

# Dynamic Modeling and Control Issues on a Methanol Reforming Unit for Hydrogen Production and Use in a PEM Fuel Cell

Dimitris Ipsakis<sup>1,2</sup>, Spyros Voutetakis<sup>1</sup>, Panos Seferlis<sup>3</sup>, Simira Papadopoulou<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.T.H.), P.O. Box 60361, 57001 Thessaloniki, Greece (Tel: +30-2310-498 317; e-mail:paris@cperi.certh.gr).

<sup>2</sup>Department of Chemical Engineering, Aristotle University of Thessaloniki, P.O. Box 1517, 54124 Thessaloniki, Greece (Tel: +30-2310-498 353; e-mail:ipsakis@cperi.certh.gr).

<sup>3</sup>Department of Mechanical Engineering, Aristotle University of Thessaloniki, P.O. Box 484, 54124 Thessaloniki, Greece (Tel: +30-2310-994 229; e-mail:seferlis@cperi.certh.gr).

<sup>4</sup>Department of Automation, Alexander Technological Educational Institute of Thessaloniki, P.O. Box 14561, 54101 Thessaloniki, Greece (Tel: +30-2310-498 319; e-mail:shmira@teithe.gr).

---

**Abstract:** The presented research work focuses on the mathematical description and control analysis of an integrated power unit that uses hydrogen produced by methanol autothermal reforming. The unit consists of a reformer reactor where methanol, air and water are co-fed to produce a hydrogen rich stream through a series of reactions. The hydrogen main stream is fed to a preferential oxidation reactor (PROX) for the reduction of CO at levels below 50ppm with the use of air. In the end, the PROX outlet stream enters the anode of a PEM fuel cell where power production takes place to serve a load demand. The operation of the two reactors is described by a combination of partial differential equations (mass and energy balances) and non-linear equations (kinetic expressions of the reactions), while the power production in the fuel cell is based on the inlet hydrogen flow and on operational characteristics. A simple case scenario is employed when a step change on methanol flowrate is imposed. Main target is to identify and analyze the changes occurring in the main variables of concern ( $H_2$ , CO and temperature levels) that affect the overall system operation. Based on the results, an insight on the challenging control scheme will be applied in order to identify possible ways of setting up a reliable and robust control structure according to the developed mathematical model.

*Keywords:* methanol reforming, preferential oxidation, hydrogen, PEM fuel cell, dynamic modeling

---

## 1. INTRODUCTION

Hydrogen can be considered an energy carrier for the future and when derived from renewable energy sources can be totally non-polluting when used in fuel cells (Ipsakis D. et al., 2008). Fuel cells advantages include (Larminie J. and Dicks A., 2003) the low operation temperatures ( $\sim 80^\circ\text{C}$ ), the  $\text{CO}_2$  tolerance by the electrolyte, the fast cold start and their few moving parts, which enhances their role as back-up units in vehicles. Nevertheless, the main disadvantage of fuel cells refers to the hydrogen supply. Natural gas, gasoline and higher hydrocarbons have been proposed for hydrogen production via steam reforming, but methanol carries the most advantages from all (Lindström B. and Petterson L.J., 2001). Methanol is a liquid that does not require special conditions of storage, while it is also free from high reforming temperatures and sulphur oxides that are met in methane and gasoline reforming. Moreover, methanol has a high H:C ratio and no C:C ratio and thus, prevents the soot formation (Lindström B. and Petterson L.J., 2001), while

biomass resources can be used to produce methanol (biomethanol). Production of hydrogen from methanol can be achieved in three ways: (i) steam reforming of methanol, (ii) partial oxidation of methanol and (iii) autothermal reforming of methanol (Lindström B. and Petterson L.J., 2001). Autothermal reforming has the asset of eliminating the disadvantages of steam reforming (endothermic process which requires a heating source) and partial oxidation (highly exothermic process which leads to the formation of hot spots in the catalyst) by properly selecting the reactants ratios in such a way, so that adiabatic conditions can be achieved. One of the drawbacks of hydrocarbons reforming however, is the production of CO at high levels that degrade the electrochemical performance of low temperature PEM fuel cells. 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 (Cipiti F. et al., 2007).

Most of the simulation and modeling studies on methanol reforming, focus on each subsystem as an individual part. Steam reformers have been modelled using axial distribution models (Suh J. S. et al., 2007), while PROX reactors have also been modelled using 2D models (Cipiti F. et al., 2007). In one of the very few papers that deal with an integrated system, Stamps A. T. and Gatzke E.P. (2006), developed and implemented a system level model of a vehicular reformer PEM fuel cell stack power system without the use however, of a hydrogen purification system, while the dynamic operation results were not provided explicitly. As can be seen, literature references lack in studies that deal with the detailed mathematical description of all the involved subsystems and on their overall dynamic interactions. The objective of this study is to analyze the dynamic behaviour of the two reactors based on a step change imposed in methanol flowrate. The reactors temperature and CO content will be continuously monitored, since they mostly affect the power production of the fuel cell. In the end, an analysis on the demanding task of the control of such an integrated power system will be applied, in order to identify all the necessary actions need to be taken for the development of a robust control scheme.

## 2. DESCRIPTION OF THE INTEGRATED POWER SYSTEM

Figure 1, shows the overall process flow diagram of the methanol autothermal reforming unit.

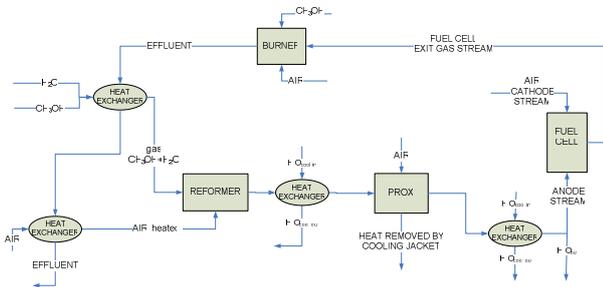


Fig. 1: Overall operation scheme of the methanol autothermal reforming unit.

Methanol, air and water are co-fed to the reformer (0.15m length and 0.1m diameter) after they are preheated by the effluent gases of a burner. The main reaction that takes place at the reformer is the steam reforming of methanol (R1), but because it is an endothermic reaction, oxygen also reacts with methanol (R2) to provide the necessary heat to the system.

Table 1. Reactions taking place at the reformer

$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$ $\Delta H_{R, 298} = 49\text{kJ/mol}$ , (R1)	$\text{CH}_3\text{OH} + 0.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2$ $\Delta H_{R, 298} = -193\text{kJ/mol}$ , (R2)
$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ $\Delta H_{R, 298} = -41.2\text{kJ/mol}$ , (R3)	$\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$ $\Delta H_{R, 298} = 90.1\text{kJ/mol}$ , (R4)

The autothermal reforming of methanol is based on the effective selection of the reactants ratios at the inlet of the reformer. For the current study, it was found from steady-

state simulations using Aspen Plus<sup>®</sup> (Ouzounidou M. et al., 2008a) that the optimum values for  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  and  $\text{O}_2/\text{CH}_3\text{OH}$  are between 1.5-1.7 and 0.1-0.15 respectively. Steam reforming is considered as the sum of the water gas shift (R3) and methanol decomposition (R4) reactions.

The reduction of CO after steam reforming, takes place at the PROX reactor (0.1m length and 0.1m diameter). There, besides CO oxidation,  $\text{H}_2$  oxidation also takes place, but it is kept at low rate through the effective selection of the catalyst. The reactions of the PROX can be seen in table 2:

Table 2. Reactions taking place at the PROX

$\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$ $\Delta H_{R, 298} = -283\text{kJ/mol}$ , (R5)	$\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$ $\Delta H_{R, 298} = -242\text{kJ/mol}$ (R6)
---	---

The main objective of the PROX reactor is to keep the CO concentration at a maximum limit of 50 ppm by using efficiently the  $\text{O}_2/\text{CO}$  ratio. From ASPEN Plus<sup>®</sup> simulations (Ouzounidou M. et al., 2008a), its optimum value is 1, but could vary severely with CO concentration. The PROX reactor due to the presence of the two highly exothermic reactions is surrounded by a jacket to cool the system from undesirable extreme heat generation. The kinetic expressions for all the involved reactions can be found in (Ouzounidou M. et al., 2008b) where an analysis on their selection is provided.

Finally, the hydrogen rich stream is fed to the anode of the fuel cell where it ionises releasing protons ( $\text{H}^+$ ) and electrons ( $\text{e}^-$ ). Protons pass through the proton exchange membrane to the cathode, while electrons flow through an external electric circuit and produce current. In the cathode, oxygen is fed via air supply and reacts with the protons and electrons to form water (Table 3).

Table 3. Reactions taking place at the PEM fuel cell

$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ Anode, (R6)	$0.5\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ Cathode, (R7)
---	---

## 3. MATHEMATICAL DESCRIPTION OF THE SUBSYSTEMS

In this section, the mathematical models of the involved subsystems will be presented and discussed. All parameters, variables and symbols are explained in the nomenclature section. gPROMS<sup>®</sup> was used to simulate the operation of the integrated power system (PSE<sup>®</sup>, 2002).

### 3.1 Reformer and PROX Reactors

The model equations for the catalytic reactors consist of the standard material and energy balances for a pseudo-homogeneous system (packed-bed type). These equations are in partial differential form with spatial and radial distributions. In order to simplify the model and reduce the computational effort needed to simulate all the subsystems, a number of assumptions have been made. It is highlighted, that the description of the system does not lose its accuracy

and the crucial phenomena can be easily described by the developed mathematical model.

- The ideal gas law is applied for all gas components.
- No diffusion phenomena are assumed to take place from the gas phase to the surface of the catalyst.
- Constant reactor pressure and fluid velocity.
- Constant physical properties (component density and heat capacity) over the range of conditions.
- The temperature in the cooling jacket of the PROX reactor is approximately uniform and the resistance to heat transfer occurs primarily between the reactor contents and the wall of the tube (being at the cooling medium temperature).

#### Material Balance Equation

$$\frac{\partial C_i}{\partial t} + u \cdot \frac{\partial C_i}{\partial z} - \varepsilon_{\text{cat}} \cdot D_z \cdot \frac{\partial^2 C_i}{\partial z^2} - \varepsilon_{\text{cat}} \cdot D_r \cdot \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C_i}{\partial r} \right) = \sum_{i=1}^N \sum_{j=1}^R \nu_{i,j} \cdot R_j \quad (1)$$

#### Energy Balance Equation

$$\sum_{i=1}^N \rho_i \cdot C_{p,i} \cdot \frac{\partial T}{\partial t} + \sum_{i=1}^N \rho_i \cdot C_{p,i} \cdot u \cdot \frac{\partial T}{\partial z} - k_z \cdot \frac{\partial^2 T}{\partial z^2} - k_r \cdot \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} \right) = - \sum_{j=1}^R R_j \cdot (\Delta H_{R,T,j}) \quad (2)$$

#### Coolant Energy Balance Equation

$$\rho_c \cdot V_c \cdot C_{p,c} \cdot \frac{\partial T_c}{\partial t} = F_c \cdot C_{p,c} \cdot (T_{c,in} - T_c) + Q \quad (3)$$

$$Q = U \cdot A \int_0^{\text{ReactorLength}} (T - T_c) \cdot dz \quad (4)$$

#### Ideal Gas Law

$$P_i \cdot V = n_i \cdot R \cdot T \Rightarrow P_i = C_i \cdot R \cdot T \quad (5)$$

#### Species Flowrate

$$F_i = C_i \cdot Q_o \quad (6)$$

$$Q_o = u \cdot S = \frac{\sum F_{i,in} \cdot R \cdot T_{in}}{P_{\text{reactor}}} \quad (7)$$

#### Boundary Conditions (Eqs. 1-4)

$$z=0 \quad C_i = C_{i,in} \text{ and } T = T_{in}, \quad r \in [0, R] \quad (8)$$

$$z=L \quad \frac{\partial C_i}{\partial z} = 0 \text{ and } \frac{\partial T}{\partial z} = 0, \quad r \in [0, R] \quad (9)$$

$$r=0 \quad \frac{\partial C_i}{\partial r} = 0 \text{ and } \frac{\partial T}{\partial r} = 0, \quad z \in (0, L) \quad (10)$$

$$r=R \quad \frac{\partial C_i}{\partial r} = 0 \text{ and } -k_r \cdot \frac{\partial T}{\partial r} = h_w \cdot (T - T_c), z \in (0, L) \quad (11)$$

In the solution of the reformer,  $h_w$  is 0 and for the PROX  $\neq 0$ . For the discretization of the distributions the method of centered finite difference (2<sup>nd</sup> order) was used. The discretization of the axial and radial distribution was performed for 50 and 5 intervals, respectively. More intervals showed that the results are not affected, but the increase in the required computational effort leads to inefficient solution procedure.

#### 3.2 PEM Fuel Cell

Larminie J. and Dicks A., (2003), presented an equation that relates the power production with the hydrogen flow and the operational characteristics of the fuel cell:

$$P_{fc} = F_{H_2} \cdot n_e \cdot F \cdot \eta_F \cdot V_{\text{cell}} \quad (12)$$

The hydrogen flow predicted by the reactors mathematical model is used in the above equation to predict the power production as a function of time.  $V_{\text{cell}}$  is usually around 0.7V/cell (Larminie J. and Dicks A., 2003).

The same authors also concluded that if all the enthalpy of reaction of a hydrogen fuel cell was converted into electrical energy then the output voltage would be 1.48V (water in liquid form) or 1.25V (water in vapour form). Therefore, the difference between the actual cell voltage and this voltage represents the energy that is converted into heat instead. For the vapour case in our fuel cell, heat is calculated as:

$$Q_{fc} = P_{fc} \cdot \left( \frac{1.25}{V_{\text{cell}}} - 1 \right) \quad (13)$$

#### 3.3 Model validation

Based on the experimental results presented in (Ouzounidou M. et al., 2008b), validation with the above mathematical model (kinetic parameters and the axial and radial distributed parameters were estimated) has been performed, where it has been found that the model accurately simulates the performance of both reactors. Figures 2 and 3 show the comparison between the experimental data and mathematical model for the two reactors, respectively and the deviation between simulated and experimental values is within the expected error (less than 5%). Only in low PROX temperatures a higher deviation is detected but considered negligible, since PROX operates in temperatures  $>150^\circ\text{C}$ .

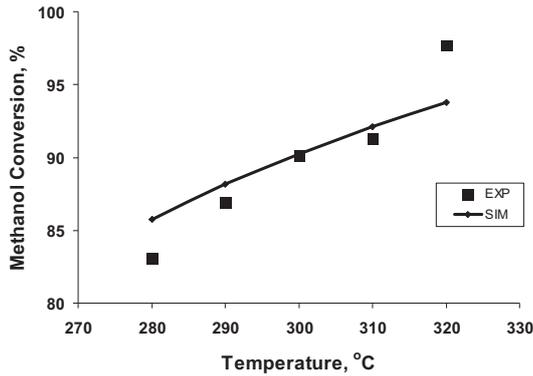


Fig. 2. Comparison between simulated and experimental results for the reformer

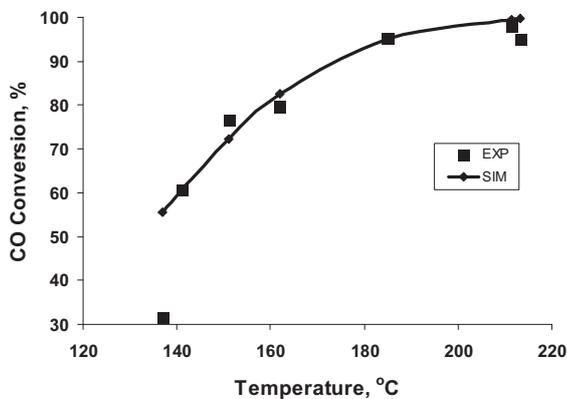


Fig. 3. Comparison between simulated and experimental results for the PROX

#### 4. SIMULATION RESULTS FROM THE DYNAMIC OPERATION OF THE INTEGRATED POWER SYSTEM

The dynamic operation of the integrated power unit will be presented based on an imposed step change. The conditions of the simulated case study are: inlet methanol at 0.02mol/s, reformer temperature at 300°C, PROX temperature at 200°C, H<sub>2</sub>O/CH<sub>3</sub>OH at 1.5, O<sub>2</sub>/CH<sub>3</sub>OH at 0.14 and O<sub>2</sub>/CO at 2. It is noted that the flowrates of the reactants and reactor temperature at the inlet of the reformer do not have a sharp constant value at the start of the simulation time, but a value that increases smoothly with time and reaches its steady state value after a few seconds. Fig.4 shows the 50% step change on the inlet methanol flowrate at t=30s (inlet water and oxygen flowrates are also increased based on the selected ratios). As can be seen, at the same time an increase at the exit hydrogen flowrate starts to appear and after 80s the increase in hydrogen flowrate is calculated at 49.6%, which shows that methanol conversion is practically unaffected by the increase in the methanol flowrate for the selected conditions.

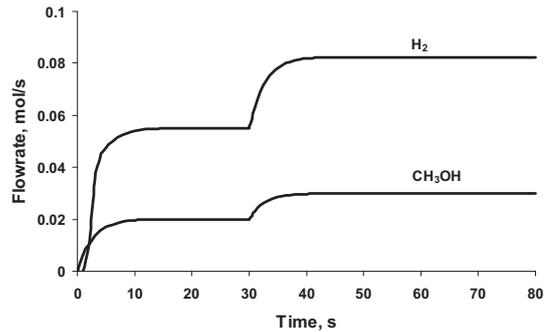


Fig. 4. Methanol inlet and hydrogen outlet flowrates

Similarly Fig.5 shows the CO content (ppm) where a 13% decrease is observed at the time that the step change occurs. This decrease is expected due to the fact that water flowrate is increased (according to the methanol step change) and the water gas shift reaction is favored. This can also be concluded by the fact that CO flowrate increase is calculated at 22.5% which differs significantly from the 50% increase detected in other products, such as hydrogen.

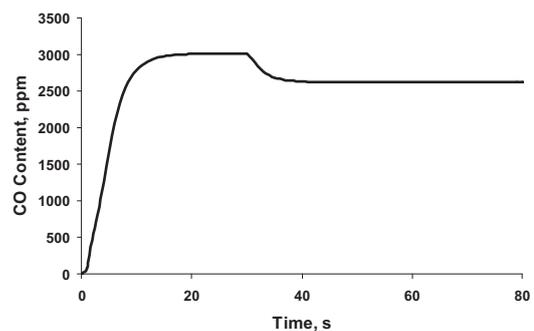


Fig. 5. Carbon monoxide content at the reformer exit

Fig.6 shows the reformer inlet and outlet temperature levels. The inlet gas temperature follows a smooth increase in order to prevent hot spots due to the rigorous exothermic partial oxidation of methanol.

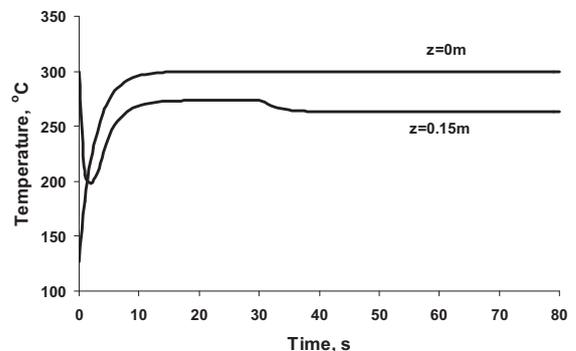


Fig. 6. Temperature levels at the reformer inlet and outlet

This smooth increase is based on the operation of the assumed preheater that heats the reactants mixture. On the

other hand, the outlet temperature of the reformer (at  $t=0$ s the reformer is assumed to be at  $300^{\circ}\text{C}$ ) is initially decreased due to the fact that low temperature gas mixture exits the reactor at  $t<10$ s, but as the reformer operation proceeds, the exit temperature is gradually increased to  $260\text{--}270^{\circ}\text{C}$ . As can be seen for the present conditions, the endothermic reactions prevail and the exit temperature is  $30\text{--}40^{\circ}\text{C}$  lower than the inlet (at steady-state conditions) and also the step change seems to affect the temperature levels by lowering them by  $10^{\circ}\text{C}$ .

Unlike the reformer, where negligible changes are observed in the radial domain, in the PROX the species concentration and temperature varies severely along the reactor radius. Fig.7 shows the CO content at the wall of the reactor, at its center and the average value that indicates the exit flow. As can be seen, the CO content is higher away from the center due to the lower temperature at that region (see Fig.8). As we move to the reactor center, the CO levels are quite low (practically zero at the reactor center) due to the increased temperature while the average value is always lower than  $50\text{ppm}$  for the current conditions. It is highlighted that the CO at the exit of the reformer is measured and according to the selected  $\text{O}_2/\text{CO}$  ratio, the air feed rate is manipulated and introduced to the PROX reactor, so as to always provide a constant  $\text{O}_2/\text{CO}$  ratio. If the  $\text{O}_2$  flow was constant based on the initial conditions, then the CO levels would have been higher indicating a possible fuel cell deterioration.

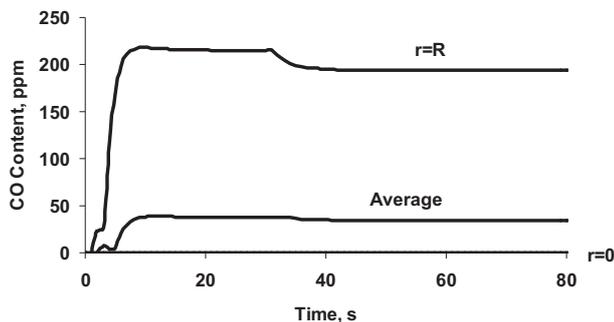


Fig. 7. Carbon monoxide content at the PROX wall, center and average value in the radial domain

Fig.8 shows the temperature levels at the wall of the reactor, at the center and the average (exit) value. Initially ( $t=0$ s), the reactor is assumed to be at  $200^{\circ}\text{C}$  and as the oxidations take place, the reactor center is found to have increased temperature in contrast with the reactor wall temperature that is maintained at low levels due to the presence of the cooling medium. Eventually, the exit (average) temperature is initially decreased, but as the gas mixture approaches the reactor exit, the temperature levels are increased. It can also be said, that at  $t=30$ s, a small increase is detected due to the increased flowrate at the inlet of the PROX which is not considered severe (less than  $15^{\circ}\text{C}$ ). The presence of a controller to maintain the reaction temperature at specific levels is of primary importance and the manipulated value will be the coolant flowrate. It is noted that the hydrogen main stream is assumed to be cooled down before entering the PROX and the fuel cell, but the dynamic simulation of the

heat exchangers is omitted for this study, since we focus on the main subsystems.

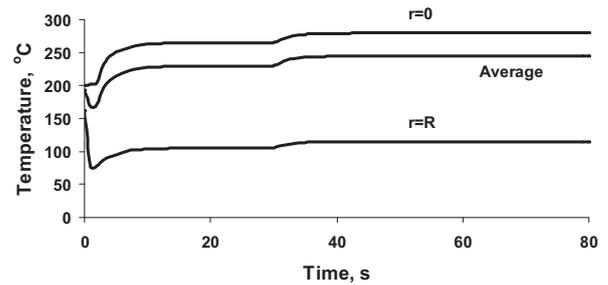


Fig. 8. Temperature levels at the PROX wall, center and average value in the radial domain

Finally, Fig. 9 shows the power and heat production levels based on the inlet hydrogen flow. As can be seen, at  $t=30$ s a  $49.8\%$  increase in power and heat production is detected, which should be taken into consideration at the developed control scheme that will always try to meet the load demand (see next section).

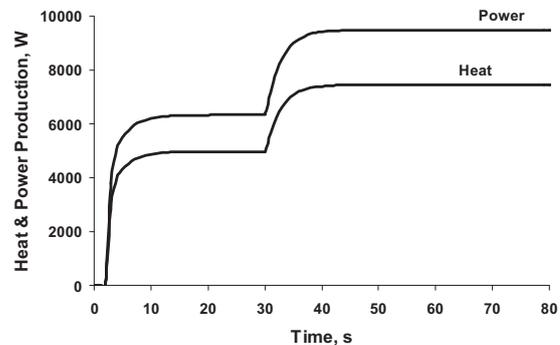


Fig. 9. Power and heat production in the fuel cell

## 5. CONTROL ISSUES ON THE INTEGRATED POWER SYSTEM

As it is obvious from the above analysis, the operation of the integrated power system, requires the development of a robust control scheme. The variables that constantly need to be monitored are: the reactor temperatures, the CO levels and finally, the power to be supplied to the load. In the reformer, the temperature will be controlled by the  $\text{O}_2/\text{CH}_3\text{OH}$  ratio and in the PROX through the coolant flowrate. The CO composition will be controlled by the effective selection of the  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  and  $\text{O}_2/\text{CO}$  ratios. Nevertheless, the main variable of concern is the power that needs to be provided to the load. Changes in the demanded load power level will be handled by manipulating the methanol flowrate in order to produce the hydrogen needed in the fuel cell to operate. As was presented, step changes in methanol flowrate affect the overall operation and model predictive control (MPC) is the more suitable control scheme of such an integrated power system. The control algorithm must also satisfy the bounds for CO and temperature levels in order to protect the various subsystems from deterioration (mainly PROX and fuel cell).

All these consequent changes will be decided based on the minimization of an objective function (MPC) that will take into account all the system necessary constraints. Special care, however, should be given to the fact that that slow and fast dynamics occur in the system (e.g. the fast PROX oxidation versus the slow coolant effect) that might need to be specially treated. Perturbation Theory is proposed to alleviate such problems, because it can be applied to mathematical systems that combine non-linear algebraic equations and differential ones (Kumar A. and Daoutidis P., 1999).

## 6. CONCLUSIONS

An integrated power system for the production of hydrogen via autothermal reforming of methanol has been studied in this paper. The developed mathematical model for the two reactors was validated and used for the simulation of the operation of the power unit where a step change was imposed. The next step will be the integration of the heat management system (burner and heat exchangers), while the developed control scheme will try to maintain the operational variables of concern at their desired values (set points).

### Nomenclature

A:	heat transfer area, m <sup>2</sup>
C <sub>i</sub> :	concentration of the component i, mol/m <sup>3</sup>
C <sub>p,c</sub> :	coolant specific heat capacity, J/K Kg
C <sub>pi</sub> :	component i specific heat capacity, J/K kg
D <sub>r</sub> :	radial effective diffusivity, m <sup>2</sup> /s
D <sub>z</sub> :	axial effective diffusivity, m <sup>2</sup> /s
F:	Faraday's constant, Cb/mol
F <sub>c</sub> :	coolant flowrate, kg/s
F <sub>i</sub> :	flowrate of the component i, mol/m <sup>3</sup>
h <sub>w</sub> :	wall heat transfer coefficient, W/m <sup>2</sup> K
i:	component that takes part at the system
in:	inlet conditions
j:	number of reaction at the reactors
k <sub>r</sub> :	radial thermal conductivity, W/m <sup>2</sup> K
k <sub>z</sub> :	axial thermal conductivity, W/m <sup>2</sup> K
n <sub>c</sub> :	number of cells of the PEM fuel cell
n <sub>e</sub> :	number of electrons
n <sub>F</sub> :	Faraday's efficiency, %
P <sub>i</sub> :	parital pressure of the component i, bar
P <sub>fc</sub> :	fuel cell power, Watt
P <sub>reactor</sub> :	reactor pressure, bar
Q:	heat removed by the cooling jacket, Watt
Q <sub>o</sub> :	volumetric flow, m <sup>3</sup> /s
Q <sub>fc</sub> :	heat, W
r:	radius of the reactor, m
R:	universal gas constant bar m <sup>3</sup> / mol K
R <sub>j</sub> :	kinetic expression of the reaction j, mol/kg <sub>cat</sub> s
S:	cross section of the reactor, m <sup>2</sup>
t:	time, s
T:	temperature, K
T <sub>c</sub> :	coolant temperature, K
u:	superficial gas velocity, m/s
U:	overall heat transfer coefficient, W/m <sup>2</sup> K
V <sub>c</sub> :	coolant jacket volume, m <sup>3</sup>
V <sub>cell</sub> :	cell voltage, V/cell
z:	length of the reactor, m
ΔH <sub>R,T,j</sub> :	enthalpy of reaction j at temperature T, J/mol
ε <sub>cat</sub> :	void fraction of the catalyst

v <sub>i,j</sub> :	coefficient of the component i in the reaction j
ρ <sub>i</sub> :	density of the component i, kg/m <sup>3</sup>
ρ <sub>c</sub> :	coolant density, kg/m <sup>3</sup>

## REFERENCES

- Cipiti, F., Pino, L., Vita, A., Laganà, M., and Recuperio V. (2007). Model-based investigation of a CO preferential oxidation reactor for polymer electrolyte fuel cell systems. *International Journal of Hydrogen Energy*, Volume 32, Pages 4040-4051
- Ipsakis, D., Voutetakis, S., Seferlis, P., Stergiopoulos, F., Papadopoulou, S., and Elmasides C. (2008). The Effect of the Hysteresis Band on Power Management Strategies in a Stand-Alone Power System. *Energy*, Volume 33, Pages 1537-1550
- Kumar A., and Daoutidis P. (1999). Control of nonlinear differential algebraic equation systems. Chapman & Hall/CRC, New York, Washington D.C.
- Larminie J., and Dicks A. (2003). Fuel Cell Systems Explained. 2nd Edition, John Wiley & Sons Ltd
- Lindström B., and Petterson L.J. (2001). Hydrogen generation by steam reforming of methanol over copper-based catalysts for fuel cell applications. *International Journal of Hydrogen Energy*, Volume 26, Pages 923-933.
- Ouzounidou, M., Ipsakis, D., Voutetakis, S., Papadopoulou, S., and Seferlis P. (2008a). Experimental Studies and Optimal Design for a Small-Scale Autonomous Power System Based on Methanol Reforming and a PEM Fuel Cell. *The AIChE 2008 Annual Meeting*, Philadelphia, PA, U.S.A., November 16-21, 2008
- Ouzounidou, M., Ipsakis, D., Voutetakis, S., Papadopoulou, S., and Seferlis P. (2008b). A combined methanol autothermal steam reforming and PEM fuel cell pilot plant unit: Experimental and simulation studies, (submitted in Energy, Special Issue for PRES08)
- Process Systems Enterprise Ltd, gPROMS Introductory User Guide, London, United Kingdom, Release 2.1.1.-15 March 2002.
- Stamps, T., and Gatzke, E.P., (2006). Dynamic modeling of a methanol reformer—PEMFC stack system for analysis and design. *Journal of Power Sources*, Volume 161, Pages 356-370
- Suh, J. S., Lee, M. T., Greif, R., and Grigoropoulos, C. P. (2007). A study of steam methanol reforming in a microreactor. *Journal of Power Sources*, Volume 173, Pages 458-466