



Research Paper

Packed bed reactor modeling of the catalytic auto-thermal reforming of synthetic crude glycerol



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ARTICLE INFO

Keywords:

Crude glycerol
 Autothermal reforming
 Nickel based catalyst
 Power law
 Reactor modeling

ABSTRACT

Modeling and simulation studies of synthetic crude glycerol auto-thermal reforming were performed in a catalytic packed bed reactor over a 5 wt% Ni/CeZrCa catalyst. The numerical model comprised of two-dimensional material and energy balance equations and an in-house developed power law kinetic rate model. The model was validated against experimental data and a close agreement between the predicted and experimentally measured values was obtained with an average absolute deviation of < 9%. Also, it was found that for the set of conditions and reactor dimensions used for this study, the effect of the axial dispersion term on the glycerol conversion was negligible. This effect is expected to be more pronounced at a larger scale and under actual operating conditions and therefore should not be neglected.

1. Introduction

Recent years have shown an increase in the alternative energy portfolio, as a solution to help meet growing energy demands, fluctuating oil prices and reduction in greenhouse gas emissions. This has led to a growth in commercialized biodiesel production. Research has shown that the crude glycerol, a byproduct of biodiesel production, is a viable source of hydrogen [1]. Steam reforming (SR) of hydrocarbons is a widely accepted industrial practice for hydrogen production and naturally, a lot of research has focused on glycerol steam reforming. Steam reforming is highly endothermic requiring high temperatures and contributing to the high operating costs of steam reformers. Auto-thermal reforming (ATR) is an alternate reforming process for hydrogen production. It involves the addition of a limited amount of oxygen to trigger an exothermic partial oxidation reaction to occur simultaneously with the steam reforming reaction. This would therefore reduce the amount of energy for the reaction and suppress coke formation [2]. Dauenhauer et al. [3] found out that addition of steam suppressed carbon monoxide (CO) formation and the main advantage of ATR is, under ideal conditions, external heat is not needed. Studies have shown differing amounts of hydrogen produced by ATR compared with SR with some observing an increase in hydrogen production [4] and others a decrease [5]. However, both cases showed increased hydrogen production with increased temperature. Douette et al. [6] observed 4.4 mol of H₂ produced for every mole of crude glycerol with coking and catalyst deactivation problems. Kinetic models have been developed in

literature to simulate catalytic ATR [7–9]. Chan and Wang [10] developed a 1-D unsteady state model incorporating heat/mass transfer with the chemical kinetics and a complete thermodynamic analysis of the system. Hoang and Chan developed a two dimension unsteady state model for the catalytic ATR of methane [11]. The development process also included chemical reaction kinetics and mass/heat transfer phenomena. Chan and Ding [12] showed how the 2-D model can be further developed by including diffusion of the reactants into the pores of the catalyst. In an earlier work, an auto-thermal reforming process was developed for reformation of synthetic crude glycerol to hydrogen [13]. The objectives of the study were catalyst development, process variable optimization and kinetic analysis. The modeling and simulations reported in this paper are based on the experimental setup, conditions, analysis and results presented elsewhere [13]. The selected catalyst was 5 wt% Ni/CeZrCa prepared by the surfactant assisted method with wet impregnation of the nickel element. Testing and characterization of the ATR of synthetic crude glycerol showed reasonable crude glycerol conversion (84.5%) and hydrogen selectivity (79.7%) [13]. Reactor modeling is needed to provide deeper comprehension of what occurs during the crude glycerol auto-thermal reforming inside a catalytic packed bed tubular reactor (PBTR). The numerical models required to simulate reactor behavior is usually simplified but not at the cost of accuracy. The proposed criteria of eliminating the axial dispersion term [14,15] for reactor modeling makes the process approach plug flow behavior. Therefore, the radial direction does not show tangible variations in temperature and component composition with no evidence

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Nomenclature*Symbols Used*

A	Reactor cross-sectional area [m ²]
AAD	Average absolute deviation [%]
D	Reactor internal diameter [m]
E	Activation energy [J mol ⁻¹]
h	Heat transfer coefficient [kJ m ⁻² s ⁻¹ K ⁻¹]
L	Length of catalyst bed [m]
M_{ave}	Average molecular weight of crude glycerol [g mol ⁻¹]
P	Pressure [atm]

R	Gas constant [J mol ⁻¹ K ⁻¹]
T	Temperature [K]
W	Weight of catalyst [g]
W/F_{AO}	Space time [h]
z	Position in reactor length [mm]

Greek Letters

$(-\Delta H)$	Heat of reaction based on component [J mol ⁻¹]
λ_{eff}	Effective thermal conductivity kJ m ⁻¹ s ⁻¹ K ⁻¹
ρ_B	Catalyst bulk density [kg/m ⁻³]
ρ_g	Gas density [kg/m ⁻³]

that the axial dispersion term in the continuity and energy balance equations had any significant effect on glycerol conversion at the studied reactor scale. This paper presents the simulation of synthetic crude glycerol auto-thermal reforming using a two dimension pseudo-homogeneous numerical model within the COMSOL Multiphysics simulation environment. The experiments [13] were carried out in the absence of mass transfer (interfacial and intraparticle diffusion) and heat transfer (internal and external) resistances so a pseudo-homogenous model was chosen. The significance of axial dispersion on the accuracy of the predicted results is also presented and discussed herein.

2. Theory

The kinetics and reactor model development for the synthetic crude glycerol ATR in a PBTR was based on the reaction kinetics of the 5 wt% Ni/CeZrCa and power law rate model developed elsewhere [13].

2.1. Kinetic rate modeling

An empirical power rate model was developed to describe the experimental observations. The development of this model is covered in detail in Abdul Ghani's thesis [13]. The power law model is as expressed in Eq. (1):

$$r_A = A_0 e^{\frac{-E}{RT}} C_A^{0.5} C_C^2 \quad (1)$$

where r_A = kg-crude glycerol kg-cat⁻¹ h⁻¹; A_0 = frequency factor; E = activation energy, J mol⁻¹; R = gas constant, 8.314 J mol⁻¹ K⁻¹; T = temperature, K; C_A = crude glycerol concentration, mol m⁻³; C_B = steam concentration, mol m⁻³; C_C = oxygen concentration, mol m⁻³

2.2. Numerical reactor modeling

A numerical model was developed and implemented for simulating the temperature and concentration profiles inside the reactor. The model was set up using mass and heat balance partial differential equations (PDEs) around the reactor geometry at steady state in the presence of the pseudo-homogenous chemical reaction represented by Eq. (1). The steady mass conservation equation for a species of concentration, c , may be described as:

$$\frac{\partial \partial c}{\partial t} + \nabla \cdot (uc + D_{eff} \nabla c) = \rho_B v_i r_A \quad (2)$$

In cylindrical coordinate system, assuming no variations along the angular coordinate, the above equation for species i may be expanded as;

$$\frac{\partial \partial C_i}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left(-D_{eff} r \frac{\partial C_i}{\partial r} + u_r C_i r \right) + \frac{\partial}{\partial z} \left(-D_{eff} \frac{\partial C_i}{\partial z} + u_z C_i \right) = \rho_B v_i r_A \quad (3)$$

where C_i is the concentration of species i , mol/m³, r is the reactor

radius, m, D_{eff} is the effective diffusivity, m²/s, u_r and u_z are the superficial velocities in the radial and axial directions, respectively, and r_A is the reaction rate and v_i is the stoichiometric coefficient of reacting species i . The radial convective flux is negligible compared to the diffusive flux and can be eliminated. Therefore, $u_r = 0$ and the radial flux consists primarily of the diffusion term.

$$\frac{\partial \partial C_i}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left(-D_{eff} r \frac{\partial C_i}{\partial r} \right) - \frac{\partial}{\partial z} \left(-D_{eff} \frac{\partial C_i}{\partial z} + u_z C_i \right) = \rho_B v_i r_A \quad (4)$$

u_z is constant throughout the reactor and equal to the inlet velocity

$$\frac{\partial \partial C_i}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left(-D_{eff} r \frac{\partial C_i}{\partial r} \right) + D_{eff} \frac{\partial^2 C_i}{\partial z^2} - u_z \frac{\partial C_i}{\partial z} = \rho_B v_i r_A \quad (5)$$

Expanding and redistributing the terms gives the final form of the mass balance equation

$$\frac{\partial \partial C_i}{\partial t} + u_z \frac{\partial C_i}{\partial z} - D_{eff} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) - D_{eff} \frac{\partial^2 C_i}{\partial z^2} = \rho_B v_i r_A \quad (6)$$

For energy balance, assume the flux of species i across any area takes the form

$$F_i = -D_i \nabla C_i + u C_i \quad (7)$$

The steady energy equation, therefore may be written as

$$\sum \frac{\partial \partial C_i h_i}{\partial t} + \sum \nabla \cdot F_i h_i - \nabla \cdot \lambda_{eff} \nabla T = \Delta H \rho_B v_i r_A \quad (8)$$

where λ_{eff} is the effective thermal conductivity of the reaction mixture, J/m s K, ΔH and is the heat of reaction, kJ mol⁻¹, h_i is the enthalpy of species i . Upon expansion in cylindrical coordinate system, assuming no variations in the angular direction, the above equation takes the form

$$\begin{aligned} \sum \frac{\partial \partial C_i C_{pi} T}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left[r \sum \left(-D_i \frac{\partial C_i}{\partial r} + u_r C_i \right) C_{pi} T \right] \\ + \frac{\partial}{\partial z} \left[\sum \left(-D_i \frac{\partial C_i}{\partial z} + u_z C_i \right) C_{pi} T \right] \frac{\lambda_{eff}}{r} \frac{\partial}{\partial r} \left(\frac{r \partial T}{\partial r} \right) - \lambda_{eff} \frac{\partial^2 T}{\partial z^2} \\ = \Delta H \rho_B v_i r_A \end{aligned} \quad (9)$$

where C_{pi} is the heat capacity of species i , J mol⁻¹ K⁻¹, T is the temperature, K. Simplifications assuming $u_r = 0$, u_z constant throughout the reactor length and the axial convective flux is greater than the axial diffusive flux

$$\begin{aligned} \sum \frac{\partial \partial C_i C_{pi} T}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left[r \sum \left(-D_i \frac{\partial C_i}{\partial r} \right) C_{pi} T \right] + \frac{\partial}{\partial z} \left[\sum (u_z C_i) C_{pi} T \right] \\ - \frac{\lambda_{eff}}{r} \frac{\partial}{\partial r} \left(\frac{r \partial T}{\partial r} \right) - \lambda_{eff} \frac{\partial^2 T}{\partial z^2} = \Delta H \rho_B v_i r_A \end{aligned} \quad (10)$$

It was further assumed that the diffusive flux of species i in the radial direction is negligible compared with the convective flux along the axial direction, the above equation, therefore reduces to:

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