FEASIBILITY STUDY ON HYDRO-THERMAL CONVERSION OF LOW-GRADE GLYCEROL TO ALCHOLS FOR USE IN BIODIESEL PRODUCTION

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The purpose of this project was to conduct a feasibility study on converting the low-grade glycerol derived from biodiesel production to short-chain alcohols such as methanol, ethanol, or propanols, or their mix and applying back to the biodiesel production process. The specific objectives were (1) to explore whether controlled thermal cracking of glycerol alone is suitable for alcohol conversion; (2) to determine the feasibility of hydro-thermal cracking of glycerol for targeted alcohols; and (3) to evaluate process parameters to maximize alcohol production if the process is feasible.

Trial experiments indicated that it is possible to convert glycerol hydro-thermally into primary alcohols that are potentially applied back to the biodiesel production. If achieved, this would be a break-through in utilizing alternatively low grade glycerol for value-added applications. However, the results from the feasibility testing were far away from satisfaction: the product yield was low, the reactions were lack of consistency, and the process efficiency needs to be improved greatly.

Future work will involve an improved reactor system that will provide the ability to design a through experimental procedure and systematically test the effects of operating parameters and fine tune the analytical procedures to improve repeatability and sensitivity.
TABLE OF CONTENTS

INTRODUCTION .......................................................................................................................... 1

PROJECT OBJECTIVES .............................................................................................................. 4

    Materials and Methods ........................................................................................................... 4

RESULTS AND DISCUSSIONS ..................................................................................................... 6

FUTURE WORK ............................................................................................................................ 12

ACKNOWLEDGEMENT ................................................................................................................ 12
INTRODUCTION

Biodiesel production in the United States have been increasing dramatically recently, from 500,000 gallons in 1999 to 30 million gallons in 2004 (National Biodiesel Board, 2005). The federal biodiesel tax incentive that went into effect January 2005 is causing biodiesel demand to climb even more and encourages entrepreneurs to invest in more biodiesel production facilities. The immediate production capacity of biodiesel is estimated to be 150 million gallons/year, and this capacity can be doubled or tripled in a time frame of 12 months (National Biodiesel Board, 2005).

The principal by-product of biodiesel production is glycerol, also known as glycerol. It occurs in vegetable oils at a level of approximately ten percent by weight. For each gallon of biodiesel produced, approximately 0.34 kg (0.68 lb) of crude glycerol accompanies. For a biodiesel production of 150 million gallons/year in the U.S., the by-product glycerol produced will approximately be 50 million kg (100 millions lb).

High purity glycerol is a very important industrial feedstock. Its applications are found in food, drug and toothpaste, cosmetic, packing material, and tobacco products. In the past decade, industrial glycerol price was in the range of $1.28 to $1.65/kg. This price has been lowered due to the surplus, partially because of the larger quantity produced from biodiesel industry. However, crude glycerol derived from biodiesel production possesses very low value because of the impurities. Further refining of the crude glycerol will depend on the economy of production scale and/or the availability of a glycerol purification facility. Larger scale biodiesel producers refine their crude glycerol and move it to markets in other industries. It is generally treated and refined through filtration, chemical additions, and fractional vacuum distillation to yield various commercial grades. If it could be used in food, cosmetics, and drugs, further purifications are needed such as bleaching, de-odorizing, and ion exchange to remove trace impurities. Purifying it to that stage, however, is very costly and generally out of the range of economic feasibility for the small to medium sized plants.
As more and more crude glycerol is continuously generated from the biodiesel industry, it is very important that economical ways of the low-grade glycerol utilization be explored to further defray the cost of biodiesel production in the growing global market. Researchers have been actively exploring alternative ways to utilize the low-grade glycerol for value-added applications. The current research activities on glycerol utilization has been reviewed (Pachauri and He, 2006) and attached to this report.

A possible way being proposed here is to convert the glycerol (a polyhydric alcohol or triol) thermochemically to short-chain monohydric or primary alcohols, such as methanol and ethanol or their mix, and other possible alcohols. Then these alcohols can be re-introduced back to the biodiesel production process. The thermochemical conversion processes available for this application include pyrolysis and liquefaction. Pyrolysis is a chemical reforming process of biomass or other organic matters which are depolymerized and reformed in a heated and free oxygen-absent enclosure. Depended on heating rate and operating temperature, pyrolysis is also further categorized as flash pyrolysis (400 to 600°C at >100°C/s heating rate) and fast pyrolysis (>600°C but lower heating rate). The products of pyrolysis are liquid (hydrogenated oils), solid (char), and some gaseous (methane, carbon monoxide, carbon dioxide, etc). The proportions of the products are dependent on factors such as operating temperature, pressure, oxygen content and biomass feedstock type. Liquefaction is another thermochemical conversion process of biomass or other organic matters into primarily liquid oil products in the presence of a reducing reagent, e.g., carbon monoxide or hydrogen. Liquefaction is usually conducted in an environment of moderate temperatures (300 to 400°C) and high pressures (e.g., 5~20 MPa or 720~2900 psi). Liquefaction is superior to pyrolysis if liquid products are targeted and the carbon is fully utilized (pyrolysis sacrifices some carbons to char in exchange of liquids). The PI has conducted and gained experience on thermochemical conversion of waste biomass for hydrogenated oils in a liquefaction process (He et al., 2000a,b; 2001a,b,c).

Compared to lingo-cellulosic biomass, glycerol is a perfect feedstock for thermochemical conversion and its consistent constituents would lead to consistent products. To convert glycerol to monohydric alcohols, a combination of pyrolysis and hydro-reforming under a reducing environment is needed. The hypothesis is that the three-carbon chain of glycerol is thermally
cracked into one- or two-carbon molecules, and hydroxyl groups (-OH) are partially removed as CO₂ and/or H₂O, depending the reducing agent added. The candidate reducing agents include carbon monoxide and hydrogen. In an idealized scenario, each mole of liquid glycerol, if cracked between C₁ and C₂ bond, would yield one mole methanol and one mole ethanol, which would account for two thirds of the alcohol requirement for biodiesel production from vegetable oils. Even more ideally, each mole of liquid glycerol, if cracked between the three C-C bonds, would yield three moles of methanol. Therefore, the alcohol required for biodiesel production could be made self-sustainable from vegetable oils. The possible chemical conversion and products are illustrated below.

\[
\text{Reducing agent} \quad (\text{H}, \text{CO})
\]

However, the composition of the products is heavily affected by the operating conditions. Other products that are also possibly derived from this process include methane (CH₄), 1-propanol (CH₃CH₂CH₂-OH), 2-propanol (CH₃CH-OHCH₃), char, etc.
PROJECT OBJECTIVES

The purpose of this project is to conduct a feasibility study on converting the low-grade glycerol derived from biodiesel production to short-chain alcohols such as methanol, ethanol, or propanols, or their mix and applying back to the biodiesel production process. The specific objectives are (1) to explore whether controlled thermal cracking of glycerol alone is suitable for alcohol conversion; (2) to determine the feasibility of hydro-thermal cracking of glycerol for targeted alcohols; and (3) to evaluate process parameters to maximize alcohol production if the process is feasible.

Materials and Methods

1. Chemicals / reagents
   - Glycerol, chemical pure
   - Carbon monoxide (CO), chemical pure; purchased by compressed cylinder

2. Experimental setup
   - the reaction setup is as illustrated in Fig. 1.
   - gaseous samples are taken using a setup as shown in Fig. 2.
   - basic requirements
     a. temperature control (± 5°C)
     b. pressure control (± 20 psi)

![Figure 1. Illustration of reactor setup](image1)
![Figure 2. Illustration of gas sampling](image2)
3. Process variables and exploration ranges

- operating mode: batch
- working capacity: 500 ml or agitation impeller submerges in the middle of liquid.
- operating temperature: 270 - 330°C
- initial CO pressure: 50 ~ 200 psi
- holding time at operating temperature: 15 ~ 60 min. The temperature raising time is not included, but kept consistent from batch to batch.
- operating pressure: monitored / recorded but not controlled; with a safety pressure set at 2000 psi.

4. Product analysis (GC, GC/MS, PHLC)

- gaseous samples: for CO, CO$_2$, CH$_4$, and methanol
- liquid samples: for any primary alcohols (methanol, ethanol, propanols, etc.)

5. Test procedure

The reactor is filled with 500 g glycerol. After sealing, the head space of the reactor is flushed with CO at least three times to remove air/oxygen, the reactor is then pressurized to a initial CO pressure (50 ~ 200 psi) depending on the test case. The reactor is heated up and the temperature is carefully controlled. System pressure is monitored throughout the experiment. After the holding time is reached, the reactor is put in an ice bath to immediately cool it down. The liquid products are collected for chemical analysis using GC/MS.

Liquid samples will be analyzed for alcohol components using an HP Model 5890 Series II Gas Chromatograph (Palo Alto, Calif.) with a flame-ionization detector and a DB-624 capillary column from Agilent J&W Scientific (Agilent Technologies, Palo Alto, Calif.). Acetonitrile was used as the internal standard for all samples and quality controls. Specific detection was focused on methanol, ethanol, 1-propanol, and 2-propanol. Standard chemicals were purchased from AccuStandard, Inc. (New Haven, Conn.).
RESULTS AND DISCUSSIONS

According to various literature, glycerol will decompose if it is heated to its boiling temperature of 290-297°C under atmospheric pressure (table 1). Therefore, the trial experiments were determined to start in temperature intervals of 270°C and 290°C. The experiments at 270°C and 290°C were conducted first and the temperature profiles for the tests are shown in Figs. 3 and 4. It took about 30-40 min to reach the desired operating temperatures. Heating was slightly accelerated by placing the reactor in a preheated furnace. It took about 30 min to cool the reactor below 50°C. Then, the reactor was depressurized before samples can be taken. No gas samples were collected from these tests.

Table 1. Basic properties of pure glycerol.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Propane-1,2,3-triol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trivial names</td>
<td>Glycerol, glycerol, glycerole</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₃H₈O₃</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>CH₂-CH-CH₂</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>92.09 g/mol</td>
</tr>
<tr>
<td>Melting point</td>
<td>17.9°C</td>
</tr>
<tr>
<td>Boiling point (decompose)</td>
<td>290 – 297 °C</td>
</tr>
<tr>
<td>Flash point</td>
<td>188-199 °C (370-390 °F)</td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>370 °C (698 °F)</td>
</tr>
<tr>
<td>Density</td>
<td>1.261 kg/m³</td>
</tr>
<tr>
<td>CAS number</td>
<td>56-81-5</td>
</tr>
</tbody>
</table>
Figure 3. Operating temperature profiles. The operating conditions are: (a). 50 psi initial CO, 15 min holding time; (b). 200 psi initial CO pressure, 60 min holding time.

It was observed that once the system was cooled to room temperature, there was no noticeable change in pressure after the processing compared to the initial pressure, which is an indication that no chemical change occurred.

Figure 4. Temperature and pressure profiles with respect to time.
Additional tests were conducted at elevated temperatures. The initial CO pressure of 100 psi was employed. Example temperature and pressure profiles with respect to time are shown in Fig. 4. At 305°C, the pressure appeared to peak at about 200 psi without much change with respect to the holding time. It is likely that there was not much chemical reaction happening. The liquid product at 305°C was a tinge darker than glycerol feedstock but other characteristics remained virtually the same as the processed glycerol from the tests at 270°C and 290°C.

At 325°C, pressure was found to increase as soon as the operating temperature was reached. By the end of the 60 min holding time, the pressure reached 500 psi. This is an indication that chemical reactions may have occurred. The low boiling point products formed through the reaction, along with unreacted CO, contributed to this pressure increase. As shown in Fig. 4, the pressure was decreased to about the same level as the initial CO pressure once cooled to 50°C or below. This analysis is supported by the characteristics of the liquid products obtained at the end of the test. Gaseous product had a distinct smell unlike that of the odorless starting glycerol. The liquid product was dark brown in color and had a smell of varnish or lacquer. It also appeared to be less viscous than feed glycerol. This liquid product was analyzed for its chemical composition.

Figure 5 shows a photo of pure glycerol (99.9 percent) and samples obtained from the tests. The color of the products can be seen to change with respect to temperature. The viscosity change was most notable at 325°C; the product was less viscous. The smell of the products were also different, the ones produced at 325°C had a more distinguishable solvent-like smell.

Figure 5. Photo of pure glycerol and processed products at different operating temperatures. (a) glycerol, (b) processed at 305°C, (c) at 315, and (d) at 325°C.
The liquid products were analyzed for detection of primary alcohols, i.e., methanol, ethanol, 1-propanol, and 2-propanol. Examples of the GC analysis spectra are shown in Fig. 6. It is evident that the glycerol feedstock underwent certain thermal cracking and the primary alcohols were among the products. It is also shown that the chemical species of products after reaction were as expected, namely, they are the primary alcohols of methanol, ethanol, and propanols. Relatively, propanols were produced in a larger quantity than methanol and ethanol. Many other chemical reactions are likely to occur depending on the operating conditions.

Table 2 summarizes the analytical results of liquid products from the preliminary experiments. Although literature reports that glycerol decomposes at 290°C or lower temperature, results from these preliminary experiments showed that glycerol remained virtually intact at 305°C or lower. No glycerol decomposition occurred. The presence of small quantities of methanol and ethanol, which were all less than 500 ppm, may result from minor side reactions. This phenomenon might be caused by the reducing environment of carbon monoxide in the head space.

Table 2. Results of liquid product analyses – example 1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Temp (°C)</th>
<th>RT (min)</th>
<th>CO (psi)</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>1-Propanol</th>
<th>2-Propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>270</td>
<td>15</td>
<td>50</td>
<td>&lt; 500 / &lt; 0.05</td>
<td>non-detectable</td>
<td>non-detectable</td>
<td>non-detectable</td>
</tr>
<tr>
<td>2</td>
<td>290</td>
<td>15</td>
<td>50</td>
<td>&lt; 500 / &lt; 0.05</td>
<td>non-detectable</td>
<td>non-detectable</td>
<td>non-detectable</td>
</tr>
<tr>
<td>3a</td>
<td>305</td>
<td>60</td>
<td>100</td>
<td>&lt; 500 / &lt; 0.05</td>
<td>&lt; 500 / &lt; 0.05</td>
<td>non-detectable</td>
<td>&lt; 500 / &lt; 0.06</td>
</tr>
<tr>
<td>3b</td>
<td>305</td>
<td>60</td>
<td>100</td>
<td>&lt; 500 / &lt; 0.05</td>
<td>&lt; 500 / &lt; 0.05</td>
<td>non-detectable</td>
<td>non-detectable</td>
</tr>
<tr>
<td>4a</td>
<td>325</td>
<td>60</td>
<td>100</td>
<td>2700 / 0.27</td>
<td>1700 / 0.17</td>
<td>3200 / 0.32</td>
<td>&lt; 500 / &lt; 0.05</td>
</tr>
<tr>
<td>4b</td>
<td>325</td>
<td>60</td>
<td>100</td>
<td>5000 / 0.50</td>
<td>3300 / 0.33</td>
<td>5800 / 0.58</td>
<td>&lt; 500 / &lt; 0.05</td>
</tr>
</tbody>
</table>
To see any thermal cracking of glycerol, the operating temperature needs to be increased much higher than that of reported decomposing temperature (i.e., 290°C). The experiments at 325°C proved this. The concentrations of methanol, ethanol, and 1-propanol reached much higher levels when the operating temperature increased 325°C. Although the mechanism is much more complicated, these alcohols are possibly formed through the following chemical reactions:

\[
\begin{align*}
2 \text{CH}_2\text{OH} + \text{CO} \xrightarrow{\text{heat}} & \text{CH}_3\text{OH} + 2\text{CH}_3\text{CH}_2\text{OH} + 2\text{CO}_2 + \text{C} \\
2 \text{CH}==\text{OH} + 4 \text{CO} \xrightarrow{\text{heat}} & \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_3 + 4\text{CO}_2
\end{align*}
\]

To confirm the finding of primary alcohol formation, additional experiments were conducted with “enhanced” operating conditions (table 3). The operating temperature was increased to 330°C (not higher due to the safety concern and the reactor’s temperature capacity), the reaction time was held for 60 min, and the initial CO pressure was filled to 400 psi. The experiments yielded relatively consistent results. The total primary alcohol concentration was total about 1.5 percent weight or higher.

Table 3. Results of liquid product analyses – example 2.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Temp (°C)</th>
<th>RT (min)</th>
<th>CO (psi)</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>1-Propanol</th>
<th>2-Propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC0807</td>
<td>330</td>
<td>60</td>
<td>400</td>
<td>4900 / 0.49</td>
<td>3000 / 0.30</td>
<td>6900 / 0.69</td>
<td>190 / 0.019</td>
</tr>
<tr>
<td>GC0807[a]</td>
<td>330</td>
<td>60</td>
<td>400</td>
<td>5500 / 0.55</td>
<td>3100 / 0.31</td>
<td>8800 / 0.88</td>
<td>non-detectable</td>
</tr>
<tr>
<td>GC0811</td>
<td>330</td>
<td>60</td>
<td>400</td>
<td>5900 / 0.59</td>
<td>5200 / 0.52</td>
<td>8600 / 0.86</td>
<td>680 / 0.068</td>
</tr>
<tr>
<td>GC0814</td>
<td>330</td>
<td>60</td>
<td>400</td>
<td>1100 / 0.11</td>
<td>550 / 0.055</td>
<td>2500 / 0.25</td>
<td>non-detectable</td>
</tr>
</tbody>
</table>

[a] duplicate.

This is a promising indication that it is possible to convert glycerol hydro-thermally into primary alcohols that are potentially applied back to the biodiesel production. If achieved, this would be a break-through in utilizing alternatively low grade glycerol for value-added applications. However, the results from the feasibility testing were far away from satisfaction: the product yield was low, the reactions were lack of consistency, and the process efficiency needs to be improved greatly.
It is this investigator’s belief that the process can be improved by designing precise testing procedures and by applying an appropriate catalyst, both of which are now under this investigator’s consideration. The new testing procedures may require a reaction system that has a better temperature control and more powerful heating mechanism. Application of an effective catalyst will be the key to the success to high conversion rate.
FUTURE WORK

The following measures will be taken to bring this feasibility study to a full research project:

- To build an improved reactor system to achieve better reactivity of glycerol hydro-thermal conversion
- To explore wide reaction conditions and identify the key influential parameters
- To design a thorough experimental procedure and systematically test the effects of operating parameters
- To optimize the operating conditions to achieve best primary alcohol yield
- To fine tune the analytical procedures to improve repeatability and sensitivity.

ACKNOWLEDGEMENT

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