental results, with respect for start (TOS=0 min) and equilibrium state of process (TOS=270 min), it can be concluded high influence of diffusion flux (Fig.2.).

The distribution of the components due to the impact of different processes can be managed by: 1) diffusion effects; 2) mixing effects due to eddy turbulence; 3) thermocatalytic surface decomposition and 4) volumetric reactions. Hydrogen mole fraction distribution at the eight single microchannels with an inlet into the package and an outlet from the package has been presented in Fig. 3.

As is highlighted in Fig. 3 the three main areas can be distinguished for the whole package: Firstly, the diffusion flux area before microchannels (between $L = -10$ mm and $L = 0$ mm); secondly, the thermocatalytic reaction area (between $L = 0$ mm and $L = 25$ mm) and thirdly, the flow mixing area (between $L = 25$ mm and $L = 35$ mm). It is worth mentioning that average Reynolds number in domain is equal to 0.06 while maximum value is around 0.2. The maximum of the methanol mole fraction is located at the beginning of the inlet package and decreases between the centre of the diffusive flux area and the thermocatalytic area in the microchannels, while further diminishing due to the surface catalytic reaction on the Ni$_3$Al thin foil, as is presented in Fig.4. It should be understood that a decrease of methanol concentration in the direction of the outlet from the package is related directly to the decomposition effects connected with the properties of the intermetallic phase of Ni$_3$Al, which is highlighted in Fig. 4. The view of the local changes in the field of the hydrogen mole fraction in both
the axial-sectional and the cross-sectional directions is illustrated in Fig. 3, thus the effects of the diffusion and the chemical reaction are clearly demonstrated.

![Figure 4. Change of the averaged cross-sectional mole fraction of hydrogen, methanol, carbon monoxide, steam, methane and carbon dioxide as a function of reactor length $L$.](image)

5. Conclusions
This paper is concerned with of the modelling of hydrogen production by methanol decomposition in the thermocatalytic reactor based on the intermetallic phase of Ni$_3$Al. The numerical simulation has been performed via CFD procedure with extensions including the increased chemical reactions rate at the interphase between fluid and solid. Analysis presented should be considered as having demonstrated a promising concept in chemical processing possibilities. Results obtained through numerical calculations were calibrated and compared with experimental data to receive satisfactory agreement, however a more sophisticated approach will be considered which includes the effects of deposit growth on the reaction conditions and temperature field at the wall. Influence of the temperature will be added as soon as new experimental data will be available which will allow to enhance the code accordingly. Carbon formation could be modelled by introducing Lagrange formulation. Therefore, the boundary conditions including fluid-solid interactions should be extended with respect of carbon nanotubes formation.

The original methodology of the 3D numerical analysis for thermocatalytic micro-reactor used in the decomposition of methanol has been presented in this paper. The data extrapolated via the implemented numerical model have made it possible to assess the minimal length of the microreactor channels, which provide a full conversion of methanol at the system outlet.

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