Open Access Journal

Journal of Power Technologies 9x (x) (2013) 1–7

journal homepage:papers.itc.pw.edu.pl

Biofuels as Fuels for High Temperature Fuel Cells

Jarosław Milewski*, Janusz Lewandowski

Warsaw University of Technology, Institute of Heat Engineering
21/25 Nowowiejska Street, 00-665 Warsaw, Poland

Abstract

Based on mathematical modeling and numerical simulations, influences of various biofuels on high temperature fuel cell performance are presented.

Governing equations of high temperature fuel cell modeling are given. Adequate simulators of both SOFC and MCFC have been done and described. Performances of these fuel cells with different biofuels are shown. Some characteristics are given and described. Advantages and disadvantages of various biofuels from system performance point of view are pointed out.

An analysis of various biofuels as fuels for Solid Oxide Fuel Cell (SOFC) and Molten Carbonate Fuel Cell (MCFC) is presented. The results are compared with Natural Gas (NG) as a reference fuel. The biofuels are characterized by both lower efficiency and lower fuel utilization factors in comparison with NG. The presented results are based on a 0D mathematical model in design point calculation. The governing equations of the model are presented.

Keywords: biogases, molten carbonate fuel cell, mathematical model

1. Introduction

Fuel price inflation and a long-term increase in electricity consumption have provided added impetus to the search for ultra-effective power generation systems. Classical power stations meet their highest possible efficiency [1–4], and it is not predicted that significant improvements are possible here. Fuel cells generate power in electrochemical reactions with potentially ultra-high efficiency by coupling them with a gas turbine [5, 6]. High-temperature fuel cells (mainly SOFC [7–11] and MCFC [12–14]) are considered as future electricity sources. Presently, state-of-the-art hybrid systems including SOFC and MCFC are being built in the 250 kW–11 MW power range. Research and development in this field is predicted to result in an increase in the power of those kinds of systems in the future.

Hydrogen and Natural Gas are currently considered to be the main fuels for fuel cells. Hydrogen is an ideal fuel with respect to fuel cell working conditions [15]. Unfortunately, hydrogen is not present in the environment in an uncombined form and there are difficulties with production, transportation and storage. Natural Gas, meanwhile, is considered to be an interim fuel due to limited resources.

The most plausible future scenarios in the power markets are as follows:

1. Abandoning gas/liquid/solid fuels in favour of electricity generated by renewable sources and/or nuclear plants. In this case, the energy distribution role will be provided by the power

Email address: milewski@itc.pw.edu.pl (Jarosław Milewski*)

grid, and the storage role by consumers.

2. Production of plant-derived gas/liquid fuels based on the cultivation of plants and shrubs [16, 17], such as e.g. Salix Viminalis and their conversion into fuel, e.g. alcohols.

Using electricity only can be problematic (e.g. airplanes), the cultivation of “energy” seems to be one of the most possible scenarios for the future.

2. Biofuels

Biofuel is defined as a solid, liquid or gaseous fuel obtained from relatively recently lifeless or living biological material and is differs from fossil fuels, which are derived from long dead biological material. The use of biogases in fuel cells has been relatively poorly investigated. Some data can be found in [18–20]. The presented analysis considers biofuels obtained by biomass gasification as well as fermentation processes. Taken into consideration were the following biofuels: biogases (Anaerobic Digester Gas—ADG, Landfill Gas—LFG); bio-liquids (methanol, ethanol, canola oil); solids—wood. Hydrogen and methane were used as the reference fuels.

Anaerobic digestion is series of processes in which microorganisms break down biodegradable material in the absence of oxygen. The presented analysis considers ADG produced by wastewater treatment plants.

Landfill gas is produced by wet organic waste fermentation under anaerobic conditions in a landfill site. The waste is covered and compressed both mechanically and by the weight of the material that is deposited from above. This material prevents oxygen from accessing the waste thereby encouraging anaerobic microbes to thrive and produce gas, which slowly escapes and is captured.

The composition of LFG and ADG are listed in Table 1, those types of gases consist mainly of methane and carbon dioxide.

Canola is one of two cultivars of rapeseed or Brassica campestris. The canola oil is considered an alternative fuel to diesel, and is so-called a bio-diesel. It is made by extracting oil from the seeds. The process can take place at an elevated temperature what gives an oil which consists mainly of long-chain hydrocarbon fatty acids (see Table 3.)

Table 1: Typical compositions of biogases

Component	Landfill Gas	Anaerobic Digester Gas
CH_4	54%	63%
CO_2	33%	35%
Other	13%	2.0%
Initial s/c ratio	0.15	0.02

Wood is composed mainly of lignin, cellulose, and hemicelluloses (see Table 3). The structure of hemicelluloses is very similar to the cellulose itself, so in the presented analysis it was assumed that the wood delivered to the gasifier consisted only of cellulose (75%) and lignin (25%).

Carbon deposition is a harmful process that causes very rapid degradation of fuel cells and the reformer [24] by carbon covering fuel cell area. To avoid this process, adequate amount of steam is necessary to be added to the fuel. This can be realized by re-cycling some part of anode-off gases [25]. Various kinds of factors are used to describe adequate steam content in hydrocarbon fuel to avoid carbon deposition. For gaseous hydrocarbon fuel, the most commonly used factor is the steam-to-carbon ratio (s/c ratio). Mostly, the s/c ratio is set at about 2 and above this value no carbon deposition takes place. Boundary values of the s/c ratio are dependent on temperature. Based on a review of the literature, typical factors and theirs definitions for various fuels are listed in Table 4.

3. Theory

The presented results are based on calculations made using an order reduced mathematical models [26, 27]. Those calculations are based on the Lee-Kesler equation of the state and minimization of Gibbs free energy [28].

The maximum voltage of the fuel cell depends on the type of reaction occurring on the electrode surfaces. Biogases in reaction with oxygen can give various maximum voltages. Mixtures of various components occur in the case of the analyzed fuels. The maximum voltages for various reactions are listed in Table 5.

Table 2: Typical composition of Canola oil

Component	Chemical structure	Molar fraction, %
Oleic acid	CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$-COOH	75
Linoleic acid	CH_3-$(CH_2)_4$-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH	15
α-Linolenic acid	CH_3-CH2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH	10

Table 3: Typical composition of wood

Component	Chemical structure	Molar fraction, %
Cellulose	…-OH-CH_2-$(CH\text{-}O)_2$-$(CH_2O)_2$-CH-…	50
Hemicelluloses	…-OH-CH_2-$(CH\text{-}O)_2$-$(CH_2O)_2$-CH-…	24
Lignin	…-OH-CH_2-CH=CH-$(CH{=}C)_2$-OH-CH=C-CH_3O-…	23

Table 4: Factors used for steam content calculations

Bio-fuel	Factor name and reference	Definition (by molar fractions)	Value assumed during calculations
Biogases, Canola Oil Syngas, Wood Syngas	steam to carbon ratio [21]	$\frac{H_2O}{CH_4+CO}$	1.4
bio-Methanol	steam to methanol ratio [22]	$\frac{H_2O}{CH_3OH}$	1
bio-Ethanol	steam to ethanol ratio [23]	$\frac{H_2O}{C_2H_5OH}$	3

Table 5: Maximum voltages for various reactions

Component	Chemical Reaction	Maximum Voltage, E_{max}, V
H_2	H_2 + 1/2O_2 H_2O	1.23
CH_4	CH_4 + 2O_2 CO_2 + H_2O	1.06
CH_3OH	CH_3OH + 3/2O_2 CO_2 + 2H_2O	1.22
C	C + O_2 CO_2	1.03
C	C + 1/2O_2 CO	0.72
CO	CO + 1/2O_2 CO_2	1.34

Table 6: Main parameters of fuel cell models

	SOFC	MCFC
Anode inlet pressure, bar	1	1
Cathode inlet pressure, bar	1	1
Working temperature, °C	800	650

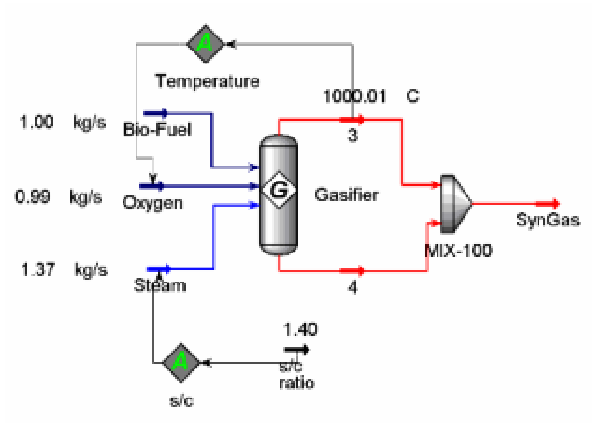

Figure 1: Gasifier model

The governing equations of the SOFC model are presented in the previous works [26, 29], whereas for the MCFC in paper [27].The presented analysis considers a design point estimation of the SOFC and MCFC. This means that the value of maximum current density (i_{max}) is constant. The other model assumptions are listed in Table 6.

The mixture of various hydrocarbons enters into the SOFC anode, so the fuel utilization factor is calculated based on an equivalent hydrogen molar flow. The equivalent hydrogen molar flow at the anode inlet is defined by the following relationship:

$$\begin{aligned} \dot{n}_{H_2,equivalent} &= \dot{n}_{H_2} + \dot{n}_{CO} \\ &+ 3 \cdot \dot{n}_{CH_3OH} + 4 \cdot \dot{n}_{CH_4} \\ &+ 6 \cdot \dot{n}_{C_2H_5OH} \end{aligned} \quad (1)$$

where: $\dot{n}$ —molar flow at anode inlet.

From Table 5 it can be seen that biogases in reaction with oxygen can give various maximum voltages. Mixtures of various components occur in the case of the analyzed fuels.

Some types of bio-fuels cannot be delivered to the fuel cells directly. In those cases, the gasifier was applied. The gasifier is fed simultaneously by oxygen and steam to achieve the auto-thermal process. For safe operation of the fuel cell, steam is added to carbon-containing fuels to prevent carbon deposition on the cell surfaces. The gasifier was modelled as adiabatic unit and oxygen is delivered to the gasifier in adequate quantity to maintain the assumed temperature. The gasifier model was created in the software used [28] and is presented in Fig. 1.

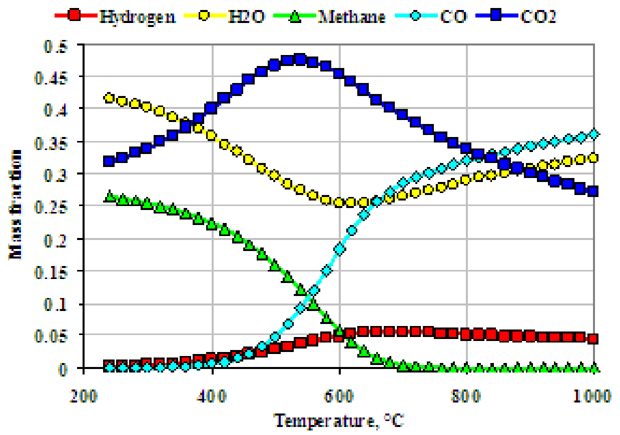

Figure 2: Canola Oil Syngas composition as a function of temperature

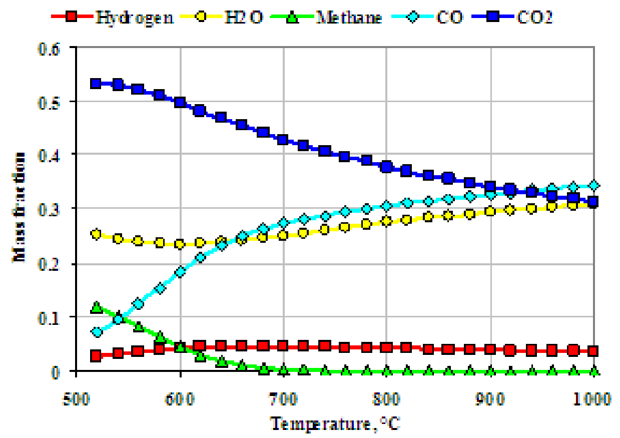

Figure 3: Wood Syngas composition as a function of temperature

Based on the built model the gasifier characteristics were generated for both fuels: canola oil and wood. The characteristics are presented in Fig. 2 and 3.

The syngas obtained by biomass gasification is characterized by a high content of carbon monoxide (35%) and steam (30%) and a low content of hydrogen (5%). There is almost no methane in the syngas.

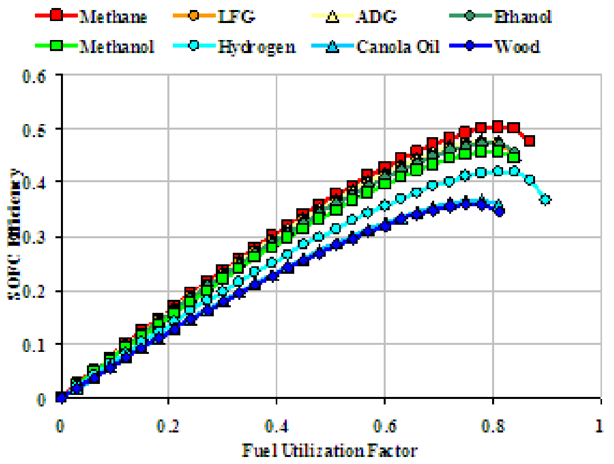

Figure 4: SOFC efficiency vs. fuel utilization factor for various biofuels

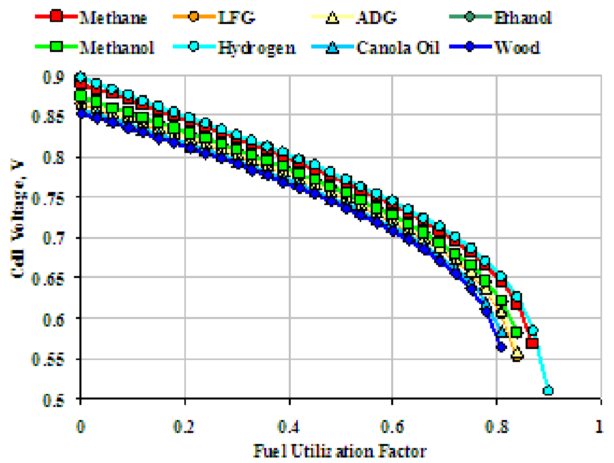

Figure 5: SOFC cell voltage vs. fuel utilization factor for various biofuels

A high inert gases content are also observed (carbon dioxide: 35%), which decreases the Higher Heating Value of the syngas.

4. Results and discussion

SOFC voltages and obtained efficiencies for various fuels are shown in Fig. 4 and 5. The figures contain the cell voltages and efficiencies for various fuels as a function of the fuel utilization factor. The SOFC efficiency curves are shown in Fig. , the highest values (50%) are obtained for methane as a fuel, syngases are characterized by much lower performances (35%). The highest optimum fuel utilization factor is for hydrogen as a fuel (80%) whereas the lowest one

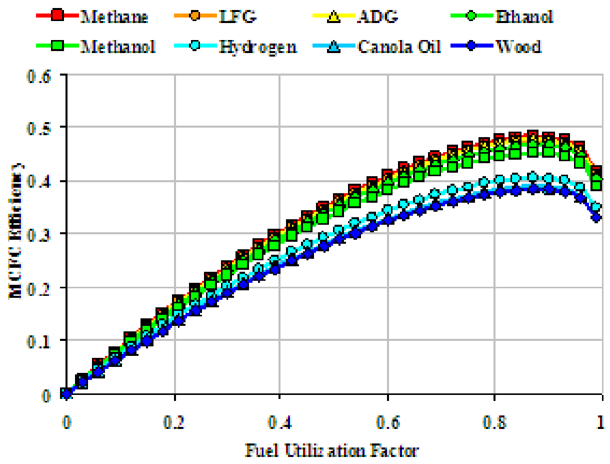

Figure 6: MCFC efficiency vs. fuel utilization factor for various biofuels

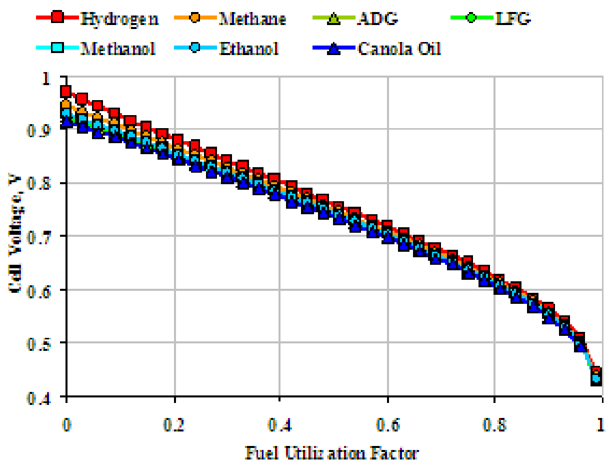

Figure 7: MCFC cell voltage vs. fuel utilization factor for various biofuels

is for Canola Oil Syngas (75%).

MCFC voltages and obtained efficiencies for various fuels are shown in Fig. 6 and 10. The figures contain the cell voltages and efficiencies for various fuels as a function of the fuel utilization factor. The highest values MCFC efficiency (50%) are obtained for methane as a fuel, just behind the ADG and LFG, syngases are characterized by lower performances (40%). The optimum values of fuel utilization factor are very similar for all analyzed fuels. Models were made of a molten carbonate fuel cell and a biomass fueled gasifier. The MCFC characteristic for various bio-fuels were obtained and commented.

5. Conclusions

The presented analysis regards a design-point model in which the fuel utilization factor represents the fuel cell load. It should be noted that the same fuel utilization factor can be obtained for various cell areas, which can additionally influence cell performances.

Generally speaking, biofuels are characterized by lower efficiency in comparison with methane. The high temperature fuel cells fueled by LFG, ADG, and alcohols outperforms both canola oil and wood. The highest open circuit voltage is achieved with hydrogen, but that does not automatically translate into greatest efficiency for higher fuel utilization factors. Internal reforming of methane means chemical conversion of process heat into a fuel (hydrogen and carbon monoxide), which achieves higher fuel cell efficiency than is the case with dry hydrogen.

Acknowledgments

The work was part of the "Scientists for the Mazovia economy" co-financed by the European Union under the European Social Fund:

http://www.bioenergiadlaregionu.eu/pl/naukowcy-dla-gospodarki-mazowsza

References

[1] . Bartela, A. Skorek-Osikowska, J. Kotowicz, Integration of a supercritical coal-fired heat and power plant with carbon capture installation and gas turbine, Rynek Energii 100 (3) (2012) 56–62.

[2] K. Janusz-Szymańska, Economic efficiency of an igcc system integreted with ccs installation [efektywność ekonomiczna układu gazowo-parowego zintegrowanego ze zgazowaniem węgla oraz z instalacjaą CCS], Rynek Energii 102 (5) (2012) 24–30.

[3] M. Kawabata, O. Kurata, N. Iki, C. Fushimi, A. Tsutsumi, Analysis of igfc with exergy recuperation and carbon dioxide separation unit, Vol. 3, 2012, pp. 441–448.

[4] M. Kawabata, O. Kurata, N. Iki, A. Tsutsumi, H. Furutani, Advanced integrated gasification combined cycle (A-IGCC) by exergy recuperation—technical challenges for future generations, Journal of Power Technologies 2 (2012) 90–100.

[5] G. De Lorenzo, P. Fragiacomo, Electrical and electrical-thermal power plants with molten carbonate fuel cell/gas turbine-integrated systems, International Journal of Energy Research 36 (2) (2012) 153–165.

[6] G. De Lorenzo, P. Fragiacomo, A methodology for improving the performance of molten carbonate fuel cell/gas turbine hybrid systems, International Journal of Energy Research 36 (1) (2012) 96–110.

[7] S. Bozorgmehri, M. Hamedi, Modeling and optimization of anode-supported solid oxide fuel cells on cell parameters via artificial neural network and genetic algorithm, Fuel Cells 12 (1) (2012) 11–23.

[8] H. Marzooghi, M. Raoofat, M. Dehghani, G. Elahi, Dynamic modeling of solid oxide fuel cell stack based on local linear model tree algorithm, International Journal of Hydrogen Energy 37 (5) (2012) 4367–4376.

[9] P. Pianko-Oprych, Z. Jaworski, Numerical modelling of the micro-tubular solid oxide fuel cell stacks [przeglad metod modelowania numerycznego mikrorurowych stał otlenkowych stosów ognhw paliwowych], Przemysl Chemiczny 91 (9) (2012) 1813–1815.

[10] J. Milewski, A. Miller, Mathematical model of SOFC (Solid Oxide Fuel Cell) for power plant simulations, in: ASME Turbo Expo, Vol. 7, 2004, pp. 495–501.

[11] J. Milewski, Mathematical model of SOFC for complex fuel compositions, in: International Colloquium on Environmentally Preferred Advanced Power Generation, no. ICEPAG2010-3422, 2010.

[12] G. Discepoli, G. Cinti, U. Desideri, D. Penchini, S. Proietti, Carbon capture with molten carbonate fuel cells: Experimental tests and fuel cell performance assessment, International Journal of Greenhouse Gas Control 9 (2012) 372–384.

[13] H. Jeong, S. Cho, D. Kim, H. Pyun, D. Ha, C. Han, M. Kang, M. Jeong, S. Lee, A heuristic method of variable selection based on principal component analysis and factor analysis for monitoring in a 300 kw mcfc power plant, International Journal of Hydrogen Energy 37 (15) (2012) 11394–11400.

[14] J. Milewski, J. Lewandowski, A. Miller, Reducing co_2 emissions from a coal fired power plant by using a molten carbonate fuel cell, in: Proceedings of the ASME Turbo Expo, Vol. 2, 2008, pp. 389–395.

[15] G. Marban, T. Valdes-Solis, Towards the hydrogen economy?, International Journal of Hydrogen Energy 32 (2007) 1625–1637.

[16] W. Budzianowski, Negative carbon intensity of renewable energy technologies involving biomass or carbon dioxide as inputs, Renewable and Sustainable Energy Reviews 16 (9) (2012) 6507–6521.

[17] A. Sobolewski, . Bartela, A. Skorek-Osikowska, T. Iluk, Comparison of the economic efficiency of chp plants integrated with gazela generator [porównanie efektywności ekonomicznej układów kogeneracyjnych z generatorem gazu procesowego gazela], Rynek Energii 102 (5) (2012) 31–37.

[18] D. J. Brett, A. Atkinson, D. Cumming, E. Ramirez-Cabrera, R. Rudkin, N. P. Brandon, Methanol as a direct fuel in intermediate temperature (500–600°c) solid oxide fuel cells with copper based anodes, Chemical Engineer-

ing Science 60 (21) (2005) 5649–5662.
[19] R. J. Kee, H. Zhu, D. G. Goodwin, Solid-oxide fuel cells with hydrocarbon fuels, Proceedings of the Combustion Institute 30 (2) (2005) 2379–2404.
[20] L. Fryda, K. Panopoulos, E. Kakaras, Integrated chp with autothermal biomass gasification and sofc-mgt, Energy Conversion and Management 49 (2) (2008) 281–290.
[21] J. V. Herle, F. Marchal, S. Leuenberger, Y. Membrez, O. Bucheli, D. Favrat, Process flow model of solid oxide fuel cell system supplied with sewage biogas, Journal of Power Sources 131 (1-2) (2004) 127 – 141.
[22] S. Assabumrungrat, N. Laosiripojana, V. Pavarajarn, W. Sangtongkitcharoen, A. Tangjitmatee, P. Praserthdam, Thermodynamic analysis of carbon formation in a solid oxide fuel cell with a direct internal reformer fuelled by methanol, Journal of Power Sources 139 (1–2) (2005) 55–60.
[23] G. Rabenstein, V. Hacker, Hydrogen for fuel cells from ethanol by steam-reforming, partial-oxidation and combined auto-thermal reforming: A thermodynamic analysis, Journal of Power Sources 185 (2) (2008) 1293 – 1304.
[24] K. Chaichana, Y. Patcharavorachot, B. Chutichai, D. Saebea, S. Assabumrungrat, A. Arpornwichanop, Neural network hybrid model of a direct internal reforming solid oxide fuel cell, International Journal of Hydrogen Energy 37 (3) (2012) 2498–2508.
[25] D. A. Brunner, S. Marcks, M. Bajpai, A. K. Prasad, S. G. Advani, Design and characterization of an electronically controlled variable flow rate ejector for fuel cell applications, International Journal of Hydrogen Energy 37 (5) (2012) 4457 – 4466.
[26] J. Milewski, K. Świrski, M. Santarelli, P. Leone, Advanced Methods of Solid Oxide Fuel Cell Modeling, 1st Edition, Springer-Verlag London Ltd., 2011.
[27] J. Milewski, M. Wołowicz, A. Miller, R. Bernat, A reduced order model of molten carbonate fuel cell: A proposal, International Journal of Hydrogen Energy in press.
[28] H. Corporation, HYSYS.Plant 2.1 User guide (1996).
[29] J. Milewski, The influence of fuel composition on Solid Oxide Fuel Cell obtained by using the advanced mathematical model, Journal of Power Technologies 91 (4) (2011) 179–185.