Dynamic Modeling and Control of a Steam Reformer-Fuel Cell Power System Operating on LPG for Vehicular Applications

Dimitris Ipsakis[a], Spyros Voutetakis*[a], Simira Papadopoulou[a,b], Panos Seferlis[a,c], Costas Elmasides[d], Krystalia Papadaki[e], Spyros Mastrogeorgopoulos[e], Alexios Kyriakides[a]

[a]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, Thermi-Thessaloniki, Greece
[b]Automation Department, Alexander Technological Educational Institute of Thessaloniki, P.O. Box 141, 57400 Thessaloniki, Greece
[c]Department of Mechanical Engineering, Aristotle University of Thessaloniki, P.O. Box 484, 54124 Thessaloniki, Greece
[d]Systems Sunlight SA, 67200, Neo Olvio, Xanthi, Greece
[e]Department of Chemical Engineering, Aristotle University of Thessaloniki, P.O. Box 1517, 54124 Thessaloniki, Greece
Spyros Voutetakis, paris@cperi.certh.gr

The core aim of this study is to develop a control scheme based on a rigorous mathematical model that will be able to capture the dynamic features of a 1 kW$_p$ fuel cell power system based on LPG reforming that satisfies acceptably power variations in vehicular applications. The integrated system consists of an LPG steam reformer followed by a water-gas-shift reactor. A high temperature PEM fuel cell accompanies the system and receives the produced hydrogen having high tolerance in CO levels (up to 1000 ppm). A burner that exploits the anode off-gas and an additional supply of fresh LPG meets system's heat requirements, while further stream heat integration and individual coolers complement system autonomy and efficiency. Material and energy balances fully apply in system reactors and fuel cell (no axial/radial distributions are introduced), while energy balances for the cold and hot streams are developed for the intensive heat exchanging network. Model validation with available experimental data and thermodynamic results confirm the accuracy of the proposed mathematical modeling scheme. A set of simulations of the integrated system including closed loops of predefined conventional PI controllers is applied in order to evaluate the effectiveness of the respective control scheme.

1. Introduction

LPG (liquefied petroleum gas) is a widely used propane-butane mixture that is readily available from petroleum refineries, is convenient in storage and transportation and recently provided in low prices (Zeman et al., 2011). A medium scale pilot plant unit based on LPG reforming was presented by Recupero et al. (2005), and highlighted the effect of inlet composition and operating temperature on LPG conversion rates. Further thermodynamic analysis identified desired operating ranges for steam/carbon ratios and operating temperatures for autonomous LPG reforming units (Wang et al., 2010; Kale et al., 2009). Despite providing valuable insights on the overall process of LPG reforming,

the aforementioned studies fall short in describing complex dynamic interactions that could be exploited in developing effective control schemes that could minimize system operation & maintenance costs and simultaneously ensure safety during dynamic transitions. Several modeling studies on hydrocarbon reforming systems are presented in literature (Wu and Pai, 2009; Lin et al., 2006; Ipsakis et al., 2012), with main initiative the development of accurate dynamic models that are able to provide a rigorous framework in advanced process control and optimization studies. Following such specifications, the proposed study is organized in two levels. First, an accurate dynamic mathematical model of an integrated LPG reforming system is presented and evaluated. Secondly, according to engineering knowledge and process availability a number of PI control loops of specific system variables are included in the system dynamics. The control actions are imposed by selected manipulated variables in order to operate within the required operating limits.

2. Process Flowsheet Description

The main objective is to design, simulate and control a power system based on LPG reforming that could provide efficiently and uninterruptedly power to a forklift or other vehicles through a fuel cell. The power requirements are considered to vary significantly during a simple operating day and therefore, dynamic transients and control flexibility policy is of primary importance in such a complex problem. The chemical system is necessary to be accompanied by a Li-Ion battery for absorbing power excess from the system (charging) and for providing power deficit (discharging) during extreme operating load demands (Ipsakis et al., 2009). As seen from Figure 1, water is evaporated in heat exchanger E1 with the use of the burner effluent. The gas mixture water-LPG (mixer) is further heated in E2 by the reformer outlet before entering the plug flow reformer for hydrogen production. The reformer outlet (after E2) is air-cooled in E3 and enters the high temperature shift reactor (HTS) for CO minimization (less than 1000 ppm). Due to significant amount of water contained at HTS outlet, a condenser is utilized for water removal and simultaneous heating of the hydrogen rich stream (~75 %) in E4 before entering the anode of the high temperature fuel cell. There, power generation takes place and the anode effluent along with fresh LPG is used as main fuels in the burner. The overall reaction scheme is shown in Table 1.
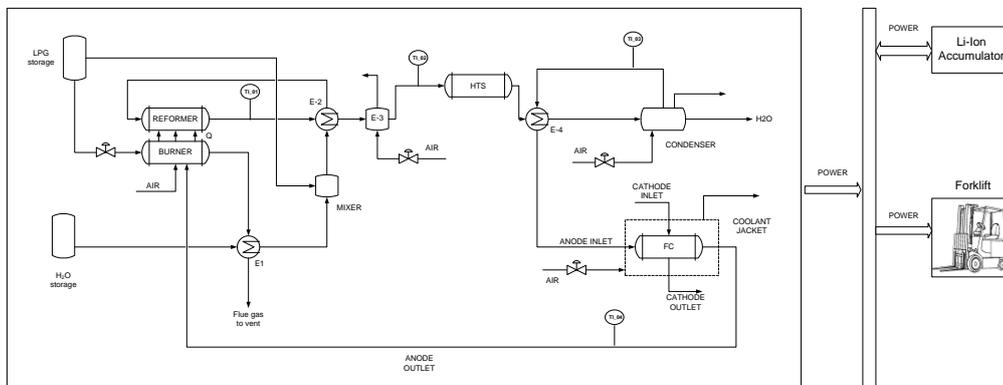

Figure 1: LPG reforming and fuel cell power system

Table 1: Reaction scheme of the LPG reforming and fuel cell power system

Subsystem	Reaction	Subsystem	Reaction
Reformer	$C_3H_8 + 3 \cdot H_2O \rightarrow 3 \cdot CO + 7 \cdot H_2$	**Burner**	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
	$C_4H_{10} + 4 \cdot H_2O \rightarrow 4 \cdot CO + 9 \cdot H_2$		$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$
	$CO + H_2O \leftrightarrow H_2 + CO_2,$		$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
	$CO + 3 \cdot H_2 \rightarrow CH_4 + H_2O$		$CO + 0.5O_2 \rightarrow CO_2$
			$H_2 + 0.5O_2 \rightarrow H_2O$
Water Gas Shift	$CO + H_2O \leftrightarrow H_2 + CO_2$	**Fuel Cell**	$H_2 + 0.5O_2 \rightarrow H_2O$

3. Mathematical Modeling

The nonlinear dynamic model consists of: a) component molar balances, b) energy balances that identify temperature dynamics of streams and subsystems and c) constitutive equations that fully complement the mathematical modeling. The assumptions that follow the overall mathematical model refer to: a) ideal gas behavior, b) no spatial variation is considered, c) negligible system pressure drop and e) pseudo-homogeneous kinetics.

Equations 1, 2 provide the molar and energy balances respectively:

$$\frac{dn_i}{dt} = \frac{d(C_{i,out}V)}{dt} = C_{i,in}Q_{in} - C_{i,out}Q_{out} \pm \sum v_{i,j}r_{i,j} \tag{1}$$

$$\frac{d(\rho_{out}c_p V T_{out})}{dt} = c_p(\rho_{in}Q_{in}T_{in} - \rho_{out}Q_{out}T_{out}) \pm \sum Q_{th} \tag{2}$$

where n_i the ith component moles in mol, C_i the ith component concentration in mol/m^3, V the mixture volume in m^3, Q the volumetric flowrate in m^3/s, $r_{i,j}$ the j reaction rate of component i in mol/m^3·s, $v_{i,j}$ the stoichiometric coefficient of i in reaction j, T_{out} is the fluid outlet stream temperature in K, c_p the specific heat capacity in J/K·kg, ρ_{out} the mixture total density in kg/m^3 and ΣQ_{th} the sum of the total heat exchange (e.g. environmental losses, heat radiation, heat of reaction, heat due to electrochemical phenomena, heat exchange between streams) in W.

In the case of reformer-burner coupling an additional set of equations is needed in order to derive the dynamics of the wall temperature interaction….

$$(mc_p)_{burner}\frac{dT_{burner,wall}}{dt} = UA_{burner,in}(T_{burner,out} - T_{burner,wall}) - UA_{reformer,wall}(T_{burner,wall} - T_{reformer,wall}) \tag{3}$$

$$(mc_p)_{reformer}\frac{dT_{reformer,wall}}{dt} = UA_{reformer,wall}(T_{burner,wall} - T_{reformer,wall}) - UA_{reformer,in}(T_{reformer,wall} - T_{reformer,out}) \tag{4}$$

where m the subsystem mass in kg, c_p the subsystem specific heat capacity in J/K·kg, $T_{burner,wall}$ and $T_{reformer,wall}$ the subsystem wall temperature in K, $T_{burner,out}$ and $T_{reformer,out}$ the fluid outlet temperature in K (Eq.2), $UA_{burner,in}$ and $UA_{reformer,in}$ the overall heat transfer coefficient from bulk to wall in W/K, and $UA_{burner,wall}$ and $UA_{reformer,wall}$ the overall heat transfer coefficient from wall to wall in W/K

The volumetric flowrate, concentration and molar flowrate are associated with the following scheme:

$$Q_{in/out} = \frac{\sum_{i=1}^{N} F_{i,in/out}RT_{in/out}}{P} \tag{5}$$

$$C_{i,in/out} = \frac{F_{i,in/out}}{Q_{in/out}} \tag{6}$$

where in/out denote the inlet/outlet of a subsystem and F_i the i-th component flowrate in mol/s.

In the case of the fuel cell, there is a linear dependence of current draw and hydrogen consumption via the Faraday's law:

$$R_{fc} = \frac{n_c \cdot I_{fc}}{n_e \cdot F} \cdot n_f \tag{7}$$

where R_{fc} the reaction rate in mol/s, n_c are the number of cells, I_{fc} the operation current in A, n_e the number of electrons, F the Faraday's constant in Cb/mol and n_f is the fuel cell electrical efficiency.

The fuel cell operating voltage (V_{fc}, Volt) is based on a group of non-linear equations (Ipsakis et al., 2012) that is dependent on various system variables such as temperature (T_{fc}, K), component concentrations ($C_{i,fc}$, mol/m^3), operating current (I_{fc}, A), design characteristics (d) and electrochemical parameters (p):

$$V_{fc} = f(T_{fc}, C_{i,fc}, I_{fc}, d, p) \tag{8}$$

4. Model Validation

Model validation based on experimental data is a prerequisite stage of the mathematical model development. To this end, an experimental run regarding the following operating conditions was performed by (HELBIO S.A., 2012) LPG to reformer: 1.75ml/min, LPG to burner: 1.05 mL/min, water to reformer (liquid): 14.2 mL/min, air to burner: λ=1.4 (40 % excess). Furthermore, in order to compare several results that are not measured or cannot be derived from experiments (heat exchange, various temperatures, etc) and in this way ensure the model validity, Aspen Plus simulations in steady state mode were performed (Figure 1) and compared with the dynamic simulations. In Table 2, only the similar results are presented and comprise: experimental data/Aspen Plus Simulation/Dynamic Simulation. As can be seen, the accuracy of results is acceptable and indicates the further use of the model in control studies.

Table 2: Comparison between simulated (dynamic model and Aspen Plus) and experimental data

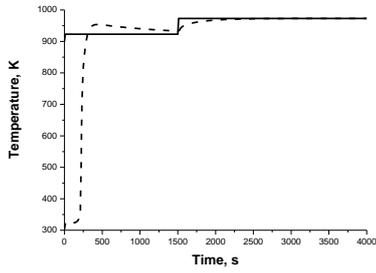|	Reformer	HTS
H_2	71.5 / 72.7 / 72.5 %	73 / 75.8 / 75.8%
CO_2	13.5 / 12.1 / 12 %	23 / 22.05 / 22.3 %
CO	12.5 / 14.2 / 14.2 %	1.15 / 1.26 / 1 %
CH_4	1.5 / 1 / 1 %	1.5 / 0.9 / 0.9 %

5. Control Analysis

The PI controllers (discrete velocity form) that are used in the mathematical model are introduced in specific closed loops of the system according to current engineering knowledge of the integrated system. Table 3 presents the selected pairs of controlled and manipulated variables and the respective parameters of the included controllers in the process flowsheet of Figure 1.

Table 3: System Controlled and Manipulated variables for sampling time T_s=5s

| Controlled Variables	Manipulated Variables	Controller Parameters
Reformer operating temperature	LPG flow at burner	K_c=100, $\tau_{I,fast}$=60 s, $\tau_{I, slow}$ =120 s
HTS inlet temperature	Coolant flow rate at E3	K_c=10, $\tau_{I,fast}$ =300 s, $\tau_{I, slow}$ =3000 s
Fuel cell operating temperature	Coolant flow rate at cooling jacket	K_c=50, $\tau_{I,fast}$ =300 s, $\tau_{I, slow}$ =3000 s
Fuel cell inlet temperature	Coolant flow rate at condenser	K_c=10, $\tau_{I,fast}$ =200 s, $\tau_{I,slow}$ =800 s

As seen from Figures 2 and 3, arbitrary selected set-point trajectories were imposed to the system and a set of closed loop simulation was performed. As was found, a very aggressive integral action (fast action) causes the system at the start up to promote a very high overshoot that could eventually deteriorate catalyst performance or material that operate at higher than desired operations. Also, manipulated variables are forced to increase their action, possibly near their maximum limits. After achieving steady state operation however, the aggressive PI action is considered quite satisfactory for this operating scheme. Providing a slow action though at start-up, the overshoot is eliminated but, steady state is achieved much later. To this end, a combined action of the two is proposed with slow action at first 2000 s and higher at the second stage as seen from controller parameters at Table 3.
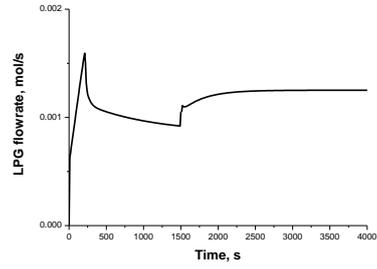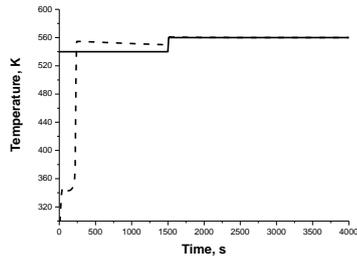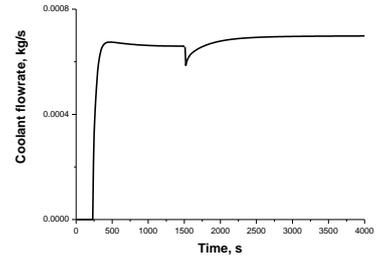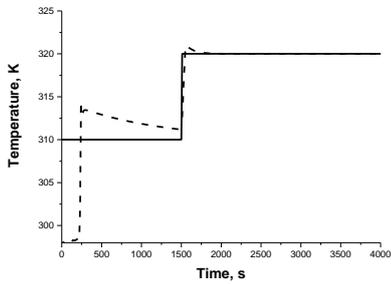
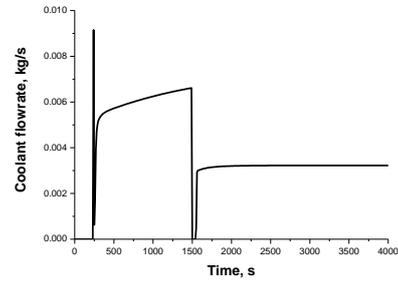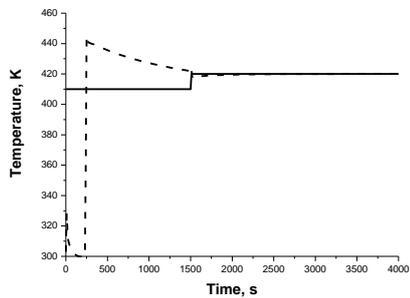*Figure 2: a) Reformer temperature dynamics, b) LPG feed flowrate manipulation, c) HTS inlet temperature dynamics and d) E3 coolant flowrate*
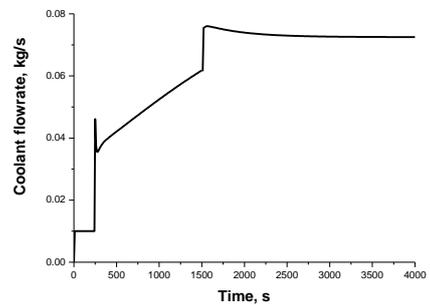

Figure 3: a) Fuel cell inlet temperature dynamics, b) condenser coolant flowrate manipulation, c) Fuel cell operating temperature dynamics and d) coolant flowrate manipulation

6. Conclusions

A control-oriented mathematical model for an integrated LPG reforming and PEM fuel cell power generation system was presented in this study. Experimental results were used to evaluate the accuracy of the proposed model scheme and specific PI control loops were introduced in the process flowsheet. As was found, a "clamped" operating control policy is required in order to offset between high overshoots and low start-up times. Based on this outcome, the next step should be the development of a model-based advanced control framework on the premises of model predictive (nonlinear) control. Such an approach, aims to the maintenance of process control targets in specified trajectories by manipulating in a centralized scheme selected process variables. Fuel minimization and prolonged battery life is considered important in hybrid applications (fuel cell and Li-Ion battery) that involve complex interactions along with a combination of slow and fast dynamics. Until steady state is reached, battery as a fast subsystem could provide power to the system and afterwards the integrated reforming-fuel cell system can support the overall operation.

Acknowledgment

References

HELBIO S.A., 2012. Hydrogen and Energy Production Systems <www.helbio.com>, Accessed 30.05.2012

Ipsakis D., Voutetakis S., Papadopoulou S., Seferlis P., 2012, Optimal operability by design in a methanol reforming-PEM fuel cell autonomous power system, International Journal of Hydrogen Energy, doi:/10.1016/j.ijhydene.2012.02.134.

Ipsakis D., Giannakoudis G., Papadopoulos A.I., Voutetakis S., Seferlis P., 2009, Design and optimization of a Stand-Alone Power System based on renewable energy sources, Chemical Engineering Transactions, 18, 147-152.

Kale G.R., Kulkarni B.D., Joshi A.R., 2009, Thermodynamic study of combining chemical looping combustion and combined reforming of propane, Fuel, 89(10), 3141-3146.

Lin S.T., Chen Y.H., Yu C.C., Liu Y.C., Lee C.H., 2006, Dynamic modeling and control structure design of an experimental fuel processor, International Journal of Hydrogen Energy,31(3), 413-426.

Recupero V., Pino L., Vita A., Cipitì F., Cordaro M., Laganà M., 2005, Development of a LPG fuel processor for PEFC systems: Laboratory scale evaluation of autothermal reforming and preferential oxidation subunits, International Journal of Hydrogen Energy, 30(9), 963-971.

Wang X., Wang N., Zhao J., Wang L., 2010, Thermodynamic analysis of propane dry and steam reforming for synthesis gas or hydrogen production, International Journal of Hydrogen Energy, 35(23),12800-12807.

Wu W., Pai C.C., 2009. Control of a heat-integrated proton exchange membrane fuel cell system with methanol reforming, Journal of Power Sources, 194(2), 920-930.

Zeman H., Url M., Hofbauer H., 2011, Autothermal reforming of hydrocarbon fuels, Chemical Engineering Transactions, 24,169-174.