Catalytic utilization of unconventional fuels in a gas turbine

M Stajnke¹² and J Badur¹³
¹Energy Conversion Department, The Szewalski Institute of Fluid-Flow Machinery PAS-cii, Fiszera 14, 80-231 Gdańsk, Poland

E-mail: ²mstajnke@imp.gda.pl, ³jb@imp.gda.pl

Abstract. In this paper, the numerical modelling of acetone utilization in the thermocatalytic reactor based on the intermetallic phase of Ni₃Al has been presented. The experimental results of mixtures containing air contaminated with acetone in a thermocatalytic reactor were used for the preliminary calibration of the Computational Fluid Dynamics “CFD” calculations. The thermocatalytic combustion reaction of acetone has been modelled by employing experimental data related to the active surface area. For more accurate application of current model into the gas turbine regime simulation was performed on three different geometrical cases. Effects regarding flows in microchannel are visible especially when “small” geometry is concerned. One should notice that a decrease of acetone concentration at inlet into package, mainly, two millimetres before the thermocatalytic area, is connected with the diffusion fluxes of the other components, mainly water and carbon dioxide. The commercial CFD code has been expanded by User Defined Functions “UDF’s” to include surface chemical reaction rates on the interphase between fluid and solid. Results obtained through numerical calculations were calibrated and compared with experimental data to receive satisfactory agreement.

1. Introduction

There are catalysts like Ni-based that exhibit very versatile spectrum of applications. In case presented in this paper one of this high catalytic potential has been utilised that is extremely high catalytic activity in harmful substances utilization. Along with the reactions with other gasses synthesis and promote the production of carbon nanostructures (mainly carbon nanotubes) [1,2]. The Ni-based, solid-state catalysts that was used in this work as is the Ni₃Al alloy [3], which combines 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]. Said that the main disadvantage of this material is the relatively high temperature of maximal hydrocarbon conversion as stated in the literature [1,5]. That is where high temperature occurring during normal work of a gas turbine can be utilized. From the thermodynamic point of view such solution would be negative on overall gas turbine performance. But in some instances this utility might be more than useful. As gas turbines are relatively easy to transport they can be used in whole spectrum of situations where this specific function might be used. The thin strips or thin foils based on the Ni₃Al intermetallic phase produced according to technology presented by Jóźwik et al. in works [1,3] could be applied inside gas turbine to fully utilize catalytic potential of mentioned material. The alloy foil package based on the intermetallic phase Ni₃Al created as an prototype used in experiment to define catalytic activity was constructed as a rolled up honeycomb structure (shown in Fig.1a).
1.1. Motivation

While foil packages and experiment data were obtained having very small dimensions in mind (as shown in Fig. 1c) there is still question how this catalyst will perform when put in gas turbine which connects with greater overall dimensions of mentioned package. Appropriate method of insertion catalytically active surface inside the hot gas stream will be crucial for performance of gas turbine and catalyst itself. However in this work as a first step to creating full model of gas turbine with catalytically active surfaces the focus was put into examining performance of the alloy foil package for different dimensions. Cases of modelling thermocatalytic processes are 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 acetone and influence of microchannel dimensions on reaction rates. Situation where catalytic surface reactions occurs in the direct vicinity of walls coated in active layers, are often present in technical situations [11,12]. In instances of thermal decomposition reactions, active layers are often built on the base of Ni alloys [2,13,14]. As previously mentioned in this paper, alloy foils based on the intermetallic phase of \( \text{Ni}_3\text{Al} \) can be widely utilized. One of the most promising potential applications is within the field of air purification and removal of harmful substances and the controlled decomposition of hydrocarbons, and extended consideration is given here. The main focus of the this paper is to describe the mathematical modelling the chemical surface reactions of the flow of mixture of air contaminated by acetone. The model has been verified and the performance of the thermocatalytic reactor with microchannels within the air purification regime has been investigated.

2. Model description

A mathematical model used in solver contain basic governing equations that include continuity, momentum, energy, evolution of kinetic energy of turbulence, evolution of dissipation of kinetic energy of turbulence and species transport. Equations were assumed in manner showed below.

2.1. Mass balance (continuity) equation

\[
\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial x_i} (\rho v_i) = 0
\]  

(1)

Where \( \rho \) is fluid density, generally dependent on time and location, \( v_i \) is fluid velocity (where \( i = x, y, z \)) and \( x_i \) as coordinates used in finite volume method, \( i = 1, 2, 3 \) (structural mesh) or \( i = x, y, z \) (non-structural mesh).
2.2. **Momentum balance equation**

\[
\frac{\partial}{\partial t} (\rho v_i) + \frac{\partial}{\partial x_j} (\rho v_i v_j + p \delta_{ij}) = \frac{\partial}{\partial x_j} (\tau_{ij} + R_{ij}) + \rho b_i
\]  

(2)

Where \( p \) is thermodynamic pressure, \( \delta_{ij} \) stands for Kronecker delta, \( \tau_{ij} \) for viscous stress flux components, \( R_{ij} \) is Reynolds turbulent stress and \( b_i \) is mass force of Earth gravity (\( b_i = -9.81 \delta_{ij} \)).

2.3. **Energy balance equation**

\[
\frac{\partial}{\partial t} (\rho e) + \frac{\partial}{\partial x_i} (\rho e v_i + p v_i) = \frac{\partial}{\partial x_i} (q_i + q_i^T + \tau_{ij} v_j + R_{ij} v_j) + \rho b_i v_i
\]  

(3)

Where \( e \) represents internal and kinetic energy (\( e = u + \frac{v^2}{2} \)), \( u \) – internal energy (\( u = c_v T \)), \( q_i \) is molecular heat flux and \( q_i^T \) turbulent heat flux.

2.4. **Equation for turbulent kinetic energy evolution** \( k \)

\[
\frac{\partial}{\partial t} (\rho k) + \frac{\partial}{\partial x_j} (\rho k v_j) = \frac{\partial}{\partial x_j} (J^k_j) + \rho S_k
\]  

(4)

2.5. **Equation for turbulent dissipation energy evolution** \( \varepsilon \)

\[
\frac{\partial}{\partial t} (\rho \varepsilon) + \frac{\partial}{\partial x_i} (\rho \varepsilon v_i) = \frac{\partial}{\partial x_i} (J^\varepsilon_i) + \rho S_\varepsilon
\]  

(5)

Where \( J^k_i \) and \( J^\varepsilon_i \) are respectively diffusive flux of \( k \) and diffusive flux of \( \varepsilon \) with sources \( S_k \) and \( S_\varepsilon \).

2.6. **Equation for species transport**

\[
\frac{\partial}{\partial t} (\rho Y_m) + \frac{\partial}{\partial x_i} (\rho Y_m v_i) = \frac{\partial}{\partial x_i} (J_{m,i}) + \rho S_m
\]  

(6)

Where, \( Y_m \) is mass fraction of gas component \( m = N_2; C_3H_6O; CO; H_2O; CO_2 \). \( S_m \) is creation/destruction sources of species \( m \) and \( J_{m,i} \) define flux of \( m \) components of mixture. More detailed description of Eq. (1-6) is presented in [6].

2.7. **Chemical reaction**

The main products of the acetone combustion reaction over the Ni\(_3\)Al foils are water and carbon dioxide. The by-products were omitted in this work but are further investigated in works [5,13,14]. For this simplest case focusing on model verification based on experiment results only one equation was implemented:

\[
C_3H_6O + 4O_2 \rightarrow 3H_2O + 3CO_2
\]  

(7)

Some of the by-products, especially water (also present in air), can oxidize the Ni\(_3\)Al catalyst surface. As described in 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 aluminum hydroxide.
2.8. Acetone combustion source

As it was already mentioned, changes in the components 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). There are numerous works describing models including flow with chemical reactions [6-8] but it mostly refers to mechanical, thermal and chemical issues of the phenomena occurring in volume. Phenomena occurring on the surface of the combustion chamber are characterized by complete anisotropy. Separately from the volumetric reaction resulting in 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].

In this first approach in modelling complex flow and chemical reactions cases it is assumed in the numerical case that the products of thermocatalytic oxidation are not deposited on the catalyst surface. As it was previously stated all chemical reactions are considered irreversible. In the future, the wall boundary conditions such as temperature and emissivity should be enhanced to account for the effects of this deposit accumulation under the conditions of this reaction. The source term for acetone reaction, $S_{C_3H_6O}$, can be formulated in cells strictly adjacent to the catalyst surface. By the means of UDF (User Defined Functions) we formulated algorithm which can identify finite volumes in direct proximity to the reactor walls. Inside identified in this way cell the source of the acetone oxidation ($S_{C_3H_6O}$) could be implemented which can be expressed via the following equation:

$$S_{C_3H_6O} = W_{C_3H_6O} \nu_{C_3H_6O} (k_{Ni_{3-Al}}[X_{C_3H_6O}] \frac{A_{Ni_{3-Al}}}{V_{cell}})$$

(8)

where: $\nu_{C_3H_6O}$ - the molar stoichiometric coefficient for $C_3H_6O$ and $\alpha$-th non-reversible reaction and $W_{C_3H_6O}$ molecular mass of acetone, kg/kmol. To obtain the volumetric source term, $S_{C_3H_6O}$, independent from the different mesh sizes occurring in discretization process and only include catalytic surface area, 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 acetone combustion $S_{C_3H_6O}$ is then usually given as a function of acetone molar concentration $[X_{C_3H_6O}]$ 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 acetone conversion to reaction time characteristics diagram that is often available for a particular thermocatalytic micro-reactor.

3. Analysis

3.1. Experiment and constant to calibration

In the examinations the thin Ni$_3$Al foils with thickness about 50$\mu$m and average grain size about 15$\mu$m were taken. The stability test for Ni$_3$Al catalyst in acetone utilization effectiveness been carried out under atmospheric pressure and under the lowest possible temperature, 600 °C, which was sufficient to obtain a full conversion from the initial mole fraction i.e. 2000 ppm. Basic information regarding experiment are shown in table 1. More detailed description of the experiment as well as data obtained can be found in mentioned earlier work [10]. Others parameters have been treated as boundary conditions for CFD calculations.

**Table 1.** An experimental thermocatalytic decomposition rate of acetone $q_{C_3H_6O}$ over Ni$_3$Al foil estimated at GHSV = 40000h$^{-1}$ under the lowest possible temperature of the catalysis process which is sufficient to obtain a full conversion from the initial mole fraction i.e. $X_{C_3H_6O}$=2000 ppm.

| Parameter                  | Unit | Value |
|----------------------------|------|-------|
| Total mass of catalytic specimens | g    | 0.5   |
| Conversion of acetone      | %    | 100   |
| Experimental reaction rate of acetone | g / (g$_{cat}$ s) | 0.124 |
3.2. Numerical boundary condition

The recalculations 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). However to verify the model for gas turbine usefulness the dimensions of analyzed microchannel were changed. To compare changes in reaction effectiveness and flow behavior the geometry was scaled twice, once dimensions in every direction were multiply by two and after that once again multiply by two. This way we obtained 3 geometries of the same microchannel but in different sizes. The results of scaling and its effect on reactor volume and mass flow can be seen in Table 2.

Table 2. Change in parameters (reactor volume and mass flow) for different scale factor for assumed geometry (basic dimensions shown in Fig. 1c).

| Parameter  | Reactor volume [m³] | Volume multiple [-] | Mass flow rate [kg/s] | Mass multiple [-] |
|------------|----------------------|----------------------|-----------------------|-------------------|
| Scale_1    | 7.04E-08             | 1                    | 1.19E-07              | 1                 |
| Scale_2    | 5.63E-07             | 8                    | 4.77E-07              | 4                 |
| Scale_3    | 4.50E-06             | 64                   | 1.91E-06              | 16                |

Microchannels coupled at the inlet and outlet are shown in Fig. 1 b). The velocity was assumed at the level $v = 0.07$ cm/s. As known from the experimental data that the lowest possible temperature of the catalysis process which is sufficient to obtain a complete conversion occurred at $T = 600$ °C. Mixture used in simulation consist of air contaminated with acetone in concentration of 250 ppm. For the calculations steady state flow state was assumed and analysis was performed by a CFD commercial code. This finite volume based code permits one to solve the three-dimensional fluid and heat flow problems concerned with turbulent structures and chemical reactions [17-20]. However, it also allows for the addition of user defined subroutines programmed in C++ for problems that fall outside the capability of the standard version of code. As has been demonstrated in recent works [21-23], in modelling flows with a strong interaction of surface and liquid material, boundary conditions and appropriate closure in mathematical models are essential.

The grid used in the numerical calculations presented here consist of $1 \times 600 \times 000$ finite volumes for basic geometry case “Scale_1”. For geometry “Scale_2” and “Scale_3” number of finite elements were accordingly increased, respectively to $2 \times 000 \times 000$ and $3 \times 400 \times 000$ finite elements of structural mesh. This enables the model to maintain a high accuracy of the results, without consuming unnecessary computing power. 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. It has been assumed that the micro-reactor walls are constantly under influence of a heater, thus assuring a constant temperature conditions. Although the temperature change with this slight acetone concentration will not change much even without additional heater assistance. 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 utilization of acetone in a single package micro-reactor is considered as a complicated phenomenon where the main products of the reaction are water and carbon dioxide (see Eq. (7)).

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 and 3) thermocatalytic surface utilization. However with relatively small level of air contamination (250 ppm) the diffusion effects are less visible.
with cases of larger geometry (Fig. 3). This effect can be seen before air stream reaches the reactor and despite that the acetone mole fraction is reduced. For better illustration additional measuring surface was added and placed 2 mm before package inlet.

As can be seen in Fig. 2 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). As can be seen in Fig. 3 despite significant scale increase the utilization of acetone still is very effective. It should be mentioned that case where harmful substances (in this case acetone) concentration is equal to 250 ppm is quite extreme, but at the same time useful regarding simulation and model preparation.

![Acetone mole fraction expressed in ppm $X_{C_3H_6O}$ distribution at the eight single microchannels beginning at inlet into the package and terminating at the outlet from the package.](image1)

**Figure 2.** Acetone mole fraction expressed in ppm $X_{C_3H_6O}$ distribution at the eight single microchannels beginning at inlet into the package and terminating at the outlet from the package.

![Change of the averaged cross-sectional mole fraction expressed in ppm of acetone as a function of reactor length $L$.](image2)

**Figure 3.** Change of the averaged cross-sectional mole fraction expressed in ppm of acetone as a function of reactor length $L$. 

---

XXIII Fluid Mechanics Conference (KKMP 2018)  
IOP Publishing  
IOP Conf. Series: Journal of Physics: Conf. Series 1101 (2018) 012038  
doi:10.1088/1742-6596/1101/1/012038
Although it might seem like different scaling only affect this case in almost non-dimensional way the influence of scale on flow is much more significant. This effect is seen mostly in multicomponent diffusion affecting results of molar concentration of acetone before entering the reactor. For larger scale models and much greater flow speed like in gas turbine the effects of this diffusion will not have such strong influence on gas flow as in micro scale. The important issue in this case would be ability of surfaces to effectively utilize toxic compound without generating much pressure loss.

5. Conclusions
This paper is concerned with of the modelling of acetone utilization which represent harmful substances present in the air in the thermocatalytic reactor based on the intermetallic phase of Ni₃Al. 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, increased number of chemical reactions and temperature field at the wall.

Acknowledgments
The work results were obtained in studies co-financed by the National Research and Development Centre in the project PBS 3 ID 246201 titled : "The development of innovative technology, thin foils of alloys based on intermetallic phase Ni₃Al with high activity thermocatalytic in the field of purification of air from harmful substances or controlled decomposition of hydrocarbons.”

6. References
[1] Jóźwik P, Grabowski R, Bojar Z, 2010. Catalytic activity of Ni₃Al foils in methanol reforming Mater. Sci. Forum 636-637 p 895–900.
[2] Olafsen A, Daniel C, Schuurman Y, Raberg L B, Olsbye U, Mirodatos C 2006 Light alkanes CO₂ reforming to synthesis gas over Ni based catalysts Catal. Today 115 p 179-185
[3] Jóźwik P, Polkowski W, Bojar Z, 2015 Applications of Ni₃Al based intermetallic alloys—current stage and potential perceptivities Materials 8 p 2537-2568
[4] Moussa S O, El-Shall M S, 2007 High-temperature characterization of reactively processed nanostructure nickel aluminate intermetallics. J. Alloys Compd. 440 p 178-188
[5] Xu Y, Ma Y, Sakurai J, Teraoka Y, Yoshigoe A, Demura M, Hirano T 2014 Effect of water vapor and hydrogen treatments on the surface structure of Ni₃Al foil Appl. Surf. Sci. 315 p 475-480
[6] Badur J 2003 Numerical modelling of sustainable combustion in gas turbines IFFM Publishers Gdańsk
[7] Kuo K K and Acharya R 2012 Applications of turbulent and multiphase combustion John Wiley & Sons, Inc. New Jersey
[8] Williams F A 1965 Combustion theory Addision Wesley Massachusetts.
[9] Chen G-B, Chen C-P, Wu C-Y, Chao Y-C 2007 Effects of catalytic walls on hydrogen/air combustion inside a micro-tube Appl. Catal. A 332 p 89–97
[10] Jóźwik P, Badur J and Karcz M 2011 Chemical and Process Engineering vol 32 (3) p 215-227
[11] Aoki N, Yube K, Mae K, 2007 Fluid segment configuration for improving product yield and selectivity of catalytic surface reactions in microreactors Chem. Eng. J. 133 p 105-111
[12] Duran J E, Mohseni M, Taghipour F, 2010 Modeling of annular reactors with surface reaction using computational fluid dynamics (CFD) Chem. Eng. Sci. 65 p 1201-1211
[13] Mitani H, Xu Y, Hirano T, Demura M, Tamura R, 2017 Catalytic properties of Ni-Fe-Mg alloy nanoparticle catalysts for methanol decomposition Catalysis Today 281 p 669–676
[14] Michalska-Domańska M, Bystrzycki J, Jankiewicz B, Bojar Z 2017 Effect of the grain diameter of Ni-based catalysts on their catalytic properties in the thermocatalytic decomposition of methanol *Comptes Rendus Chimie* **20** p 156-163

[15] Badur J, Ziółkowski PJ and Ziółkowski P 2015 On the angular velocity slip in nano-flows *Microfluid Nanofluid* **19** p 191-8

[16] Badur J, Ziółkowski P, Sławiński D, Kornet S 2015 An approach for estimation of water wall degradation within pulverized-coal boilers *Energy* **92** p 142-152

[17] Ziółkowski P, Stajnke M and Jóźwik P 2018 Modeling of a mixture flow of helium and methanol in thermocatalytic reactor and chemical reactions on the intermetallic phase of Ni$_3$Al *Transactions IFFM*, accepted to publication

[18] Flaszyński P, Doerffer P, Szwaba R, Kaczyński P, Piotrowicz M 2015 Shock wave boundary layer interaction on suction side of compressor profile in single passage test section. *Journal of Thermal Science* vol **24**(6) p 510-515

[19] Badur J, Ziółkowski P, Zakrzewski W, Sławiński D, Kornet S, Kowalczyk T, Hernet J, Piotrowski R, Felicjancik J, Ziółkowski P J 2014 An advanced Thermal–FSI approach to flow heating/cooling *J. Phys.: Conf. Ser.* **530** 10.1088/1742-6596/530/1/012039.

[20] Pianko-Oprych P, Kasilova E, Jaworski Z, 2014 CFD analysis of heat transfer in a microtubular solid oxide fuel cell stack *Chemical and Process Engineering* **35** p 293-304

[21] Badur J, Karcz M, Lemański M, Nastałek L 2011 Enhancement transport phenomena in the Navier-Stokes shell-like slip layer *CMES: Computer Modeling in Engineering & Sciences* **73** p 299–310

[22] Ziółkowski P, Badur J 2018 A theoretical, numerical and experimental verification of the Reynolds thermal transpiration law. International Journal of Numerical Methods for Heat and Fluid Flow vol **28**(1) p 64-80.

[23] Lewandowski T, Ochrymiuk T, Czerwińska J 2011 Modeling of heat transfer in microchannel gas flow *ASME Journal of Heat Transfer* **133** 022401-1