Steam reforming of glycerol for hydrogen production: Modeling study

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ABSTRACT

A phenomenological model that predicts the operation of a packed bed reactor for glycerol steam reforming (GSR), in terms of glycerol conversion and products generation (first time to our knowledge), especially H_2, was built and used to perform a parametric analysis (range of conditions: 748−848 K, water-to-glycerol feed ratios (WGFRs) of 3−12 and 1−5 atm). First, the model was validated in terms of glycerol conversion, products yields and selectivities, having been observed very good agreement. Regarding the parametric study, higher temperatures, WGFRs and pressures were found to be more beneficial in terms of glycerol conversion. Moreover, the H_2 yield and selectivity are enhanced when higher temperatures and lower WGFRs and pressures are employed. Still, the maximum amount of 4.93 mol of H_2/mole of glycerol fed to the reactor was observed at 848 K, WGFR of 9 and 2 atm.

Introduction

Nowadays hydrogen is seen by many authors as the energy carrier of the future due to its potential to fulfill many of our society needs without ignoring some of the environmental problems that fossil fuels, the main energy carriers of the present, cannot avoid. Therefore, several distinct processes for hydrogen production have been researched. While during the last century the focus was manly on using fossil fuels-based feedstock (e.g.: natural gas), in the last decades the interest has shifted towards cleaner raw materials such as methanol, ethanol and glycerol, among others. Glycerol, in particular, can be produced as a by-product during the biodiesel production process and converted into hydrogen through steam reforming (Eq. (1)).

$$C_3H_8O_3 + 3H_2O \rightleftharpoons 7H_2 + 3CO_2 \quad (\Delta H_r^{298K} = 128 \text{ kJ·mol}^{-1}) \qquad (1)$$
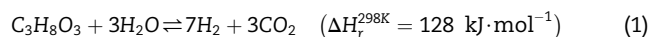
However, the formation of secondary products of a more complex mechanism than Eq. (1), such as CO and CH_4, must be considered as well, according to some works reported in the literature regarding glycerol steam reforming (GSR) [1−4]. The use of glycerol as feedstock would prove itself advantageous compared to methanol or ethanol since it would decrease its disposal and associated costs, thus valorizing biodiesel.

Even though there has been done a huge amount of work regarding the search of GSR catalysts and there are several thermodynamic assessments that have been done [5],

Notation and glossary

A	kinetics pre-exponential factor, mol/(m^{2}s kPa$^{(\beta+\gamma)}$)
A_{ij}	dimensionless parameter for the mixture of i and j
$A_{metal\ surface}$	metal surface area of the catalyst, m^2/kg$_{cat.}$
C	total concentration of species, mol/m^3
C_i	molar concentration of compound i, mol/m^3
$C_{p,i}$	molar heat capacity of species i, J/(mol K)
$C_{p,f}$	Mass heat capacity of gas mixture, J/(kg K)
C_1	Sutherland constant, kg/(m s K$^{0.5}$)
D_{ax}	mass axial dispersion coefficient, m^2/s
$D_{C_3H_8O_3,j}$	binary diffusivity of $C_3H_8O_3$ when diffusing into species j, m^2/s
$D_{C_3H_8O_3,mix}$	molecular diffusivity of $C_3H_8O_3$ in the reaction mixture, m^2/s
d_p	catalyst particles diameter, m
E_a	activation energy, J/mol
F	dimensionless parameter
F_i	molar flux of species i, mol/(m^{2}s)
g	dimensionless parameter of steam kinetics
h	convective wall-fluid heat transfer coefficient, W/(m^{2}K)
L	reactor length, m
M_i	molar mass of species i, mol/kg
P	reactor total pressure, Pa
p_i	partial pressure of component $i = C_3H_8O_3$ and H_2O, kPa
R	ideal gas constant, J/(K mol)
R_i	consumption/formation rate of component i, mol/(kg$_{cat.}$s)
R_0	reactor inner radius, m
S	Sutherland temperature, K
S_i	selectivity of species i

s_i	temperature based parameter for component i, K
T	bed absolute temperature, K
T_{bi}	normal boiling point of species i, K
$T_{i,0}$	reference temperature for species i in Sutherland's equation, K
T_w	reactor wall absolute temperature, K
u_s	superficial velocity of the gas mixture, m/s
V_R	volume of the reactor bed, m^3
W_{cat}	mass of catalyst in the reactor bed, kg$_{cat.}$
x	dimensionless axial coordinate
X_G	conversion of $C_3H_8O_3$
Y_i	yield of species i
y_i	molar fraction of species i

Greek letters

β	partial reaction order for $C_3H_8O_3$
$\Delta H_{f,i}$	heat of formation of species i, J/mol
ε_b	void fraction of the catalyst bed
ϕ_{ij}	dimensionless parameter for the mixture of i and j
γ	partial reaction order for H_2O
λ_{ax}	heat axial dispersion coefficient, W/(m K)
λ_i	thermal conductivity of species i, W/(m K)
λ_f	thermal conductivity for the gas mixture, W/(m K)
ρ_f	gas mixture density, kg/m^3
μ_i	viscosity of species i, Pa s
μ_f	gas mixture viscosity, Pa s
v	atomic diffusion volume
v_i	unitary constant that indicates if i is consumed or produced

List of acronyms

GSR	glycerol steam reforming
WGFR	water-to-glycerol feed ratio

phenomenological models that allow describing the GSR reaction system in packed bed reactors, for example, are still too few. To the best of our knowledge there are only a couple of works where such models are reported [6−8]. Even though all these are 2D models that allow consequently to do an interesting analysis of the several variables profiles (e.g. contours over the 2D domain [8]), they only predict the consumption of glycerol. There is one work in which the generation of products (and by-products) is predicted; however, it is for the sorption-enhanced GSR process and assumes theoretical yields [9], which is not realistic for conditions far from those employed by the authors. With the aim of covering up this hole, a phenomenological model capable of predicting accurately the real operation of a GSR packed bed reactor in terms of consumption of glycerol and production of the main products (H_2 and CO_2) and by-products (CO and CH_4), based on actual individual products generation kinetics, has been developed and will be target of analysis here. First a critical comparison between the model's predictions and the experimental results obtained by Cheng et al. [10] for a Co-Ni/Al$_2$O$_3$ catalyst is done, being then followed by a parametric analysis considering different temperatures (748−848 K), water-to-glycerol feed ratios (WGFRs) (3−12) and pressures (1−5 atm).

Phenomenological model

Model and governing equations

The pseudo-homogeneous model here proposed for describing the GSR reaction in a packed bed reactor considers the following assumptions:

- Steady state;
- Axially dispersed plug flow;
- Non-isothermal operation;
- Pressure drop along the bed described by the Ergun equation;
- Non-constant velocity along the bed;
- Ideal gas behavior.

The governing equations used to simulate such system are the following, being composed by 7 differential equations (one for each species - partial mass balances), 1 differential equation for the total mass balance (required due to the non-constant velocity along the reactor bed), as well as 2 other differential equations to obtain temperature and total pressure profiles: