

# **Experimental Studies and Optimal Design for a Small-Scale Autonomous Power System Based on Methanol Reforming and a PEM Fuel Cell**

*Martha Ouzounidou<sup>1</sup>, Dimitris Ipsakis<sup>1,2</sup>, Spyros Voutetakis<sup>1</sup>, Simira Papadopoulou<sup>1,3</sup> and Panos Seferlis<sup>1,4</sup>*

<sup>1</sup> *Chemical Process Engineering Research Institute (C.P.E.R.I.), Centre for Research and Technology – Hellas (CE.R.TH.), 6th km Charilaou-Thermi Road, P.O. Box 60361, 57001 Thermi-Thessaloniki, Greece*

<sup>2</sup> *Department of Chemical Engineering, Aristotle University of Thessaloniki, P.O. Box 1517, 54124 Thessaloniki, Greece*

<sup>3</sup> *Department of Automation, Alexander Technological Educational Institute of Thessaloniki, P.O. Box 14561, 54101 Thessaloniki, Greece*

<sup>4</sup> *Department of Mechanical Engineering, Aristotle University of Thessaloniki, P.O. Box 424, 54124 Thessaloniki, Greece*

## **Abstract**

An experimental and preliminary design study on the production and purification of hydrogen derived from autothermal reforming of methanol is examined in this paper. Methanol, air and water are co-fed in the reformer reactor to produce hydrogen that is intended to be used in a polymer electrolyte membrane (PEM) fuel cell. However, due to the presence of CO at levels that are poisonous to the anode (Pt) of the PEM fuel cell, the effluent of the reformer is treated at a preferential oxidation (PROX) reactor for the minimization of CO at acceptable levels (<50ppm). The present study, deals with the examination of the catalysts performance at both reactors for various temperatures, flowrates (reformer) and ratios of reactants (PROX). The PEM fuel cell is also examined for various operation temperatures. Furthermore, the design study investigates three possible configurations (modeled at ASPEN Plus<sup>®</sup>), as far as heat management is of concern, in order to identify which could be the optimal solution for an autonomous power unit with minimal auxiliary supplies.

## **Introduction**

Greenhouse gases, mainly produced by power plants that use conventional fuels such as lignite, oil and natural gas, have increased the global warming effect the past decades. Hydrogen is considered as an energy carrier for the future and can be totally non-polluting when used in fuel cells (water is the exhaust), while it becomes economically competitive with gasoline or diesel. Moreover, hydrogen can prevent the depletion of fossil fuel reserves and can result in the reduction of greenhouse gases.

Despite the many benefits that hydrogen carries, there are also constraints on its direct use to the various applications [1]. Consequently, hydrogen must be produced by fuels that could directly feed it to fuel cells. Nowadays, hydrogen is mainly produced from non-renewable sources, such as natural gas and petroleum fractions. These fuels however, lead to high CO<sub>2</sub> emissions that further contributes to the greenhouse effect. On the other hand, methanol is a liquid which is easily available in the market, it does not require special conditions of storage, while it is also free from high reforming temperatures and sulphur oxides that are usually met in natural gas reforming. Moreover, methanol has a high

hydrogen-to-carbon ratio and no carbon-to-carbon ratio and thus, prevents the soot formation [2], while biomass resources can be used to produce methanol (bio-methanol).

Currently, there are three main processes for producing hydrogen from methanol: (i) steam reforming of methanol, (ii) partial oxidation of methanol and (iii) autothermal reforming of methanol [3]. Although steam reforming produces a high level of hydrogen at the outlet stream (~75%), it is a reaction that is endothermic and requires heat to be provided by an external source (e.g. burner) [1, 3]. Partial oxidation is highly exothermic, which leads to the formation of hot spots in the catalyst and resulting in sintering and deterioration of the overall catalytic process, while the produced hydrogen remains at low levels (~45%). In the autothermal steam reforming, oxygen, water and methanol are co-fed to the reformer and the reactants ratios are chosen in such a way in order to have a slightly exothermic or thermally neutral reaction [3]. Therefore, autothermal reforming contains most of the advantages of the above procedures and is currently the most reliable process for hydrogen production at an autonomous power unit.

A drawback of reforming hydrocarbons like methanol, is the production of CO at levels that are very poisonous to the electrocatalyst at the Pt-anode of the fuel cells [4]. CO is preferentially adsorbed onto the surface of the catalyst, blocking its access to H<sub>2</sub> and degrading the electrochemical performance of fuel cells operating at temperature below 100°C [5, 6]. Several processes used for the minimization of CO content at acceptable levels (less than 50ppm) have been discussed in the past where among them preferential oxidation is considered to be the simplest and the least expensive method [7].

The present study will focus on the experimental study of the reformer and PROX reactor and on the analysis of various configurations schemes that deal with the heat integration on important sections of the unit. The results will form the basis of enhancing the already developed mathematical model of the integrated system [8].

### ***Description of the Integrated System***

In order to obtain realistic data for an integrated system, a pilot plant was constructed (Fig.1) and the main parts of the pilot plant are the following:

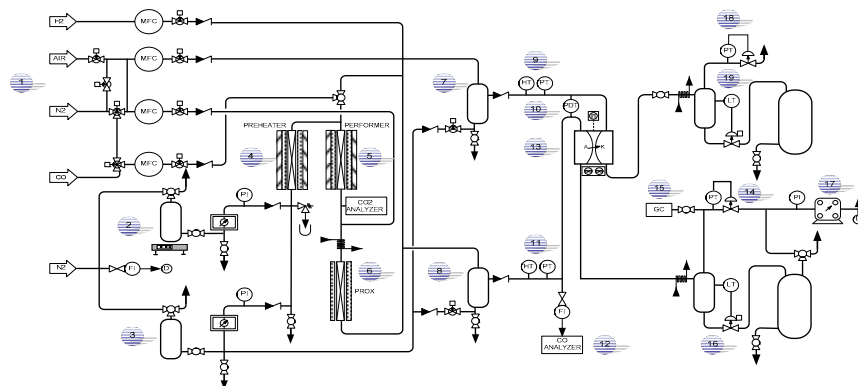
- The system of the fuel processing that includes the preheater, the methanol steam reformer reactor and the PROX reactor.
- The PEM fuel cell.
- The electronic system for the automation of the pilot plant.

Within two diaphragm pumps, methanol and water (liquid phase) with N<sub>2</sub> as carrier gas, are preheated and evaporated before they are introduced to the reformer simulating the operation of a catalytic burner. The effluent line of the preheater is mixed with air, creating a new stream for the autothermal reforming of methanol. The methanol steam reformer used in this work is a fixed bed reactor and was constructed from stainless steel with an inside diameter of 10 cm and a length of 15 cm. The catalyst used for methanol reforming is a copper-based catalyst in the form of CuO-MnO and is able to process a hydrogen-rich stream composed of 55-65% H<sub>2</sub>, 15-25% CO<sub>2</sub>, 12-18% N<sub>2</sub>, 1-3% CO in dry basis [11]. The outlet stream is analyzed by a gas chromatograph (HP-6890 Series GC System).

The reactions that take place at the reformer are a combination of endothermic and exothermic reactions. Partial oxidation of methanol is allowed to take place due to the highly endothermic reaction of steam reforming in order to provide the necessary heat to the system. With a proper selection of the oxygen/methanol (O<sub>2</sub>/CH<sub>3</sub>OH) ratio the whole

process at the reformer can be considered to be adiabatic [3, 8, 9]. The other two reactions that take place are the water gas shift reaction and the decomposition of methanol [8]. As mentioned in the introduction section, the high levels of CO at the reformer outlet, render it unsuitable for using the hydrogen stream straight to the anode of the PEM fuel cell. Therefore, the PROX reactor becomes a necessity to the system in order to minimize CO with oxidation. The PROX reactor constructed from the same material as the reformer, has an inside diameter of 10 cm and a length of 10 cm. The catalyst used at the PROX reactor is an oxide catalyst in the form of CuO-CeO<sub>2</sub> [12]. CO is analyzed by a CO Analyzer (Horiba VA-3000 Gas Analyzer). The reactions that take place are the CO oxidation and the inevitable H<sub>2</sub> oxidation. The main objective of the analysis of the PROX reactor is to keep the CO concentration at a maximum limit of less than 50 ppm.

The pilot plant unit is fully automated and based on the continuous supervisory control and data acquisition system (SCADA) with the industrial software iFIX by GE Fanuc. For ease of identification and operation, a status display is provided on the screen of a computer where the flow diagram of the system is graphically represented. Pumps, heaters, valves, power e.t.c., are controlled through the computer system by on/of commands or by pre-programmed start-up commands. The computer control system acts to automatically maintain the system parameters, to allow programmed keyboard operations, to provide safety management and to perform parametric retrieval.



**Fig. 1:** Schematic diagram of the controlled pilot plant unit for hydrogen production and power generation

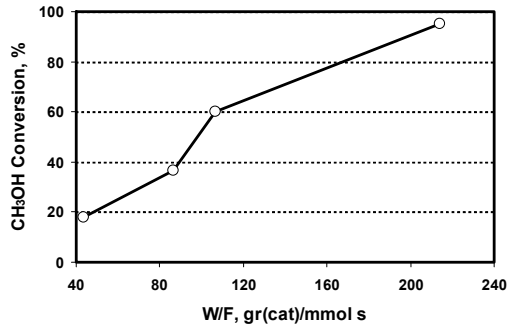
1. Feedstock lines: H <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> , CO	10. Pressure indication among anode and cathode of the fuel cell
2. Feedstock vessel of methanol	12. CO Analyzer
3. Feedstock vessel of water	13. PEM Fuel Cell
4. Preheater	14, 18. Pressure indicators
5. Reformer reactor	15. Gas Chromatograph Analyzer of the reformat gas
6. PROX reactor	16, 19. Level transmitters
7, 8. Saturators	17. Wet Test Meter (WTM)
9, 11. Humidity and Pressure Indicators	

## Results of the Integrated System

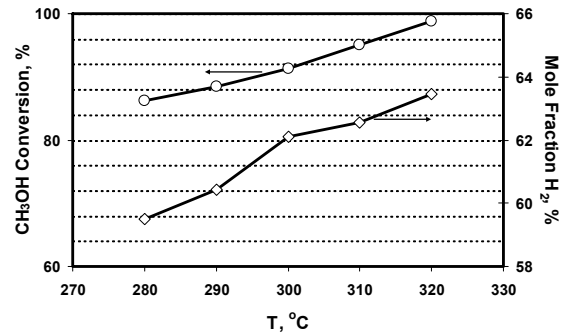
### Experimental Studies on the Integrated Power System

The catalyst loading in the reformer was 90 gr and methanol conversion in various methanol flowrates and temperature was studied. Fig. 2 presents the experimental results performed in the range of W/F<sub>CH<sub>3</sub>OH</sub> ratio 43.4-214.1 gr/mmol·s. The ratios of

steam/methanol ( $H_2O/CH_3OH$ ) and of oxygen/methanol ( $O_2/CH_3OH$ ) ratios are 1.5 and 0.1 respectively, unless stated otherwise. Furthermore, Fig.3 presents the effect of temperature at the methanol conversion and consequently hydrogen production.



(2)

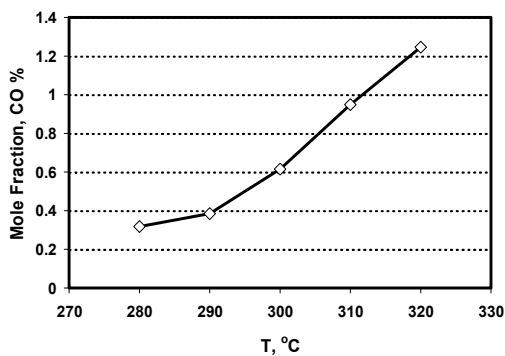


(3)

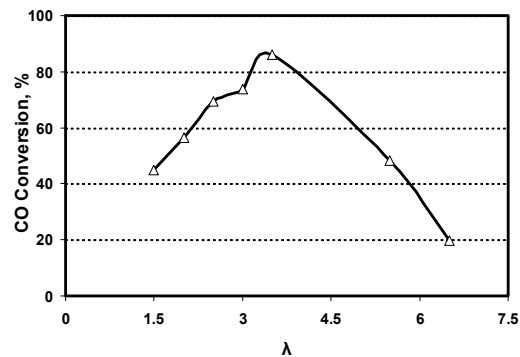
**Fig. 2:**  $CH_3OH$  conversion as a function of  $W/F_{CH_3OH}$  at the temperature of  $T=300\text{ }^\circ\text{C}$ .

**Fig. 3:**  $CH_3OH$  conversion and hydrogen production (% mole) as a function of temperature at  $F_{CH_3OH}=1.013\text{ ml/min}$ .

From the above figures, it is obvious that with the decrease of the methanol feed, methanol conversion is increased and a methanol conversion of 95% was achieved at the temperature of  $300\text{ }^\circ\text{C}$  and  $W/F_{CH_3OH}=214.1\text{ gr/mmol}\cdot\text{s}$ . Moreover, based on the results presented in Fig. 3, a maximum methanol conversion of 98.9% was obtained at the temperature of  $320\text{ }^\circ\text{C}$  for a methanol flowrate feed of  $1.013\text{ ml/min}$ . The hydrogen production reached 63% mole, which is sufficient for a power generation of 140 W. Such a power generation is considered very low for the design of the system, since the system is capable of providing power up to 10kW based on the inlet methanol flowrate. Thus, a better analysis and study of the catalyst performance is needed in order to achieve  $>90\%$  of methanol conversion for much higher flowrates than  $1.013\text{ ml/min}$ . Fig. 4 presents the dependence of CO formation on temperature where it was found that higher temperatures favors CO production and this needs to be taken into account at PROX reactor analysis.



(4)



(5)

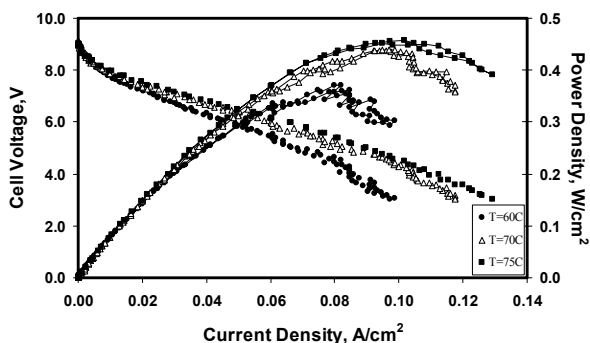
**Fig. 4:** CO production as a function of temperature ( $280\text{--}320\text{ }^\circ\text{C}$ ).

**Fig. 5:** CO conversion as a function of  $\lambda = 2[O_2]/[CO]$  ( $F_{CH_3OH}=0.5\text{ ml/min}$ ,  $T=211\text{ }^\circ\text{C}$ )

Experiments in order to minimize the CO concentration of the reformer effluent were done in the PROX reactor at a temperature range of  $180\text{--}220\text{ }^\circ\text{C}$ . In Fig. 5 the conversion of CO is

presented as a function on the ratio  $\lambda = 2[\text{O}_2]/[\text{CO}]$ . At the temperature of  $T=211\text{ }^\circ\text{C}$  [12] and  $\lambda=3.5$  a conversion of 86% was achieved, but with hydrogen losses up to 6.5%. As can be seen in Fig.5, the increase of  $\lambda$  causes an increase in CO conversion. However, after a certain value of  $\lambda$ , the conversion decreases because in hydrogen oxidation water is produced and blocks active sites of the catalyst and thus, CO cannot reach them.

Finally, the performance of a small-scale PEM fuel cell stack consisted of 10 cell was investigated. Pure  $\text{H}_2$  was fed to the anode and air to the cathode. In order to examine the hysteresis phenomena the experiments were conducted both by increasing and by decreasing the current density. As shown in Fig. 6, no hysteresis phenomena occur and increased temperatures favors the operation of the fuel cell because the overvoltages are decreased. At the temperature of  $T=75\text{ }^\circ\text{C}$  a maximum power density was observed at  $0.48\text{ W/cm}^2$  at a cell voltage of  $4.5\text{ V}$  and current density  $0.106\text{ A/cm}^2$ .



**Fig. 6:** Power density and cell voltage as a function of current density at  $T= 60,70,75\text{ }^\circ\text{C}$ .

### *Optimal design based on proposed process flow diagrams*

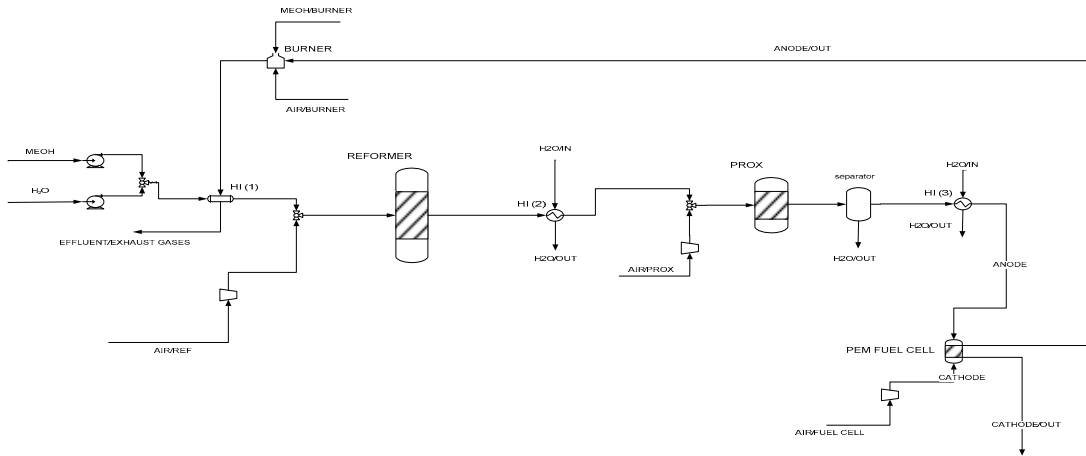
The production of hydrogen via autothermal reforming of methanol, reveals that besides the aforementioned basic components of the two reactors and the fuel cell, there are numerous other parameters that need to be considered. Two of the most important are the start-up of the unit, where the evaporation of the reactants should take place, and the cooling on the outlet of the reformer and PROX reactors. For the current study, we will discuss on three configurations where heat integration is needed for the evaporation of methanol and water and for the cooling of the outlet streams of the reformer and PROX reactors. The proposed schemes were studied with the use of the simulation tool ASPEN Plus<sup>®</sup> for a power generation of 1kW and design specifications were used in order to ensure that the reactants ratios at the reformer and PROX reactors produced the desired conditions (adiabatic conditions at reformer, minimal CO at PROX reactor outlet, methanol and air addition for the burner e.t.c.).

### *Description of the Process Flow Diagrams (PFDs)*

In general, it can be said for all the configurations that methanol and water are mixed and the product stream is being evaporated by the exhaust gases from the burner (H1 (1)). Then, the hot stream (gaseous form of methanol and water) is mixed with air and enters the reformer for the hydrogen production. The outlet stream from the reformer is cooled and mixed with air for hydrogen purification (removal of CO) at the PROX reactor. Then, the outlet stream from the PROX reactor (after water is removed) is further cooled and enters the anode of the fuel cell. Finally, all the hydrogen that has not reacted along with the other

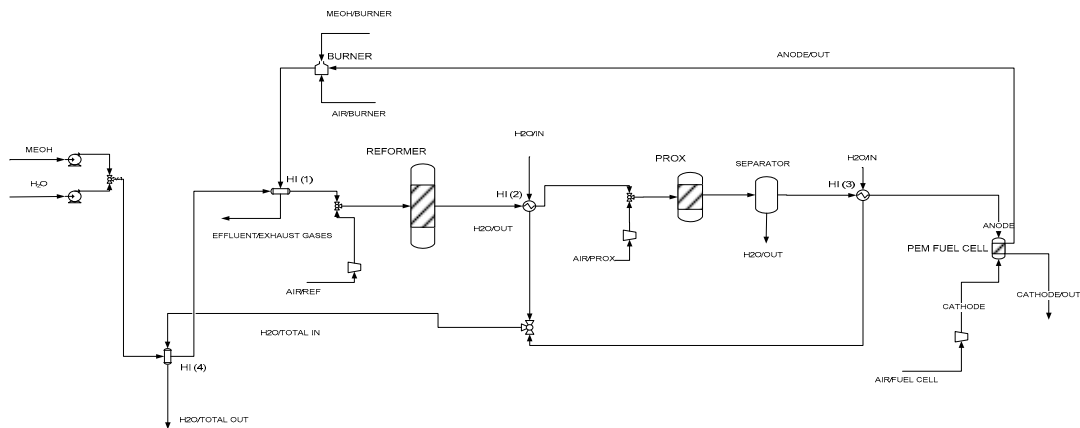
components ( $\text{CH}_3\text{OH}$ ,  $\text{CO}_2$ ,  $\text{N}_2$  etc.) is fed at the burner where additional methanol and air are used for providing the required energy (exhaust gases) for evaporating the reactants methanol and water. The configurations for the current study will be based on minimizing the methanol and air addition at the burner by using possible integration and/or recycling of process streams.

Fig.1 presents the first configuration. The outlet stream of the reformer and the PROX reactors are cooled using water that is regarded as an auxiliary unit in HI (2) and HI (3), respectively. With this configuration, the results for the used water and the additional methanol and air at the burner are shown in table 1 and discussed later.



**Fig.7:** Description of the 1<sup>st</sup> process flow diagram (PFD1)

Trying to improve the first operation scheme, some modifications were made and shown in Fig.8. Specifically, the water hot streams after HI(2) and HI (3) are mixed and used to heat up (1<sup>st</sup> stage) the inlet methanol and water in HI (4). After the 1<sup>st</sup> stage, methanol and water are further heat by the exhaust gases at the burner to meet a temperature around the reaction temperature (HI (1)). With this configuration, the methanol and air in the burner can be reduced as shown in table 1.



**Fig. 8:** Description of the 2<sup>nd</sup> process flow diagram (PFD2)

For the third configuration (Fig.9), the inlet methanol and water stream is heated up and evaporated at three stages in order to avoid using water as a coolant medium. In the first stage, the outlet stream of the reformer is used for heating up the reactants in HI (2) which are then further heated up by the outlet stream of the PROX reactor in HI (3). In the 3<sup>rd</sup> stage, the reactants are being heated by the exhaust gases from the burner in HI (1).



reaches 63 (% mole) in the effluent of the reformer at  $T=320\text{ }^{\circ}\text{C}$ . A maximum  $\text{CH}_3\text{OH}$  conversion (98.9%) was also obtained at  $T=320\text{ }^{\circ}\text{C}$  and  $W/F_{\text{CH}_3\text{OH}}=214.1\text{ gr/mmol}\cdot\text{s}$ . The experimental results from the investigation of the performance of the PROX reactor showed a CO conversion of 86% with hydrogen losses up to 6.5% but increased  $\text{O}_2/\text{CO}$  ratios can deteriorate the performance of the catalyst due to the inevitable hydrogen oxidation. The maximum power density at the PEM fuel cell was  $0.48\text{ W/cm}^2$  and increased for higher temperatures. The preliminary design study, showed many possibilities for using process streams in the unit. The cooling of the reactors outlet is of major concern, while efforts on methanol and air minimization at the burner showed that recycling and heat integration is necessary for the operation of an autonomous power system. All the above results are going to be used for the enhancing the already developed dynamic mathematical model of the power unit.

## References

- [1] S.K. Kamarudin, W.R.W. Daud, A.Md. Som, M.S. Takriff, A.W. Mohammad, Y.K. Loke, Design of a fuel processor unit for PEM fuel cell via shortcut design method, *Chemical Engineering Journal*, Volume 104, (2004), 7-17
- [2] B. Lindström and L.J. Petterson, Hydrogen generation by steam reforming of methanol over copper-based catalysts for fuel cell applications, *International Journal of Hydrogen Energy*, Volume 26, (2001), 923-933.
- [3] B. Lindström and L.J. Petterson, Development of a methanol fuelled reformer for fuel cell applications, *Journal of Power Sources*, Volume 118, (2003) 71-78.
- [4] L. Gubler, G.G. Scherer, A. Wokaun, Effects of cell and electrode design on the CO tolerance of polymer electrolyte fuel cells, *Phys. Chem. Chem. Phys.*, Volume 3, (2003), 325-329.
- [5] T.E. Springer, T. Rockwald, T.A. Zawodzinski, S. Gottesfeld, Model for polymer electrolyte fuel cell operation on reformat feed-Effects of CO, H<sub>2</sub> dilution, and high fuel utilization, *Journal of the Electrochemical Society*, Volume 148 (2001), 11-23.
- [6] R. K. Ahluwalia, E. D. Doss, R. Kumar, Performance of high-temperature polymer electrolyte fuel cell systems, *Journal of Power Sources*, Volume 117, Issues 1-2, 9( 2003), 45-60
- [7] F. Mariño, C. Descorme, D. Duprez, Noble metal catalysts for the preferential oxidation of carbon monoxide in the presence of hydrogen (PROX), *Applied Catalysis B: Environmental*, Volume 54, Issue 1, (2004), 59-66
- [8] D. Ipsakis, P. Kechagiopoulos, C. Martavaltzi, S. Voutetakis, P. Seferlis, P. Daoutidis, F. Stergiopoulos, Study of an integrated system for the production of hydrogen by autothermal reforming of methanol, *Computer Aided Chemical Engineering*, Volume 24, (2007), 913-918
- [9] S. P. Asprey, B. W. Wojciechowski, B.A. Peppley, Kinetic studies using temperature-scanning: the steam-reforming of methanol, *Applied Catalysis A: General*, Volume 179, Issues 1-2, (1999), 51-70
- [10] G.Sedmak, S. Hozvevar, J. Levec, Kinetics of selective CO oxidation in excess of H<sub>2</sub> over the nanostructured  $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_{2-y}$  catalyst, *Journal of Catalysis*, Volume 213, Issue 2, (2003), 135-150
- [11] J. Papavasiliou, G. Avgouropoulos, T. Ioannides, Combined steam reforming of methanol over Cu–Mn spinel oxide catalysts, *Journal of Catalysis*, Volume 251, Issue 1, (2007), 7-20
- [12] J. Papavasiliou, G. Avgouropoulos, Th. Ioannides, Production of hydrogen via combined steam reforming of methanol over  $\text{CuO–CeO}_2$  catalysts, *Catalysis Communications*, Volume 5, Issue 5, (2004), 231-235