Acta Mechanica Slovaca
ISSN 1335-2393
www.actamechanica.sk

Numerical Simulation of Cooling the Adsorbent During Hydrogen Storage Process at 77 K

Tomáš Brestovič [1], Natália Jasminská [1,*] Marián Lázár [1] and Ľubica Bednárová [1]

[1] Faculty of Mechanical Engineering, TU Košice, Department of Power Engineering, Vysokoškolská 4, 042 00 Košice, Slovakia

Abstract: The article describes the layout of thermal fields of activated carbon in the pressure steel tank at 77 K. The technology of adsorption hydrogen on the carbon materials is effective only at cryogenic temperatures. Therefore was used liquid nitrogen with temperature 77 K for the decrease of temperature device for storage. To properly assess the kinetics of the process is necessary to determine the correct time, which is necessary to compensate for the temperature field. Simulation program ANSYS CFX was used for the determination the thermal fields.

Keywords: *adsorbent, adsorption storage hydrogen, numerical simulation, Ansys CFX.*

1. Introduction

A Hydrogen storage is a key problem at application of hydrogen technology and assessing of economics of usage this element in energetics and transport. However, proposed methods of pressure and cryogenic hydrogen storage are not enough safe and do not have the high storage capacity. For obtaining of high pressures (storage of the composite pressure vessels), respectively low temperature (liquid storage) is needed a large amount of energy. Major advantage adsorption storage of hydrogen is a high kinetics of the adsorption-desorption cycles, cyclical stability and low cost adsorbent [1,2,3,4].

Use of cryogenic temperature and the absorbent materials leads to considerably reduced of pressure hydrogen storage. Therefore, this method is suitable for hydrogen storage. Target of further development the materials for storage is to obtain the greatest abilities of hydrogen storage with the lowest weight of the whole device mainly for transport applications [5,6,7,8,9].

The advantage of carbon materials is mainly their low density, extensive structure of the pore and chemical stability. Adsorption and desorption of hydrogen in the carbon nanotubes, in the nanoporous materials and in the active carbon show low or no hysteresis and they have relatively fast kinetics.

2. Laboratory equipment for measurement of hydrogen adsorption at 77 K

Of the base part of laboratory equipment for determination of capacity storages is thick-walled steel pressure tank with volume 10^{-5} m^3, which is filled by adsorbent and at the top of the neck is sealed with polyurethane foam. This allows a continuous flow of hydrogen without blow molding of fine particles filling. For isolation of thread was used Teflon, which resists cryogenic temperatures. The tank is immersed into the liquid nitrogen, which is in Dewar tank with volume 10^{-3} m^3.

*** Corresponding author:** Natália Jasminská, ***E-mail address:*** *natalia.jasminska@tuke.sk*

The laboratory equipment is used to measure the adsorption with the hydrogen pressure of 2 MPa with the possibility of decrease of temperature in pressure tank with active carbon at the 77 K.

Fig. 1: *The pressure tank with active carbon.*

The equipment consists from the pressure tank with hydrogen at 20 MPa and purity 3.0 (99.9%). While Purity hydrogen, which is used, is sufficient for using at the adsorption, given that the activated carbon is not susceptible to the degradation of the storage abilities by the various impurities in the gas, (especially O_2), as in certain types of metal hydrides. For decrease and regulation of hydrogen pressure from the pressure tank to maximum 2 MPa, is used reducing valve FC 2000 5-H-200 that complies with norm EN ISO 2503. The distribution of gas is realized by brass pipe MS 63.

3. Determination of thermal fields

When measuring the absorption curves is necessary to cool the adsorbent to the cryogenic temperature 77 K. Due to the complexity and voluminousness problems heat transfer from liquid nitrogen to core of active carbon is not possible to solve heat transport by an analytical method. Therefore were used the numerical methods of solving.

The main requirement numerical simulation in ANSYS CFX is the establishment of non-stationary temperature field of activated carbon, in a steel container with a capacity of 20 ml. To monitor the temperature of the adsorbent at selected points is possible to determine the minimum time that is needed to immersing tank into the liquid nitrogen until the start of measurement of adsorption of hydrogen. The weight of used carbon is 1.3 g. In view of the dramatically changing the physical properties of materials during decrease to the temperature of liquid nitrogen were used functional dependence on the temperature.

Physical properties of active carbon needed for numerical calculation:

a) Density: $\rho = 269\ kg{\cdot}m^{-3}$.

b) Specific heat capacity:

$$c_p = -1{,}67154 + 0{,}2789 \cdot T - 0{,}00895 \cdot T^2 + 1{,}44866 \cdot 10^{-4} \cdot T^3 - 3{,}52803 \cdot 10^{-7} \cdot T^4 + \\ + 6{,}70024 \cdot 10^{-11} \cdot T^5 + 3{,}74615 \cdot 10^{-13} \cdot T^6 \qquad (\mathrm{J{\cdot}kg^{-1}{\cdot}K^{-1}}) \tag{1}$$

c) Thermal conductivity:

$$\lambda = 0{,}01 \cdot \left(-16{,}8 + 0{,}73 \cdot T - 1{,}9 \cdot 10^{-3} \cdot T^2 + 1{,}53065 \cdot 10^{-6} \cdot T^3\right) \qquad (\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}) \tag{2}$$

d) Porosity of material: $\varepsilon_b = 0{,}49$

Physical properties of steel:

a) Density: $\rho = 7\,854\ kg{\cdot}m^{-3}$.

b) Specific heat capacity:

$$c_p = 2{,}2467 - 1{,}71591 \cdot T + 0{,}11268 \cdot T^2 - 0{,}00106 \cdot T^3 + 4{,}4132 \cdot 10^{-6} \cdot T^4 - 8{,}74117 \cdot 10^{-9} \cdot T^5 + \\ + 6{,}69455 \cdot 10^{-12} \cdot T^6 \qquad \left(\mathrm{J{\cdot}kg^{-1}{\cdot}K^{-1}}\right) \tag{3}$$

Thermal conductivity of tank from the steel has been selected on the basis of known data at three temperatures by Table 1. Thermal conductivity at a specific temperature of the solved element is obtained by linear interpolation. Figure 2 shows the process of thermal capacities of carbon and steel depending on temperature.

Table 1: *Thermal conductivity of steel.*

t (°C)	-197	0	100
λ ($W \cdot m^{-1} \cdot K^{-1}$)	10	59,3	52,3

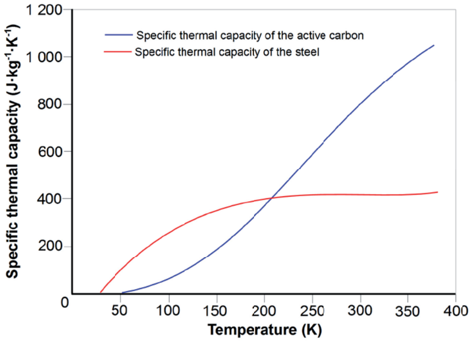

Fig. 2: *Dependence of specific heat capacity for steel and carbon.*

3.1 Creating of models and the simulation of thermal fields

The shape and dimensions of the steel tank are shown in Figure 3. The activated carbon in the container reaches the height of 47 mm from the inner bottom of the container.

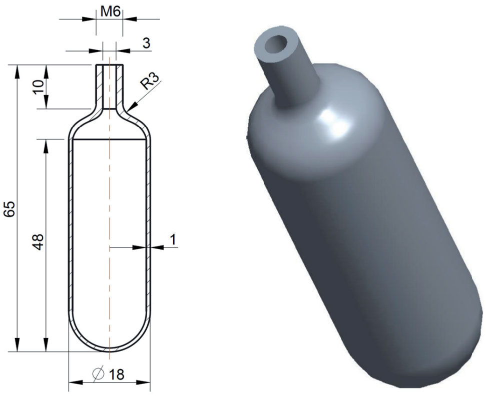

Fig. 3: *Pressure tank from steel for the storage of adsorbent.*

After sealed of the steel tank with Teflon it is screwed into the threaded brass holder whom dimensions and shape are shown on Figure 4.

Creating 3D model of composition contains four domains: active carbon, hydrogen (above the carbon in steel tank and brass holder), steel tank, brass holder. The task is possible to solve with symmetric to the longitudinal plane, therefore the rate of calculation is doubled. Figure 5 shows models with highlighted of the symmetry plane.

The mesh created by discretization individual

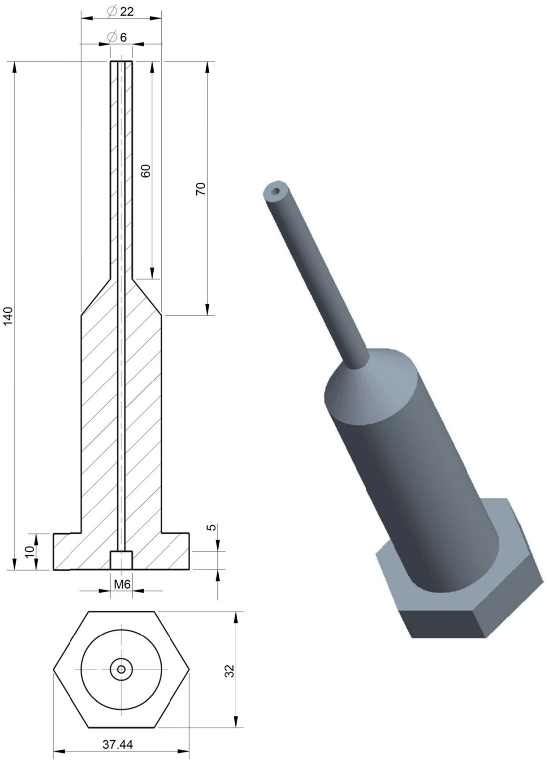

Fig. 4: *Brass stand for the steel tank.*

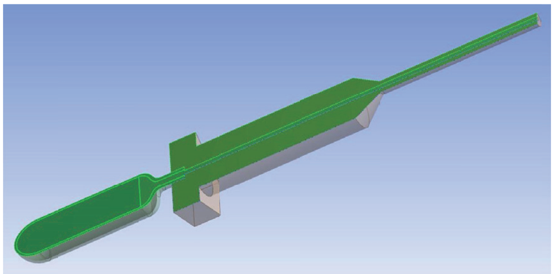

Fig. 5: *3D geometry solid and fluid domain with highlighted plane of symmetry.*

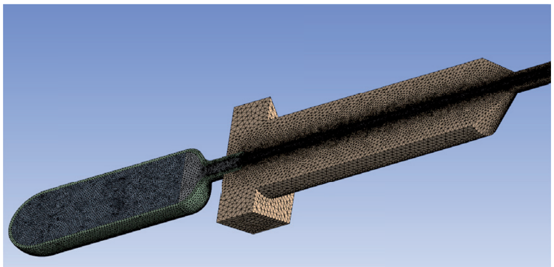

Fig. 6: *Discretization of domain by creation of a mesh.*

domains contains $1.45 \cdot 10^6$ of elements with tetrahedron type. The individual contact surfaces between the domains were using the tool "Name selection" named for ease of setup interface. The network is shown on Figure 6.

3.2 Result of simulation of thermal fields

Numerical simulation was solved as time-dependent with total time 60 s and time step 0.2 s. The initial time step was only 0.05 s with and subsequently it was increased to the 0.02 s, due to the overflow prevention solver.

Each time step was conducted 20 iterations. At time 0 Sec. was temperature 20°C, it was the initialization condition all of the domains. On the contact area of liquid nitrogen with tank (Fig. 8) was entered the third type boundary condition. The heat transfer coefficient is considered at 3 000 $W \cdot m^{-2} \cdot K^{-1}$ (calculated from criteria equation [10]) and temperature of liquid nitrogen at 77 K. At the top of the container acts on the surface the gas nitrogen, which is evaporated off having a temperature of 77 K (it is marked with green colour in Fig. 9) and the average heat transfer coefficient also takes account of the radiation of the 14 $W \cdot m^{-2} \cdot K^{-1}$. On the upper side of brass holder is defined heat transfer coefficient 12 $W \cdot m^{-2} \cdot K^{-1}$ at ambient temperature of air 20°C.

For evaluation of the time-variable thermal field was selected 3 points in axis of carbon as on Figure 7. Point 1 is situated at height 47 mm from the inside bottom of the tank. Point 2 is situated at height 24 mm and point 3 at 1 mm from the inside bottom of the tank. For evaluation of the thermal field across the thickness the line passing through the point 2 was used. This line is perpendicular to the axis, of the tank.

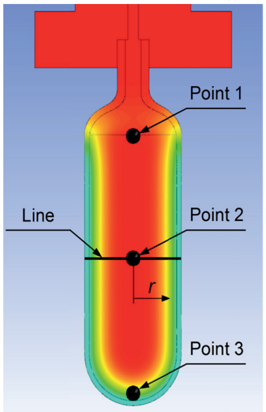

Fig. 7: *Location of the evaluation points.*

Change of temperature in individual points in depending on time is a depending to height immersion into liquid nitrogen. For numerical calculation has been studied the two variants:

1.) Total immersion at height of active carbon (48 mm from the inside bottom of the tank),

2.) 2 / 3 immersion from the bottom of the tank (32 mm).

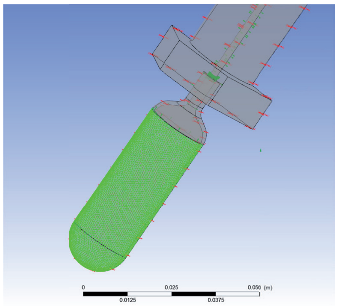

Fig. 8: *Cooled surface by total immersion of the tank into liquid nitrogen.*

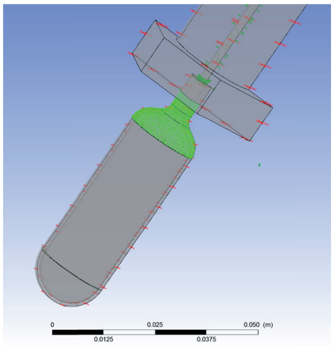

Fig. 9: *Cooled surface by total immersion of the tank into fluid nitrogen.*

Figure 10 shows the time development of temperatures in the studied points for total immersion of the tank solved in ANSYS CFX. Development of temperatures shows that the basic stabilization of temperature field takes place after 8 s.

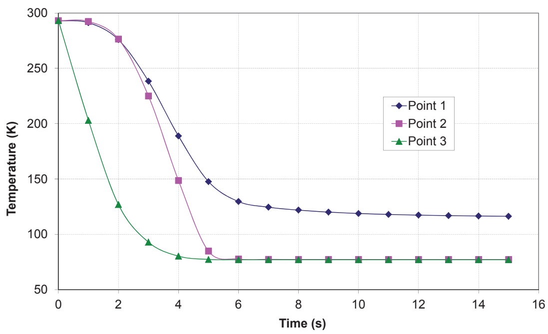

Fig. 10: *Development of temperature in selected points in dependence on time at total immersion into LH2.*

The temperature in point 1 does not reach a stable value, even after 60 s. Therefore, it was performed the simulation “steady state” which showed a stabilized temperature in point 1 to value 100 K. Heat transport from ambient through the neck of the steel tank does not allow complete cooling of the adsorbent. This can have an impact of the total capacity of hydrogen storage.

The results of the simulation show necessity the immersion tank above of the top layer of carbon to allow for the complete cooling of the adsorbent.
In point 3 there is the fastest cooling. The point 3 is situated only 1 mm from the surface of the steel tank. Development of temperature on the line which is perpendicular to the axis of the tank and passing through point 2 is shown on Figure 11. Dependence the temperature is it relevant to distance from the axis of the tank (radius r).

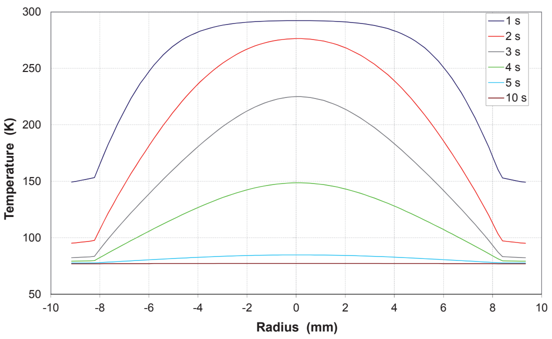

Fig. 11: *Development of temperature on a line which is perpendicular to the axis of the tank passing through the center of the tank depending on time.*

The temperature fields in the section plane passing through the axis of rotation of a steel tank in the different time points are shown in Figure 12.

Simulation of the 2/3 immersion of tank was done for comparison. The thermal fields simulation of 2/3 immersion of tank are shown on Figure 13 (steady state) and on. Figure 14 (non-stationary temperature field).

Figure 15 shows that, at 2/3 immersion is problem with hypothermia in point 2, which is situated in the middle of carbon. After stabilization the temperatures is at the point 1: 142 K; point 2: 82 K; point 3:77 K.

Figure 16 shows the development of temperature along the height of active carbon for better illustration of the problem (height 0 mm is on the underside of a sphere of carbon).

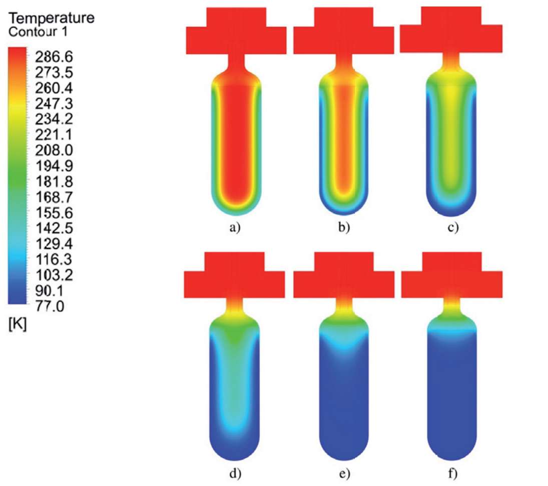

Fig. 12: *The thermal fields in cut the tank during total immersion in nitrogen at the time a) 1 s, b) 2 s, c) 3 s, d) 4 s, e) 5 s, f) 10 s.*

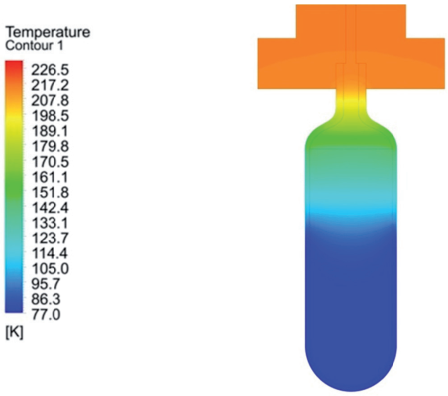

Fig. 13: *The thermal fields in steady state for 2/3 immersion into liquid nitrogen.*

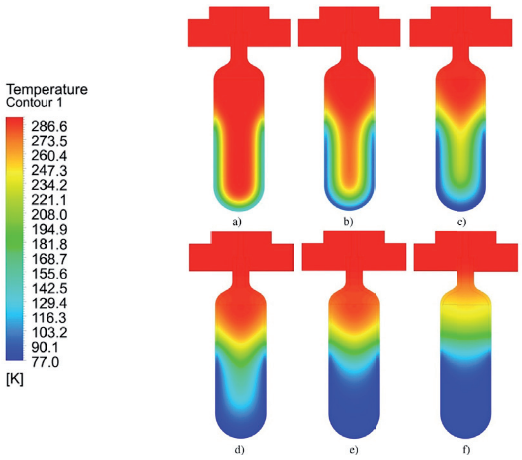

Fig. 14: *The thermal fields in cut the tank for 2/3 immersion into liquid nitrogen at the time a) 1 s, b) 2 s, c) 3 s, d) 4 s, e) 5 s, f) 10 s.*

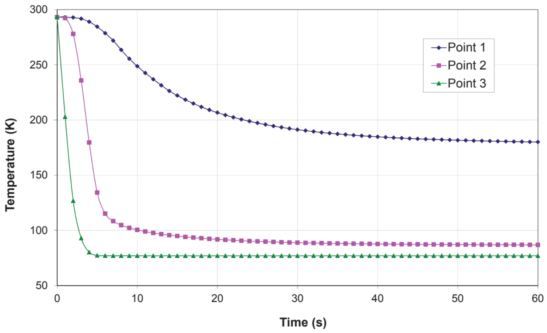

Fig. 15: *Development of temperature for 2/3 immersion into LH_2 depending on time in selected points.*

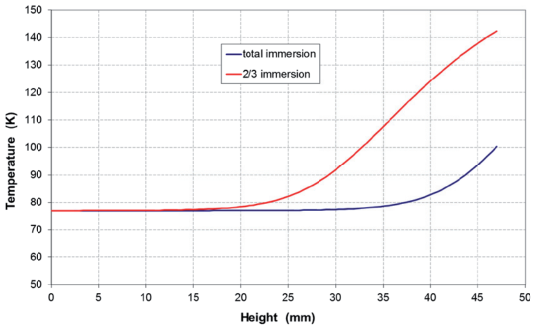

Fig. 16: *Development of temperature along height of active carbon during total and 2/3 immersion.*

To ensure reproducibility of individual measurements it is essential to observe the amount of liquid nitrogen at a minimum height of 48 mm. In the case of evaporating nitrogen due to heat flows into the tank is necessary decrease of the level of LN_2 to amend and the immersion maintain the same level.

4. Conclusions

Based on numerical simulation, it can be reported, that kinetics of heat transfer during cooling of the tank are on high level. However, during cooling is needed to keep sufficient height of liquid nitrogen to ensure constant temperature along all height of tank. During the process of measurement of the hydrogen storage capacities occurs to a gradual decrease in the level of liquid nitrogen (slow evaporation).

This state is due to supplying heat flux over the insulation of Dewar tank and holder steel tank. By reducing the level about 1/3 the height of the storage tank there is a significant temperature increase in the upper layers of the carbon material. This result decreases Van der Waals attractive forces which it binds hydrogen to the surface of carbon by adsorption. This increases the pressure of hydrogen and the process of measurement of storage capacity may exhibit distorted and inaccurate data. Given the above facts, it must be observed it is necessary to observe the constant height level of liquid nitrogen during measuring.

5. Acknowledgments

The authors would like to express their gratitude to Scientific Grant Agency APPV for the support of this work under projects No. APVV-15-0202, to Scientific Grant Agency VEGA for the support of this work under projects No. 1/0752/16 and to Scientific Grant Agency KEGA for the support of this work under projects No. 005TUKE-4/2016.

References and Notes

[1] BRESTOVIČ, T., JASMINSKÁ, N., LÁZÁR, M., KORBA, J. Adsorpcia vodíka na materiály s veľkou plochou povrchu. In: Plynár, vodár, kúrenár + klimatizácia. Roč. 12, č. 6 (2014), s. 40-42. ISSN 1335-9614.[2] COP, V.: Development projects of production techniques and technologies. SPINEA s r.o., Presov, 2005.

[2] BRESTOVIČ, T., JASMINSKÁ, N. Uskladňovanie vodíka v uhlíkových štruktúrach. In: 5. Cassotherm. Elsewa, 2013 S. 46-51. ISBN 978-80-89385-24-9.

[3] XIAO, Z. CH., ZHI, P. CH., YI, J. Z., et al. Adsorption dynamics of hydrogen and deuterium in a carbon molecular sieve bed at 77 K. In: Separation and Purification Technology, Vol. 146, 2015, p. 168-175.

[4] JASMINSKÁ, N., BRESTOVIČ, T. et al. Evaluation of hydrogen storage capacities on individual adsorbents. In: Measurement. No. 56 (2014), p. 219-230. ISSN 0263-2241.

[5] JASMINSKÁ, N., BRESTOVIČ, T., ČARNOGURSKÁ, M. Vodíkové technológie na TUKE. In: 32. stretnutie katedier mechaniky tekutín a termomechaniky. Žilina, 2013 s. 95-98. ISBN 978-80-554-0715-9.

[6] XIAOFENG, Y., RAAEN, S. The influence of potassium doping on hydrogen adsorption on carbon nanocone material studied by thermal desorption and photoemission. In: Applied Surface Science, Vol. 270, 2013, p. 364-369.

[7] JASMINSKÁ, N., BRESTOVIČ, T. New trends in hydrogen adsorption storage. In: Abidance of scientific evolution. Roč. 2, č. 1 (2013), s. 13-18. ISSN 1338-4996.

[8] ZHEVAGO, N. K. Other methods for the physical storage of hydrogen. Compendium of Hydrogen Energy, 2016, p.189-218.

[9] HE, L., MELNNICHENKO, Y. B. et al. Investigation of morphol-

ogy and hydrogen adsorption capacity of disordered carbons. In: Carbon, Volume 80, December 2014, Pages 82-90.

Biographical notes

Tomáš Brestovič, doc. Ing., PhD.: *(1982). Associate professor in the program Power Engineering Machinery and Equipment. He works as Deputy Head of Department of Power Engineering at Faculty of Mechanical Engineering at Technical University in Košice. He is graduate at Faculty of Mechanical Engineering at Technical University in Košice in 2006. He vindicated the dissertation thesis in 2009 and he habilitated in the program Power Engineering Machinery and Equipment in 2012. The focus of hisscientific research area is the area of hydrogen technology, heat and mass transfer and fluid flow simulation. He is principal investigator of the project VEGA and APVV and he is a deputy of investigator of the project KEGA. He engaged in six national projects (VEGA and AV) and six projects OP VaV from structural funds EU as co-solver He participated on ten assignments for practice as co-solver. The hitherto results of the scientific research work have been published in 80 indigenous works in the domestic and foreign journals and scientific. Eight of them was publicized in the current content and nine articles was publicized as indexed in Scopus.*

Natália Jasminská, doc. Ing., PhD.: *(1983). Personal assistant in the Department of Power Engineering. She habilitated on the Faculty of Metallurgy in 2007 on Technical University in Košice. She vindicated the dissertation thesis in 2010 in the program Power Engineering Machinery and Equipment. She focuses in the area of thermal technique, hydrogen technology and alternative sources of energy. She is principal investigator of the grant project KEGA. She engaged in six domestic projects (VEGA, APVV, AV) and five projects OP VaV from structural funds EU and five problems from practise as co-solver. Within solution of the research tasks she has authored and co-authored more than 85 indigenous works in domestic and foreign journals and collections. Five of these works was publicized in the current content and nine works was publicized as indexed in Scopus.*

Marián Lázár, doc. Ing., PhD.: *(1985). He is a research scientist and graduate of Faculty of Mechanical Engineering, Technical University in Košice. His scientific and research work focuses on the field of waste treatment by plasma technology, renewable energy resources and in the area of production and storage of hydrogen.*

Ľubica Bednárová, Ing.: *(1990). Doctoral student of the energy technique. She is graduate at Faculty of Mechanical Engineering at Technical University in Košice (2015) on Department of Power Engineering. She focuses to area of hydrogen technology and renewable source of energy. She engaged in the three domestic grant projects (VEGA, KEGA, APVV) as a co - solver. The hitherto results of the scientific research work have been published in domestic and foreign scientific journals and collections. One of these works was publicized in current content and one works was publicized as indexed in Scopus.*