

***Study of an Integrated System for the Production of Hydrogen by Autothermal Reforming of Methanol***

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All the developed as well as the developing world today is greatly concerned about the continuous problems of the environmental pollution as well as for the continuous increase on the price of oil. For this reason, the study and development of applications that deal with the production of alternative fuels and aim in the reduction of dependence from conventional fuels like oil and in the reduction of air pollutants acquire particular importance.

A methanol reforming fuel cell system, which consists of a methanol auto-thermal fuel reactor, a preferential oxidation reactor and a PEM fuel cell system has been designed and developed at C.P.E.R.I. (Laboratory of Environmental Fuels and Hydrocarbons). The main target of the project is the design of an autonomous integrated system with a capacity of 1-10 kW<sub>e</sub> electric energy and also the development of a mathematical model that will be used for system evaluation.

The process of hydrogen production via autothermal reforming of methanol, consists of the methanol reformer and the preferential oxidation reactor for CO removal. Thus, the pilot plant in C.P.E.R.I. comprises the preheater, the autothermal reformer, the preferential oxidation reactor and a PEM fuel cell. The produced hydrogen along with other gaseous products (CO<sub>2</sub> and CO) is fed to the preferential oxidation reactor for the removal of CO at levels of 20-50 ppm, as it is well known that higher quantities of CO can poison the anodic electrode of the fuel cell and degrade its performance. The effluent stream of the preferential oxidation reactor consists of a gas mixture with a typical composition of 55-65% H<sub>2</sub>, 15-25% CO<sub>2</sub>, 15-20% N<sub>2</sub>, 20-50 ppm CO in dry basis, which is introduced to the PEM fuel cell anode chamber. One of the most important advantages of this proposed method is that the process is taking place at lower temperatures compared with the reforming temperatures of other organic compounds like methane.

This integrated system has been studied from a theoretical and from an experimental scope at CPERI (Chemical Process Engineering Research Institute). The developed mathematical model consists of the energy and material balances that describe the behavior of the autothermal reformer and the preferential oxidation reactor. In the first steps of the theoretical analysis, the steady-state performance was studied where the various H<sub>2</sub>O/CH<sub>3</sub>OH ratios and various reaction temperatures revealed the same behavior as with the experimental study. The main variables that are concerned for the theoretical study are the concentrations of methanol, carbon monoxide, carbon dioxide and hydrogen as a function of the response time and the reactor length at both reactors. Moreover, the present work examines the effect of the inlet H<sub>2</sub>O/CH<sub>3</sub>OH and O<sub>2</sub>/CH<sub>3</sub>OH ratios and of the reforming temperature on methanol conversion and CO selectivity. From preliminary studies, it was found that higher temperatures led to higher H<sub>2</sub> concentrations but the CO level increased.

Furthermore the increase of the  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$  ratio proved efficient as the CO reduced due to the water gas reaction and  $\text{H}_2$  is slightly increased.

For future studies, the dynamic model will be developed in order to describe better the transient responses on the system. The evaluation of the mathematical model with experimental data will be another crucial step towards the development of a “plant wide” model based control. Dynamic simulations of the integrated system as a whole after studying each subunit separately, are used as the basis of developing and evaluating a “plant wide” model based control strategy. This strategy will exploit the inherent time scale separation in such integrated systems and involves the stabilization of individual subsystems in a fast time scale and supervisory control of the overall integrated system in a slow time scale.

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