Hydrogen Production from Glycerin Reforming

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1-Abstract

Following a factorial experimental design, a series of tests were performed to investigate the effects of operating parameters; oxygen to carbon ratio (O/C), steam to carbon ratio (S/C) and temperature (T), on reforming glycerin to a H₂ rich gas. A mathematical model defining the effect of those three variables was derived, and used for improving the reaction hydrogen yield. From the range of experimental conditions tested it was concluded that O/C, as well as the interaction between O/C and temperature had the most important effects on H₂ yield. 4.5 mole of hydrogen were produced per mole of glycerin at experimental conditions of O/C=1, S/C=2.2, and T=804°C. This is 65% of the maximum theoretical yield, and 90% of the yield predicted by thermochemical equilibrium. 1.4 moles of carbon monoxide per mole of glycerin were also produced, presenting a potential for an additional 1.4 mole hydrogen per mole glycerin. A water gas shift reaction was then used, and its operating temperature optimized, in order to convert the reformate gas CO into hydrogen by combining it with water. Results were satisfying, with a final yield of 5.3 moles H₂ / mole glycerin, which is 75% of the maximum stoichiometric hydrogen yield. Crude glycerin, obtained from biodiesel production, was finally tested (without a water gas shift) as a feed to compare it with pure glycerin used throughout the tests. The initial results were very encouraging, almost identical to those of pure glycerin, but carbon formation quickly became a problem. Possible contaminants causing the coking may include methanol, chloride and sodium cations, and free fatty acids, all present in crude glycerin as byproducts of biodiesel synthesis.
2 - Introduction

Society is increasingly looking for clean and renewable fuels to offset the negative effects of fossil fuel use including greenhouse gas emissions and consumption of limited resources. This is even truer for a community like Hawaii that relies on fossil energy resources (~90%), \(^1\) primarily imported oil, and has limited space for waste disposal. Two possible renewable energy supplies are biodiesel and hydrogen. Biodiesel is produced on two islands (Maui and Oahu) by the company Pacific Biodiesel and is made from used cooking oil and grease trap waste obtained from Hawaii’s many restaurants. At present, this biodiesel is used by state vehicles and buses on the island of Oahu in a blend with regular diesel. The most common mix is B20 (20% biodiesel and 80% diesel). One of the major difficulties facing widespread biodiesel use on the mainland U.S. is its cost (~$2.60/gal), which is significantly higher (depending on the source of oil, size of the facility, etc.) than fossil fuel based diesel (~$2.00/gal). \(^2\)

However, biodiesel in Hawaii is a good and competitive alternative due to soaring gas prices as well as fossil fuel shipping cost to the islands. In the week of February 20, 2005, retail diesel prices at the pump were $2.69/gal (Chevron) whereas biodiesel from Pacific Biodiesel was priced at $2.59/gal.

Annually, 180 million pounds of biodiesel are produced nationwide, generating about 18 million pounds of glycerin. \(^3\) The U.S. consumption of diesel for transportation is 340 billion pounds per year and the U.S. demand for glycerin is 453 million pounds per year. \(^4\) Thus, the U.S. glycerin demand could be met from the production of 4.53 billion pounds of biodiesel annually (~1.33% transportation diesel used). \(^3,4\)
Glycerin prices have been going down (from $1.08/lb in 1995 to less than $0.80/lb in 2004) and have stabilized with production meeting demand. The additional supply of glycerin from increasing biodiesel production could further decrease glycerin market prices.

2-1 Hydrogen

Another potentially renewable and clean energy source is hydrogen. Hydrogen has a number of uses, from ammonia production (50%) to petroleum processing (hydrocracking of heavy fractions, hydrotreatment, [7] hydrodenitrogenation, [7] and hydrodemetallization [8]) and hydrogenation of oils and fat. Hydrogen could also be used as a fuel as it is a clean burning element (only water being produced), but a more promising use for hydrogen as a fuel would be using it in fuel cells. The demand for clean and efficient energy and initiatives by the federal government are pushing the development of fuel processing technologies for producing hydrogen for power generation in fuel cells. A variety of fuel cells can be fueled with hydrogen. These include polymer electrolyte membrane (PEM), phosphoric acid, alkaline, and molten carbonate types. [9]

2-2 Hydrogen Production Methods

As of 2003, 48% of the hydrogen worldwide was produced from natural gas, 30% from oil, 18% from coal, and 4% from electrolysis. [10] Electrolysis produces hydrogen
from water, basically using electricity to break water molecules into oxygen and hydrogen. A number of methods are available including PEM electrolysis, alkaline electrolysis \(^{11}\) (very expensive due to high electricity demand), or nuclear electrolysis \(^{12}\) (not used yet due to low energy efficiency processes, but promising for future production). Hydrogen could also be produced in a bioreactor from biological cells and research in this area is underway. The biotech firm Infotech stated in a news letter that “The most likely method for low-cost production of massive quantities of \(H_2\) as an alternate energy source is hydrogen production using clostridia bacteria, which produces hydrogen as a by-product.” \(^{13,14}\) Hydrogen could also be produced from solar energy using photoelectric cells to power water electrolysis, \(^{15}\) but this method is too dependent on light intensity and uncontrollable variables. For the future, photobiological cells are very promising but major breakthroughs are still needed. \(^{16}\) This method uses microalgae to produce hydrogen from photosynthesis, but the efficiency is still very low (1% of energy received), and the systems are expensive to build and run. The most common way of producing hydrogen today is reforming, which consist of producing hydrogen from hydrocarbons. A variant of this, glycerin reforming, is the topic of this thesis.

2-3 Steam Reforming

Steam reforming is a potential method for obtaining hydrogen from hydrocarbons. A two step global reaction mechanism is presented below in which the carbohydrate (glycerin) undergoes thermal decomposition in the first reaction to form \(CO\) and \(H_2\). The
CO then reacts with steam (oxidizer) in the second reaction to form CO₂ and additional H₂.

\[
\begin{align*}
C_3H_8O_3 & \rightarrow 3 \text{CO} + 4 \text{H}_2 \quad [1] \\
3 \text{CO} + 3 \text{H}_2\text{O} & \rightarrow 3 \text{CO}_2 + 3 \text{H}_2 \quad [2]
\end{align*}
\]

Reactions 1 and 2 can be added to yield:

\[
C_3H_8O_3 + 3 \text{H}_2\text{O} \rightarrow 3 \text{CO}_2 + 7 \text{H}_2 \quad [3]
\]

Equilibrium must be reached between those two reactions and will depend on the amount of steam and oxygen added to the reactor, as well as the temperature and pressure of the reaction. Oxygen may be added to steam reforming reaction, but glycerin oxygen content is sufficient in reaction [1] to balance the reaction. Reforming will be explained more thoroughly in the next section.

2-4 Glycerin Characteristics

The chemical formula of glycerin is C₃H₆O₃. Pure glycerin has a flash point of 199°C (lowest temperature at which a liquid gives off enough flammable vapor to ignite and produce a flame when an ignition source is present), a boiling point of 290°C, and a high viscosity at room temperature (1490 cP at 20°C compared to 1.002 cP for water). Glycerin is nonhazardous.

Crude glycerin obtained from the biodiesel plants may contain impurities, such as water, soap, salts, and other elements. Table 1 below shows the results for ultimate analysis performed by Hazen Research, Inc. [18] on crude glycerin obtained from Pacific Biodiesel Oahu’s plant. Two samples were submitted for analysis. Sample A was a well
mixed 0.5 L sample from a five gallon (18.9 L) tank. Sample B was 0.5 L obtained from the same tank after being centrifuged and contained less suspended solids.

Table 1. Results of ultimate analysis of crude glycerin samples obtained from Pacific Biodiesel

<table>
<thead>
<tr>
<th>Ultimate (% by weight)</th>
<th>Sample A crude glycerin (w/ suspended solids)</th>
<th>Sample B crude glycerin (reduced suspended solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>16.6</td>
<td>16.7</td>
</tr>
<tr>
<td>ash</td>
<td>1</td>
<td>1.34</td>
</tr>
<tr>
<td>sulfur</td>
<td>0.006</td>
<td>0.056</td>
</tr>
<tr>
<td>carbon</td>
<td>48.54</td>
<td>49.22</td>
</tr>
<tr>
<td>hydrogen</td>
<td>8.82</td>
<td>9.09</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.16</td>
<td>0.2</td>
</tr>
<tr>
<td>oxygen</td>
<td>24.87</td>
<td>23.39</td>
</tr>
<tr>
<td>Total</td>
<td>99.996</td>
<td>99.996</td>
</tr>
</tbody>
</table>

The chemical composition of the two samples is not drastically different. The reason for the higher sulfur content of Sample B is not readily apparent. Considering the chemical formula of glycerin is C₃H₅O₃, a ratio based on one mole of carbon would be C₁H₂.7O₁. The results of Table 1 yield values of C₁H₂.2O₀.₄ indicating that contaminants are present and that carbon is present at higher than expected concentration. Further investigation of the composition of crude glycerin is warranted. In addition to being a chemical impurity, suspended solids may also cause operational problems for the experimental system as they can plug smaller tubing. To avoid those difficulties, initial experiments used pure glycerin and later experiments used centrifuged or filtered crude glycerin samples.
2-5 Objectives

The objectives of this research were:

(1) To use a laboratory-scale reactor to study effects of operating conditions, reactor temperature, steam to carbon ratio (S/C), and oxygen to carbon ratio (O/C), on the yield of hydrogen obtained from reforming reagent-grade glycerin based on a $2^3$ experimental design.

(2) To use the results from (1) and a "path of steepest ascent" method to identify operating conditions resulting in improved hydrogen yield from reforming reagent-grade glycerin.

(3) To use results of (1) and (2) to develop a model of the effects of reactor temperature, S/C, and O/C on hydrogen yield from reforming reagent-grade glycerin.

(4) To investigate the use of a water-gas shift reactor to improve hydrogen concentrations in the gas stream generated from reforming reagent-grade glycerin.

(5) To test the effects of using crude glycerin produced from biodiesel manufacture under the best reformer operating conditions identified in experiments using reagent-grade glycerin.
3 - Prior Work

Reforming is the most common way to produce hydrogen using hydrocarbons as feed stock. Half of the hydrogen currently produced is obtained from natural gas, which is the least expensive hydrogen production method. [19]

3-1 Steam Reforming

Reforming of natural gases has been widely studied and documented. Methane, CH₄, is the largest constituent of natural gas and reforming is carried out according to the following reaction:

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{298^\circ C} = 198 \text{ kJ/mole} \]  [4]

This reaction is endothermic requiring 198 kJ of heat per mole CH₄. Reforming reactors are usually operated at pressure between 3 and 25 bars and attain up to 85% efficiency. The most important variables in operating a reformer are the steam to carbon ratio (S/C), the oxygen to carbon ratio (O/C) and the reaction temperature. Oxygen can be added to the reaction to produce heat by burning part of the hydrocarbon. Typical reforming of natural gas produces 7.05 kg of carbon dioxide per kg of hydrogen. Reforming temperature is usually between 750 and 900°C, and S/C between 2 and 4. Hydrocarbons produces reformate containing hydrogen, carbon monoxide as shown in equation [4], as well as carbon dioxide and methane. [21] As discussed in the literature, modifying the reforming conditions will affect the reformate gas composition. Steam reforming usually yields a reformate gas with high hydrogen content. Song, et al. [21] showed that reformate H₂/CO ratio can be lowered by decreasing S/C and T, or inversely,
the hydrogen content can be increased by increasing S/C and T. By adding more steam, the equilibrium of reaction [5], below, can be shifted toward the products:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad \Delta H_{298^\circ C} = 41 \text{ KJ/mole} \quad [5]
\]

This reaction is called the water-gas shift and converts carbon monoxide and steam into hydrogen and carbon dioxide. \cite{20} Both reforming and water gas shift reactions are reversible, and due to equilibrium, the reformate inevitably contains steam and carbon oxides, which must be dealt with in the final gas product.

### 3-2 Reforming Catalyst

Catalyst is used to accelerate the reactions in the reforming process. Ni, Co, Ni/Cu, and noble metal (Pd, Pt, Rh) based catalyst all favor hydrogen production. \cite{19,21,23}

The most common reforming catalysts in use are nickel based. It is not certain how catalysts enhance the reforming reactions at the molecular level but a proposed mechanism \cite{22} is described below:

Initially, steam is adsorbed on the catalyst (s refers to catalyst active site):

\[
\text{H}_2\text{O} + s \rightarrow \text{H}_2\text{O(s)} \quad [a_1]
\]

In this case the whole water molecule attaches to the catalyst, or alternatively

\[
\text{H}_2\text{O} + s \rightarrow \text{H}_2 + \text{O(s)} \quad [a_2]
\]

the water breaks down to molecular hydrogen and oxygen atom and the oxygen remains attached to the catalyst, leaving the oxygen atom free to react with a carbon molecule.

Methane can also be adsorbed on the catalyst:

\[
\text{CH}_4 + s \rightarrow \text{CH}_4(s) \quad [b_1]
\]
The whole methane molecule attaches to the active site

$$\text{CH}_4 + s \rightarrow \text{CH}_2(s) + \text{H}_2 \text{ or } \text{CH}_4 + 3s \rightarrow \text{CH}_2(s) + 2\text{H}(s) \quad [b_2]$$

Methane is broken into CH$_2$ which attaches to the active site. An alternative pathway is

$$\text{CH}_4 + s \rightarrow \text{C}(s) + 2\text{H}_2 \text{ or } \text{CH}_4 + 5s \rightarrow \text{C}(s) + 5\text{H}(S) \quad [b_3]$$

The carbon is removed from the methane molecule and is adsorbed by the catalyst.

The products from these reactions then react with each others to form hydrogen and carbon oxides. There is no real agreement on what pathway is predominant, and it may depend on the reaction conditions. Any combination of reactions a and b are possible.

The publication by Hou and Hughes \cite{22} has a thorough discussion about the possible reaction mechanisms.

The catalyst activity (ability to support the reaction) depends on its size and more precisely on its total surface. \cite{24,25} Bigger particles catalysts are thought to be less active than small particle catalyst because they offer fewer reaction sites. A problem encountered with trying to reduce the size of the catalyst particle is that they may be hard to keep in the reformer and may be entrained with the reformate. Another issue for nickel catalyst is the presence of sulfur in the feed such as H$_2$S (formed in non-oxidizing environment) and SO$_2$ (formed in a high temperature, oxidizing environment). Poisoning a reformer feed stream with ~200 ppm sulfur has been shown to decrease hydrogen yield by has much as 40\%. \cite{34} The sulfur tends to bind with the nickel active\cite{24} site as follow:

$$\text{H}_2\text{S} + \text{Ni} \rightarrow \text{Ni-S} + \text{H}_2 \quad [6]$$

This causes the catalyst to have fewer active sites available for the reforming process.
3-3 Coke Formation

One of the major problems encountered with steam reforming is coke formation, the deposition of carbon on the catalyst, [19,25,26,28,31] which blocks the active sites and reduces reaction rates.

Coke reaction can occur when carbon is generated by any of the following mechanisms: [24]

- Pyrolytic carbon is formed by the exposure of higher hydrocarbons to high temperature (thermocracking) and results in carbon deposits in the reformer and on the catalyst surface and causes the catalyst to be deactivated by blocking its active sites.

- Encapsulating carbon (gum) is formed from heavy hydrocarbons with aromatic compounds, resulting in a thin layer of graphite covering the nickel particles. Glycerin is not aromatic so this case should not happen.

- Whisker carbon is formed if S/C is too low for higher hydrocarbons. Carbon whiskers grow by the reaction of hydrocarbons or CO at one side of the nickel particle and nucleation of graphitic carbon as a carbon whisker on the other side of the nickel particle.

Coke formation usually takes place in the following ways:

\[ \text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2 \]  
\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \]  
\[ \text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \]
\[ C_{n}H_{2n+2} \rightarrow nC + (n+1)H_{2} \] 

All of the above reactions are side reactions that may occur during reforming. The less active the catalyst becomes, the more coke forms, further deactivating the catalyst. Under this scenario, coking is an important issue in steam reforming as it can greatly decrease the reaction/fuel conversion efficiency.

3-4 Role of Water in Reforming

As shown in equations 4 and 5, steam reacts with hydrocarbons by providing the oxygen needed to form carbon monoxide during reforming, and further reacting with carbon monoxide to form carbon dioxide (although this reaction is limited at reforming temperatures due to thermochemical equilibrium). It has been shown that increasing S/C ratio in the feed (adding water) improves the reforming process and favors the production of hydrogen. This is because excess water drives reactions 4 and 5 to the right. Excess water also decreases coking by pushing reaction 9 to the left. This reaction is often believed to be the major cause of coking associated with thermal cracking at higher temperature. Nonetheless, it is beneficial to keep water content to a minimum during reforming due to the energy and economic costs of generating steam and raising it to reforming temperature – costs that can cancel the benefits of higher hydrogen yield.
3-5 Role of O/C

In reforming, oxygen reacts with the hydrocarbon to break down the carbon chain, producing carbon oxides. Oxidation \[^{[19,20,21]}\] produces heat for endothermic reactions, thereby decreasing the required external sensible energy input and, potentially, the operating costs. The process of using oxygen (or air) in reforming to produce part of the heat required is called partial oxidation \[^{[34,35]}\] and has been thoroughly documented. It should be noted that the stoichiometric oxygen requirement for glycerin is 3.5 mole \( \text{O}_2/\text{mole } \text{C}_3\text{H}_5\text{O}_3 \) and partial oxidation requires less than this amount. \[^{[36]}\] If the oxygen content is too high, hydrogen yield decreases and the reforming reaction gives way to more complete oxidation. If there is not enough oxygen, then coking may occur faster due to thermal cracking, unless more steam is used.

Another use for oxygen in reforming is to slow down coking, and even to reactivate deactivated catalyst. \[^{[37]}\] As mentioned before, catalyst deactivation is caused by excess carbon depositing on the catalyst surface. Feeding an excess of oxygen for a short time reactivates the catalyst by oxidizing the unwanted carbon in the reformer according to reaction \[^{[11]}\]:

\[
\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \quad \text{[11]}
\]
3-6 Types of Reformers: Fluidized vs Fixed Bed.

In a fixed bed reactor, reactants flow through a stationary solid catalyst formed into a high surface area geometry. In a fluidized reformer, the catalyst is made of particles designed so that the drag force between the reactants and the particles overcomes the weight of the particle and causes fluidization. A fluidized bed has the advantages of being well mixed and of having a more uniform reaction temperature profile compared to a fixed bed reactor. Temperature gradients of only 4°C have been recorded versus 15°C for fixed beds. The fluidized beds can also use much smaller catalyst pieces, in the 50-100 μm size, which potentially increases the active surface of the catalyst per unit of reactor volume. In addition, fluidized beds reach equilibrium conditions faster due to more homogeneous environment. One of the major problems in using a fluidized bed reactor is that the catalyst pieces, due to their small sizes, can sometime entrain with the reformate gas downstream of the reformer, where temperature is cooler, thus limiting the reforming process and producing more lower molecular weight hydrocarbons. Regarding coking and catalyst deactivation, studies have shown that for the first 20 hours, fixed beds showed faster catalyst deactivation, then over the next 60 hours of operation, fixed bed catalysts tend to remain stable while fluidized bed catalyst kept seeing their activity decrease, and eventually, after 120 hours on-stream, fluidized and fixed bed reactors showed the same deactivation state for their catalyst. It has been noted that fluidized beds have less carbon deposition on the catalyst than fixed beds due to constant motion of the catalyst, which can circulate to oxygen rich areas of the reformer and burn off the carbon.
3-7 Glycerin Reforming

The stoichiometric equation for glycerin reforming is:

\[ \text{C}_3\text{H}_5\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 3 \text{CO}_2 + 7 \text{H}_2 \quad [3] \]

Based on this stoichiometry, 7 mole of hydrogen could be obtained from 1 mole of glycerin (15.3 g H\textsubscript{2} / 100 g glycerin), i.e. a 15.3% yield. In practice, steam would be added as an excess reactant and the actual reaction would be expected to yield a wider variety of products.

\[ \text{C}_3\text{H}_5\text{O}_3 + a \text{H}_2\text{O} \rightarrow u \text{CO}_2 + v \text{H}_2 + w \text{CO} + x \text{H}_2\text{O} + y \text{CH}_4 + ... \quad [12-a] \]

Czernik et al. reported results from crude glycerin reforming research. [40] Crude glycerin was fed to a reformer at 78 g/hr, a rate similar in magnitude to the feed rate used in the experiments reported in the present work. Steam was injected for a S/C of 2.3 and there was no mention of air or oxygen being introduced with the glycerin. Smooth operation of the reformer was reported, with “occasional fluctuations in the liquid feed rate resulting from a non-complete homogeneity of the feed”. A gradual increase of methane in the reformate gas was reported, a normal sign of catalyst deactivation. Balances on overall mass and individual elements (carbon, oxygen and hydrogen) performed around the reformer system attained 95% closure. They indicated that the hydrogen yield “oscillated at around 77% of the stoichiometric potential, which was 23.6 g per 100 g of feed.” This would equal 18.2 g H\textsubscript{2} per 100 g feed. As noted above, the theoretical yield of hydrogen from glycerin is 15.3 g H\textsubscript{2} per 100 g C\textsubscript{3}H\textsubscript{5}O\textsubscript{3}, less than the
18 g that was reported by Czernik et al. Czernik's methods for determining theoretical yield were not clearly presented. At a S/C of 2.3, reaction 12-b could be expected:

\[ \text{C}_3\text{H}_6\text{O}_3 + 6.9 \text{H}_2\text{O} \rightarrow v \text{CH}_4 + w \text{H}_2\text{O} + x \text{CO}_2 + y \text{H}_2 + z \text{CO} + ... \] [12-b]

Methane concentration in the reformate increased from 500 to 2000 ppm over a 6 hour experiment but amounts of CO and CO\(_2\) were not reported.
4 - Apparatus

The fuel reforming test bed consists of two parts. The first part is the experimental test equipment that includes the reformer, the water-gas shift reactor, the tube furnace used to control the reformer temperature, mass flow controllers to meter reactant gases, a pump to meter glycerin, and the data acquisition and control system. The second part of the experimental set-up is the analytical equipment, a gas chromatograph, that is used to determine the composition of the reformate gas.

4-1: Reformer

The reforming reaction takes place in a stainless steel (type 316) pipe, 294 mm in length with an internal diameter of 25 mm. The reactor is placed in a tube furnace (Barnstead Thermoline) which provides temperature control via a thermocouple located between the furnace wall and the reactor; therefore the furnace temperature does not represent the temperature inside the reactor. The reactor pipe/furnace assembly is collectively referred to as the reformer. Prior to an experiment, nickel-based reforming catalyst (GW-91 from Sud-Chemie) was placed inside the reformer about 16.5 cm from the entrance to the stainless steel tube. Figure 1 shows pieces of used and unused catalyst.
Figure 1: Picture of unused catalyst piece (left) and used piece (right) (2 cm o.d.).

The reforming experiments were conducted in the reformer with metered flows of liquid phase glycerin and water and gas phase oxygen and nitrogen. A photograph of the reforming test stand is shown in Figure 2.
Oxygen and nitrogen were stored in compressed gas bottles at ~17 MPa (2500 psi) and regulated to an outlet pressure of 345 kPa (50 psi). The bottles are connected to two mass flow controllers (MFC) (Brooks S850 E series) which are controlled using Labview software run on a Toshiba laptop computer. The two MFCs were calibrated by the manufacturer for oxygen and air. The oxygen bottle was connected to the controller calibrated for oxygen and the nitrogen was connected to the controller calibrated for air. A correction factor supplied by the manufacturer was entered in the Labview program to account for the difference in air and nitrogen properties and ensure correct flow rates. The outlets of the mass flow controllers are connected to tubes entering the reformer.

Air could have been used for this experiment, but it was found (through experiment) to be more practical to separate the nitrogen and oxygen flows. Glycerin, O₂,
and N\textsubscript{2} were introduced to the reactor through three concentric tubes as shown in Figure 3. The glycerin and water mixture was injected into the reformer through the center tube that was 32 cm in length and 0.03 mm internal diameter. Initially, coking at the tip of the injector was a problem because it frequently resulted in reduced glycerin flow to the point of complete plugging. To resolve this, the nitrogen was introduced in the annulus between the glycerin injector and a 6 mm (0.25") tube, and the oxygen in the annulus between the 6 mm tube and an outer 12 mm tube. The nitrogen acted as a shroud gas to prevent the oxygen from reacting immediately with the glycerin at the injector tip.

A pump was used to meter the glycerin water mixture to the reactor. It was initially calibrated before installation and the calibration was checked before every test. The graph in Figure 4 shows the pump calibration curve.

![Figure 3: Schematic of glycerin, nitrogen and oxygen injection system.](image)
At the outlet of the reformer, the 25 mm reactor pipe is reduced to 6 mm (0.25"). An in-line filter is located 125 mm downstream of the pipe to collect any carbon that is produced in the reformer to prevent it from affecting downstream analytical equipment. The tubing at the inlet and outlet of the reformer are wrapped with resistance heating tapes and temperature is maintained at a desired set point by a controller (Omega, Mode CN 1504-TC) based on feedback received from type K thermocouples placed on the heated tube’s surface. Heat applied to the tubing upstream of the reformer preheat the reactants, vaporizes the water, and, in general, provides for more stable operation of the reformer. The tubing downstream of the reactor is heated to a temperature above 100°C.

Figure 4: Glycerin feed pump calibration curve for increasing and decreasing flow.
to prevent water from condensing. All the tubing in the system is insulated using glass wool to limit heat loss. A gauge is located upstream of the reformer, at the oxygen inlet, to measure system pressure. Three thermocouples (type K) are located inside the reformer; two upstream of the catalyst and one downstream of the catalyst, as shown in Figure 5.

![Figure 5: Thermocouples and catalyst positions inside the reformer. (Distances in cm)](image)

The thermocouples are connected to a data acquisition board linked to the Labview software that records data on the computer hard drive every three seconds.

4-2 Analysis

The gas coming out of the reformer first goes through a condenser to remove water vapor and then the gas is disposed in a laboratory fume hood. The reformate stream is sampled and analyzed using a gas chromatograph (GC) (Shimadzu, GC-14A) equipped with a thermal conductivity detector (TCD) and Supelco Carboxen 1000 column. The
carrier gas was a mixture of 8% hydrogen and 92% helium, and the pressure of the gas bottle exit line is set at 80 psi (552 kPa). The compounds making up the reformate elute from the column at different times depending on the size of the molecule and column temperature and pressure. As each compound passes the detector, an electronic signal is generated and recorded as a peak on the chromatogram. The retention time of each species for the current set-up is shown in Table 2. After calibration, it is possible to determine the composition of an unknown gas mixture based on retention time (used to identify the species) and the area of peak (proportional to concentration).

Table 2: GC retention time for reformate constituents.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.38</td>
</tr>
<tr>
<td>N₂</td>
<td>1.16</td>
</tr>
<tr>
<td>CO</td>
<td>1.65</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.15</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.44</td>
</tr>
</tbody>
</table>

The initial temperature for the GC column oven is 45°C. The GC system is equipped with an automatic valve that injects a new sample every 35 minutes. After sample injection the column is heated at a rate of 20°C per minute to 225°C. The temperature stays at 225°C for 25 minutes, after which the column is cooled to 45°C in preparation for the next sample.

To provide fresh sample to the GC sampling valve, a pump (Barnant, Model 400-1901) turns on 3 minutes before the sample is to be injected. It pulls the gas from the
condenser, through a coalescing filter (Balston, Model 31G) where remaining moisture is removed, and then to the GC sampling valve so that when the GC proceeds with the injection, the lines have been purged with sample gas from the process and gas from the previous sample has been removed. The sampling pump is controlled by the laptop computer using the Labview software. It is programmed to be synchronized with the GC sampling frequency so that it is not required to manually operate the pump during experiments and sampling. Figure 6 shows the sampling system.

Figure 6: Sample conditioning system for reformate analysis by GC.

4-3 Test Procedure

The following procedure was used to conduct a typical experiment:

1- Testing the glycerin injection needle

The glycerin injection needle is connected to a gas bottle and pressurized air is forced through to assure that it is clear. The needle is then connected to the glycerin feed pump and water is forced through (preheated as is done for experiments) to test atomization behavior. If successful, the water is then purged from the needle using compressed air. A poor atomization pattern is typically associated with pump outlet pressures above 40 psi
(276 kPa) compared to normal atomization with values of 10-20 psi (69-138 kPa). If the needle exhibits poor atomization a new needle is prepared and the procedure above is repeated.

2- Turning on the GC

The gas chromatograph is turned on at least 2 hours before sampling to allow it to preheat. During this time, the GC column temperature is set at 120°C with carrier gas flowing through it. After two hours, the GC oven temperature is set to 45°C and is ready for sampling procedure.

3- Setting up the reformer

Between each test, the reformer reactor tube is opened, catalyst from the previous experiment is removed, and the reformer is cleaned of any carbon it may contain. Fresh, pre-weighed catalyst is placed inside the reformer and all fittings are tightened. Heating tapes are put in place, the system is insulated, thermocouples are inserted into the reactor and connected to the data acquisition system, and the mass flow controllers are connected to their respective gas bottles.

4- Preheating the system

The reformer tube furnace is set to the desired operating temperature. At least 15 minutes before starting a test, the heating tapes installed on sections of the system tubing are turned on and allowed to reach their operating temperatures.

5- Checking system configuration

The system is checked to make sure all fittings have been tightened during reassembly and that the various valves are set to configure the desired flow path.
6- Starting the test

When all components are at operating temperature, the system is purged with nitrogen. The glycerin feed pump is turned on manually and the desired glycerin water mixture is drawn into the suction side of the pump. About 10 minutes are required to purge water in the pump and feed lines through the system and for the glycerin mixture to reach the reformer. There is a visible increase in the pressure between the pump and the injection needle (5-10 psi, 34-68 kPa) when glycerin begins to enter the reactor. At this time the oxygen flow to the reactor (if required) is also turned on.

7- Sampling

After glycerin feed to the reactor has begun, time is allowed for the temperatures inside the reformer to stabilize and then sampling is started. With the GC in ready mode, the sampling pump is manually turned on for 3 minutes to purge the lines, then turned off, and then set to auto mode. The GC sampling procedure is then started and thereafter the sampling pump automatically turns on for 3 minutes every 35 minutes. The time of each run was determined by the time required to reach steady state conditions and then analyze 5 to 8 gas samples.

8- Checking the experiment

During an experiment, various indicators should be monitored to ensure the safe and stable operation of the reformer system. These include: (1) the pressure after the glycerin pump to check for a plugged injector, (2) the pressure inside the reformer to check that the system after the reformer is not plugged, (3) the temperature inside the reformer to check that the temperature does not exceed the reformer maximum designed temperature
(\sim 1000^\circ C) and that the reaction is going smoothly, and (4) the GC chromatograms to
monitor the reformate gas composition, an indicator of the reformer performance.

9- Shutting down the system.

When the test is finished the system components are shut down in the following order,
starting with the glycerin pump, followed by the oxygen mass flow controller, and finally
heating tapes and the tube furnace. Nitrogen flow to the system is left on for a few
minutes to purge the system and then it is allowed to cool.
5 - Experimental Design

An initial $2^{4-1}$ factorial design was used to study the effect of oxygen to carbon ratio (O/C), steam to carbon ratio (S/C), reformer temperature, $T_{\text{ref}}$, and the interaction of the three variables on hydrogen yield and hydrogen concentration produced from reforming glycerin.

The values for the three variables were chosen from literature review and thermochemical equilibrium calculations conducted using the Factsage software. Simulations of glycerin reforming were run using Factsage at temperatures from 650 to 1000°C. The glycerin and water reactant proportions were set at stoichiometric values as in equation [3].

Figure 7 shows the results of the simulations in moles of product produced per mole of glycerin. Although Reaction [3] indicates that only CO$_2$ and H$_2$ should be produced, thermochemical equilibrium predicts that CO will be a major component.
From the Figure 7, the best temperature for hydrogen production would be around 750°C. Considering that hydrogen can also be produced from carbon monoxide (1 mole of H₂ / mole CO) by the water gas shift reaction and that over the temperature range from 750 to 1000°C, the hydrogen molar production decrease is inversely proportional to the carbon monoxide increase (-0.0011 mole H₂ / mole glycerin vs. +0.0015 mole CO / mole glycerin), the temperature starting point was chosen in this range. Initial tests used a reformer temperature of 750°C, however, due to operating problems which will be discussed later in the section 6, the reformer temperature was increased to 810°C. An O/C value of 1.05 (moles of O₂ per mole of C, including the oxygen present in the glycerin) was selected. Although this is somewhat high, it helped prevent excessive carbon formation on the catalyst.
As mentioned earlier, the glycerin was mixed with water to decrease its viscosity so that it could be easily injected into the reactor. Initially, a feed mixture composed of 63% water and 37% glycerin (by volume) was selected, which was equivalent to a molar steam to carbon ratio of 2.35.

Figure 8: Reforming conditions selected for experimental investigation.

From this initial set of operating parameters, two levels for each of the three variables were chosen by an equal increment in each direction as shown in Figure 8. The S/C was changed by ±0.35 to 2.0 and 2.7, the O/C was changed by ±0.15 to 0.9 and 1.2, and the temperature was changed by ±40°C to 770 and 850°C. Ten different conditions were tested. As shown in Figure 8, conditions 1 through 8 corresponded to the vertices of a cube defined by the $2^3$ factorial design and conditions 9 and 10 were the same and were located at the center of the design conditions.
Table 3 summarizes the experimental values of the variables and their coded units. Coding is used to make the statistical analysis easier. In coded units, the 0 value represents the center value for the variable, and +1 and -1 represent the values at the vertices of the cube as shown in Figure 8.

The performance of the experiment is defined primarily by studying the hydrogen yield. Carbon monoxide and carbon dioxide, as well as methane production are also important data in evaluating experimental success. Temperatures measured inside the reformer also provide insight into what may be happening at a given time during a test. Within the range of variables for the set of experiments, it is possible to calculate a value for the effect of each variable and the effects of the interactions between the different variables. It is possible to derive an equation that estimates the hydrogen yield (or any other measured output from the system) based on the operating conditions within the test range. An equation can then be derived to see how variables can be changed in order to improve the hydrogen yield following the path of steepest ascent. Once a directing line is
defined, it is then possible to move along it until the best operating condition is reached. When the reformer operating conditions are optimized, another variable effect analysis may be done to check that variables not so important in the first test area (inside the cube), did not become more important as they moved away from the original test conditions.

Following optimization in the reforming reactor, a water-gas shift reactor was added to the experimental process and the effect of its reaction temperature, $T_{\text{wgs}}$, on the gas composition was determined.
6 - Results and Discussion

6-1 Preliminary Tests

Initially, the system was tested at different conditions to get a feeling of how well it could perform and to identify operating problems. It took 12 practice runs to identify the various problems and to solve them. Below is a summary of the preliminary tests and the conclusions obtained from them.

Preliminary Test 1:

The water content in the glycerin feed mixture to the reformer was 10% and supplemental water was introduced to the reformer through a parallel line. Deionized water was used. Air was used to supply the oxygen required for the reaction and nitrogen to serve as a basis for gas yield calculations.

Results: No gas analyses were performed due to rapid system failure. The carbon feed rate (3ml glycerin / minute) was too high for the reformer capacity, requiring too much water to reach a S/C of 2.3, causing the reactor temperature to drop to 400°C (instead of 750°C set point). Also, the glycerin feed line quickly saw a pressure build-up that was apparently caused by the high glycerin viscosity and the small diameter tubing used in the injection needle.

Preliminary Test 2:
To remediate to the problems encountered in Preliminary Test 1, all the water required to obtain the desired S/C was mixed with the glycerin to decrease the fluid viscosity and allow easier flow through the injection needle. It also permitted a higher flow rate through the needle which was required for atomization of the feed inside the reformer while maintaining a lower carbon feed rate.

Results: No temperature drop was noticed inside the reformer but the test had to be stopped due to pressure build-up in the glycerin feed line again. Tests were performed to evaluate the spray of the glycerin/water mixture outside of the reformer and were deemed satisfactory, indicating that the needle placement inside the reformer probably caused the problem. After inspecting the needle closer, carbon deposits were found at the tip of the needle, probably due to the fuel-rich reaction of the glycerin with the oxygen at the needle tip, resulting in carbon formation, deposition, and plugging of the needle outlet.

Preliminary Test 3:

In order to keep the oxygen from reacting with the glycerin at the needle exit, separate bottles for nitrogen and oxygen were used instead of air. The injection system was modified to the configuration shown in Figure 3 so that the nitrogen flowed in the annulus between the glycerin/water mixture and the oxygen, delaying glycerin and oxygen reaction to a point further into the reactor. The tip of needle was positioned so that it was slightly recessed inside the tube carrying the nitrogen.

Results: This test was more successful. The reformer was operated for over two hours without pressure built up in the glycerin/water feed line.
Preliminary Tests 4-12:

With the glycerin feed system pressure build-up problems solved, the remaining preliminary tests were spent gaining experience to stabilize the reaction in the reformer. The thermocouples inserted in the reactor showed very unstable reaction temperatures and the analysis performed with the GC showed gas concentration varying from one sample to the next. Figure 9 shows this for preliminary run 9 that was operated for over 5 hours.

![Graph showing run 9 reformate gas concentrations](image)

Figure 9: Run 9 reformate gas concentrations.

This was not due to the GC since it had been calibrated and also successfully tested with calibration gas. Gas composition was analyzed every 35 min (25 min in the later tests) and was not particularly useful in identifying the cause of the unstable operation. The
reactor temperature and pressure data was acquired on a 3 second interval and were more helpful in diagnosing problems. Temperatures were seen to increase rapidly before slowly decreasing and rising again. Also, a significant amount of liquid glycerin was found in the inlet of the reactor tube after each run was ended. It was concluded that the liquid feed was not being smoothly injected into the reformer, and that it was accumulating in the 12 mm (0.5") tube carrying the nitrogen (i.e. the spray was hitting the inner surface of the tube) until it got hot enough to evaporate, enter the reformer, react with the oxygen, and cause the observed temperature increase. Experiments were performed with different configurations and lengths of needles. The problem was solved by making the needle exactly 32 cm long and extending it further out from the outlet of the tube carrying the nitrogen so that glycerin and water feed mixture did not impinge on the nitrogen feed tube walls and sprayed directly into the reactor. To further delay the reaction of glycerin and oxygen, the nitrogen flow was increased to 1.76 L/min so that it would shield the glycerin spray and move the reaction zone further into the reformer. After these modifications the system was ready to operate and perform the experimental plan discussed above.

A short discussion of the atomization process is given in Appendix B, part 4 (pp 86). The temperature of the glycerin and water mixture at the exit of the injector tube is not known with certainty. Measurement of the temperature profile at the reactor centerline at steady state with no flow in the reactor indicates that the temperature at the tip of the injector is \( \sim 450^\circ C \). Physical property data for the glycerin and water mixture at this condition are not readily available, however estimates were used to gain insight into
the atomization process. The analysis indicates that under the worst-case injection conditions, the liquid jet exiting the nozzle breaks up many nozzle diameters downstream and that the droplet diameters are about the same as the jet diameter (30 μm). These conditions are conducive to enhanced reaction rates and thereby allow the process to reach equilibrium faster.

6-2 Experimental Tests

**Typical Test explanation**

Preliminary Test 12 is used below to show how each test is analyzed.

Temperature: As mentioned before, three thermocouples are placed inside the reformer to monitor internal reactor temperatures as these are different from the tube furnace setpoint temperature. Reactor internal wall temperatures were not monitored but would be expected to be higher than reaction temperatures and could catalyze reactions on the reactor internal surfaces.
Focusing on the beginning of the run shown in Figure 10, the temperature goes up when the furnace is first turned on. When the reformer reaches stable temperature, the nitrogen (and oxygen) is (are) turned on, causing a slight drop in temperature, and the system pressure rises (from 0.689 to 3.10 kPa). Immediately afterward, the feeding pump is turned on and initially only water is injected into the reactor. The water injection causes the pressure and the temperature to temporarily become unstable and temperatures $T_1$ and $T_2$ decrease as water drops fall from the needle and evaporate. At ~11:10, the pressure takes a large sudden drop because the pressure at the needle is not yet high enough to induce atomization and get the feed inside the reformer, delaying vaporization of the water. The pressure then stabilizes. If after 6 minutes of water injection the pump
pressure (not shown on graph) is still below 69 kPa, the pump is then connected to the water/glycerin mixture. It takes about 7 minutes for the mixture to travel through the tubing and enter the reformer. When the glycerin gets to the injection needle (11:30), the reformer pressure again becomes very unstable while the flow makes a transition from water spray to glycerin/water spray. After about 15 minutes (11:45), the pressure at the pump stabilizes and the system begins to run smoothly. Thereafter, gas analysis can be conducted.

6-3 Test Results

As described in section 5, a first set of experiments covering 10 conditions was performed around what was hypothesized to be the best reforming settings. The reformer was used without the water gas shift reactor. For each condition, the reformate gas was analyzed for the predominant gases \( \text{N}_2, \text{H}_2, \text{CO}, \text{CO}_2 \) and \( \text{CH}_4 \), and the trace gases, \( \text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_4 \). Table 4 shows the amount of reformate gas obtained from each condition.
Table 4: Reformate gas yield, hydrogen concentration and setting values for conditions 1 through 10

<table>
<thead>
<tr>
<th>Condition Number</th>
<th>O/C</th>
<th>S/C</th>
<th>T, °C</th>
<th># of samples</th>
<th>[H₂] %</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>2</td>
<td>770</td>
<td>10</td>
<td>28.17</td>
<td>3.2±0.1</td>
<td>1±0.03</td>
<td>2±0.01</td>
<td>0.03±0.001</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>2</td>
<td>770</td>
<td>8</td>
<td>14.84</td>
<td>1.5±0.5</td>
<td>0.5±0.2</td>
<td>2.3±0.3</td>
<td>0.02±0.006</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>2.7</td>
<td>770</td>
<td>7</td>
<td>25.4</td>
<td>3.1±0.1</td>
<td>0.8±0.03</td>
<td>2±0.02</td>
<td>0.027±0.001</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>2.7</td>
<td>770</td>
<td>10</td>
<td>17.51</td>
<td>1.9±0.2</td>
<td>0.5±0.3</td>
<td>2.4±0.2</td>
<td>0.008±0.001</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>2</td>
<td>850</td>
<td>9</td>
<td>30.83</td>
<td>3.5±0.1</td>
<td>1.2±0.03</td>
<td>1.9±0.02</td>
<td>0.04±0.001</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>2</td>
<td>850</td>
<td>10</td>
<td>13.74</td>
<td>1.3±0.1</td>
<td>0.7±0.07</td>
<td>2.2±0.02</td>
<td>0.03±0.002</td>
</tr>
<tr>
<td>7</td>
<td>0.9</td>
<td>2.7</td>
<td>850</td>
<td>9</td>
<td>27.37</td>
<td>3.5±0.3</td>
<td>1±0.1</td>
<td>2±0.1</td>
<td>0.04±0.003</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>2.7</td>
<td>850</td>
<td>9</td>
<td>11.88</td>
<td>1.2±0.1</td>
<td>0.6±0.05</td>
<td>2.3±0.05</td>
<td>0.03±0.003</td>
</tr>
<tr>
<td>9</td>
<td>1.05</td>
<td>2.4</td>
<td>810</td>
<td>6</td>
<td>20.94</td>
<td>2.1±0.1</td>
<td>0.8±0.1</td>
<td>1.9±0.02</td>
<td>0.04±0.006</td>
</tr>
<tr>
<td>10</td>
<td>1.05</td>
<td>2.4</td>
<td>810</td>
<td>6</td>
<td>19.5</td>
<td>2.1±0.05</td>
<td>0.8±0.04</td>
<td>2.2±0.04</td>
<td>0.04±0.008</td>
</tr>
</tbody>
</table>
Condition 5 and 7 have the highest hydrogen yields, with 3.5 moles H₂ produced per mole of glycerin (~50% of the maximum theoretical yield of 7 moles of H₂ per mole glycerin). No great difference can be seen by varying the temperature. The hydrogen yields are respectively 2.4 and 2.3 mole per mole of glycerin at 770 and 850 °C. For S/C of 2 and 2.7, the same trend appears to be true, with respective yields of 2.3 and 2.4. The tests indicate that there are two groups of yields, one below 1.5 mole H₂ / mole glycerin and one above 3.0, which seems to be linked to the O/C ratio. The low O/C all yielded over 3 mole H₂ / mole glycerin, whereas the high O/C all yielded less than 1.5 mole H₂ / mole glycerin. The low O/C conditions also produced more CO (1 mole CO / mole glycerin vs 0.6) and less CO₂ (2 mole CO₂ / mole glycerin vs 2.3), compared to the high O/C conditions, which indicates that more oxidation takes place with more oxygen input.

Averages and standard deviations were computed using Excel for the five to eight reformate GC analyses that were performed for each condition. The standard deviation for most runs ranged from 0 to 0.3 (except for condition 2 at 0.5). Reforming conditions in the reactor changes over time due to catalyst deactivation and this contributes to the variation in gas composition and yield.

6-4 Reaction Modeling

Trends in the hydrogen concentration in the reformate gas closely matched the hydrogen yield as shown in Table 4. This is because little carbon (~1 g) was found in the reformer indicating that glycerin was nearly completely converted to gas. The ratio of hydrogen concentration over hydrogen yield was always a ratio between 9 and 10 and
this is an indicator that the gas yield was relatively constant over the range of test conditions.

A statistical analysis was performed on the data to define the effects (importance) of the dependent variables on the hydrogen yield during the reforming process and to predict the hydrogen concentration \( [H_2] \) and hydrogen yield \( Y_{H_2} \) in the reformate gas. Only hydrogen concentrations and yields were used in defining the effect of each variable, so the models do not predict CO or CO\(_2\) concentrations and yields.

The effect of each variables are shown in Table 5 and in equation \([13]\) for hydrogen concentration (%) and equation \([14]\) for hydrogen yield (mole H\(_2\) / mole glycerin) in coded units (See Appendix A, parts 1.2 and 3, pp71).

\[
[H_2] = 21.1 - 6.73 X_1 - 0.67 X_2 - 0.26 X_3 + 0.87 X_1 X_2 - 1.4
\]

\[
X_1 X_3 - 0.65 X_2 X_3 - 0.47 X_1 X_2 X_3 \tag{13}
\]

\[
Y_{H_2} = 2.3 - 0.93 X_1 + 0.034 X_2 - 0.02 X_3 + 0.06 X_1 X_2 - 0.18
\]

\[
X_1 X_3 - 0.047 X_2 X_3 - 0.08 X_1 X_2 X_3 \tag{14}
\]

Table 5: Effects of experimental variables and their interactions on reformate gas H\(_2\) concentration and yield (coded units)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Concentration</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X_1)</td>
<td>-6.7</td>
<td>-0.93</td>
</tr>
<tr>
<td>(X_2)</td>
<td>-0.6</td>
<td>0.034</td>
</tr>
<tr>
<td>(X_3)</td>
<td>-0.2</td>
<td>-0.02</td>
</tr>
<tr>
<td>(X_1 X_2)</td>
<td>0.8</td>
<td>0.06</td>
</tr>
<tr>
<td>(X_1 X_3)</td>
<td>-1.4</td>
<td>-0.18</td>
</tr>
<tr>
<td>(X_2 X_3)</td>
<td>-0.6</td>
<td>-0.047</td>
</tr>
<tr>
<td>(X_1 X_2 X_3)</td>
<td>-0.5</td>
<td>-0.08</td>
</tr>
</tbody>
</table>

The oxygen to carbon ratio is by far the most important variable in the parameter range covered by the tests, followed by the interaction between the oxygen content and the
reactor temperature. The effect of the steam to carbon ratio was minimal at this stage. But we can see that increasing S/C would decrease the hydrogen concentration in equation [13] and increase yield a little in equation [14]. This makes sense since, as mentioned before, extra water can result in additional hydrogen provided that carbon is present, i.e. all carbon has not been converted to CO$_2$. At this stage, however, changing S/C has minimal effect on reforming. Following response surface methodology (see Appendix A part 4, pp 78), a curvature check of equation 13 was performed to determine new values of the three variables that would improve the hydrogen concentration of the reformate gas. The model predicting hydrogen concentration was chosen over the one predicting hydrogen yield because they are closely related and it was thought more advantageous at this stage to obtain a high hydrogen concentration reformate. Two additional runs were performed along the line of steepest ascent. Table 6 shows the values defined for those two runs.

Table 6: Experimental conditions determined from response surface analysis and resulting H$_2$ and CO production.

<table>
<thead>
<tr>
<th>Condition</th>
<th>O/C</th>
<th>S/C</th>
<th>T (C)</th>
<th>mole/mole glycerin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H$_2$</td>
</tr>
<tr>
<td>11</td>
<td>0.8</td>
<td>2.3</td>
<td>807.0</td>
<td>3.8</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>2.2</td>
<td>804.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The table shows that the values of S/C were changed by 2 and 6%, respectively, and T was changed by less than 0.5%, indicating that they were already close to optimum values. O/C was decreased by 24% and 52% to values of 0.8 and 0.5, respectively relative to center point, conditions 9 and 10. Equation [13] suggested that it should be further decreased but this was not possible. At an O/C=0.5 (mole O$_2$ / mole C), the
oxygen feed line was shut off and all of the oxygen in the reaction was supplied from the glycerin. The hydrogen yield for condition 12 produced $4.5 \pm 0.3$ mole of $\text{H}_2$ per mole of glycerin, an increase of 28.6% relative to the 3.5 mole produced by conditions 5 and 7. This is 65% of the theoretical yield (7 mole $\text{H}_2$/mole glycerin). Also, 1.4 moles of CO were produced, which, from equation [2], could theoretically produce another 1.4 mole of $\text{H}_2$ using a water gas shift reaction. The amount of carbon monoxide increased in comparison to conditions 1 through 10, showing that the reforming process produced more CO instead of $\text{CO}_2$. Figure 11 shows the hydrogen and carbon monoxide concentrations for each condition.

![Figure 11: $\text{H}_2$ and CO molar concentration in reformate gas for conditions 1 through 12.](image)
It is clear that the reforming process was improved, producing more hydrogen as well as more carbon monoxide. As stated in the experimental equipment description in section 5, the reformer set point temperature differs from the actual reaction temperature. The actual reaction temperature at the optimized condition was 760°C. Figure 10 shows the reformer temperature over the duration of a test.

Table 7 summarizes the hydrogen yield for each condition, and the associated error. Error calculations are detailed in Appendix B, Part B3, pp 82. Error is caused by the uncertainty in the measurement of nitrogen and hydrogen concentrations in the reformate, as well as the limitation in controlling the nitrogen gas and glycerin flows into the system. As explained in Appendix B-1, nitrogen flow is used as the basis to evaluate the reformate gas yield. All runs have error below 10% of the yield value except for condition 2 which had a very low hydrogen yield, making the error large as a percentage of the value. The error for the experiments is acceptable and quite consistent among all conditions.

Table 7: H₂ yield and associated error (mole H₂ / mole glycerin)

<table>
<thead>
<tr>
<th>Condition</th>
<th>H₂ Yield (mole H₂/mole glycerin)</th>
<th>Error (mole H₂/mole glycerin)</th>
<th>Error (% of value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.2 ±0.3</td>
<td>±8.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.5 ±0.4</td>
<td>±24.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.1 ±0.3</td>
<td>±8.4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.9 ±0.2</td>
<td>±12.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.5 ±0.1</td>
<td>±2.6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.3 ±0.1</td>
<td>±7.7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.5 ±0.2</td>
<td>±4.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.2 ±0.1</td>
<td>±8.3</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2.1 ±0.2</td>
<td>±8.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.1 ±0.2</td>
<td>±7.1</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>3.8 ±0.3</td>
<td>±7.4</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>4.5 ±0.4</td>
<td>±7.8</td>
<td></td>
</tr>
</tbody>
</table>
The Factsage software was used to perform a chemical equilibrium calculation for the reaction conditions at condition 12 to see if the experimental results were in agreement. The reaction temperature measured inside the reactor directly downstream of the catalyst bed (~860°C) was used for the calculation. It predicted 5.4 moles H₂ / mole glycerin, 1.6 mole CO₂ / mole glycerin, 1.4 mole CO / mole glycerin, and 0.036 mole CH₄ / mole glycerin. The test at condition 12 therefore produced 83% of the hydrogen predicted by chemical equilibrium.

6-5 Effect of T and S/C around Condition 12

The steepest ascent method used to obtain the operating condition for run 12, was based on the model derived from conditions 1 through 10 over the following range of values:

\[
0.9 < \text{O/C} < 1.2 \quad \text{(reminder: O/C = mole O₂ / mole C)}
\]

\[
2 < \text{S/C} < 2.7
\]

\[
770°C < T < 850°C \quad \text{(furnace setpoint temperature)}
\]

The values of S/C, O/C, and T selected for condition 12 defined a point outside of the experimental cube shown in Figure 8, where the model (equation 13) derived from the first 10 tests may no longer be valid. In addition, the response surface around the point defined by Condition 12 may no longer depend on the S/C, T, and O/C variables in the same manner. To test this, two runs (13 and 14) were performed around condition 12,
keeping O/C (0.5) and T (804°C) constant, and setting S/C to 1.91 and 2.51, respectively, to determine its effect. Table 8 shows the test results.

Table 8: Reformate composition for runs 13 and 14

<table>
<thead>
<tr>
<th>Condition</th>
<th>O/C</th>
<th>S/C</th>
<th>T, °C</th>
<th>mole/mole glycerin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>13</td>
<td>0.5</td>
<td>2.5</td>
<td>804</td>
<td>4.67</td>
</tr>
<tr>
<td>14</td>
<td>0.5</td>
<td>1.9</td>
<td>804</td>
<td>4.72</td>
</tr>
</tbody>
</table>

The effect of S/C turns out to be 0.05 (in coded units) (see Effect Calculation, Appendix A3), which is very small and shows that changing S/C by a small amount can hardly improve the production of hydrogen. This does not tell us however how S/C affects catalyst deactivation, coking, CO and CH₄ production, and other performance indicators.

6-6 Water Gas Shift Results

After optimizing the reforming process, a water gas shift reactor was added downstream of the reformer to investigate its effect on hydrogen production. The water gas shift (WGS) reacts CO with H₂O to produce CO₂ and H₂ in a low temperature (~400°C) reactor. The experiments used a monolithic WGS catalyst from Nextech based on nano-particle, ceria-based, mixed oxide support. In the tests of the shift reactor performance, the temperature was the only variable that was changed. The gas stream exiting the reformer flowed immediately to the shift reactor, the two being in series (Figure 2). For the investigation of the shift reactor, the reformer was operated with operating variables set to those used for Conditions 12. Five tests were performed (16-20)
to reach an optimized WGS temperature. For each test, the reformer was initially run by itself to make sure that reformate composition was similar to that determined earlier for condition 12. When the reformer was operating stably, the reformate was directed to the water gas shift reactor. Table 9 shows the operating temperature for the shift reactor and the amount of gas produced for each of the tests.

Table 9: Mole H₂ per mole glycerin using the WGS at different temperatures, with reformer operated at Condition 12 (O/C = 0.5, S/C = 2.2 and T= 804°C)

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>mole H₂/mole glycerin</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>320</td>
<td>4.31</td>
</tr>
<tr>
<td>16</td>
<td>340</td>
<td>4.99</td>
</tr>
<tr>
<td>17</td>
<td>360</td>
<td>5.38</td>
</tr>
<tr>
<td>18</td>
<td>380</td>
<td>5.9</td>
</tr>
<tr>
<td>18</td>
<td>420</td>
<td>5.96</td>
</tr>
<tr>
<td>19</td>
<td>420</td>
<td>5.28</td>
</tr>
</tbody>
</table>

Up to two shift reactor temperature conditions were run during a single test period. Each temperature was only tested for a little over one hour to limit the effect of any change in the reformer performance over time. Three analyses were obtained per condition. The results were also dependent on the reformer operation, which were not always stable especially at the beginning of a test. This caused the results for the WGS to have greater variability than the tests using only the reformer. The shift reactor tests for temperatures of 380 and 420°C were run during the same test period, with each condition run for about an hour. Figure 12 shows the measured gas compositions for each sample, which were 25 minutes apart.
Figure 12: Run 18 reformer with WGS reformate gas composition at 380 (left) /420°C (right). Samples 1, 2, 7 and 8 are reformer gas composition.

Samples 1 and 2 are analyses of the reformer outlet gas. Samples 3 through 6 were taken at the outlet of the WGS. For samples 3 and 4 the WGS was operating at 380 C and for samples 5 and 6 it was operating at 420 C. The average H₂ yield for samples 5 and 6 was 5.96 ± 0.43 mole H₂ / mole glycerin, which is a very high yield compared to condition 17 (5.38 mole H₂ / mole glycerin) which was 40°C below. Analysis of sample 2 determined a production rate of over 5 mole of H₂ per mole glycerin, and this is higher than any other run obtained from the reformer only. Therefore, there were reasons to think that this run was overestimating the hydrogen production. To verify this, the reformer was again run while using the WGS set at 420°C, throughout the whole test (condition 18). This test was much more stable, and obtained 5.28 ± 0.41 moles H₂ / mole glycerin from the shift reactor, a more realistic result. The standard deviation was about 0.12, showing very stable reformer operation. Figure 13 shows the shift reactor outlet gas composition over the course of the condition 18 test. A set point temperature of
420°C for the WGS corresponds to an internal reactor temperature of 369°C. Table 10 shows the average gas production for run 18.

Table 10: Gas composition from reformer (O/C=0.5, S/C=2.2, T=804°C) with WGS reactor (set point T_{WGS}=420°C, internal reactor temperature = 369°C)

<table>
<thead>
<tr>
<th>Run #</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>5.3</td>
<td>0.5</td>
<td>2.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The hydrogen yield per mole of glycerin improved from 4.5 mole H₂ / mole glycerin using only the reformer to 5.3 mole H₂ / mole glycerin when the WGS was used, an improvement of 18%. Also, the amount of CO₂ produced rose from 1.4 to 2.2 mole H₂ / mole glycerin, and the CO decreased from 1.4 to 0.5 mole H₂ / mole glycerin. These
results are in keeping with the water gas shift reaction (Equation 3) since the CO₂ production increased by 0.8 moles and the CO production decreased by 0.9, showing that approximately all the CO is converted to CO₂. The hydrogen production increase of 0.8 moles, shows good operation of the water-gas shift. If the water gas shift was the only reaction taking place in the shift reactor, an additional 0.1 mole of CO₂ would be produced to complete the balance. The gas analysis showed that 0.065 mole of C₂H₆ per mole glycerin was produced, compared to 0.01 moles per mole glycerin in condition 12. Part of the carbon for C₂H₆ may be coming from the CO, and 0.065 mole of C₂H₆ per mole glycerin would account of the 0.1 difference between CO and CO₂ yields. The carbon balance computed for condition 20 was 97.6% indicating that the measurement of system inputs and outputs is being well conducted. We can then conclude that the addition of a shift reactor to a reformer is a good option, improving hydrogen yield from 64% to 75% of the maximum theoretical yield.

6-7 Catalyst Deactivation

Catalyst deactivation occurs over time mainly due to coking, as discussed in section 3-3, and results in a lower hydrogen yield. A good indicator of catalyst deactivation is an increase in methane production, and to a lesser extent, ethane. Despite the short length of these tests, the decrease in performance from the reformer was noticeable within a few hours of testing. Data for condition 12, the best operating condition for the reformer, are presented in Figures 14 and 15 and show a decrease in hydrogen yield and a corresponding increase in methane yield. The hydrogen yield in the reformate gas went
from 4.75 mole / mole glycerin to 4.49 in less than 150 min. (-0.56 % / hr). The yield for each gas and the carbon balance was estimated based on their concentration relative to nitrogen gas. Nitrogen gas flow was kept constant and is nonreactive.

Figure 14: H₂ yield (mole H₂/ mole glycerin) for each sample during condition 12 test.
Figure 15: Condition 12 methane yield (mole CH₄/mole glycerin) for each sample

Figure 15 shows the increase in methane production, which is also quite constant. It increased by 60% during the 150 min test period. Despite the increasing methane (Figure 15) and decreasing hydrogen (Figure 14) trends, it is not possible to predict long term performance.
Table 11: Methane production for run 1 through 8

<table>
<thead>
<tr>
<th>Condition</th>
<th>Mole CH₄ / mole glycerin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.027</td>
</tr>
<tr>
<td>2</td>
<td>0.038</td>
</tr>
<tr>
<td>3</td>
<td>0.038</td>
</tr>
<tr>
<td>4</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>0.028</td>
</tr>
<tr>
<td>6</td>
<td>0.032</td>
</tr>
<tr>
<td>7</td>
<td>0.01</td>
</tr>
<tr>
<td>8</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 11 shows the molar yield of methane per mole of glycerin obtained from tests 1 through 8. These data were examined to see how methane production was related to S/C or O/C. Runs 1, 2, 6 and 7 had higher S/C (2.7) while runs 3, 4, 5, 8 had lower S/C (2). Both higher and lower S/C tests averaged 0.03 mole CH₄ / mole glycerin, indicating the S/C was not useful in preventing catalyst deactivation over the range of conditions tested. A similar assessment of the data was performed to determine effects of O/C. Runs 1 through 4 had lower O/C (= 0.9) and averaged 0.033 mole CH₄ / mole glycerin. Runs 5 through 8 (higher O/C=1.2) averaged 0.023 mole CH₄ / mole glycerin, a 30% decrease. This indicates that higher oxygen input can decrease the methane yield which may correlate with decreased catalyst deactivation.

Methane production, \( Y_{CH₄} \) (mole per mole glycerin), was modeled as a function of O/C, S/C and T in coded units, resulting in equation [15],

\[
Y_{CH₄} = 0.027 - 0.0054 \times (X₁) - 0.0011 \times (X₂) + 0.006 \times (X₃) \quad [15]
\]

Equation [15] indicates that lowering O/C increases methane production, the likely result of catalyst deactivation. This was supported by runs 11 (O/C = 0.75) and run 12 (O/C = 0.5) which produced 0.04 and 0.14 mole CH₄ / mole glycerin respectively. Figure 16
summarizes these results. More tests would be needed to better understand the effect of oxygen content on catalyst deactivation.

Figure 16: Methane production as a function of O/C
Carbon deposits are often responsible for catalyst deactivation and were readily apparent when the catalyst pieces were recovered from the reformer after a test was completed. Figure 17 shows the six catalyst pieces recovered from run 12. The catalyst pieces on the left were the closest to the inlet end of the reactor and the pieces on the right were further downstream. The pieces on the left are much darker and covered with carbon, affecting their ability to enhance the reforming reaction. Over the length of each run, the catalysts farthest downstream kept their original, grayish color (and were still apparently quite active). A possible reason why hydrogen yield did not drop significantly over the test duration is that the catalyst may have been in excess of amount required for
complete reaction or the rate of carbon deposition may not have been constant over the test duration. One possible way to test this hypothesis would be to reduce the number of catalysts pieces and repeat the experiment.

Figure 18: Post-test and pre-test in-line sintered metal filters that are located downstream of the reformer.

Figure 18 shows the in-line, sintered-metal filter elements placed in the process line after the reformer (before the WGS and the GC). The filter element on the right is new while the one on the left has been used in a reforming test. The used filter is blackened from carbon collected from the reformate stream exiting the reformer. Although the amount of carbon recovered from the reformer and the filter after each test was not
significant (between 0.36g to 1g) and accounted for less than 1% of the total carbon contained in the glycerin feed, it impacted the reformer by increasing operating pressure over the test duration. Pressure started at about 20 kPa for each run, and slowly worked its way up to ≥48 kPa. A higher S/C was expected to reduce coking and slow the catalyst deactivation. From the amount of carbon collected in the reformer and the pressure recorded in the reformer, it was not possible to determine a clear effect of S/C on the carbon formation for the duration of these tests. The pressure inside the reformer varied from 27 to 48 kPa for each condition (with peaks as high as 69 kPa on some occasions during the earlier tests, probably due to poor feed injection and sudden vaporization of water).

6-8 Crude Glycerin Test

Crude glycerin is the eventual final target feed to be used for reforming. Its characteristics were discussed in the experimental part. Reforming of crude glycerin was tested at the optimal operating condition, (i.e. condition 12), without using the WGS. The conditions were as follow (same as run 12):

\[
\begin{align*}
O/C &= 0.5 \\
S/C &= 2.21 \\
T_{\text{set}} &= 804 ^\circ C
\end{align*}
\]
Figure 19: Crude glycerin reformate gas composition

Figure 19 shows the reformate composition for the crude glycerin test. The crude glycerin feed rate was measured in the same way as pure glycerin. The hydrogen yield reached 4.4 moles $H_2$ / mole crude glycerin, when the best yield reached with pure glycerin was 4.5 moles. This shows that the process worked well at first. The amount of CO and CO$_2$ produced was significantly lower though, with about 1 mole of each produced in the second sample. The amount of methane produced, 0.23 moles per mole crude glycerin, was almost twice as much as in run 12 (0.14 moles per mole glycerin). In addition, C$_2$H$_4$ was produced at levels equal to methane, where previously it was almost negligible in all runs performed using pure glycerin. The hydrogen yield decreased quickly after the second sample (-0.41 mole $H_2$ per mole glycerin per hour) and the amount of CH$_4$ and
C$_2$H$_4$ increased (+0.072 mole/hr), possibly indicating rapid catalyst deactivation and feed pyrolysis. Also, the carbon balance on this test shows that only 2.5 mole of C were recovered in the gas phase per mole of glycerin (83% recovered). This could explain the fast pressure rise in the reformer as shown in Figure 20. Increasing pressure in the system should go against the reforming process and the production of gas, favoring instead carbon formation.

![Graph showing reformer pressure during test 20 using crude glycerin as feedstock. Feeding started at 12:00 and ended at 14:24)](image)

Figure 20: Reformer pressure during test 20 using crude glycerin as feedstock. (Feeding started at 12:00 and ended at 14:24)

The pressure quickly increased past 69 kPa (the limit for the pressure sensor), causing the experiment to be stopped. After the reformer cooled down and was opened to be cleaned and to recover the used catalyst, it was found that the reformer tube was filled with rock-hard carbon deposit as shown in Figure 21. It was not possible to tell how much carbon
formed in the reformer because it could not be removed. This test showed that crude glycerin can be reformed with high hydrogen yield but that contaminants can cause severe coking during the reforming process. The major contaminants known to be present in crude glycerin are sulfur (present in the waste cooking oil), potassium/sodium cations (from either the potassium or sodium hydroxide base used as catalyst in biodiesel manufacture), free fatty acids (present in the cooking oil from animal fat based oil), and methanol (reacts with the oil and replaces the glycerin to form biodiesel). Further work was performed to determine the effects of contaminants on the reforming process performance. The approach was to add individual contaminants to pure glycerin to determine their effect on process performance, particularly coke formation. Results are described in section 6-10 (pp 63).
6-9 Comparison with Relevant Research

As mention in the prior work (p. 8), the amount of hydrogen that Czernik et al. reported to have obtained, (77% of stoichiometric yield), was not based on the actual glycerin reforming stoichiometric equation but on the relative amount of hydrogen contained in the glycerin and the water that they fed the reformer. They obtained 8 moles of hydrogen per mole of glycerin. Based on real stoichiometric value (i.e. $C_3H_8O_3 + 3 H_2O \rightarrow 3 CO_2 + 7 H_2$), their hydrogen yield was actually 115% of theoretical which is not considered possible. Nonetheless, for using a steam to carbon ratio close to the one
that was used in the best run for this experiment (2.3 vs. 2.21), their hydrogen yield was a
much higher than the one achieved during this research, 115% vs 65% of theoretical.
After giving a closer look at their experimental conditions, their ratio of steam to carbon
turned out to be 3.2 instead of the 2.3 that they reported.
Their actual reaction, given the steam flow rate of 145 g / hr, was:

\[ C_3H_8O_3 + 9.6 \text{H}_2\text{O} \rightarrow x \text{CO}_2 + y \text{H}_2 + z \text{CO} + z \text{H}_2\text{O} \] [16]

The amount of CO, CO₂, and H₂O that they recovered was not reported. Using their
stoichiometric equation, their achieved yield was not 77% but 58%, and such a large
amount of hydrogen in the reformate gas is difficult to explain.

6-10 Contaminant Analysis

Pure glycerin was contaminated with methanol, NaCl and NaOH to see the effect
of each contaminant on the reforming process. The water-gas shift reactor was not used.
The conditions for the reformer were the same as condition 12. Figure 22 shows the
system pressure for the test run with glycerin contaminated with methanol.
Figure 22: System pressure for glycerin feed contaminated with methanol (reformer set at condition 12)

The experiment performed well with the methanol, with the pressure staying within normal range (<34 kPa). The hydrogen yield averaged 4.7 mole H₂ per mole glycerin, which is close to the yield obtained from condition 12 with no contaminants.

Figure 23 shows the system pressure for a test of glycerin contaminated with sodium chloride (0.5% by weight) using condition 12 reformer settings.
Figure 23: System pressure and temperatures for glycerin feed contaminated with NaCl (reformer set at condition 12)

Although the reformer temperatures were stable, the pressure inside the system rose to over 30 kPa in about 1 hour. The pressure then started to increase more rapidly causing the experiment to be shut down, the same as happened with crude glycerin.
Similar system performance occurred in a test conducted with pure glycerin contaminated with sodium hydroxide [0.5 % by weight], as shown in Figure 24. The pressure climbed to over 45 kPa very quickly. Both tests using pure glycerin contaminated with sodium compounds at condition 12 have shown a fast pressure rise, and in both cases, the reformer was found to contain a lot of carbon built-up on the catalyst and the reformer surfaces. This may suggest that sodium hydroxide and sodium chloride are possible components causing coking.
7- Conclusion

A statistical approach to study and improve the reforming of glycerin to produce hydrogen was undertaken with the goal in mind to reform crude glycerin obtained from the transesterification of vegetable oil in the production of biodiesel. Using a fixed bed reactor of nickel based catalyst and a $2^3$ factorial design, the effects of the reformer temperature ($T$), oxygen to carbon ratio ($O/C$), and steam to carbon ratio ($S/C$) were studied and quantified, so that they could be used to improve the hydrogen yield. The two levels of $T$, $O/C$, and $S/C$ were 770 and 850°C, 0.9 and 1.2, and 2 and 2.7, respectively, and the hydrogen yield was successfully modeled in terms of these three variables. Over the range of conditions tested, oxygen to carbon ratio was found to have the greatest effect. The hydrogen yield obtained, 4.6 mole H$_2$ / mole of glycerin, was as high as 65% of the stoichiometric maximum yield (7 mole H$_2$ / mole glycerin) and 85% of the maximum theoretical yield based on chemical equilibrium (5.4 mole H$_2$ / mole glycerin). A path of steepest ascent method was used to arrive at the reformer operating conditions that produced the greatest hydrogen yield – an oxygen to carbon ratio of 0.5, a steam to carbon ratio of 2.2 and a reformer internal temperature of 760°C. A water gas shift reactor was then added after the reformer to convert carbon monoxide to hydrogen. Operating the water gas shift reactor at 369°C yielded 5.3 mole H$_2$ per mole glycerin. Crude glycerin was then tested in the reformer. The initial results were very close to that of pure glycerin, but the hydrogen yield quickly decreased due to catalyst deactivation and coking. Carbon accumulation in the reformer plugged the system and caused the pressure to rise above 10psig necessitating system shut down. Tests conducted with pure glycerin doped with potential contaminants, methanol, NaOH, and NaCl, suggest that Na may be
one of the elements responsible for the reduced performance. Methanol did not negatively affect the reforming process. Free fatty acid not converted during the transesterification process could also be responsible for poor system performance using crude glycerin but their effect was not investigated. All stated objectives (page 6, section 2-5) of this research were achieved except objective 5, which was only partially achieved since the effect of free fatty acids was not investigated.
8 – References

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[8] Fei Xiang Long and Börje S. Gevert, Modeling initial decay of hydrodemetallization catalyst with simultaneous adsorption and reaction mechanism, *Journal of Catalysis, Volume 222, Issue 1, 15 February 2004, Pages 1-5*


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Appendix A

A - Experimental design part 2: Calculation.

A-1 Effect Calculation

The initial experimental design initially shown in Figure 8 is reproduced below.

- Replacing variables real units by coded units:

The cube can be seen as having a width of 2 units, the center of it (cond 9and 10) having coordinates of (0, 0, 0).

The following names will be used for the coded variables:

\[ X_1 = O/C \]
\[ X_2 = S/C \]
\[ X_3 = T \]
Replacing the real units by coded units would be done as follow:

\[
X_1 = \frac{(O/C - 1.05)}{0.15}
\]  \[17\]

where 1.05 is the middle value for O/C and 0.15 is the deviation on each side. Similarly for \(X_2\) and \(X_3\):

\[
X_2 = \frac{(S/C - 2.35)}{0.35}
\]  \[18\]

\[
X_3 = \frac{(T - 810)}{40}
\]  \[19\]

The values for O/C, S/C and T and their values in coded units are shown in Table A1. Also included in the table are the interactions between the variables \(X_1\), \(X_2\) and \(X_3\), and the hydrogen concentration obtained for each condition. From this table, we can calculate the effects of each variable and their interaction on the hydrogen yield. Note that the center points (conditions 9 and 10) are not used in determining the effects of the variables.

Table A1: Reformer experimental variable values and coded unit values for a \(2^3\) experimental design with two center points, coded unit values for two and three variable interactions, and average hydrogen concentration at each condition.

<table>
<thead>
<tr>
<th>Condition</th>
<th>O/C</th>
<th>S/C</th>
<th>T (C)</th>
<th>(X_1)</th>
<th>(X_2)</th>
<th>(X_3)</th>
<th>(X_1X_2)</th>
<th>(X_1X_3)</th>
<th>(X_2X_3)</th>
<th>(X_1X_2X_3)</th>
<th>[(H_2)] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>2</td>
<td>770</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>28.2</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>2</td>
<td>770</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>14.9</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>2.7</td>
<td>770</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>25.4</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>2.7</td>
<td>770</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>17.5</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>2</td>
<td>850</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>30.8</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>2</td>
<td>850</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>13.7</td>
</tr>
<tr>
<td>7</td>
<td>0.9</td>
<td>2.7</td>
<td>850</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>27.3</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>2.7</td>
<td>850</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>11.9</td>
</tr>
<tr>
<td>9</td>
<td>1.05</td>
<td>2.4</td>
<td>810</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20.9</td>
</tr>
<tr>
<td>10</td>
<td>1.05</td>
<td>2.4</td>
<td>810</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>19.5</td>
</tr>
</tbody>
</table>
A-2 A Model Development for Third Order Design

The modeling equations for hydrogen concentration (analogous to hydrogen yield) will have the form:

\[ Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3 \] [20]

Where

\[ \beta_1, \beta_2, \text{and} \beta_3 \] are the coefficients for the first order effects of \( X_1, X_2 \) and \( X_3 \).

\[ \beta_{12}, \beta_{13} \text{ and} \beta_{23} \] are the coefficients for the second order effects (interaction between two variables).

\[ \beta_{123} \] is the coefficient for the third order effect (interaction between the three variables).

\[ \beta_0 \] equals the average of the hydrogen concentration for all runs, 21.1%.

A-3 Example Calculating effect of \( X_1 \): \( \beta_1 \)

The values of \( X_1 \) for each condition are multiplied by the \( H_2 \) concentration for that condition and all the results are added together. They are then divided by 8 as shown below:

\[ X_{1\text{effect}} = \frac{((-1)28.17 + (1)14.9 + (-1)25.4 + (1)17.5 + (-1)30.8 + (1)13.7 + (-1)27.3 + (1)11.9)}{8} \]

\[ X_{1\text{effect}} = -6.72 \]

The results of performing this calculation for each variable and their interactions are summarized in Table A2.
As was mentioned in the Results section 6-4 (pp 41), $X_1$ is the most influential variable, followed by the interaction between $X_1$ and $X_3$ (O/C and T). Because the interaction between the variables is deemed important for hydrogen yield and concentration, a second order design (one that includes the two variable interactions) must be used to define a polynomial model of the reforming process.

Equation 20 then becomes:

\[
Y = 21.1 - 6.73 \times (X_1) - 0.67 \times (X_2) - 0.26 \times X_3 + 0.87 \times (X_1) \times X_2 - 1.4 \times (X_1) \times X_3 - 0.65 \times (X_2) \times X_3
\]

[21]

Table A3 compares the model predicted concentration against the obtained concentration:
Table A3 Comparison of equation 21 model of reforming reaction vs. real data.

<table>
<thead>
<tr>
<th>condition</th>
<th>predicted</th>
<th>real</th>
<th>error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.15</td>
<td>28.2</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>14.81</td>
<td>14.8</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>25.4</td>
<td>25.4</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>17.4</td>
<td>17.5</td>
<td>0.57</td>
</tr>
<tr>
<td>5</td>
<td>30.8</td>
<td>30.8</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>13.7</td>
<td>13.7</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>27.3</td>
<td>27.4</td>
<td>0.37</td>
</tr>
<tr>
<td>8</td>
<td>11.9</td>
<td>11.9</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The model is always within 1% of the real data, therefore, it was deemed accurate and could be used for improving the hydrogen yield.

A-4 Path of Steepest Ascent

After determining a model equation that defines yield (or concentration), it can be used to define the path of steepest ascent toward better yield. This path is defined by the first order effects shown in equation 21 above. For each -6.73 units moved in the $X_1$ direction, $X_2$ moves by -0.67 units and $X_3$ moves -0.26 units or for every 1 unit moved in $X_1$, move 0.1 units in $X_2$ and 0.04 units in $X_3$. Following this path is called the path of steepest ascent. Changing $X_1$, $X_2$, and $X_3$ according to these results should produce a higher hydrogen yield from the reformer. Table A4 shows the improved values of the variables in coded units as well as their equivalent values in real values.
Table A4: Values for future conditions along the path of steepest ascent. Point 4 corresponds to condition 11 and condition 12 lies between point 4 and 5.

<table>
<thead>
<tr>
<th>Point #</th>
<th>coded Units</th>
<th>Real Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x1  x2  x3</td>
<td>O/C  S/C  T(°C)</td>
</tr>
<tr>
<td>1</td>
<td>0   0   0</td>
<td>1.05  2.35  810</td>
</tr>
<tr>
<td>2</td>
<td>0   -0.1 -0.04</td>
<td>0.9  2.315  808</td>
</tr>
<tr>
<td>3</td>
<td>-2  -0.2 -0.08</td>
<td>0.75 2.28  807</td>
</tr>
<tr>
<td>4</td>
<td>-3  -0.3 -0.12</td>
<td>0.6  2.245  805</td>
</tr>
<tr>
<td>5</td>
<td>-4  -0.4 -0.16</td>
<td>0.45 2.21  803</td>
</tr>
<tr>
<td>6</td>
<td>-5  -0.5 -0.2</td>
<td>0.3  2.175  801</td>
</tr>
</tbody>
</table>

Real values were obtained using equations 16, 17 and 18. Realistically, as mentioned on the result section, O/C cannot be brought under 0.5, which is the glycerin oxygen content. Therefore, it will not be possible to conduct experiments at points 6 and 7 shown in Table 15. Figure A1 shows a representation of the path of steepest ascent followed to improve the reforming process and increase hydrogen concentration, as well as the yield (mole H2 / mole glycerin) obtained at each point.
Condition 11 and 12, performed along the path of steepest ascent (red line), improved the hydrogen yield. The value of O/C was reduced by more than half. Two more runs were performed around condition 12 to see if S/C, which was only changed slightly along the path of steepest ascent, would have a greater effect on the hydrogen yield in the region of condition 12. This is done because the model was only valid inside the cube in Figure A1 and the further away from its bounds the experimental conditions are moved, the less accurate the may model become.

Tests were conducted at Conditions 13 and 14 to determine the effect of S/C around Condition 12. As mentioned previously, hydrogen yield for conditions 13 and 14 were respectively 4.67 and 4.72. Only S/C was changed in this part, by 0.3 in each direction.
around S/C=2.21, the value at condition 12. The effect of S/C was calculated in the same way as described earlier:

$$\text{S/C}_{\text{effect}} = (4.72 - 4.67) / 1 = 0.05$$

This shows that the effect of S/C is small and does not have a large impact on hydrogen concentration or yield around the region of Condition 12.
Appendix B

B-1 Reformate Gas Product Concentration \([x]\)

From the GC analysis, a normalized concentration, \([x]\), for each gas was determined:

\[
[H_2] + [CO] + [CO_2] + [N_2] + [CH_4] + [C_2H_4] + [C_2H_6] + \ldots = 100
\]  \[22\]

The molar flow rate for \(N_2\), \(N_{N_2}\), is known from the input mass flow controller setting and is constant because it does not react in the reformer. Knowing \(N_{N_2}\), as well as \([N_2]\) and the concentration of all other compounds, \([x]\), the molar flow rate \(N_x\) for each of the other gases can be calculated.

For each gas, \(N_x\) equals:

\[
N_x = [x] \frac{N_{N_2}}{[N_2]} \quad \text{[23]}
\]

Where

- \([x]\) = molar concentration of \(x\) in the reformate
- \(N_x\) = molar flowrate of \(x\) in the reformate
- \([N_2]\) = molar concentration of \(N_2\) in the reformate
- \(N_{N_2}\) = molar flow rate of \(N_2\) = 0.078 [mole / min]

For each test, the molar flow rate for glycerin \(N_{glyc}\) is known:

\[
N_{glyc} = V_{\text{feed}} \times X_{C_3H_6O_3} \frac{d_{glyc}}{M_{glyc}}
\]

\(V_{\text{feed}}\) = volume flow rate of the feed (glycerin and water mixture), controlled by pump, ml/min, determined from initial and final weight of glycerin water feed mixture and the test duration.

\(X_{C_3H_6O_3}\) = volumetric fraction of \(C_3H_6O_3\) in the feed

81
\( d_{glyc} = \text{glycerin density (1.26 g/ml)} \)

\( M_{glyc} = \text{glycerin molar weight (92 g/mole)} \)

The mole of gas produced per mole of glycerin \( Y_x \) then:

\[
Y_x = \frac{N_x}{N_{glyc}}
\]  \[24\]

**B-2 Carbon Balance Calculation**

The initial \( (W_{initial}) \) and final \( (W_{final}) \) weight of the glycerin/water feed bottle were used to determine the weight of mixture fed to the reformer:

\[
W_{final} - W_{initial} = W_{used}
\]  \[25\]

The volume is determined using the density of the mixture:

\[
D_{mix} = X_{glycerin} \times D_{glycerin} + X_{water} \times D_{water}
\]  \[26\]

Where:

- \( D = \) density of the subscript fluid
- \( X_i = \) volume fraction of water or glycerin in the feed mixture

The volume (ml) of the mixture \( (v_{mix}) \) fed to the reformer can be calculated as:

\[
v_{mix} = \frac{W_{used}}{D_{mix}}
\]  \[27\]

Multiplying \( v_{mix} \) by \( X_{glycerin} \) yields:

\[
v_{mix} \times X_{glycerin} = v_{glycerin}
\]  \[28\]

\( v_{glycerin} = \) volume (ml) glycerin used during the test

Knowing the duration of the experiment \( (t, \) time elapsed from when the pump was turned on and off\), we get the flow rate of the glycerin injected in the system.

\[
V_{glycerin} = \frac{v_{glycerin}}{t}
\]  \[28\]
Where $V_\text{glycerin}$ is the average volumetric flow rate of glycerin during the test.

From the glycerin flow rate and the time, the total number of moles of carbon ($\Sigma_{\text{Cin}}$) fed to the reactor can be calculated, knowing that each mole of glycerin contains three moles of carbon.

$$\Sigma_{\text{Cin}} = v_\text{glycerin} \cdot d_\text{glycerin} \left( \frac{1}{M_{\text{glyc}}} \right) \left( \frac{3 \text{ moles carbon}}{1 \text{ mole glycerin}} \right)$$  \[29\]

To determine the number of moles of carbon accounted for in the reformate ($\Sigma_{\text{Cout}}$), we sum the products of the molar flow rates, $N_x$, the number of C atoms in each species, and the duration of the experiment.

$$\Sigma_{\text{Cout}} = (N_{\text{CO}} + N_{\text{CO2}} + N_{\text{CH4}} + 2 N_{\text{C2H4}} + 2 N_{\text{C2H6}}) \cdot t$$

The carbon balance, $C_{\text{balance}}$, (% of C input recovered as C in the reformate) is calculated as:

$$C_{\text{balance}} = 100 \frac{\Sigma_{\text{Cin}}}{\Sigma_{\text{Cout}}}$$

**B-3 Error Calculation**

There are four variables affecting the accuracy of the hydrogen yield calculation. These are:

1) The GC estimated concentration of nitrogen in the reformate, $[N_2]$

2) The GC estimated concentration of hydrogen in the reformate, $[H_2]$

3) The $N_2$ molar flow rate going into the reformer controlled by the mass flow controller, $V_{N_2}$
4) The glycerin volumetric flow rate going into the reformer controlled by the pump, 

\[ V_{\text{glycerin}} \]

The error associated with each is as follow:

\[ [N_2] = \text{GC} \% \text{ N}_2 \text{ value } \pm 2\% \text{ (of value)} \]

\[ [H_2] = \text{GC} \% \text{ H}_2 \text{ value } \pm 2\% \text{ (of value)} \]

\[ V_{N_2} = 0.078 \text{ mole/min } \pm 0.00078 \text{ mole/min (obtained from manufacturer)} \]

\[ V_{\text{glycerin}} = \text{Pump set value } \pm 0.001 \text{ ml/min (precision of pump).} \]

Below is an example of the error calculation for run 12:

The hydrogen yield \( Y_{H_2} \) was 4.6 mole \( H_2 \)/mole glycerin

The yield is equal to the hydrogen flow rate out of the reformer divided by the glycerin flow rate in the reformer.

From the calculations of yield outlined above, it can be shown that:

\[ Y_{H_2} = ([H_2] * V_{N_2}) / ([N_2] * V_{\text{glycerin}}) \]  \[ \text{[30]} \]

To determine the error for \( Y_{H_2} \), the derivative for each of the four variables on the right hand side of equation 30 are calculated:

\[ \Delta Y/\Delta[H_2] = V_{N_2} / ([N_2] * V_{\text{glycerin}}) \]  \[ \text{[31]} \]

\[ = 0.078 / (35.2*0.014) = 0.133 \]

\[ \Delta Y/\Delta V_{N_2} = [H_2] / ([N_2] * V_{\text{glycerin}}) \]  \[ \text{[32]} \]

\[ = 60.06 \]

\[ \Delta Y/\Delta [N_2] = -([H_2]* V_{N_2}) / (V_{\text{glycerin}} * [N_2]^2) \]  \[ \text{[33]} \]

\[ = -0.13 \]

\[ \Delta Y/\Delta V_{\text{glycerin}} = -([H_2]* V_{N_2}) / ([N_2] * V_{\text{glycerin}}^2) \]  \[ \text{[34]} \]

\[ = -407 \]
The error ω for each variable is shown below:

\[ \omega_{[H_2]} = [H_2]*2\% = 35.2 * 2\% = 0.7 \]
\[ \omega_{[N_2]} = [N_2]*2\% = 41.2 * 2\% = 0.824 \]

(35.2 and 41.2 are the gas concentration in the reformate.)

\[ \omega_{VN_2} = 0.00078 \]
\[ \omega_{Vglycerin} = 0.001 \]

The final error \( W_R \), for the hydrogen yield, \( Y_{H_2} \), is:

\[ W_R = \left[ \sum (\omega_i^2 * (\Delta Y/\Delta i)^2) \right]^{1/2} \]  \[35\]

where \( i \) represent the four different variables

For run 12, the error is ± 0.35 mole \( H_2 \) / mole hydrogen

\( Y_{H_2} = 4.6 \pm 0.35 \) mole/mole glycerin

**B-4 Atomization Insight**

To find out more about the atomization of the glycerin water mixture inside the reactor, calculations were made on the characteristics of the injection process based on an approach outlined in A. Lefebvre's book: Atomization and Sprays. \[43\]

The Reynolds number (Re) for the flow inside the injection needle was computed to determine the state of the flow at the injection point, inside the reformer.

\[ Re = \rho VD/\mu \]  \[36\]

Where:
\( \rho \) is the density of the fluid,

\( V \) is the average velocity of the fluid inside the tube,

\( D \) is the inside diameter of the tube, and,

\( \mu \) is the viscosity of the fluid.

\( \rho = 0.0011 \text{ kg/cm}^3 \) (based on a 40\% glycerin volume fraction and 60\% water volume fraction in the feed solution)

\( V = \sim 70 \text{ m/s} \) (based on the superficial velocity of a 3 ml / min feed mixture flow in the injector)

\( D = 0.003 \text{ cm} \) (injection needle)

The value for viscosity was estimated from data \[44\] for water, glycerin, and water-glycerin mixtures. The viscosity for a 40\% glycerin, 60\% water mixture at 100°C is 0.668 cP (0.000668 kg/m/s). \[44\] Calculating Re based on these data yield a value of

\[ \text{Re} = (1100 \text{ kg/m}^3) (70.7 \text{ m/s}) (0.00003 \text{ m}) / (0.000668 \text{ kg/m/s}) = 3500 > 2100 \]

This indicates that the flow inside the tube is fully turbulent.

To characterize the atomization mode, the Ohnesorge number must be computed in addition to Re. The Ohnesorge number, \( (\text{Oh}) \) is defined as

\[ \text{Oh} = \mu / (\rho \sigma D)^{0.5} \]

where \( \sigma \) is the surface tension of the fluid in kg/s\(^2\). Available data for surface tension of glycerin and water are limited, especially at elevated temperature. The surface tension of glycerin at 90°C and water at 100°C are 0.059 and 0.059 kg/s\(^2\), respectively. Using these values, Oh can be calculated as

\[ \text{Oh} = (0.000668 \text{ kg/m/s}) / ((1100 \text{ kg/m}^3) (0.059 \text{ kg/s}^2) (0.00003 \text{ m}))^{0.5} = 0.015 \]
According to the text by Lefebvre\textsuperscript{[43]}, values of $\text{Re} = 3500$ and $\text{Oh} = 0.015$ place the jet leaving the 30 $\mu$m injection tube in the atomization mode called "first wind-induced breakup". Jet break up is expected to occur many jet diameters downstream of the nozzle and the drop diameters are about the same size as the jet diameter. Note that values of Re and Oh are computed using values of surface tension and viscosity at $\sim100^\circ\text{C}$. A temperature profile at the reformer centerline was made using a thermocouple as shown in Figure B1. From this, the temperature at the feed tube injection point (located at 28 cm on the graph) was estimated to be $\sim450^\circ\text{C}$.

Figure B1: Temperature profile at the feeding tube centerline in the reformer (injection tube exit located at 28 cm)
At higher temperatures, both viscosity and surface tension are expected to decrease. The viscosity of a 40% glycerin / 60% water mixture is plotted against temperature. (from 0 to 100°C data) in Figure B2. An exponential trendline and regression equation are shown and indicate decreasing viscosity with increasing temperature. Data for surface tension also indicate a linear decline with increasing temperature. Decreasing viscosity will increase Re and the combined effects of decreasing viscosity and surface tension will result in reduced values of Oh. The effects of these changes on atomization mode are difficult to assess due to (1) the lack of data for viscosity and surface tension for glycerin water mixtures at elevated temperature, (2) uncertainty in the actual temperature of the glycerin water mixture at the point of injection, and (3) uncertainty in the phase of the glycerin water mixture at the point of injection. Extrapolation of viscosity and surface tension data from ~100°C was performed to temperatures up to 400°C as shown in Table B1. Values of Re and Oh were computed using these data and the values compared to the atomization mode curves. The range of Re and Oh covered in the atomization curves do not extend over the range of values shown in Table B1, however, comparing the tabulated values with the curve indicates that elevated temperature would be expected to improve the atomization process.
Figure B2: Regression of 40% glycerin / 60% water mixture viscosity as a function of temperature

Table B1. Extrapolated data for $\mu$, $\sigma$, Re, and Oh at elevated temperature.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$, kg/m/s</td>
<td>0.000668</td>
<td>4.8241E-05</td>
<td>4.2047E-06</td>
<td>3.6649E-07</td>
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<tr>
<td>$\sigma$, kg/s²</td>
<td>0.0612</td>
<td>0.0467</td>
<td>0.0323</td>
<td>0.0178</td>
</tr>
<tr>
<td>Oh</td>
<td>0.014870</td>
<td>0.00123</td>
<td>0.00013</td>
<td>0.00002</td>
</tr>
</tbody>
</table>