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Supercritical Water Reformation of Crude Glycerol Solution for Hydrogen Production

by

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The logo for NUTC R203, featuring a stylized, dark silhouette of a person's head and shoulders against a bright yellow background. The text "NUTC" and "R203" is overlaid in a white, serif font.

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Supercritical Water Reformation of Crude Glycerol Solution for Hydrogen Production

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Abstract

Glycerol, also known as glycerin, is a less desirable byproduct formed in the production of biodiesel via the transesterification of triglycerides and presents a nontrivial issue in terms of developing other beneficial end uses. With an inflated glycerol market and rapidly increasing demand for the production of biodiesel, innovative utilization of the crude glycerol solution produced by biodiesel plants is paramount to the success of biodiesel as an alternative fuel. Supercritical water reformation of crude glycerol solution presents a unique non-catalytic means of converting unwanted glycerol into hydrogen for use in energy and transportation applications, hence increasing the amount of usable transportation fuel that may be produced from triglycerides in biodiesel production. An ongoing experimental study of the supercritical water reformation of crude glycerol solution is being conducted to explore the effects of multiple variables important to the chemical reactions involved in the reformation process. Reaction variables include temperature, pressure, water-to-glycerol ratio, reactor space times, and the impact of other chemical species found in crude glycerol solution, such as salts, alcohols, and soaps.

Background

Biodiesel is an alternative liquid transportation fuel that has the potential to readily displace its petroleum counterpart, since it can be used in conventional diesel engines with little to no modifications.¹ Biodiesel is made through the transesterification of fatty acids with methanol or ethanol to make three moles of biodiesel and one mole of glycerol. After biodiesel is taken from the solution, the crude glycerol solution is made up of water, glycerol, and small amounts of salts and ethanol or methanol.²

In the United States production of biodiesel increased from ~75 million gallons in 2005 to over 200 million gallons in 2006.¹ The amount of biodiesel production is expected to grow further with more states passing laws requiring a certain blend of biodiesel in their diesel fuels, such as Minnesota requiring that 2 % blend on all diesel fuel sold in the state. If all states were to pass such requirements and 2% of petrochemical diesel was replaced by biodiesel, an extra 800 million pounds of glycerol per year would be produced, surpassing the United States market need of 600 million pounds per year.¹ A substantial portion of a biodiesel plant's revenue comes from selling the byproduct glycerol that is produced. With the glycerol market so inflated, biodiesel plants will not be as profitable until there is some way to utilize the excess glycerol.

Supercritical water reformation is one possible way to utilize this excess glycerol. The process of supercritical water reformation uses water above its critical temperature and critical pressure to react with the glycerol to create hydrogen and carbon monoxide. Carbon monoxide can further react in the water gas shift reaction to make more hydrogen. The reformation process is non-catalytic and is applicable a variety of hydrocarbons, such as alcohols or biodiesel which can be found in crude glycerol solution. Currently, few studies have been conducted on the supercritical reformation of glycerol, even fewer non-catalytically.³⁻⁶

Chemical Reactions

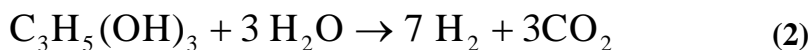
There are many chemical reactions that occur during the supercritical water reformation of glycerol. The five principal reactions discussed in this paper are the pyrolysis reaction, methanation reaction, reformation reaction, the water gas shift reaction, and the Boudouard reaction. The pyrolysis reaction involves the dismantling of glycerol into smaller hydrocarbons, such as methane, ethylene, and ethane. The ethane produced can still be reformed to make hydrogen or pyrolyzed even further to produce methane. While this reaction does not consume hydrogen, it does competitively consume the reactant for reformation, limiting hydrogen production.

The methanation reaction is a reversible reaction that involves carbon oxides and hydrogen reacting to become methane and water. The forward reaction consumes hydrogen, and therefore is detrimental to the reformation process. The methanation reaction and pyrolysis reaction are the only sources of methane for the purposes of this paper.



The reformation reaction is endothermic and involves the reaction of water with glycerol to produce hydrogen as well as carbon monoxide. The reformation of hydrocarbons is commonly performed with the aid of a noble metal catalyst. The experiments presented in this paper were performed non-catalytically, with no catalyst loaded into the reactor, except potential monolithic catalytic effects from the reactor wall made of high-nickel alloy of Haynes® 230.

The forward water gas shift reaction (WGS) is fourth major reaction in the supercritical water reformation of glycerol. The reaction is reversible in nature, and involves the combination of water and carbon monoxide to make hydrogen and carbon dioxide. The forward reaction is thermodynamically favored at temperatures of 815°C or below.⁷ Using the assumption that all carbon monoxide produced in the reformation reaction subsequently undergoes in the WGS reaction, the overall reaction would yield seven moles of hydrogen per mole of glycerol. The overall reaction is shown below.



This reaction means the maximum amount of hydrogen production is seven moles per mole of glycerol fed. Another possible reaction that could be happening is the Boudouard reaction. The Boudouard reaction is a reversible reaction that involves two carbon monoxide molecules combining to make a carbon dioxide molecule and elemental carbon. The effect of the Boudouard reaction is limited at higher temperatures; the equilibrium constant favors carbon monoxide production at temperatures above 680°C.⁷⁻¹¹ This means that the Boudouard reaction will only influence the experimental runs with lower temperatures. Increasing amounts of carbon dioxide and lower carbon monoxide and carbon gasification values can be indicative of the Boudouard reaction.



Current Research

There have already been many experimental runs conducted on the reformation of pure glycerol in a water solution. Determining the reformation properties of pure glycerol is the first step toward determining the reformation potential of crude glycerol. After a thorough analysis of the pure glycerol experimental runs is complete, that data can then be used as a baseline to compare the reformation of a crude glycerol solution against. This will allow for a better analysis of the effects each additional species in the crude glycerol solution will have on its reformation.

The chemicals used for the experiments were deionized water and 99.7% pure glycerol from thechemistrystore.com. Glycerol above 80 wt-% in purity will absorb ambient water vapor from the air; therefore the bulk glycerol was diluted to 75.9 wt-%. The physical properties of glycerol and water may be found in Table 1.

Table 1. Physical Properties of Glycerin and Water^{12,13}

| Property | Glycerol | Water |
|---|----------|-------|
| Molecular Weight (g/mol) | 92.09 | 18.02 |
| Density at 25 °C and 1 bar (g/cm ³) | 1.26 | 0.99 |
| Melting Point (°C) | 17 | 0 |
| Boiling Point (°C) | 287 | 100 |
| Critical Temperature (°C) | 577 | 647 |
| Critical Pressure (atm) | 74.02 | 217.7 |

The supercritical water reformation system used for these experiments consists of a water feed system, reactant preheater, Haynes® Alloy 230 reactor with a heater, liquid collection system, gas sampling system, and a data acquisition and control system. Figure 1 is a representative process flow diagram of the supercritical water reaction system. The Haynes® Alloy 230 reactor has an internal volume of 383 mL, and is an alloy of mostly nickel, chromium, tungsten, and molybdenum, along with other elements.¹⁴ The stress-strain, creep, and rupture properties of Haynes® Alloy 230 allows

the reactor to operate at a temperature of 800°C at a pressure of 36.2 MPa. The samples collected of the gaseous effluent at ambient conditions were analyzed using a HP 5890 Series A gas chromatograph with a thermal conductivity detector. The gas chromatograph is calibrated to detect hydrogen, nitrogen, carbon monoxide, methane, carbon dioxide, acetylene, ethylene and ethane.

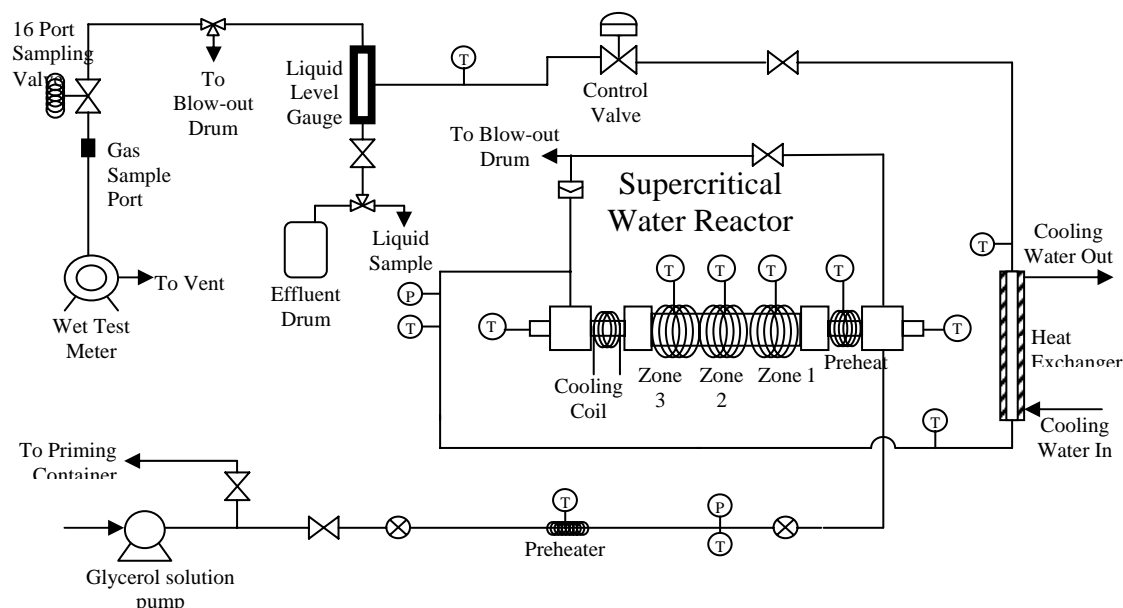


Figure 1. The supercritical water reformation system at the Missouri University of Science and Technology.

An experimental study of the supercritical water reformation of pure glycerol was conducted using a tubular 0.4-L Haynes® Alloy 230 reactor at a constant pressure of 22.4 MPa. The study explored the effects of temperatures from 500°C to 700°C, water-to-glycerol molar ratios from 3:1 to 24:1, and reactor space times between 30 and 150 seconds. The list of experimental runs that were conducted and their run conditions are shown in Table 2 below.

The results of the experiments listed in Table 2 were very promising. Most experiments resulted in over 90% carbon gasification, with the exception being experimental runs at the lower temperature of 500°C and experimental runs using the very rich 3:1 water-to-glycerol ratio. The hydrogen gas yields for those experimental runs were quite good as well, with most runs producing at least 30% of the theoretical maximum of 7 moles of hydrogen gas per mole of glycerin fed. Many experimental runs achieved close to 50% yield, and the only runs that had poor yields were the same as those that had poor carbon gasification.

Table 2 Experimental Run Matrix

| Run No. | Temp (oC) | Res time (sec) | Pressure (psig) | Solution (g/min) | W/G | glycerin wt % |
|---------|-----------|----------------|-----------------|------------------|------|---------------|
| WG-8 | 698 | 110 | 3476 | 14.3 | 24 | 17.5% |
| WG-9 | 700 | 55 | 3511 | 28.7 | 24 | 17.5% |
| WG-10 | 599 | 127 | 3503 | 14.8 | 24 | 17.5% |
| WG-11 | 599 | 65 | 3505 | 29.1 | 24 | 17.5% |
| WG-12 | 591 | 31 | 3503 | 61.5 | 24 | 17.5% |
| WG-13 | 699 | 113 | 3466 | 15.7 | 12 | 29.9% |
| WG-14 | 704 | 60 | 3501 | 29.7 | 12 | 29.9% |
| WG-15 | 497 | 100 | 3486 | 29.0 | 12 | 29.9% |
| WG-16 | 696 | 147 | 3470 | 10.7 | 24 | 17.5% |
| WG-17 | 698 | 102 | 3483 | 15.4 | 24 | 17.5% |
| WG-18 | 598 | 145 | 3491 | 12.9 | 24 | 17.5% |
| WG-19 | 601 | 98 | 3481 | 18.9 | 24 | 17.5% |
| WG-20 | 601 | 100 | 3489 | 20.9 | 13.5 | 27.5% |
| WG-21 | 600 | 143 | 3482 | 14.5 | 13.5 | 27.5% |
| WG-22 | 700 | 100 | 3501 | 17.4 | 13.5 | 27.5% |
| WG-23 | 696 | 150 | 3476 | 11.6 | 13.5 | 27.5% |
| WG-24 | 705 | 49 | 3499 | 35.2 | 13.5 | 27.5% |
| WG-25 | 498 | 146 | 3497 | 16.8 | 24 | 17.5% |
| WG-26 | 695 | 151 | 3486 | 19.5 | 3 | 63.0% |
| WG-27 | 698 | 102 | 3501 | 28.7 | 3 | 63.0% |
| WG-28 | 597 | 157 | 3507 | 24.0 | 3 | 63.0% |
| WG-29 | 595 | 101 | 3502 | 37.5 | 3 | 63.0% |
| WG-30 | 496 | 98 | 3511 | 25.3 | 24 | 17.5% |
| WG-31 | 492 | 151 | 3507 | 19.1 | 13.5 | 27.5% |
| WG-32 | 497 | 50 | 3506 | 56.1 | 13.5 | 27.5% |
| WG-33 | 501 | 101 | 3515 | 27.6 | 13.5 | 27.5% |
| WG-34 | 504 | 49 | 3499 | 48.6 | 24 | 17.5% |
| WG-35 | 695 | 147 | 3493 | 11.9 | 13.5 | 27.5% |
| WG-36 | 698 | 100 | 3497 | 17.4 | 13.5 | 27.5% |
| WG-37 | 692 | 145 | 3504 | 11.0 | 24 | 17.5% |

Future Research

With the data gained from the supercritical water reformation of pure glycerol in the experimental runs listed on the above table, the next step is to move on to a crude glycerol solution. The same experimental equipment and process from the pure glycerol experiments will be used, and the experimental runs in Table 2 will serve as a template for the crude glycerol experiments by running at the same temperatures, space times, and water-to-glycerol ratios. The primary difference in the crude glycerol experiments will be factoring in the variable composition of crude glycerol solutions.

Crude glycerol solution created in the production of biodiesel has different compositions dependent on many variables. These variables include the type of feed oil, the amount of excess alcohol fed, what type of alcohol (ethanol or methanol) is fed, and the concentration of the weak base catalyst. In general, the composition of crude glycerol

contains from 50-80 wt-% glycerol with the balance being a mix of methanol, soaps, salts, and small quantities of water. With so many possible crude glycerol solutions, multiple sets of experimental runs will have to be conducted which span the entire spectrum of possible crude glycerol solution compositions.

Using the pure glycerol runs as a baseline, the effect on reformation caused by the other species that make up crude glycerol can be determined. These runs will also allow for an analysis into the feasibility of supercritical water reformation as a solution for what to do with the excess crude glycerol produced by biodiesel.

Conclusion

For the biodiesel industry to see any substantial growth, a solution for what to do with the excess glycerol is necessary. One potential solution to that problem is reforming the crude glycerol solution using supercritical water. The reformation process is straight forward due to the absence of a catalyst, no need to purify the crude glycerol solution, and water being the only other species necessary for the reaction.

Experiments have already been conducted using pure glycerol and the results have been promising. Many experimental runs with pure glycerol resulted in total carbon gasification and reached almost 50% of the maximum possible yield of hydrogen gas. The next step of this research is to perform experiments using different crude glycerol solutions encompassing the range different possible compositions. The results of these experiments will show the effect that the alcohols, salts, and soaps have on the reformation process, as well as the overall potential of supercritical water reformation as an alternative use for crude glycerol.

- (1) Johnson, D.T.; Taconi, K.A. The Glycerin Glut: Options for the Value-Added Conversion of Crude Glycerol Resulting from Biodiesel Production. Published online Oct. 1, 2007 in Wiley InterScience
- (2) Bournay, L.; Casanave, D.; Delfort, B.; Hillion, G.; Chodorge, J.A. New heterogeneous process for biodiesel production: a way to improve the quality and value of the crude glycerin produced by biodiesel plants. *Catal. Today* **2005**, *106*, 190-192.
- (3) Byrd, A.J.; Pant, K.K.; Gupta, R.B. Hydrogen production from glycerol by reforming in supercritical water over Ru/Al₂O₃ catalyst. *Fuel* **2008**, *87*, 2956-2960.
- (4) Xu, X.; Matsumura, Y.; Stenberg, J.; Antal, M.J. Carbon-catalyzed gasification of organic feedstocks in supercritical water. *Ind. Eng. Chem. Res.* **1996**, *35* (8), 2522-2530.
- (5) Kersten, S.R.A.; Potic, B.; Prins, W.; Van Swaaij, W.P.M. Gasification of model compounds and wood in hot compressed water. *Ind. Eng. Chem. Res.* **2006**, *45*, 4169-77.
- (6) Buhler, W.; Dinjus, E.; Ederer, H.J.; Kruse, A.; Mas, C. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. *J. of Supercrit. Fluids* **2002**, *22*, 37-53.
- (7) Lee, S. *Alternative Fuels*, Taylor & Francis, Philadelphia, **1996**; pp.140-151.

- (8) McIntosh, S.; Gorte, R.J. Direct Hydrocarbon Solid Oxide Fuel Cells. *Chem. Rev.* **2004**, *104*, 4845-4865.
- (9) Murray, E. P.; Tsai, T.; Barnett, S. A. Adirect-methane fuel cell with a ceria-based anode *Nature* **1999**, *400*, 649.
- (10) Garcia-Serna, J.; Garcia-Merino, E.; Cocero, M.J. Gasification of charcoal using supercritical CO₂ at high pressure. *J. of Supercritical Fluids* **2007**, *43*, 228-235.
- (11) Mondal, K.; Lorethova, H.; Hippo, E.; Wiltowski, T.; Lalvani, S.B. Reduction of iron oxide in carbon monoxide atmosphere-reaction controlled kinetics. *Fuel Processing Technology* **2004**, *86*, 33-47.
- (12) Glycerin Phase Change Properties. National Institute of Standards and Technology.
<http://webbook.nist.gov/cgi/cbook.cgi?ID=C56815&Units=SI&Mask=4#Thermo-Phase>
- (13) Water Phase Change Properties. National Institute of Standards and Technology.
<http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=4#Thermo-Phase>
- (14) *Haynes*[®] 230 Alloy, Haynes High-Temperature Alloys International, 2004 pp. 2.