ELSEVIER

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod



Water vapor plasma technology for biomass conversion to synthetic gas

V. Grigaitienė*, V. Snapkauskienė, P. Valatkevičius, A. Tamošiūnas, V. Valinčius

Plasma Processing Laboratory, Lithuanian Energy Institute, Breslaujos Str. 3, LT-44403 Kaunas, Lithuania

ARTICLE INFO

Article history:
Received 15 June 2010
Received in revised form
19 November 2010
Accepted 6 December 2010
Available online 26 January 2011

Keywords:
Water vapor plasma jet
DC plasma torch
Optical emission
Biomass conversion technology
Thermal treatment

ABSTRACT

This study presents the results of experimental investigation on the development of water vapor plasma technology for conversion of biomass and destruction of hazardous substances. Similar plasma technology is also foreseen for the synthesis of micro- and nanostructured catalytic coatings for wide range of applications.

An experimental DC plasma torch with button type hot cathode and step formed copper anode, operating at atmospheric pressure has been developed, tested and employed. The following main tasks of this research have been solved: (i) experimental facility was constructed and water vapour plasma generation process was practically realized; (ii) thermal and electrical characteristics of water vapour plasma generator were investigated and plasma jet characteristics were established; (iii) the real operating condition of plasma facility was analyzed.

This work includes the analysis of operating characteristics of water vapour plasma system which were investigated in the following range of plasma source parameters: power of plasma torch was 25–45 kW; arc current was 140–180 Å, the arc voltage was 172–231 Å, the efficiency was 0.5–0.78, the average temperature of water vapour plasma jet in exhaust nozzle was 2600–3500 K, and the plasma jet velocity was 200–310 m s⁻¹. Holding the temperature above 2300 K and water vapour flow rate at 1321 min⁻¹, it is possible to reach the sufficient conditions for the biomass conversion to syngas. Spectral analysis of plasma jet outflowing from plasma torch exhaust nozzle showed that water vapour plasma contains an increased amount of hydrogen that is usable in many plasma chemical processes. The summarized results can help to calculate and design gasification systems of biomass, to establish optimal parameters for stable operation of plasma generator and regulate the process parameters.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Waste management is an important issue in the European countries nowadays. Lithuania is one of the leading countries in the European Union according to the amount of biomass per one habitant [1]. One of the biggest potential is solid biomass (residues of forest logs and energetic plants), also straw, municipal waste, domestic residues, etc. which need destruction or recycling. The most promising are technologies allowing not only to destruct waste or to reduce their volume, but which are also capable of obtaining products for further commercial use. A great deal of methods and technologies of biomass conversion into bio-fuels have been created and developed recently in the world (Fig. 1).

One of the latest and less explored technologies is plasma gasification which is an advanced and environmentally friendly process of converting different kinds of waste materials to further usable by-products. Plasma is considered as a 4th state of matter with unique properties that cannot be found in nature. The existing

designs of plasma generators can be divided into two basic groups: direct current (DC) plasma torches [2] and alternating current (AC) plasma torches [3,4]. A DC plasma torch consists of two water cooled electrodes and anode which is shaped in the form of a nozzle. Gasification using this plasma technology offers some unique advantages for biomass conversion, such as providing high temperature and heating rate, in comparison to other thermal methods. It also offers the possibility of decomposition of biomass by pure pyrolysis in the absence of oxygen. When the waste is exposed to the plasma, it is heated to a high temperature above 2000 °C. A very intensive heat exchange causes the organic compounds in the waste to dissociate into very simple atoms and molecules such as hydrogen, carbon dioxide, carbon monoxide, methane, water vapor, etc. very quickly and provide a potential solution for the problems that occur in conventional pyrolysis processes [5,6].

The production of synthetic gas from wood using AC air plasma torches is discussed in [7]. However, AC plasma torches are not used widely yet. This is related to additional difficulties caused by the variation of electrical parameters used for the plasma generation with time. The coal gasification and production of hydrogen in air and steam plasma using both the DC and AC torches were studied in several papers [8,9] and were found to be a very effective method.

^{*} Corresponding author. Fax: +370 37 351271. E-mail address: vika@mail.lei.lt (V. Grigaitienė).

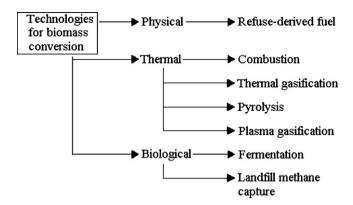


Fig. 1. Technology alternatives for biomass conversion.

Biomass is an organic compound mostly made of carbon and hydrogen molecules, which participate in chemical reactions. Some authors [10,11] proposed that there are few main reactions of biomass plasma gasification.

Reactions in the presence of oxygen:

$$C + O_2 \rightarrow CO_2 + 406 \,\text{MJ} \,\text{kmol}^{-1},$$
 (1)

$$2C + O_2 \rightarrow 2CO + 246 \,\text{MJ} \,\text{kmol}^{-1};$$
 (2)

Boudouard reaction:

$$CO_2 + C \rightarrow 2CO + 173 \,\mathrm{MJ \, kmol^{-1}};$$
 (3)

Water shift reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O - 41 \text{ MJ kmol}^{-1};$$
 (4)

Water steam reaction at 500–600 °C temperature:

$$C + 2H_2O \rightarrow CO_2 + 2H_2 - 90 \,\text{MJ} \,\text{kmol}^{-1};$$
 (5)

and at >900 °C temperature:

$$C + H_2O \rightarrow CO + H_2 + 130 \,\text{MJ} \,\text{kmol}^{-1};$$
 (6)

Methane production reaction:

$$C + 2H_2 \rightarrow CH_4 - 75 \,\text{MJ} \,\text{kmol}^{-1}$$
. (7)

It is visible from the reactions listed above that water steam content can increase the production of H_2 and CO_2 . The main reactions show that heat is required during the reaction process. The organic compounds are thermally decomposed into simple compounds, such as synthetic gas (CO and H_2) or their constituent elements. As an example, the composition of synthetic gas after plasma gasification of crushed wood is 61.6% of hydrogen and 35.2% of carbon monoxide; enthalpy is 22.8 MJ kg $^{-1}$ [12].

The main advantage of plasma gasification is a better control of the composition of synthetic gas and reduction of the amount of unwanted tar, carbon dioxide and hydrocarbons [13]. The advantages of thermal plasma based technologies over conventional incineration include higher temperatures, independence of additional fuel and shorter residence times [14], also, the prevention or reduction undesired pollutants in the by-products and final product [15].

It is well known that mass enthalpy of water vapor is about six times higher than the mass enthalpy of air at temperatures of 4000–5000 K (Fig. 2). Several times more power than the same amount of air is necessary to heat water vapor up to the required temperature. In comparison, the distribution of oxygen and hydrogen enthalpies is showed in Fig. 2 which suggests that the reaction of hydrogen formation requires very high energy.

It means that decomposition of biomass by water vapor is a highly endothermic process. Therefore, the temperature of water

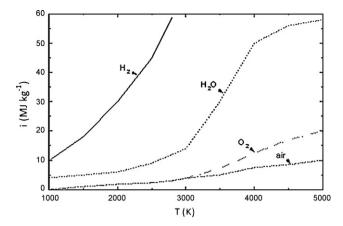


Fig. 2. The dependence of hydrogen, water vapor, oxygen and air enthalpies on the temperature at 1 bar pressure.

vapor has to be much higher than the temperature of chemical reactions. Thus, electrical energy provides the energy need for the plasma torch which then transfers it to the substances to be treated.

Water vapor begins to dissociate above 2000 K [16] (Fig. 3) and at 4000 K it is no longer water vapor. The plasma flow consists only of O_2 , H_2 molecules and O, H, OH radicals.

The optical emission spectroscopy method was applied to identify the species present in the plasma jet. Optical emission spectroscopy, which measures the light emitted from the plasma as a function of wavelength, time and location, is the most commonly used plasma diagnostic probe for plasma processing. Since it is non-intrusive, inexpensive, and can be easily applied into plasma processing system, it quickly gains popularity in the plasma spraying industry for monitoring the plasma processing. However, large information content makes the interpretation of the spectra difficult. For this reason, it is primarily used as a "fingerprint" of the plasma species identification. As a research and development tool, it can be very useful in understanding the basic processes within plasma. It can be quite effective and quantitative if combined with other measurements. According to the stated above, the main goal of this work is to develop a water vapor plasma torch for conversion of biomass and organic waste.

2. Methodology and equipment

The experimental water vapor plasma system was projected and designed at Lithuanian Energy Institute by the staff of Plasma Pro-

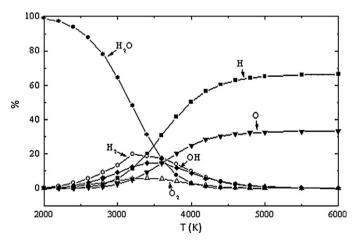


Fig. 3. The dependence of the percentage composition of water vapor on the temperature at 1 bar pressure.

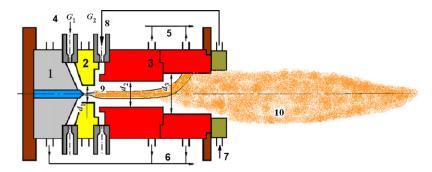


Fig. 4. A schematic view of water vapor plasma torch. (1) Cathode junction, (2, 4, 8) neutral section, (3) step formed anode, (5) cooling water supply, (6) water exhaust, (7) water vapor supply, (8) overheated water vapor, (9) electric arc, (10) plasma jet, (G_1) argon gas supply, (G_2) water vapour supply.

cessing Laboratory (Fig. 4). It consists of a linear DC plasma torch $30\text{--}40\,\text{kW}$ of power with button type hot tungsten cathode (Fig. 4, position 1) and a step-formed copper anode (Fig. 4 position 3). The equipment also contains the systems of power supply and regulation, torch cooling, water vapour and gas feeding. The system is operating under the atmospheric pressure. The electrodes of plasma torch are separated by insulation rings (Fig. 4, position 2), which have an inlet hools for tangential supply of shielding gas and main plasma forming gas. The DC water vapor plasma torch, operating at atmospheric pressure at arc current strength I = 140– $180\,\text{A}$, arc voltage U = 180– $250\,\text{V}$, power P = 25– $45\,\text{kW}$, Argon gas flow rate G_1 = $18.2\,\text{l}\,\text{min}^{-1}$, and water vapor flow rate G_2 = 128– $133\,\text{l}\,\text{min}^{-1}$, has been employed. The average temperature of flow at the torch outlet nozzle varied within the limits of T = 2600– $3500\,\text{K}$.

When a DC arc is ignited between the cathode and anode and the feeding gas is introduced in the reaction chamber of the plasma torch, the arc is pushed through the nozzle and high temperature, and high velocity plasma jet is generated. Due to the arc shunting process suppression and the life-time of the electrode prolongation, the stair-step shape to the copper anode has been provided. The dynamical stabilization of electric arc and protection of the cathode from erosion has been applied using argon (Ar) as shielding gas. The amount of shield Ar to ensure good shielding effect depends on the current strength and type of plasma forming gas used, which is about 10-20% of the total mass flow rate. The main plasma forming gas is the overheated water vapor, which is produced using a 5 bar of pressure water steam generator. The mass flows of the source gases as water vapor and shielding gas are regulated by the mass flow controllers. The characteristics of the plasma torch and parameters of plasma jet were determined from the heat conservation calculations while measuring current strength in the circuit, voltage drop and gas flow rates. Heat lost to the cooling water was determined, average flow temperature and velocity was calculated and the value of efficiency η of the plasma torch was established. The electrical characteristics of the linear, sectional plasma generator with step-formed anode are generalized employing the theory of similarity of electrical processes as follows [17]:

$$\frac{Ud}{I} = A \left(\frac{I^2}{Gd}\right)^m \left(\frac{G}{d}\right)^n (pd)^k \left(\frac{l}{d}\right)^r \tag{8}$$

where U is arc voltage (V); I, arc current (A); d, anode diameter (m); G, total gas flow rate (kg s⁻¹); p, pressure in the arc chamber (Pa); I, length of the anode (m); A, m, n, k and x constant values depending on plasma torch construction and operating regime.

The performance of plasma torch can be evaluated by its efficiency η , which indicates what part of the generated energy is transferred to the gas:

$$\eta = Gd(UI). \tag{9}$$

Generalization of the thermal characteristics of the plasma torch is similar to the generalization of electrical characteristics:

$$\frac{(1-\eta)}{\eta} = B\left(\frac{I^2}{Gd}\right)^{m2} \left(\frac{G}{d}\right)^{n2} (pd)^{k2} \left(\frac{I}{d}\right)^{r2} \tag{10}$$

where ${\it B}$ is a constant established from the dependence of efficiency from arc current.

In order to understand plasma chemistry, optical emission spectroscopy (OES) for various plasma processes diagnostic was used. OES was developed to quantify various reactive species in the plasma and provides a non-intrusive analysis to investigate atoms, ions and molecules within plasma, and information about plasma properties.

Spectral analysis was provided using an acousto-optic emission spectrometer IFU AOS4, which operates on the basis of a tuneable acousto-optical filter (AOTF). The spectrometer has a solid state monochromator/grating, which measures emission wavelengths between 250 and 800 nm with an excellent spectral resolution between 0.05 nm (250 nm) and 0.5 nm (800 nm). The schematic view of the optical emission analysis system is shown in Fig. 5. It consists of an initial optical system, a spectrometer with a photomultiplier detector system, including computer control. The optical lens collimator of 5 mm diameter and 2 m long optical fiber was used to focus the axial center of the flowing plasma jet. The focal distance was 0.08 m. The fiber directs emission from plasma into the optical interface located at the entrance pinhole of the grating spectrometer. In this manner, the spectra from emitting plasma jet are observed.

3. Results and discussion

The measurements were carried out varying the arc current strength and overheating it up to $473-573 \, \text{K}$ temperature, water vapor flow rate G_2 , tangentially injected into the plasma torch. Generated plasma jet was slightly unstable. The main operational

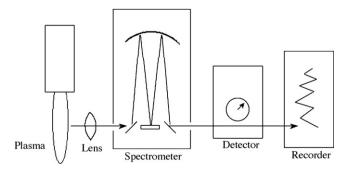


Fig. 5. The schematic presentation of an optical system for the analysis of photoemission from plasma.



Fig. 6. Water vapor plasma torch in operation.

Table 1Experimental parameters of water vapor plasma torch and plasma jet.

Arc current (A)	138-182
Arc voltage (V)	179-260
Arc power (kW)	29-39
Power loss to the cooling water (kW)	11-16
Power available for plasma jet (kW)	16-26
Torch efficiency, η (%)	51-70
Argon gas flow rate, G_1 (1 min ⁻¹)	18.2
Water vapor flow rate, G_2 (1 min^{-1})	128-133
Total mass flow rate, $G(1 \text{ min}^{-1})$	146-152
Average temperature of plasma jet at the torch outlet nozzle (K)	2600-3500
Velocity of plasma jet at the torch exhaust nozzle (m s ⁻¹)	211-311
Diameter of stair-step anode, d_2 (10 ⁻³ m)	8
Diameter of stair-step anode, d_3 (10 ⁻³ m)	14

characteristics of plasma torch and plasma jet were established and are given in Table 1 and Fig. 6 which shows water vapor plasma processing in operation. The magnitude of applied current, voltage and the total mass flow rate are selected as the prime variables in experiments.

To ensure a stable work of the water vapor plasma torch, rising or steady voltage-current characteristics (VCC) are desirable. A general estimating equation for determination of VCC were estimated using the theory of similarity and is presented below in (11). The general results are depicted in Fig. 7.

The VCC of water vapor plasma torch are strongly dependent on the type of working gas and shield gas and their mass flow rate. It also depends on the physical characteristics of the gas, i.e. density, viscosity, conductivity and etc. The VCCs of the PG investigated are described by the following relationship:

$$\frac{Ud_2}{I} = 3 \times 10^3 \left(\frac{I^2}{Gd}\right)^{-0.6} \tag{11}$$

where U is voltage (V); d_2 , diameter of anode (m); I, the arc current (A); G, the total mass flow rate (kg s⁻¹).

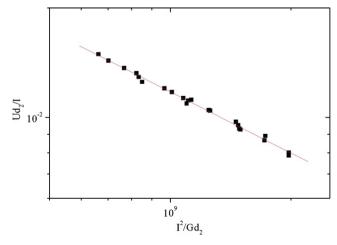


Fig. 7. Voltage-current characteristics of water vapor plasma torch.

The knowledge of geometry of plasma generator and its VCC helps to determine the temperature and velocity of the plasma jet at the exhaust nozzle.

The general results of plasma torch thermal efficiency (Fig. 8) were estimated using the theory of similarity for thermal processes and were summarized into one equation. The general estimated equation for determination of efficiency is presented below in (12).

$$\frac{(1-h)}{h} = 1.65 \times 10^{-3} \left(\frac{I^2}{Gd_2}\right)^{0.26}.$$
 (12)

It enables estimating any magnitude of plasma torch thermal efficiency. The results from Fig. 8 and (12) are taken into account when designing plasma generator for decomposition of biomass and organic waste.

Thermal and dynamic parameters of plasma jet have the most influence on the effective thermal plasma gasification of biomass and organic waste. The additional regulating resistors are not required and the thermal efficiency of water vapor plasma torch increases while increasing the water vapor flow rate. The plasma torch works steady then the flow rate of water vapor-Ar is in the range of 148, 150 and 152 l min⁻¹ at the current strength of electric arc variation in the range of 138–174 A.

This newly designed water vapor plasma torch has some advantages such as there are no hot moving parts with additional mechanisms to wear them out and the cooling system is not complicated, the plasma torch can work stable at low flow rates of Ar as shielding gas or without Ar if hafnium cathode is used.

To investigate the processes occurring in the water vapor plasma flow, the OES has been employed as well. Figs. 9 and 10 present the optical emission spectrum, measured for water vapour-Ar plasma jet at the 5 mm from exhaust nozzle. The measured field was approximately 4° . The experiment conditions in emission spectra measuring (Fig. 9) were the following: power of plasma torch P=31.8 kW, argon gas flow rate $G_1=18.2$ l min $^{-1}$ and water vapor flow rate $G_2=146$ l min $^{-1}$. The measurements performed to obtain the results depicted in Fig. 10 were established accordingly to

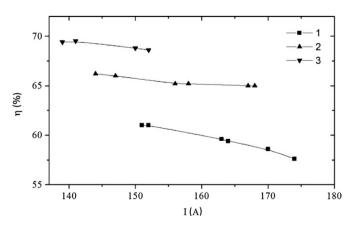


Fig. 8. The dependence of plasma torch thermal efficiency on the current strength and water vapor-Ar flow rate, I min⁻¹: 1–148; 2–150; 3–152.

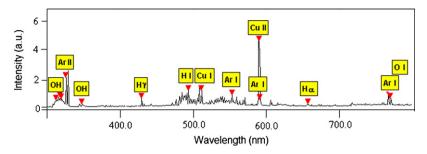


Fig. 9. Optical emission spectrum of Ar (as shield gas)—water vapor plasma at P = 31 kW, water vapor flow rate $G_2 = 129$ l min⁻¹.

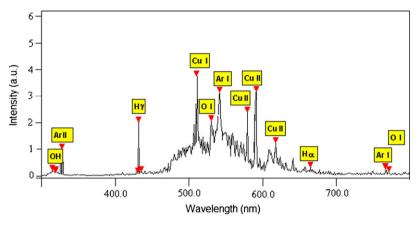


Fig. 10. Optical emission spectrum of Ar (as shield gas)—water vapor plasma, power of plasma torch at P = 37 kW, water vapor flow rate $G_2 = 133 \text{ l min}^{-1}$.

P=37 kW, $G_1=18.21$ min⁻¹ and $G_2=1331$ min⁻¹. It can be seen that the most intense spectral lines are situated in the zones of cyan, green and orange part of the spectrum around 500–590 nm. The emission spectra consisted of OH, hydrogen (HI), excited argon (Ar I), copper (Cu I) and oxygen (O II) lines. The intensity of Cu was much larger than those of H and O. It is considered that the copper anode is emitting copper radicals in the plasma. The major OH peak is located at 306.4 nm band, the Hγ peak, which belongs to the Balmer series, is located at 434.0 nm and O peak is located at 533.1 nm. The H peak is extremely prominent (Fig. 10). Therefore, it was confirmed that the water vapor plasma was decomposed into H, OH and O radicals. Beside these important groups of spectral lines, the spectrum contains a large number of other lines with variable intensities, making the plasma emission spectrum rather complicated.

It appears that the water vapor plasma discharge emits quite a complicated spectrum. Indeed, as the review papers usually report on glow discharge analytical spectrometry, e.g. [18,19], one of the advantages of mass spectrometry, as an analytical technique compared with the optical emission spectrometry, is that the mass spectra are much simpler than line-rich optical spectra; thus, they suffer less from spectral interferences.

In the world-wide scientific sources some other researches report about using OES for water vapor plasma flow [5,20]. However, these studies have been performed in the vacuum conditions; thus, the lack of information in water vapor plasma at atmospheric pressure still exists. Additionally, an exact comparison of the results is not possible due to the different discharge conditions in the reacting arc zone and plasma torch constructional particularities and geometries; therefore, different positions of the spectral line intensities were recorded.

4. Conclusions

An experimental linear DC water vapor plasma torch with hot button-type cathode step-formed anode operating at atmospheric pressure has been designed, tested and found to be suitable for biomass conversion. The average temperature of flow at the torch exhaust nozzle varied within the limits of $T=2600-3500 \, \text{K}$. The maximal plasma torch thermal efficiency was up to 0.7.

Analyzing the electrical and thermal characteristics of water vapor plasma torch, it has been determined that the rising arc current leads to the decrease of arc resistance. Thus, the arc voltage decreases due to the reduced resistance, which ensures the stable work of the plasma torch.

The $\rm H_2O$ vapor plasma was characterized by the optical emission spectrum analysis and was observed to surely decompose into H, OH and O radicals. The present study shows that the most intense lines in the emission spectrum are situated between 434 and 620 nm.

The presented plasma torch is absolutely suitable for biomass conversion purpose. To conclude, it is important to notice that water vapor plasma is very attractive for production of high-energy synthetic gas from different organic matters which could be used in the heat exchangers of different assignments.

Although important research progress in this area has been made in recent years, there are still considerable technical challenges to be faced in developing and modifying thermal plasma pyrolysis process for industrial applications. Summarized results can help to calculate and design gasification systems of biomass, to establish optimal parameters for stable operation of plasma generator and regulate the process parameters.

Acknowledgements

The research was partly supported by the Research Council of Lithuania and the European Union (European Regional Development Fund). Thanks to COST Action CM0903 for supporting cooperation among scientists and researchers.

References

- Report of Lithuanian Biomass Energy Association LITBIOMA, 2010–2020. Plan of Promotion of Lithuanian Renewable Energy Sources, Vilnius, 2008, pp. 50–59.
- [2] A.S. Koroteev, V. Mironov, Yu. S. Mand Svirchuk, Plasma Generators: Designs, Characteristics, Calculation, Moscow, 1993, p. 84 (in Russian).
- [3] I.A. Glebov, Ph.G. Rutberg, Powerful Plasma Generators, Moscow, 1985.
- [4] Ph.G. Rutberg, A.A. Safronov, V.L. Goryachev, Strong-current arc discharge of alternating current, IEEE Trans. Plasma Sci., 26 ITPSBD, 1998, pp. 1297–306, ISSN 0093-3813.
- [5] H. Nishikawa, M. Ibe, M. Tanaka, M. Ushio, T. Takemoto, K. Tanaka, N. Tanahashi, T. Ito, Vacuum 73 (2004) 589–593.
- [6] M. Tendler, P. Rutberg, G. van Oost, Plasma based waste treatment and energy production, Plasma Phys. Contr. F. 47 (5A) (2005) A219–A230.
- [7] P.G. Rutberg, A.N. Bratsev, A.A. Ufimtsev, Plasmachemical technologies for processing of hydrocarbonic raw material with syngas production, J. High Temp. Process 8 (3) (2004) 433–446.
- [8] B. Mikhailov, in: O.P. Solonenko, M.F. Zhukov (Eds.), Plasma Gasification of Coal, Thermal Plasma and New Materials Technology, vol. 2, Cambridge Interscience Publishers, Cambridge, 1995, pp. 345–369.
- [9] I.M. Zasypkin, G.V. Nozdrenko, Production of acetylene and synthesis gas from coal by plasma chemical methods, in: O.P. Solonenko (Ed.), Thermal Plasma Torches and Technologies, vol. 2, Cambridge Interscience Publishers, Cambridge, 2001, pp. 234–243.

- [10] A. Demirbas, Hydrogen production from biomass by the gasification process, Energy Sources 24 (2002) 59–68.
- [11] CH.Y. Wereko-Brobby, E.B. Hagan, Biomass Conversion and Technology, Chichester, John Willey & Sons, 1996, 203 p, ISBN 0-471-96426-5.
- [12] R. Juskevicius, P. Valatkevicius, Thermal and Plasma Gasification of Solid Fuel, Energetic 4 (1997) 24–28.
- [13] G. Van Oost, M. Hrabovsky, V. Kopecky, M. Konrad, M. Hlina, A. Chumak, E. Beeckman, J. Verstraeten, Pyrolysis of waste using a hybrid argon-water stabilized torch, Vacuum 80 (2006) 1132–1137.
- [14] R. Kezelis, V. Mecius, V. Valinciute, V. Valincius, High Temp. Mater. 8 (2004) 273–282.
- [15] M. Hlina, M. Hrabovsky, V. Kopecky, M. Konrad, T. Kavka, S. Skoblja, Chech. J. Phys. 56 (2) (2006) B1179–B1184.
- [16] N.B. Vargaftik, Handbook of Physical Properties of Liquids and Gases, Moscow, Nauka, 1972, 625 p, ISBN 0-470-90310-4.
- [17] M.F. Zhukov, A.S. Anjshakov, I.M. Zasipkin, J.V. Kurochkin, V.P. Lukashov, A.V. Pustogarov, Electric Arc Generators with the Interelectrode Inserts, Novosibirsk, Nauka, 1981.
- [18] W.W. Harrison, K.R. Hess, R.K. Marcus, F.L. King, Anal. Chem. 58 (1986) 341A.
- [19] W.W. Harrison, C.M. Barshick, J.A. Klingler, P.H. Ratliff, Y. Mei, Anal. Chem. 62
- [20] İ. Serdyukov, Yu. Poplavskii, A.L.N. Sinitsa, Investigation of the water vapor emission spectrum in the region 9600–12,000 cm⁻¹, Opt. Spectrosc. 4 (101) (2006) 532–536