The Feasibility of Glycerol Steam Reforming to Produce Hydrogen in a Fixed Bed Reactor

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Abstract- The growing demand of hydrogen needs renewable sources of raw materials to produce it. Glycerol, by-product of biodiesel synthesis, could be a bio-renewable substrate to obtain hydrogen. Momentous amount of glycerol is produced as a by-product during bio-diesel production by the transesterification of vegetable oils, which are available at low cost in large supply from renewable raw materials. As hydrogen is a clean energy carrier, conversion of glycerol to hydrogen is one among the most attractive ways to make use of glycerol. Production of hydrogen from glycerol is environmentally friendly because it adds value to glycerol generated from biodiesel plants. This study investigates a review on the feasibility of glycerol steam reforming in an industrial sized fixed bed reactor. Also, investigating the extent of the transport resistances that would occur in a fixed bed reactor.

Keywords: Biodiesel, Hydrogen, Glycerol, Steam reforming

I. INTRODUCTION

For the past decade, the production of biodiesel has significantly increased along with its byproduct, glycerol. Biodiesel-derived glycerol massive entry into the glycerol market has caused its value to plummet. Newer ways to utilize the glycerol by-product must be implemented or the biodiesel industry will face serious economic problems. The biodiesel industry should consider steam reforming glycerol to produce hydrogen gas. Steam reforming is the most efficient way of producing hydrogen and there is a lot of demand for it in the petroleum and chemical industries. This study investigates the feasibility of glycerol steam reforming in an industrial sized fixed bed reactor. In this paper, a review of computational fluid dynamic (CFD) simulations, the extent of the transport resistances that would occur in an industrial sized reactor can be visualized. An important parameter in reactor design is the size of the catalyst particle. The size of the catalyst cannot be too large where transport resistances are too high, but also not too small where an extraordinary amount of pressure drop occurs. The goal of this paper is to find the best catalyst size under various flow rates that will result in the highest conversion. Computational fluid dynamics simulated the transport resistances and a pseudo-homogenous reactor model was used to evaluate the pressure drop and conversion.CFD simulations showed that glycerol steam reforming has strong internal diffusion resistances resulting in extremely low effectiveness factors. Due to the low effectiveness factors and high carbon deposition rates, a fluidized bed is recommended as the appropriate reactor to carry out glycerol steam reforming. Also the effects of average linear velocity of fluid, heat of reaction, permeability, porosity on distribution of velocity, temperature, and mass inside the fixed bed reactor were investigated. Here three important parameter one is best size of catalyst particle, second using active metal. The third way of improving the conversion is by using a fluidized bed reactor is studied.

II. COMPUTATIONAL FLUID DYNAMICS MODEL

The field of computational fluid dynamics (CFD) is central to chemical reaction engineering, as the modeling of fluid-phase systems is essential to the study and design of continuous chemical processes.CFD has proven to be very accurate in predicting complex flow fields, extending its applicability to many heterogeneous reaction systems [1]. Typically a pseudo-homogeneous approach is taken, where the catalyst is not explicitly modeled but is accounted for with effectiveness factors that represent its impact on the fluid phase. Steam reforming in a fixed bed, however, has demonstrated that severe intra-particle diffusion limitations are one of its defining characteristics [2]. Furthermore, the computational demands of a three-dimensional CFD simulation necessitate the use of a very small reactor segment, usually containing one to several catalyst particles [3].This capture the full profile of chemical and physical behavior along a fixed bed reactor.

III. REACTOR DESIGN RECOMMENDATIONS

A. Diffusion Limitation and Effectiveness Factor

It is known empirically that in steam reforming the reaction rate is proportional to the outer (geometric) surface area of the catalyst particles, rather than the much larger true surface area that includes the pore walls within the catalyst support [4]. This indicates that the intrinsic reaction rate proceeds much faster than the diffusion of reactants into the pellet's pores, limiting the active region of each catalyst particle mainly to its exterior. It was suspected that steam reforming of glycerol would display similar behavior [5], and the results of this simulation confirm that. At a suggested set of optimal conditions—T_{in}=823K, P_{in}=2.02kPa, q_W=21000W, u=5m/s, which gives a nearly isothermal system—glycerol concentration and reaction rate within the catalyst domain were both limited to the outside of the pellet. The graphs shows glycerol concentration and reaction rate as a function of scaled radial position within a spherical catalyst particle at the reactor inlet and at a point one meter down the length of the tube

B. *Reactor to Catalyst Pellet Radius Ratio*

The ratio of the reactor radius to the catalyst pellet radius was studied by keeping the catalyst pellet size constant and varying the reactor size, and vice versa. An analysis of an optimal reactor radius was inconclusive, therefore it is suggested that the monetary tradeoff between higher energy use and higher pressure drop occurring during the process should be assessed. Similarly, a study on the tradeoff between higher active catalyst use and higher pressure drop should be made in order to assess an optimal catalyst Pellet radius for glycerol steam reforming.

C. Heating the feed vs Heating the reactor

Since glycerol reforming is highly endothermic and benefits from high temperature operation, a similar setup to the one typically used for methane steam reforming should be considered. Applying heat to the reactor as well as the feed in order to balance the energy consumption of the chemical reaction is sensible, so as to maintain thermodynamically favorable conditions throughout the reactor. The distribution of heat application between the feed and the actual reactor, however, is a process variable that is free to be manipulated. Ideal operation involves adding a significant amount of heat directly to the reactor, so that despite the heat sink created by the reacting catalyst pellets, the fluid and catalysts both increase in temperature down the length of the reactor. The reason for this is that high glycerol conversion is a desirable process quality, so an effective reactor will have a significantly lower concentration of glycerol near the end of the tube. Thus, a higher temperature is more useful near the effluent side to drive the reaction toward completion when glycerol becomes less abundant. Two different heating distributions are examined below

Figure 1. Glycerol Concentration as a Function of Radial Position in Catalyst

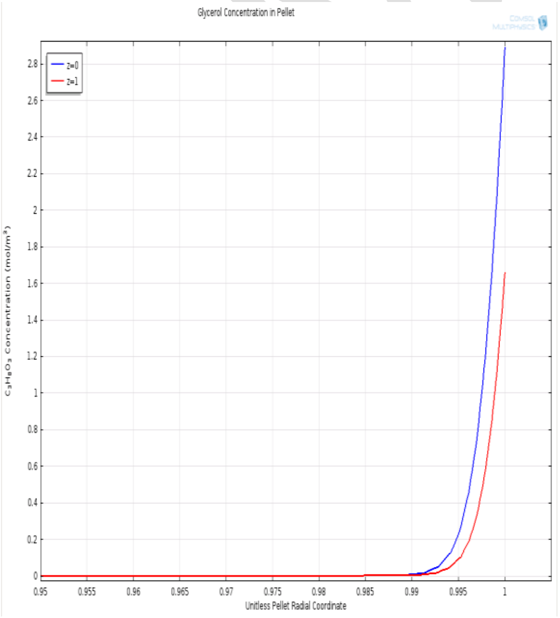
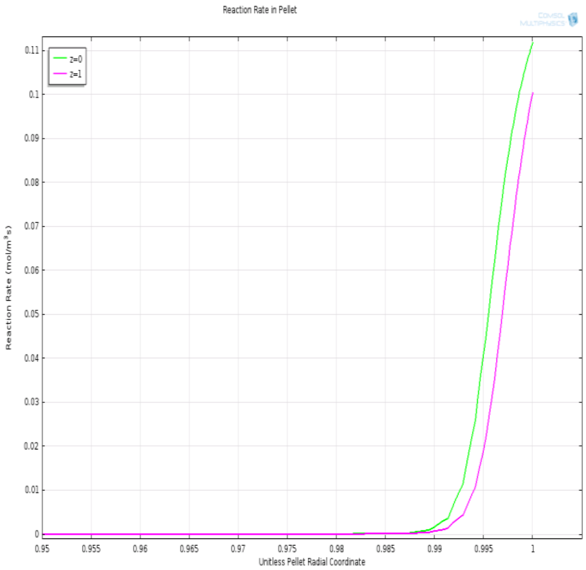


Figure2. Reaction Rate as a Function of Radial Position in Catalyst Pellet



The conversion at the entrance of the tube is slightly higher for the second case (green line), due to the higher feed temperature. However, farther along the reactor segment, where the partial pressure of glycerol depreciates significantly, the effect of the temperature of the bulk fluid becomes more pronounced and a higher conversion is obtained for the first case (blue line). With lower feed temperature and larger heat flux, higher conversion was obtained, despite lower bulk fluid average temperature. If the difference in bulk fluid average temperature is taken to be negligible and it is assumed that a similar amount of energy is supplied to system in each case, then supplying a larger amount of heat to the reactor instead of the feed creates a more efficient process. This result makes a strong case for using energy resources mostly on the reactor rather than the feed, but other factors beyond the scope of this simulation must be considered. It may be more effective to supply energy to the process stream pre-reaction in a heat exchanger that can be designed solely for the purpose of providing efficient heat transfer than rely on heavily on the heat transfer rate.

D. *Wall flux and Radial temperature gradient*

Glycerol steam reforming demands operating pressures significantly lower than other reforming processes, making the thermal conductivity of the fluid considerably lower in comparison. As a result, radial temperature gradients, which were not accounted for in this axial reactor model, will be even more impactful for this process, calling for caution in design a reformer with substantial wall heating.

E. Turbulence

In laminar flow, mass transport relies on molecular diffusion and mixing is limited, whereas eddies present in turbulent flow greatly aid in chemical dispersion. on the basis of This model assumed a well-mixed fluid, thus, its applicability relies on the maintenance of turbulent flow conditions. The complex void pattern created by a randomly packed reactor promotes turbulence. Typically, in such reactor, a Reynolds number of 200 is high enough to prevent true laminar flow, and a Reynolds number of 1900 will induce full turbulent flow [6][7]. At a temperature of 823K, pressure of 2atm, particle diameter of 0.0254m, and a molar composition based on a 30% reaction extent, the Reynolds number varies with the fluid's velocity shows that true laminar flow only exists at fluid velocities below 1m/s, and a velocity of 5m/s is sufficient to create fully turbulent flow. Therefore, while the system should not operate at excessively low flow rates, the fluid flow will not exhibit laminar behavior in the observed range.

F. Reactor to catalyst pellet radius ratio

The ratio of the reactor radius to the catalyst pellet radius was studied by keeping the catalyst pellet size constant and varying the reactor size, and vice versa. An analysis of an optimal reactor radius was inconclusive, therefore it is suggested that the monetary tradeoff between higher energy use and higher pressure drop occurring during the process should be assessed. Similarly, a study on the tradeoff between higher active catalyst use and higher pressure drop should be made in order to assess an optimal catalyst pellet radius for glycerol steam reforming

Figure 3: Improved Catalyst Shapes [8]

IV. CONCLUSION

This study has demonstrated that the steam reforming of glycerol in fixed bed reactor with a catalyst has strong internal diffusion resistances and low conversion. In order to arrive at these conclusions that on the basis of commercial CFD software, Fluent, One way of improving the conversion is by changing the design of the catalyst. Since the reaction is mainly occurring near the surface of the catalyst, a better shape can be used to maximize the geometric surface area of the catalyst per reactor volume. A better shape can also help reduce the pressure drop in the reactor. Also, the expensive catalytic active metals (Nickel) should be placed only on the rim of the pellet because the poor diffusion will prevent the reactants from reaching the active metals in the center of the particle [9].A second way of improving the conversion is by using a different active metal is the most popular catalyst used in steam reforming due to its good activity and low cost, however, work by Chiodo et al has shown that steam reforming glycerol is much different than other compounds. The study discovered that glycerol is thermally unstable and portion of it is decomposing into mostly carbon monoxide and olefins before reaching the catalysts. Finally, the third way of improving the conversion is by using a fluidized bed reactor. In fluidized bed reactors, the catalyst particle diameters can average less than 100 µm which will greatly improve the effectiveness factor. Fluidized bed reactors also can continuously regenerate coked catalysts. Glycerol steam reforming catalysts will need this continuous regeneration. In a study by Chiodoet al, all the catalysts tested drastically deactivated from carbon deposition during the first 2hours of reaction.

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