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Study of an integrated system for the production of hydrogen by autothermal reforming of methanol

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Abstract

In this study a mathematical model is developed and evaluated in order to describe an experimental methanol fuel processor (a combination of autothermal reformer and preferential oxidation reactor) for the production of hydrogen to be used it as the main fuel of a Proton Exchange Membrane Fuel Cell (PEMFC) for the generation of 1kW electrical power. This integrated system has been studied from a theoretical and an experimental point of view where different parameters were studied in order to maximize hydrogen production and keep in a low content carbon monoxide. The main variables that are of concern in this study, are the temperature and the concentrations of the reactants and products as a function of the length of the reactors. By utilizing kinetic expressions developed for this catalytic system, the results of the simulations are found in good agreement with the results obtained from the experimental implementation.

Keywords: autothermal reforming, preferential oxidation, fuel cell, integrated systems

1. Introduction

Hydrogen constitutes a promising form of alternative fuel for the future because its production and utilization can be free of greenhouse gas. The lack of a safe and cost effective hydrogen storage however, is currently a significant obstacle to its direct use in a fuel cell. To overcome this difficulty, hydrogen can be produced by easily stored raw materials in a combined hydrogen producting and fuel cell system.

Hydrogen is conventionally manufactured in large scale by the steam reforming of hydrocarbons like methane or naphtha oil; for small and medium scales users produce it from methanol [1]. Methanol is easily available in the market; it does not require special conditions of storage, while it is also free from sulphur oxides that exist in natural gas. Currently, there are three available processes for extracting hydrogen from methanol. Among them autothermal reforming exhibits the most significant advantages and is currently the most reliable process for hydrogen generation from methanol [2].

A drawback of reforming hydrocarbons is the production of CO at levels that are very poisonous to the electrocatalyst at the anode of the fuel cell. Several processes that are used for the minimization of CO content at allowable levels (20-50ppm) have been discussed in the past, where among them preferential oxidation is considered to be the simplest and the least expensive method [3].

Previous studies regarding the modeling of the system, have been dealing with each subsystem individually. Reformer and Preferential Oxidation reactor (PROX) modeling has been studied for other hydrocarbons like n-decane and methane [4,5].

In this work, pseudo-homogeneous models that accurately predict the axial profiles of radially averaged temperatures and concentrations at both catalytic fixed bed reactors are developed and presented.

2. Model Description

The principle reactions that take place in the reformer are steam reforming of methanol, water gas shift reaction, methanol decomposition and partial oxidation of methanol. These reactions are not independent. In fact, steam reforming is considered to be the sum of the water gas shift reaction and methanol decomposition reaction [6].

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 for the ignition of the reforming reaction. The reformer is considered to be adiabatic at a temperature of 300 ^{o}C and pressure of 1.8 bar.

In this study, the ratios of steam over methanol (S/C) and of oxygen over methanol (O_2/C) at the reformer inlet are set equal to 1.5 and 0.13 respectively, unless stated otherwise.

The CO composition is reduced in the preferential oxidation reactor at a temperature of 180 ^{o}C and pressure of 1.5 bar. In this reactor besides the CO oxidation, hydrogen oxidation (kept at slow rate) and water gas shift reaction also take place [7]. These reactions are highly exothermic and therefore is essential to have a water bath or a jacket with a cooling fluid (e.g. water) for the removal of the produced heat.

The mathematical model consists of the component material and energy balances in the two reactors.

$$\frac{\partial C_i}{\partial t} + \varepsilon_{cat} \cdot \frac{\partial (u \cdot C_i)}{\partial z} = \sum_{j=1}^{R} \nu_{ji} (r)_j \qquad (1)$$

$$\frac{\partial (\sum_{i=1}^{N} \rho \cdot c_p \cdot T)}{\partial t} + \varepsilon_{cat} \cdot \frac{\partial (u \cdot \sum_{i=1}^{N} \rho \cdot c_p \cdot \rho \cdot c_p \cdot T)}{\partial z} = -\sum_{j=1}^{R} r_j \cdot (\Delta \mathrm{H}_{R,T}) + \frac{4 \cdot U}{D} \cdot \Delta \mathrm{T} \qquad (2)$$

where:

i: component that takes part at a reaction (1,…7)

j: number of reaction (1,…4)

Kinetic expressions for the principal reactions in each reactor were taken from the literature [6-8].

The assumptions made for the simulation study are the following:

- Constant pressure at the reactors.
- Equal solid and vapor phase temperature.
- Ideal gas behavior of each component.
- Thermal capacity of the gas in the reactor is negligible, as compared to that of the solid catalyst.

3. Model Solution and Results

The analysis that is presented in this section is for steady state conditions where the independent variable is the length of the reactors.

3.1. Experimental Arrangement

The overall experimental study was conducted at the reforming hydrocarbons pilot plant at CPERI/CERTH [9]. In table 1, experimental data for the reformer's outlet are presented, where the effect of steam over methanol and temperature effect was studied. An increase in the reforming temperature leads to an increase in the CO production, whereas an increase in S/C ratio leads to a decrease in CO production. The weight hourly space velocity, WHSV ($gr_{methanol}$ /gr_{cat} hr) and O_2/C ratio are equal to 19.3 and 0.13 respectively.

H_2O/CH_3OH (S/C)	**1.5**			**2.5**		**3.5**
T (°C)	**285**	**315**	**320**	**320**	**330**	**320**
CO_2 (%)	22.59	21.02	20.96	22.32	22.13	22.41
H_2(%)	66.11	65.79	65.30	63.99	64.08	62.23
CO(%)	1.72	3.73	3.98	1.44	1.86	0.88

Table 1: Experimental data (dry basis) obtained at the outlet of the reformer for various temperatures and S/C ratios [10]

3.2. Simulated Results

The equations were solved simultaneously in order to give the results for the profiles at the reactors (reformer and PROX reactor). It is highlighted that the differential equations to be solved are stiff. Numeric solution of the mathematical equations (1) and (2) was performed by using MATLAB® 2006. Figures 1 and 2 show the temperature profile and the components mole fraction (dry basis) along the reactor path of the reformer, respectively.

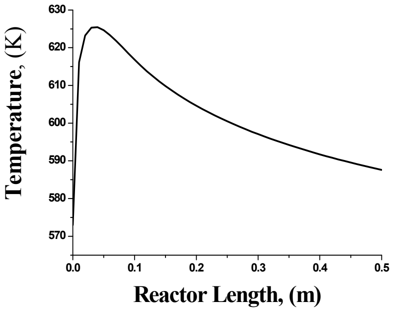

Figure 1: Temperature profile along the length of the reformer

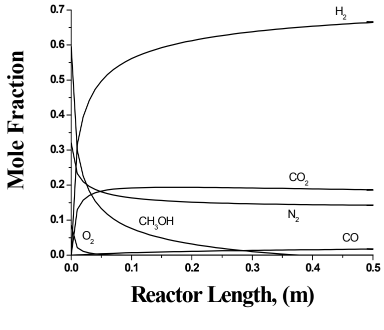

Figure 2: Components mole fraction along the length of the reformer

At the beginning of the reactor the partial oxidation of methanol provides the necessary heat to ignite the reforming reaction and after air is consumed, there is a sharp decrease due to the endothermic steam reforming reaction. At the outlet of the reformer hydrogen composition is 66% per mole (in dry basis) and carbon monoxide is 1.8% per mole (in dry basis). Figure 3 shows the effect of the S/C ratio in CO selectivtity. As can be seen, CO selectivity decreases with a higher steam over methanol ratio. The increase of steam at the inlet of the reformer, however leads to the design of a larger reformer.

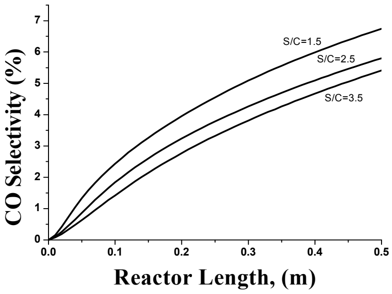

Figure 3: CO Selectivity for various steam to methanol ratios (S/C) at the reformer

Furthermore, figures 4 and 5 show the temperature profile and components mole fraction (dry basis) along the PROX reactor path. The highly exothermic oxidation reactions are responsible for the sharp increase of the temperature and the decrease at 450 K is due to the heat removal from the cooling fluid of this reactor. From the components mole fraction (dry basis) profile it can be shown that reverse water gas shift reaction and the two oxidation reactions are taking place at the first 5cm of the reactor where there is a slight decrease at H_2 mole fraction and an increase at CO mole fraction. Water Gas Shift Reaction (WGS) is responsible for the increase of H_2 and the decrease of CO mole fraction, at 68% and 0.00017% respectively.

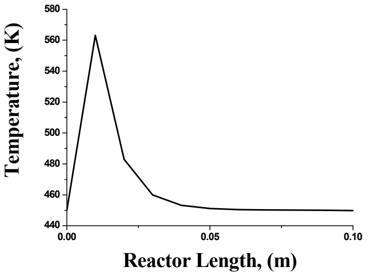

Figure 4: Temperature profile along the length of the PROX reactor

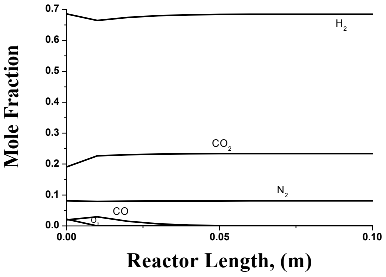

Figure 5: Components mole fraction along the length of the PROX reactor

3.3. Results & Discussions

The experimental results revealed that a Cu-based catalyst had a very satisfactory performance in hydrogen production via autothermal steam reforming. Temperatures around 300 ^{o}C were chosen, due to the high hydrogen percentage at the outlet of the reformer. CO contents around 1.5-2 % (in dry basis) are considered to be satisfactory at the outlet of the reformer since higher percentage leads to the design of a larger PROX reactor. The effect of the reactants ratios at the inlet of the reactors remains also a critical issue since they can lead to CO content below its lowest limit of 20 ppm.

4. Conclusions

In this work a mathematical model for an integrated system for the production of hydrogen for usage in a PEM fuel cell was developed. The results of the steady state simulation study were the basis for the design of an experimental methanol reforming system. The next step of this research study will be the development of a dynamic mathematical model and the development and evaluation of a ''plant wide'' model based control strategy

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