Chemical Engineering Journal 146 (2009) 128–135

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Design of a CO preferential oxidation reactor for PEFC systems: A modelling approach

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ARTICLE INFO

Article history:
Received 11 January 2008
Received in revised form 4 September 2008
Accepted 5 September 2008

Keywords:
Fuel processor
CO preferential oxidation
Hydrogen oxidation
Hydrogen production
Two-dimensional catalytic modeling

ABSTRACT

This paper presents a two-dimensional model of a preferential oxidation (PROX) reactor to be used in a beta 5 kWe hydrogen generator (HYGen II), to integrate with Polymer Electrolyte Fuel Cells (PEFCs). PROX reactors require careful temperature control systems, in order to enhance optimization and control of the unit. The model concerns chemical kinetics and heat/mass transfer phenomena occurring in the reactor. Aim of the model is to investigate the effects of the molar ratio O_2/CO, the gas hourly space velocity (GHSV) and the inlet temperature on process performance of the reactor, in order to obtain high CO conversion and high selectivity with respect to the undesired H_2 oxidation. The model plays a key role in overcoming the issues of system design, by evaluating the temperature and the gas concentration profiles in the reactor. Simulation results showed the strong dependence of the overall performance upon the operating conditions examined.

1. Introduction

Fuel cell technology has been recently recognized as the most effective method to produce energy by both industrial R&D departments and academia. The Polymer Electrolyte Fuel Cell (PEFC) fuelled by hydrogen appears to be the key option for both transport and small scale combined heat and power applications, due to its compactness, modularity, higher conversion efficiencies and low emissions of noise and pollutants [1,2]. A growing interest for small stationary applications (in the 0.5–10 kW electrical output range) is developing; a large increase in the number of installed units in the world, as a decentralized power supply, grid support, peak shaving, power back-up or uninterruptible power supply (UPS), can be derived [3].

The absence of a hydrogen refuelling infrastructure and problems concerning hydrogen storage has led to the development of fuel processors able to convert available fuels (hydrocarbons and/or alcohols) into hydrogen rich reformate gas [4]. The choice of a suitable fuel processor and fuel, during the transition phase to a hydrogen economy, are key aspects to the successful implementation of direct-hydrogen fuel cell systems.

The key requirements for a fuel processor include rapid start-up, good dynamic-response to change in hydrogen demand, high fuel-conversion, small size and weight, simple design (construction and operation), stable performance for repeated start-up and shut-down cycles, maximum thermal integration, low cost and maintenance, high reliability and safety [5].

In small scale applications, natural gas remains the fuel most commonly employed for its wide availability and related infrastructure. For some niche markets, such as electricity production in remote sites, LPG could be an interesting optional fuel [6,7]. However, to utilize the reformate gas as a reactant for PEFC systems, clean-up steps must be considered to reduce the CO concentration to an acceptable level (10 ppm), since the fuel cell performance is progressively degraded by CO poisoning of the anode catalyst [8,9]. The reformate stream is purified using a two-stage process. The first stage is the water gas shift reaction, that reduces the carbon monoxide, increasing hydrogen content. The CO conversion is limited by equilibrium at the outlet temperature of the reactor. In the second stage the amount of carbon monoxide is further reduced using preferential oxidation reaction, which is the most compact of all the purification methods. Alternative technologies for the last clean-up step, such as Pressure Swing Adsorption (PSA) or Metal Separation Membranes, are not suitable for small scale applications, because high pressure requirements mandate the use of an additional compressor, and the need to re-humidify the hydrogen prior to use in fuel cells. Furthermore a desiccant must be used to adsorb water from the incoming wet gas stream in a PSA unit [10].

Because the PROX reaction is exothermic, the main drawback of a preferential oxidation reactor is complex temperature control system, in order to minimize parasitic hydrogen oxidation, since selectivity of oxygen to carbon monoxide deteriorates with

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doi:10.1016/j.cej.2008.09.004

Nomenclature

c_i	concentration of species i (mol m^{-3})
c_i^0	inlet concentration of the species i (mol m^{-3})
C_{pj}	heat capacity of air in the jacket (J kg^{-1} K^{-1})
C_{pr}	heat capacity of gas in the reactor (J kg^{-1} K^{-1})
$D_{i,eff}$	effective diffusion coefficient of species i (m^2 s^{-1})
D_{ij}	binary (species i, j) gas diffusion coefficients (m^2 s^{-1})
$D_{ij,eff}$	effective binary (species i, j) gas diffusion coefficients (m^2 s^{-1})
F_i	molar flow rate of the species i (mol s^{-1})
h_i	molar enthalpy of the species i (J mol^{-1})
ΔH_{CO}	enthalpy for the reaction of CO oxidation (J mol^{-1})
ΔH_{H_2}	enthalpy for the reaction of H_2 oxidation (m^2 s^{-1})
k_f	thermal conductivity of the fluid (W K^{-1} m^{-1})
k_{eff}	effective thermal conductivity in the reactor (W K^{-1} m^{-1})
k_j	thermal conductivity in the jacket (W K^{-1} m^{-1})
k_s	thermal conductivity of the solid (W K^{-1} m^{-1})
k_w	thermal conductivity of the wall (W K^{-1} m^{-1})
N_i	flux vector of species i (mol m^{-2} s^{-1})
p_{O_2}	oxygen partial pressure (Pa)
q_j	heat flux vector in the jacket (mol m^{-1} s^{-3})
q_r	heat flux vector in the reactor (mol m^{-1} s^{-3})
Q	heat generation rate per unit volume of the catalyst bed (J m^{-3} s^{-1})
r_{CO}	rate of CO oxidation (mol kg_{cat}^{-1} s^{-1})
r_{H_2}	rate of H_2 oxidation (mol kg_{cat}^{-1} s^{-1})
R_g	gas constant (J mol^{-1} K^{-1})
R_i	net species' reaction term (mol m^{-3} s^{-1})
T_j	jacket temperature (K)
T_r	reactor temperature (K)
T_0	inlet temperature of the reagent gas mixture (K)
T_j^0	inlet temperature of the air (K)
u_j	air velocity in the jacket (m s^{-1})
u_r	velocity of the fluid in the reactor (m s^{-1})
U_k	film coefficient (W K^{-1} m^{-2})

Greek symbols

δ_w	thickness of the wall (m)
ε	void fraction of the catalyst bed
ρ_b	catalyst bulk density (kg_{cat} m^{-3})
ρ_{gr}	gas density in the reactor (kg m^{-3})
ρ_{gj}	gas density of the air in the interspace (kg m^{-3})

Subscripts

cat	catalyst
eff	effective
f	fluid
g	gas
i	gas species, i = CO, O_2, CO_2, H_2, H_2O
in	inlet
j	jacket
r	reactor
s	solid
out	outlet

increasing operating temperatures [11]. The consequent oxidation of hydrogen causes a decrease in the process efficiency and increases water management issues. Multi-stage PROX reactors have been proposed [12–14], but complex hardware is required to control temperatures, using staged air injections along the catalyst bed. A single-stage PROX process could be an optimal solution, as reported by Echigo et al. [15]. It has been reported that Pt/Al_2O_3 catalysts showed higher CO removal performance than conventional Ru/Al_2O_3 catalysts in a temperature range 448–523 K [16–18].

During the last few years, research activity on the PROX reaction for small scale applications has focused on catalyst development/testing and reactor design optimization, in order to reduce the CO concentration to below 10 ppm to meet the fuel purity requirements for PEFC stacks.

Previous experimental tests with our 2 kWe LPG-based fuel processor (HYGen I) [19], designed for integration with a PEFC, showed some drawbacks in the CO preferential oxidation step: the CO content in the output of the reactor reached a CO level of 0.2% (dry basis). This content, incompatible with a PEFC system, showed the need of improving the prototype engineering, focusing on further efforts to achieve optimized design of the PROX subsystem, in terms of temperature control.

The objective of this study is to theoretically investigate the PROX kinetics by a modeling approach. A 2D steady state reactor model was developed, driving the design of a single-stage multi-tube reactor to overcome the system issues of heat management, considering Pt/Al_2O_3 catalysts (pellets form 3 mm × 3 mm). This geometrical configuration, with a cocurrent air in the cooling jacket (interspace), is used as a case study in developing a beta 5 kWe hydrogen generator [20–22]. Simulation studies on the influence of reactor geometrical parameters [23,24], comparing process performance with other two configurations (without a cooling jacket and with a countercurrent air flow in the interspace), showed that an optimal temperature control can be achieved using a configuration with a cocurrent air flow in the interspace. The model-based analysis make it possible to gain insight into the factors that limit PROX performance.

2. Reactor concept and design

The HYGen II system can generate hydrogen for Polymer Electrolyte Fuel Cells for small stationary applications. The prototype is able to convert light hydrocarbons (methane, LPG, butane) with a nominal hydrogen production of 5 N m^3 h^{-1} and a maximum hydrogen production of 8 N m^3 h^{-1}. The net size (mm) of the fuel processor is 636 (width) × 868 (length) × 1350 (height).

The unit is based on three catalytic reaction steps: the Autothermal Reforming (ATR), the Intermediate Water Gas Shift (ITWS) and the preferential oxidation (PROX). The diagram of the integrated system is shown in Fig. 1; the processing unit is coupled with a heat exchanger, a static mixer, a water reservoir, manual/automatic valves, pressure regulators/transducers, flow meters and ancillaries.

The main issues in developing a commercially viable fuel processor are high energy efficiency, compact size and low cost for manufacturing and maintenance. Consequently, the system has been engineered, focusing on the design of every single component and the integration of the system, to minimize size, while improving thermal and mass transfer and system efficiency. The reformer uses a new design concept for integrating the CO preferential oxidation process and the heat transfer management into a suitable configuration, namely, a single-stage multi-tube reactor geometry. Hence the resulting unit is a single-stage multi-tube reactor, filled with pellet catalysts with a total volume of 4.38 l.

The single-stage multi-tube PROX reactor consists of 10 parallel and cylindrical tubes (Fig. 2): the product gas mixture from the previous water gas shift step enters into a static mixer where it is mixed with air and then reaches the heating zone, that consists of an inert bed heated by electrical heating elements only during start-up