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Bioethanol steam reforming for ecological syngas and electricity production using a fuel cell SOFC system

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Abstract

A bioethanol processing system to feed a 200 kW solid oxide fuel cell (SOFC) is simulated and evaluated in the present paper. The general scheme of the process is composed of vaporization, heating, bioethanol steam reforming (ESR) and SOFC stages. The performance pseudo-homogeneous model of the reactor, consisting of the catalytic ESR using a Ni/Al_2O_3 catalyst, has been developed based on the principles of classical kinetics and thermodynamics through a complex reaction scheme and a Lagmuir-Hishelwood kinetic pattern. The resulting model is employed to evaluate the effect of several design and operation parameters on the process (tube diameter between 3.81 and 7.62 cm, catalyst pellets diameter 0.1–0.5 cm, temperature 673–873 K, space time (θ) 1–10 (g min/cm^3) and water/ethanol molar ratio (R_{AE}), 1–6). It can be concluded that higher water/ethanol ratio ($R_{AE} = 5{:}1$) and temperatures (above 773 K) favors hydrogen yield ($Y_H = 4.1$) and selectivity ($S_H = 91\%$), while the heat consumed in vaporization and heating stages is strongly increased at the same conditions. At temperatures above 773 K and $R_{AE} > 6$, the reforming efficiencies exhibit a plateau because of the thermodynamics constraints of the process. The SOFC stack is arranged in parallel and needs 83 cells of 0.4 A/cm^2 and 1 m^2.

Keywords: Bioethanol; Steam reforming; Fuel cells; Reactor modeling

1. Introduction

Nowadays catalytic steam reforming is a new interest focus as the main pathway to obtain hydrogen from hydrocarbons or alcohols to be supplied to a fuel cell (FC). The mentioned above is based fundamentally on the low emissions and high efficiency levels obtained from the operation of FC systems and hydrogen combustion engines as well [1–3]. The environmental compatibility of hydrogen energy is limited by the primary fuel, because of this ethanol present several advantages when is compared with other fuels [1], since it is easier to store, handle and transport in a safe way due to its lower toxicity and volatility. In addition, this alcohol could be bio-produced from a wide variety of biomass sources, including sugar cane molasses, lignocelluloses and waste materials from agro-industries [4]. On the other hand, if the fermentation of biomass is used to obtain the bioethanol, the total emissions of CO_2 could be neutral, since the dioxide emitted in the reforming to FC process is consumed for biomass growth, being the contribution to the total warming null.

Moreover, bioethanol steam reforming is the cheapest and efficient way to produce hydrogen from biomass, both reactants (water and ethanol) includes H atoms that contribute to the total yield and the thermal efficiency obtained is considerably good (>85%) [2]. From thermodynamic studies [5,6], the feasibility of hydrogen production from bioethanol steam reforming at temperatures higher than 500 K have been proved. Besides these studies has shown that the increment of temperature and water/ethanol feed molar ratio (R_{AE}) favors the hydrogen production while high pressures reduces considerably the total yield.

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Nomenclature

A_{is}	shell inner transfer area (cm^2)
A_{os}	shell exterior heat transfer area (cm^2)
A_{refm}	mean area of heat transfer surface of refractory (cm^2)
A_s	shell flow area (cm^2)
A_{sm}	mean area of heat transfer surface of shell (cm^2)
A_t	tube flow area (cm^2)
A_{wm}	mean area of heat transfer surface of metal (cm^2)
Ac	SOFC stack surface (cm^2)
ac	single cell surface (cm^2)
C_{pm}	reacting mixture heat capacity (J/g K)
C_{pg}	hot gasses heat capacity (J/g K)
$C_{E\text{-}Exp}$	experimental bioethanol conversion
$C_{E\text{-}Model}$	predicted bioethanol conversion
D_p	pellet diameter (cm)
D_{to}	tube outer diameter (cm)
D_s	shell inner diameter (cm)
DI	current density (A/cm^2)
F_j	molar flow of component *j* (mol/s)
F_{obj}	optimization function
G_g	hot gasses mass flow (g/s)
G_m	reacting mixture mass flow (g/s)
h_{cr}	convection–radiation coeff. between surface and surroundings (W/cm^2 K)
h_{is}	convection–radiation film coeff. between shell and tubes (W/cm^2 K)
h_i, h_o	heat transfer film coeff. for inside and outside of tubes surface (W/cm^2 K)
$\Delta H_{(i)}$	heat of reaction *i* (J/mol)
I	current (A)
K_{eff}	effective thermal conductivity (W/cm K)
K_m, K_i	thermal conductivity of mixture and component *i* (W/cm K)
K_{tref}	thermal conductivity of refractory (W/cm K)
K_{ti}	thermal conductivity of insulating (W/cm K)
K_w	thermal conductivity of metal (W/cm K)
M_i	molecular weight of component *i* (g/mol)
n	carbon atoms in the products (1 for CO, CO_2, CH_4 and 2 for C_2H_6)
$n(z,j)$	moles of component *j* at (*z*) position (mol/s) ($j=1$ C_2H_6O, $j=2$ CH_4, $j=3$ CO, $j=4$ H_2, $j=5$ CO_2, $j=6$ H_2O, $j=7$ C)
$n(O_2)_{CON}$	oxidant feed to SOFC (mol/s)
N_c	cells number
N_{tub}	tube number
p_E	C_2H_6O partial pressure (atm)
p_w	H_2O partial pressure (atm)
p_H	H_2 partial pressure (atm)
p_{ME}	CH_4 partial pressure (atm)
p_D	CO_2 partial pressure (atm)
p_M	CO partial pressure (atm)
P	total pressure (atm)
P_c	stack power (kW)
Qa	heat consumed in the conditioning (kJ/h)
Qr	heat consumed in the reforming (kJ/h)
Qv	heat consumed in the vaporization stage (kJ/h)
Qc	heat consumed in the heating stage (kJ/h)
$r(z,i)$	rate of reaction *i* at *z* position, $i=5, 6, \ldots, 10$ ($mol/s\,cm^3$)
Re	Reynolds number
R_{do}, R_{di}	dirt scale for outside and inside of tubes (cm^2 K/W)
$S_{j\text{-}Exp}$	experimental selectivity of component *j*
$S_{j\text{-}Model}$	predicted selectivity of component *j*
T_a	environment temperature
T_g	hot gasses temperature (K)
T_m	reacting mixture temperature (K)
T_{tw}	tube wall temperature (K)
U_t	overall heat transfer coefficient (tubes) (W/cm^2 K)
U_s	overall Heat transfer coefficient (shell) (W/cm^2 K)
V_c	single cell voltage (V)
x_{ref}	thickness of refractory material (cm)
x_{im}	thickness of insulating material (cm)
X_{sw}	thickness of shell (cm)
y_i	mol fraction of component *i*
$Y_{j\text{-}Exp}$	experimental yield of component *j*
$Y_{j\text{-}Model}$	predicted yield of component *j*
z	reactor length (cm)

Superscripts

in	enter to the reactor
out	living the reactor

Greeks letters

α	stoichiometric coefficient of component (*j*) within reaction (*i*)
ε	bed porosity
η_{ref}	reforming efficiency (%)
η_{cell}	cell efficiency (%)
ρ_m	reacting mixture density (g/cm^3)

The bioethanol steam reforming is an endothermic reaction, for this reason the necessary heat has to be supplied from an external source; it could be represented in the simplest case by the following stoichiometry equation:

$$C_2H_5OH + 3H_2O \Leftrightarrow 2CO_2 + 6H_2 \qquad \Delta H^\circ = +173.5\,\mathrm{kJ\,mol^{-1}}$$

However, during the process a series of side reactions take place (ethanol dehydration and decomposition) producing byproducts (CH_3CHO, C_2H_4, CH_3COOH), which compete for hydrogen atoms causing the reduction of the global yield; because of this the use of stable and selective catalytic formulations is an important issue for the process development.