Modeling and design of a microchannel reformer for efficient conversion of glycerol to hydrogen

CrossMark

*Ozgur Yasar Caglar, C. Doga Demirhan, Ahmet K. Avci**

Department of Chemical Engineering, Bogazici University, Bebek 34342, Istanbul, Turkey

ABSTRACT

The objectives of this study are to investigate steam reforming (SR) of glycerol, by-product of biodiesel synthesis, in a wall-coated catalytic microchannel by a detailed mathematical model and design an adiabatic microchannel reformer that can be integrated into a biodiesel production plant with an annual capacity of 4×10^3 m^3/year. Modeling and simulation studies are based on Finite Element Method (FEM) technique. Sizing and design of the multichannel reactor involving wall-separated arrays of parallel microchannels is based on converting a minimum of 85% of the glycerol obtained as a by-product of the biodiesel production. The results show that the microchannel architecture enables fast and uniform transfer of the sensible heat of the feed stream to the catalyst layer. This phenomenon, which is more pronounced by using thick and high thermal conductivity walls between channels, allows SR to run without external heat supply and leads to glycerol conversions above 85%. It is demonstrated that a multichannel unit of 1×10^{-2} m^3 volume, operating without external energy supply, is sufficient to convert ca. 90% of the glycerol produced in a biodiesel plant with a capacity of 4×10^3 m^3/year.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The importance of renewable fuels as alternatives to their existing, non-renewable counterparts is becoming more significant due to the increasing cost of obtaining high quality crude oil as a result of the depleting oil reserves [1]. One of the most attractive renewable fuels is biodiesel whose global use is expected to increase continuously. Biodiesel can be produced by catalytic trans-esterification of animal-based or vegetable oils with methanol (or ethanol) [2]. In this process, 1 mol of glycerol is produced for every 3 moles of biodiesel. This stoichiometry, however, causes undesirably high supply of glycerol. Due to the rising demand of biodiesel, the amount of by-product glycerol that will be produced by 2020 is expected to increase up to 3 megatons, whereas the total glycerol demand will be less than 500 kilotons [2]. The significant gap between the demand and supply of glycerol will eventually increase the cost of biodiesel, as well as biodiesel blended diesel fuel due to the elevated cost of glycerol removal.

Solution of this problem requires efficient conversion of glycerol into value-added products such as hydrogen, which is the feedstock for many petrochemical processes as well as for the fuel cells delivering efficient electricity generation. One of the most well known techniques for producing hydrogen from glycerol is by its reforming with steam, which is carried out at temperatures in excess of ca. 600 K over a supported catalyst:

$$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2 \quad \Delta H^0 = 346.4 \text{ kJ/mol} \tag{1}$$

Catalysis of glycerol SR is well investigated. Most of the studies involve the use of Ni-based catalysts [3–6], which are demonstrated to deliver glycerol conversions above ca. 90% depending on the reaction temperature, molar steam-to-carbon ratio at the inlet and contact time. In addition to Ni-based ones, the performance of noble metals such as Rh, Pt, Ru, Pd, Ir [7–9] are also investigated. Apart from the type of active metal, the nature of the catalyst support is found to have significant impact on glycerol conversion and hydrogen selectivity. Adhikari et al. [10] compared the use of CeO_2, MgO and TiO_2 as supports for Ni in glycerol SR and reported that hydrogen selectivity followed the order of Ni/CeO_2 > Ni/MgO > Ni/TiO_2. Pompeo et al. [11] reported that glycerol SR over Pt/γ-Al_2O_3 and Pt/ZrO_2 led to carbon formation and the catalysts are deactivated rapidly due to the acidic nature of both supports. The same authors showed that the use of SiO_2, a support with neutral properties, with Pt gave stable operation together with high activity and hydrogen selectivity [11]. An extensive review of catalysts and supports studied for glycerol-to-hydrogen conversion is reported elsewhere [2].

Hydrogen production from glycerol requires high temperatures and external energy demand, both of which depend strongly on the catalyst type and reactor geometry. Even though the effect of catalyst on glycerol SR is studied extensively, the reactor type is limited to the conventional packed bed configuration. Recent studies on non-oxidative and oxidative steam reforming of methane to synthesis gas showed that structuring the reactor and catalyst by using the microchannel technology can provide methane conversions and CO selectivities higher than those obtained in a packed-bed reactor operated under equivalent conditions [12–14]. Similar results, demonstrating the superior properties of microchannel reactors in terms of improved conversions and high product selectivities are reported by other groups [15–17]. Microchannel reactors are defined as units involving parallel channels with hydraulic diameters below 1×10^{-3} m [18]. Inner walls of the channels are coated with porous catalyst layers with less than ca. 1×10^{-4} m thickness which offers minimum resistance to heat and mass transfer within the catalyst (Fig. 1a). Since the reactor block is mostly a metal and the surface area-to-volume ratio is very high (between ca. $1–5 \times 10^4$ m^2/m^3) due to tiny channels, heat distribution along the reactor and the coated catalyst layers, which are in direct contact with the reactor block, is much faster than observed in a typical packed-bed reactor [19]. These features allow efficient use of the catalyst and lead to higher reactant conversions.

The objective of this study is to investigate steam reforming of glycerol to hydrogen in a microchannel reactor by a FEM-based mathematical model that can successfully describe detailed flow and catalytic reaction phenomena in the micro-scale, and to understand temperature distribution and glycerol conversion at different configurations of the reactor. The mathematical model is then used to estimate the size of a multichannel reformer that can convert glycerol produced in a plant producing 4×10^3 m^3 of biodiesel annually. The studies are planned to provide insight into the
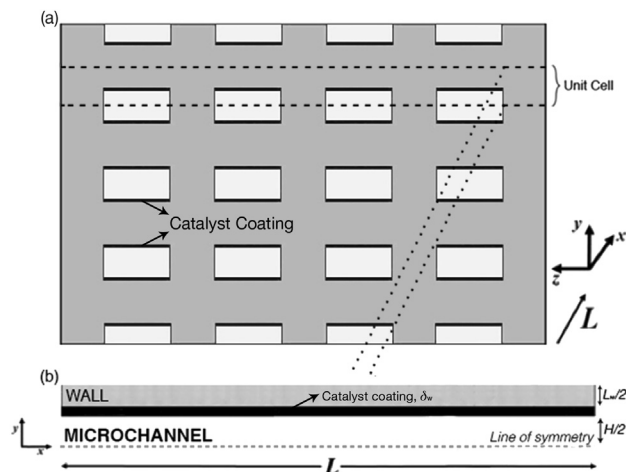

Fig. 1 – Description of the parallel microchannel reactor configuration (a) and the characteristic unit cell (b).

microchannel enabled heat distribution properties of the endothermic glycerol SR and to understand the degree of compactness that can be achieved by the microchannel architecture. Details of the microchannel reactor and the modeling technique are provided in the 'System description and mathematical modeling' section. The outcomes of the study and their discussion are given in the 'Results and discussion' section.

System description and mathematical modeling

The microchannel reactor is composed of parallel groups of identical channels separated by the reactor wall. Each channel, which is rectangular in shape, has dimensions of 6.5×10^{-4} m (Height) $\times 1 \times 10^{-2}$ m (Width) $\times 1 \times 10^{-1}$ m (Length), and 5×10^{-5} m thick layers of Ni/CeO_2 catalyst are being coated onto opposite inner walls of each channel (Fig. 1). Channel dimensions are chosen to yield an aspect ratio (channel height/channel width) of 0.065, since this value ensures wide and shallow channels leading to reduced axial dispersion and uniform diffusion mixing [20]. Any given channel is part of a horizontal array of channels, each of which has the same reaction occurring within, as shown in the frontal view of the microchannel array on the y-z plane in Fig. 1a. Since the height of the channel is much smaller than its width, the share of reactor wall material in the y-direction becomes higher than that in the z-direction. Therefore, due to the chosen aspect ratio, any gradients in z-direction can be neglected and the reactor can be modeled as a 2D reactor in the x-y plane. This simplification allows the description of the whole reactor block by a repeating unit cell (Fig. 1b) that comprises halves of one channel and wall and a washcoated catalyst layer. The validity of employing a 2D unit cell to describe the whole microreactor block can also be found in the literature where the difference between 2D and 3D simulation of a similar microreactor configuration is reported to be negligible [21]. Moreover, the microchannel block is assumed