Energy 34 (2009) 1733–1743

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

A combined methanol autothermal steam reforming and PEM fuel cell pilot plant unit: Experimental and simulation studies

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ARTICLE INFO

Article history:
Received 8 January 2009
Received in revised form
12 June 2009
Accepted 13 June 2009
Available online 16 July 2009

Keywords:
Methanol autothermal steam reforming
Preferential oxidation of CO
Hydrogen production
PEM fuel cell
Modeling
Integrated systems

ABSTRACT

An integrated system for hydrogen production via autothermal steam reforming of methanol and consequent power generation in a polymer electrolyte membrane (PEM) fuel cell has been developed and operated at C.P.E.R.I. The pilot plant comprises an autothermal reforming reactor to produce hydrogen, a preferential oxidation reactor (PROX) to reduce CO concentration below 50 ppm and a PEM fuel cell for power generation.

The present paper deals with the study of this system, both from an experimental and a theoretical point of view. The experimental work aims to: (a) examine the effect of the reforming temperature on methanol conversion and on the effluent stream concentration, (b) investigate the effect of reaction temperature and O_2/CO ratio on the performance of the PROX reactor, and (c) evaluate the operation of a 10-cell PEM fuel cell, using pure hydrogen and air at three temperature levels. The experimental data are subsequently utilized for the validation of one-dimensional pseudo-homogeneous models that have been developed for the two reactors and also for the identification of the voltage–current characteristic curve of the PEM fuel cell. The validated models are then used to investigate the behavior and explore the interactions, both static and dynamic, among the various process subsystems.

1. Introduction

Power generation using a fuel cell can be achieved with zero greenhouse gas emissions when hydrogen is produced by renewable energy sources [1–3]. Advantages of fuel cells include their few moving parts, the low operation temperature (~80 °C) and the fast cold start [4,5]. Nevertheless, the main disadvantages of fuel cells refer to the high investment and operating cost (due to the presence of Pt in the electrodes and the compression of supply gases) and the hydrogen supply.

An autonomous power system requires that hydrogen should be produced reliably and continuously. Candidate fuels for use in integrated hydrogen-based power systems are natural gas, methanol, ethanol, higher hydrocarbons and dimethyl ether (DME) [6–9]. Methanol does not require special conditions of storage, has a high H:C ratio and no C:C ratio [10], while biomass resources can be used to produce methanol (bio-methanol) [11]. Moreover, methanol reforming requires moderate temperature levels and is free of sulphur oxides that usually appear in methane and gasoline reforming.

Hydrogen production from methanol can be achieved via steam reforming, partial oxidation and autothermal reforming [6,12,13]. Steam reforming of methanol produces a rich in hydrogen outlet stream (~75%), but the endothermic nature of the reactions requires the supply of heat by an external source (e.g., a burner). On the other hand, partial oxidation of methanol is a highly exothermic reaction that could lead to the formation of hot spots in the catalyst, while hydrogen remains at relatively low concentration levels (~45%). In the autothermal steam reforming, methanol, oxygen and water are co-fed in appropriate ratios so that the reforming and oxidation reactions are properly balanced to create slightly exothermic or thermally neutral conditions [12,13]. Steam reforming of hydrocarbons however, leads to the production of the undesired CO at levels that are poisonous to PEM fuel cells [4,14,15]. Several processes used for the minimization of CO content at acceptable levels (less than 50 ppm) have been extensively studied, and preferential oxidation appears to be the simplest and the most economically attractive method [16,17].

Extensive research showed that Cu-based catalysts are probably the most suitable choice for high hydrogen production rates

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doi:10.1016/j.energy.2009.06.031

Nomenclature

A_T	Tafel slope for the PEM fuel cell, V
C	Concentration, mol/m^3
C_p	Specific heat capacity, J/(K · kg)
D	Diameter of the reactor, m
E_{fc}	Thermodynamic voltage for the PEM fuel cell, V
E	Arrhenius activation energy, J/mol
F	Faraday constant, Cb/mol
F	Flowrate, mol/s
G_f	Gibbs free energy of formation, J/mol
$H_{R,T}$	Enthalpy of reaction, J/mol
i_{fc}	Current density for the PEM fuel cell, A/m^2
i_o	Tafel parameter for the PEM fuel cell, A/m^2
$K_{eq,wgs}$	Equilibrium constant for the water gas shift (WGS) reaction
k_o	Arrhenius constant for the reactions in the reformer and PROX
l	Parameter for the overvoltage due to mass transport limitations for the PEM fuel cell, m^2/A
m	Parameter for the overvoltage due to mass transport limitations for the PEM fuel cell, V
Power	Power, W
P	Partial pressure, bar
$P_{reactor}$	Reactor pressure, bar
Q_o	Volumetric gas flow in the reactors, m^3/s
R	Universal gas constant, (m^3 · bar)/(mol · K)
R_{fc}	Resistance for the PEM fuel cell, Ω·m^2
r	Kinetic expression, mol/(kg$_{cat}$ · s)
S	Cross section of the reactor, m^2
T	Temperature, °C or K
t	Time, s
u	Superficial gas velocity, m/s
U	Overall heat transfer coefficient, J/(m^2· K · s)
V_{act}	Activation losses, V
V_{fc}	Operation cell voltage for the PEM fuel cell, V
V_{mtl}	Mass transport or concentration losses, V
V_{ohmic}	Ohmic losses, V
z	Length of the reactor, m

Greek symbols

Δ	Difference from a reference value
ϵ_{cat}	Void fraction of the catalyst
ν	Stoichiometric coefficient
ρ	Density, kg/m^3

Subscripts

i	Component index: 1, …, 7: CH_3OH, H_2O, O_2, H_2, CO_2, CO, N_2
in	inlet conditions
j	Reaction index

[10,18,19]. Regarding process characteristics and equipment, reformers are reactors mainly based on plug flow conditions [20,21] and several studies investigated the effect of the operation temperature, the reactants feed ratio and the reactants flowrate in order to identify those conditions that achieve high methanol conversion and low CO selectivity. Similar experimental studies conducted on PROX reactors [22,23], calculated the suitable conditions (e.g., temperature, suitable O_2/CO ratio and so forth) to achieve low CO concentrations at the outlet stream. Integrated power systems of small scale have been presented in [24,25] and comprise a reformer, a PROX reactor and a hydrogen combustion unit, where a power production up to 150 W was achieved. Medium to large scale systems that employ a reformer, a catalytic burner, a gas cleaning unit and a PEM fuel cell have also been studied for long-term operation [26]. Similarly, Liu et al. [27] integrated an autothermal reformer, a water-gas-shift and a PROX reactor into a 75 kW_{el} PEM fuel cell that further utilized anode offgas to an evaporator. On the other hand, Lindström and Pettersson [28], effectively combined a methanol reformer and a PROX reactor with a 5 kW fuel cell that achieved start-up times at the region of 4–6 min, but nevertheless high CO levels were observed in some cases.

From a simulated point of view, thermodynamic analysis identified all the possible by-products of the methanol steam reformer and a parametric sensitivity analysis with respect to the reactants ratios and operation temperature has been reported in [29,30]. Simulation models that predict the steady-state operation of the reformer can be found in [31,32], while a dynamic model for a methane fuel processor, which can also be adapted for similar fuels such as methanol, can be found in [33]. Furthermore, PROX reactors have been modeled using two-dimensional [34] and one-dimensional [35] models.

As can be seen, the study of the overall integrated system has attracted limited attention, as most studies focused on the individual subsystems either experimentally or mathematically. In an integrated system the degree of interactions among the various process units and power generating devices can be quite large. Therefore changes in process (e.g. temperature increase) affect all other units, and the ability of the system to meet a change in the power load depends on the response of both upstream and downstream units for heat integrated systems or systems with recycles. The main focus of this work lies on the investigation of the performance of the various process units through experimental studies, the development and validation of reliable and accurate process models and the comprehensive exploration of the interactions among the various subsystems through effective simulation studies. Therefore, the behavior of a reformer with a Cu–MnO catalyst is studied under various operating conditions with an ultimate goal to identify those conditions that maximize hydrogen production, but simultaneously result in low CO content in the outlet reactor stream. Similar studies are carried out for a PROX reactor with a CuO–CeO_2 catalyst that aim to investigate the effect of the $\lambda = 2[O_2/CO]$ ratio, as well as, the suitable range of temperature levels on the CO conversion. Furthermore, the effect of temperature on the operation of a 10-cell PEM fuel cell is studied for the determination of the voltage-current (V–I) characteristic curve. Process models are then developed for both reactors assuming a one-dimensional mathematical relation for temperature and species concentration and validated using the available experimental data. In addition, a process model is also developed and validated with the experimental data for the PEM fuel cell. Two simulated cases that utilize the validated models explore the interactions between the two reactor units. The main emphasis is directed on the phenomena taking place inside the reactors (steady-state operation), as well as, on the dynamic operation of the system for changes in the feed stream conditions. Results analysis leads to significant conclusions regarding the static and dynamic behavior of the integrated system and is considered a necessary step for the development of efficient control and operating policies.