Experimental studies and comprehensive reactor modeling of hydrogen production by the catalytic reforming of crude ethanol in a packed bed tubular reactor over a Ni/Al$_2$O$_3$ catalyst

Ahmed Aboudheir[a], Abayomi Akande[a, b], Raphael Idem[a, *], Ajay Dalai[b]

[a]Process Systems Engineering Laboratory, Faculty of Engineering, University of Regina, Regina, Canada S4S 0A2
[b]Chemical Engineering Department, University of Saskatchewan, Saskatoon, Canada S7N 5C5

Abstract

A rigorous numerical model was developed to simulate the production of hydrogen from the reforming of crude ethanol in a packed bed tubular reactor (PBTR). The model was based on the coupling of mass and energy balance equations as well as a new kinetic model developed for the process. The simulation results for crude ethanol conversion were found to be in accordance with the experimental data obtained at various operating conditions. This confirms the validity of the numerical model. A further validation of the model was obtained by using the model to simulate a well-documented reaction process. In addition, the predicted variations of the concentration and temperature profiles for our process in the radial direction indicate that the assumption of plug flow and isothermal behavior is justified within certain kinetics operating conditions. However, even within these operating conditions, our results have proven that the axial dispersion terms in both the mass and the energy balance equations cannot be neglected.
© 2005 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

Keywords: Hydrogen; Crude ethanol; Reforming; Kinetics; Tubular reactor modeling

1. Introduction

Strong efforts are being made to commercialize the use of fuel cells such as the proton exchange membrane (PEM) fuel cell for the generation of electric power for both electric vehicles and distributed stationary applications [1,2]. The major reason for the interest is the high-energy efficiency of the fuel cell, which in some cases, is reported to have an overall energy efficiency of about 85% [3]. Also, with an equally strong interest in the use of hydrogen (H$_2$) as the fuel, PEM fuel cells are the most certain to meet future ultra low NO$_x$, SO$_x$, CO, CH$_4$ and CO$_2$ emissions targets [1]. Thus, H$_2$ has a significant future potential as an alternative fuel that can solve the problems of CO$_2$ emissions as well

as the emissions of other air contaminants. It is well known that H$_2$ production can be accomplished by gasification or reforming of fossil fuels [4,5] or biomass [6]. However, if a global cycle of clean and sustainable production of energy is envisaged, a new eco-friendly reservoir of hydrogen is needed [7,8].

In this context, ethanol (a form of biomass) satisfies most of these requirements since it is easy to produce, and is also safe to handle, transport and store [9,10]. As such, ethanol provides an environmentally responsible energy source that can significantly reduce greenhouse gas emissions [8]. It is also known that the application of ethanol for the production and use of H$_2$ energy is CO$_2$ neutral [11]. Furthermore, since ethanol does not contain heteroatoms and metals, its use as source of energy does not result in emissions of NO$_x$, SO$_x$, particulates and other toxics. In addition, ethanol is mostly an oxygenated hydrocarbon, which leads to complete

---

* Corresponding author. Fax: +1 306 585 4855.
  E-mail address: Raphael.idem@uregina.ca (R. Idem).

combustion during its application to produce power. As such, little or no CO is produced. These attributes have made H_2 obtained from ethanol reforming a very good energy vector, especially in fuel cells applications. H_2 production from ethanol has advantages when compared with other H_2 production strategies, including steam reforming of methanol and hydrocarbons. Unlike hydrocarbons, ethanol is easier to reform and is also free of sulfur, which is a catalyst poison in the reforming of hydrocarbons [9]. Also, unlike methanol, which is sourced from hydrocarbons [12] and has a relatively high toxicity, ethanol is completely biomass based and has low toxicity.

The production of hydrogen by steam reforming of pure ethanol has been widely investigated [13–16]. In all these cases, water is needed as a co-feed to the process. Consequently, there is no need to reduce the water and organic contents of wet or crude ethanol (i.e. fermentation broth produced from a fermentation process) since this contains approximately 12% v/v ethanol, which is within the range of water to ethanol molar ratios used for the literature cited ethanol reforming processes. Besides, by using crude ethanol, the other organic compounds present in the fermentation broth could equally be reformed to produce additional H_2. Also, this process would eliminate the large amount of energy wasted during distillation to remove water from fermentation broth in order to produce dry or pure ethanol. Haga et al. [8] suggested that in order to obtain a widespread use of ethanol for hydrogen production, the economics and energetics of the ethanol production process have to be greatly improved. Thus, by circumventing the distillation and drying step, our process [17,18] of reforming crude ethanol (i.e. fermentation broth) provides us with the ability to produce H_2 from crude ethanol solution in a cost-effective manner. We recently developed the catalytic process for H_2 production from the reforming of crude ethanol based on $Cu/Mn/Al_2O_3$ and Ni/Al_2O_3 catalysts [17–19].

Because of weight and engineering problems, on-board reforming to produce H_2 no longer appears to be the most attractive way to deliver H_2 to the fuel cell in electric vehicles. Instead, there are strong efforts to deliver the H_2 to the fuel cell for this application by means of H_2 refueling stations. Several such stations already exist, for example, the Hydrogenics station in Toronto, Canada, as well as the ones in Perth, Australia and in Japan. A very important aspect for the actualization of the PEM fuel cell powered electric vehicles and distributed stationary PEM energy application (especially in remote locations where biomass is abundant) that would use crude ethanol based H_2 is the proper design of the crude ethanol reformer. It is well known that the simulation and design of any reactor requires information on both the thermodynamic and kinetic properties of the reaction of interest. In this regard, we have recently developed the kinetics for the production of hydrogen by the reforming of crude ethanol in a packed bed tubular reactor (PBTR) over 15% Ni/Al_2O_3 catalyst prepared by coprecipitation techniques [19].

It is well known that catalytic PBTRs are usually used for the reforming of hydrocarbons [20] or the reforming of oxygenated hydrocarbons such as methanol and ethanol. The performance of these reactors (tubular and membrane) depends on the mass transport characteristics and temperature distribution in the reactor. Most of the reported design models in the literature are based on unrealistic assumptions such as plug flow behavior, perfectly isothermal or adiabatic condition, or negligible radial gradients [21–23], which were imposed mainly to obtain a simple model to solve in terms of ordinary differential equations. However, this simplification may be a serious deficiency when reactions with pronounced heat effects are involved such as in the hydrocarbon or oxygenated hydrocarbon reformation processes. Only few recent papers exist in the literature, which have reported models that take into consideration the variations of the concentration and temperature in both the axial and radial directions. However, these models still apply several assumptions such as negligible pressure drop, ideal behavior of gases, constant reactor wall temperature, negligible diffusion resistance of particle of catalyst, or negligible axial dispersion [24,25]. It is well known that the more unrealistic the assumptions imposed on the model are, the less accurate will the model be able to predict the behavior of the process. In this paper a comprehensive numerical model was solved and compared with experimental results in order to investigate the validity of some of these assumptions for the production of hydrogen from the reforming of crude ethanol in a PBTR.

2. Theory

2.1. Numerical modeling

The numerical model developed and used for modeling and simulation of the PBTR is based on the steady state mass and energy balances (Eqs. (1) and (2), respectively) around the reactor in the presence of chemical reactions. Based on the general mass and energy balance equations reported by Bird et al. [26] and the geometry of the PBTR depicted in Fig. 1, which represents a schematic diagram of the catalytic PBTR used in the experimental work, the model equations can be presented in cylindrical coordinates for z components as in Eqs. (1) and (2):

$$v_Z \frac{\partial C_i}{\partial z} = D_r \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) + D_z \frac{\partial^2 C_i}{\partial z^2} + \rho_B r_j, \quad (1)$$

$$\rho_g C_p v_Z \frac{\partial T}{\partial z} = \lambda_r \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right)$$
$$+ \lambda_z \frac{\partial^2 T}{\partial z^2} + \rho_B \left[\sum -\Delta H_j r_j \right], \quad (2)$$