

GLYCERIN STEAM REFORMING FOR HYDROGEN PRODUCTION

S. Adhikari, S. D. Fernando, A. Haryanto

ABSTRACT. Biodiesel production is expected to grow steadily in the future. In converting vegetable oils into biodiesel, approximately 10% (w/w) of glycerin is produced as a by-product. With the increasing production of biodiesel, there would be glut of glycerin in the world market; therefore, it is essential to find useful applications for this by-product. Glycerin is a potential feedstock for hydrogen production because one mole of glycerin can produce up to four moles of hydrogen. The objective of this study was to develop, test, and characterize promising catalysts for hydrogen production from steam reforming of glycerin. The following five catalysts were prepared on ceramic foam monoliths (92% Al₂O₃, 8% SiO₂): rhodium-cerium, rhodium-cerium-platinum, ruthenium-yttrium, nickel, and iridium. The catalysts were prepared by the incipient wetness technique. This article discusses selectivity data of the selected gases resulting from the glycerin steam reforming process. The study found that the rhodium-cerium-platinum catalyst was the most selective towards hydrogen under the experimental conditions investigated (700 °C, 1 atm, and gas hourly specific velocity of $9.2 \times 10^4 \text{ h}^{-1}$). The glycerin conversion was 100% with all the catalysts tested.

Keywords. Catalyst, Glycerin, Hydrogen, Steam reforming.

After the energy crisis of the 1970s, considerable attention was given to the development of alternate energy resources. Currently, biomass has received much attention as an alternate energy source because it is renewable and carbon dioxide (CO₂) neutral. Fuels produced from biomass such as ethanol and biodiesel appear to be good substitutes for gasoline and diesel. With the environmental benefits and national energy security, use of biodiesel and its production have gained worldwide momentum (Thompson and He, 2006). For example, biodiesel production in the U.S. has increased dramatically from 0.5 million gallons in 1999 to 75 millions in 2005 (National Biodiesel Board, 2006).

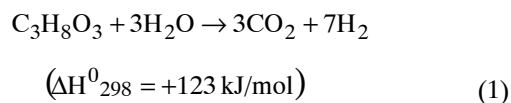
In converting vegetable oils into biodiesel, approximately 10% (w/w) of glycerin is produced as a by-product. With increased production of biodiesel, a glut of glycerin is expected in the world market; therefore, it is essential to find useful applications for glycerin. Glycerin can be used to produce a variety of products, such as 1,3 propanediol, succinic acid, polyesters, lactic acid, and polyglycerols. A detailed review on glycerin utilization can be found elsewhere (Pachauri and He, 2006).

One possibility is using glycerin as a source for hydrogen (H₂) production. To date, only a handful of studies (Cortright et al., 2002; Czernik et al., 2002; Davda et al., 2005; Hirai et al., 2005; Huber et al., 2003; Shabaker and Dumesic, 2004;

Soares et al., 2006) have been performed on glycerin reforming for hydrogen production. Cortright et al. (2002) produced hydrogen from biomass-derived oxygenated hydrocarbons including glycerin in an aqueous phase reforming (APR) process. Although catalyst (Pt/Al₂O₃) performance was stable for at least a week, the process required high pressure. On the other hand, a steam reforming process can be carried out at atmospheric pressure. Czernik et al. (2002) reported steam reforming of crude glycerin using a commercial nickel-based naphtha reforming catalyst (C11-NK), but detailed results were not given. Recently, Hirai et al. (2005) reported the performance of catalysts loaded with groups 8-10 metals, such as Ru, Rh, Pd, and Pt, on glycerin reforming.

The catalysts used in all the aforementioned studies were in powder form. Although the use of powder catalysts could easily produce higher surface area and perhaps, higher glycerin conversions, extreme pressure drops make powder catalysts less feasible for practical applications. In addition, thermodynamically, high pressures reduce hydrogen yield from the steam reforming process. In this study, we have used monoliths instead of powder to reduce the pressure drop in the reactor. The performance of platinum metal-based catalysts and their alloys were tested, including one of the best catalysts (i.e., Rh-Ce) for the ethanol steam reforming process (Deluga et al., 2004; Haryanto et al., 2005).

The glycerin steam reforming process is endothermic ($\Delta H^0_{298} = +123 \text{ kJ/mol}$), and thermodynamically, high temperatures favor the reaction. Ideally, the steam reforming reaction could be represented as follows:



Although the steam reforming of glycerin (C₃H₈O₃) can be represented by equation 1, in reality several intermittent steps occur. The gas stream also consists of carbon monoxide

Submitted for review in April 2006 as manuscript number FPE 6453; approved for publication by the Food & Process Engineering Institute Division of ASABE in January 2007.

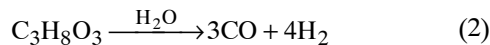
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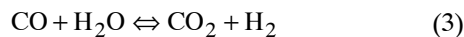
Figure 1. Ceramic foam monolith loaded with a catalyst.

(CO), methane (CH₄), and other gases in addition to CO₂ and H₂. According to Hirai et al. (2005), the process proceeds according to the following steps:

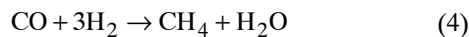
Steam reforming of glycerin:



Water-gas shift reaction:



Methanation reaction:



This article discusses glycerin conversion and gas composition during steam reforming of glycerin in the presence of the following catalysts:

- Rhodium-cerium (Rh-Ce): one of the best catalysts for ethanol steam reforming for hydrogen production (Haryanto et al., 2005).

- Rhodium-cerium-platinum (Rh-Ce-Pt): Pt was used for the APR process (Cortright et al., 2002), and Rh-Ce-Pt was chosen to analyze the effect of the Rh-Pt alloy.
- Ruthenium-yttrium (Ru-Y): the best catalyst for glycerin steam reforming (Hirai et al., 2005).
- Nickel (Ni): a commonly used catalyst for steam reforming (Czernik et al., 2002).
- Iridium (Ir): offers good resistance to carbon formation (Zhang et al., 2006).

EXPERIMENTAL METHODOLOGY

CATALYST PREPARATION

All catalysts were prepared on alumina (92%) ceramic foam monoliths containing 8% silica (Vesuvius Hi-Tech Ceramics, Champaign, Ill.), which had a nominal surface area of approximately 1 m² g⁻¹ with a void fraction of approximately 0.8. All the catalysts [precursors as Rh(NO₃)₃, PtO₂, Ni(NO₃)₂·6H₂O, H₂N₄O₁₀Ru, IrO₂, and Ce(NO₃)₃·6H₂O] were loaded with metal up to 2.5 wt % of the monoliths, except in the case of ruthenium where 1.25 wt % was loaded. Chemicals used for preparation of the catalysts were purchased from Sigma-Aldrich (St. Louis, Mo.). The monoliths were dried at 125 °C for 1 h and then calcined at 700 °C for 4 h in a furnace before they were placed in the reactor. The monoliths were left overnight in the furnace for cooling and reweighed to confirm the required metal loading based on the mass of the monoliths. Figure 1 depicts a catalyst-impregnated ceramic monolith.

CATALYSTS CHARACTERIZATION

X-ray diffraction (XRD), BET (Brunauer, Emmett, and Teller) surface area, metal dispersion, active metal surface area, crystallite size, and the adsorption isotherms were analyzed as a part of the catalysts characterization. XRD analysis was performed in AMIA Labs (Leesburg, Va.), and surface area analyses were done at Quantachrome Instruments (Boynton Beach, Fla.). Detailed methods for these analyses can be found elsewhere (Chorkendorff and Niemantsverdriet, 2003; Lowell et al., 2006).

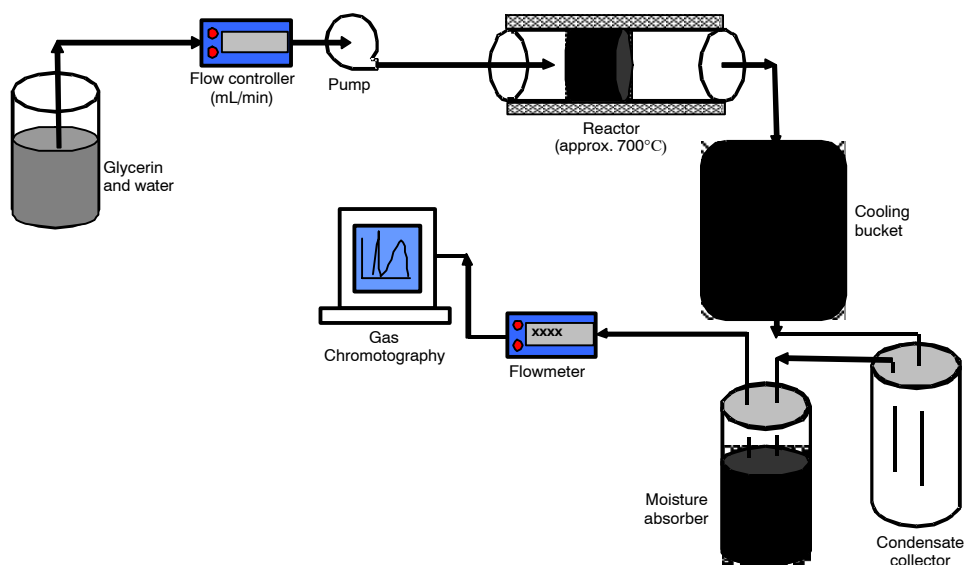


Figure 2. Schematic of glycerin steam reforming setup.

CATALYST TESTING

Figure 2 shows a schematic of the glycerin steam reforming process. All experiments were carried out at 700 °C with a flow rate of 0.9 mL/min in a tube furnace that could reach temperatures up to 1100 °C. As depicted in figure 2, the coated monoliths were placed in the middle of the tubular reactor. The reactor was made of alumina (99.8%) tubing of 19 mm inner diameter and 0.6 m (2 ft) long. The alumina tubes were obtained from McDanel Advanced Ceramic Technologies LLC (Beaver Falls, Pa.). Monoliths were held at the center of the reactor with the help of snap rings. Gas hourly specific velocity (GHSV) was held constant at $9.2 \times 10^4 \text{ h}^{-1}$ throughout the experiments. The experiments were run for 9 h for each catalyst. Molar concentration of glycerin and water was 1:6 and was also held constant throughout the experiments. The stream of gases produced by the reaction was cooled with an ice-water bath before being sent to the gas chromatograph.

The condensates of the gases were collected and analyzed for glycerin conversion. A high-pressure liquid chromatograph (GC6890, Agilent Technologies, Inc., Palo Alto, Cal.) was used to analyze the glycerin conversion with a Zorbax carbohydrate column ($4.6 \times 150 \text{ mm}$) using acetonitrile and water as a mobile phase. The mixture of gases was sent through a moisture trap before purging to the gas chromatograph. Only four gases (CO, CO₂, CH₄, and H₂) were analyzed via the GC, although small amounts of ethane and ethylene were identified in the glycerin reforming, as mentioned elsewhere (Soares et al., 2006). The H₂ content in the outlet gas was analyzed by a thermal conductivity detector with an HP-Plot Molecular Sieve column. Similarly, concentrations of CO, CH₄, and CO₂ were analyzed by a flame ionization detector with an HP-Plot Q column.

RESULTS AND DISCUSSION

Figures 3 through 7 show the selectivity of H₂, CO, CO₂, and CH₄ with different catalysts. Selectivity is defined as the volumetric composition of the gas in the mixture. With all catalysts, the selectivity towards CO was higher than CO₂, which implies that the reforming process is mainly governed by reaction 2. The higher H₂ selectivity is perhaps due to the water gas shift reaction, as shown in reaction 3. CO₂ selectivity was below 7% with Ru-Y and Ir, whereas Ni, Rh-Ce, and Rh-Ce-Pt showed selectivity in the range of 15% to 20%. CO selectivity with the Rh-Ce, Rh-Ce-Pt, and Ni catalysts was in the neighborhood of 15% to 25%, whereas

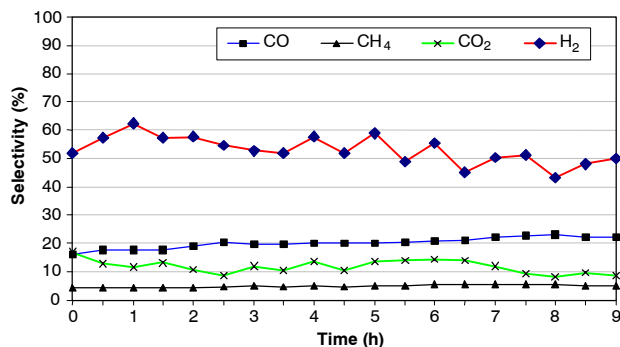


Figure 3. Gas composition from glycerin reforming with Rh-Ce.

it was almost 50% with the Ru-Y and Ir catalysts. Similar results were reported with lower percentage of Ru loading (Hirai et al., 2005).

With all the catalysts, CH₄ selectivity was less than or equal to 5%, whereas Ir showed the highest selectivity

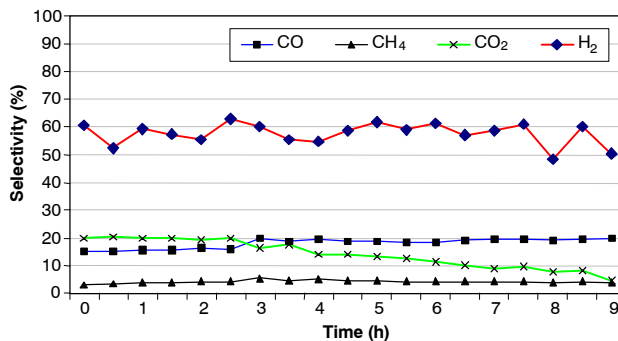


Figure 4. Gas composition from glycerin reforming with Rh-Ce-Pt.

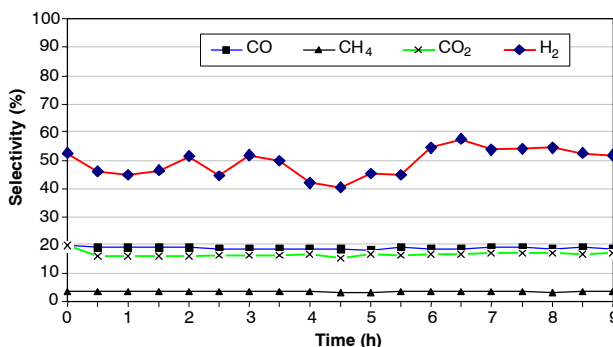


Figure 5. Gas composition from glycerin reforming with Ni.

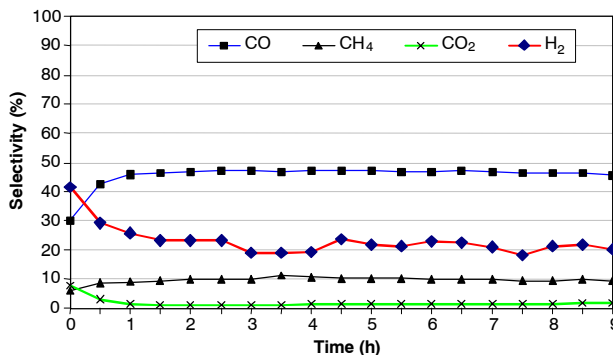


Figure 6. Gas composition from glycerin reforming with Ru-Y.

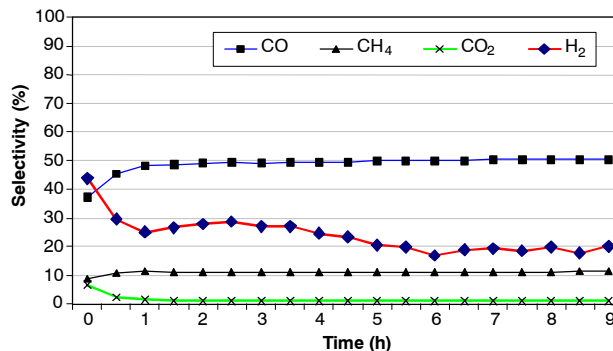


Figure 7. Gas composition from glycerin reforming with Ir.

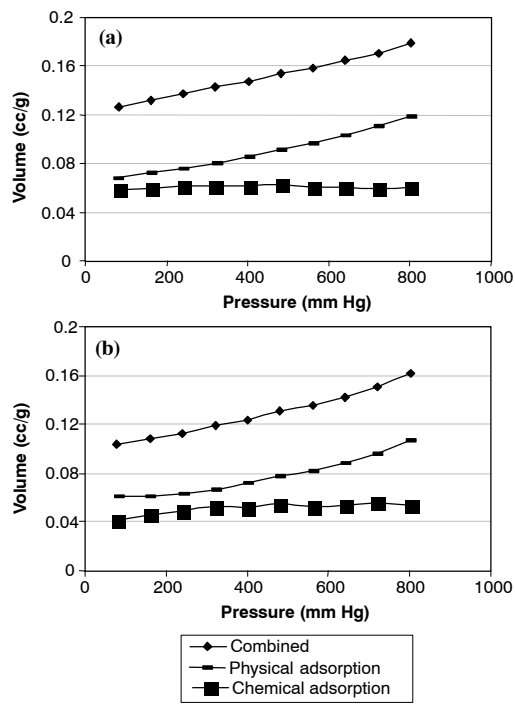


Figure 8. Adsorption isotherms for (a) Rh-Ce and (b) Rh-Ce-Pt.

Table 1. Catalysts characteristics.

Parameters	Rh-Ce/Al ₂ O ₃	Rh-Ce-Pt/Al ₂ O ₃
Active metal surface area (m ² g ⁻¹)	4.886E-01	3.878E-01
Percent of metal dispersion (%)	4.44	3.52
Average crystallite size (Å)	2.476E+02	3.119E+02
BET surface area (m ² g ⁻¹)	9.486E-01	8.332E-01

(approx. 11%). Reducing CH₄ production is very important in any steam reforming process because CH₄ contains two moles of H₂. H₂ selectivity was found to be higher (45% to 60%) with the Rh-Ce, Rh-Ce-Pt, and Ni catalysts, whereas Ru-Y and Ir showed poor selectivity (15% to 30%). During 9 h operation, the selectivity towards H₂ decreased with time, which was attributed to catalyst deactivation (figs. 3 through 7). With almost all catalysts, a deactivation phenomenon was noticed; however, Rh-Ce-Pt seemed to be more stable throughout the experimental period (fig. 4). After 6 h, the selectivity towards H₂ increased with the Ni catalyst; this may have been due to the self-activation of the catalyst (fig. 5). The Ru-Y and Ir catalysts deactivated faster in the beginning and remained almost constant thereafter (figs. 6 and 7). Among the catalysts tested, Rh-Ce-Pt was found to be the best for hydrogen production. The glycerin conversion was found to be 100% with all the catalysts. It should also be noted that the sum of the four gases (H₂, CO, CO₂, and CH₄) analyzed in this study never added up to 100%. As mentioned earlier, this could be attributed to trace amounts of ethane, ethylene, and/or other unknown gases.

In ethanol steam reforming, a low amount of Rh loading showed a high activity and selectivity towards H₂ compared to that of Pt, Pd, and Ru. In contrast, at 5% Ru/Al₂O₃ loading, the results from Ru and Rh towards H₂ selectivity and activity were comparable (Liguras et al., 2003). Therefore, as a less costly alternative for glycerin steam reforming, Ru is worth investigating in the future.

Most of the catalysts used for steam reforming are in metallic form. However, our catalysts were prepared in metal oxide form. Usually, metal oxides are reduced to metallic form by exposing them to H₂ gas at an elevated temperature for a certain period of time. The H₂ gas reacts with the oxygen present in the metal oxides, and the metal oxides are converted to metallic form. Although our catalysts were not reduced with hydrogen prior to the experiment, the H₂ selectivity was found to be comparable with the results published elsewhere for reduced catalysts (Hirai et al., 2005). This is a significant finding, indicating that it is not necessary to reduce the catalysts each time a batch has to be run.

Catalysts characterization was performed for the two best performing catalysts, i.e., Rh-Ce and Rh-Ce-Pt. Figure 8 and table 1 show the results after these catalysts were characterized. As can be seen from figure 8, physical adsorption was significant in the catalysts compared to chemical adsorption. Although metal dispersion in Rh-Ce was slightly higher than in Rh-Ce-Pt, both catalysts had very low metal dispersion (table 1). BET surface area was slightly lower than 1 m² g⁻¹. The XRD analysis revealed that the catalysts that were tested had formed a complex crystalline phase that consisted of respective metal oxides (not shown here).

CONCLUSIONS AND FINAL REMARKS

Performance of the following catalysts was investigated for glycerin steam reforming: rhodium-cerium (Rh-Ce), rhodium-cerium-platinum (Rh-Ce-Pt), ruthenium-yttrium (Ru-Y), nickel (Ni), and iridium (Ir). It was found that Rh-Ce-Pt showed the highest hydrogen yield among the catalysts studied. The order of catalyst based on H₂ selectivity is as follows: Rh-Ce-Pt > Rh-Ce > Ni > Ir > Ru-Y. The glycerin conversion was 100% with all the catalysts under the experimental conditions investigated. We also found that metal oxide catalyst reduction was not necessary for glycerin reforming; however, we have not done a rigorous analysis to compare the performances of metal oxides and metals. The oxide forms that were confirmed by X-ray diffraction analyses would be sufficient to perform the reforming. It is recommended that experiments should be continued on selected catalysts for longer durations, perhaps with trace amounts of promoters, to test catalyst stability in terms of selectivity and conversion.

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