

CONTINUOUS-FLOW REACTOR SYSTEM FOR IMPROVED CATALYTIC GLYCEROL CONVERSION

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EXECUTIVE SUMMARY

Currently, converting the surplus, low quality glycerol, a byproduct from biodiesel production, to valuable products remains an important topic of interest in both the industry and research communities. One value added product we can produce from glycerol is ethanol. Our previous research showed improved ethanol yields from glycerol by applying the Raney nickel catalyst. With the promising results, further investigation was recommended to improve the productivity and yield using a continuous-flow reactor system. A continuous-flow reactor typically provides better unit productivity, more consistent product quality, and much improved process efficiency since the frequent heating and cooling in batch processes are eliminated, reactions occur under optimized conditions, and the products are collected continuously. Therefore, it is worthwhile to conduct a study on catalytic conversion of glycerol to valuable products in a continuous-flow reactor system. This report summarizes the results of our attempts to improve the process efficiency of glycerol processing using a continuous-flow process.

A continuous-flow reactor system was modified from the existing 300 mL PARR bench scale batch reactor system and used for conducting this research. Aqueous glycerol was pumped to the reactor system continuously using a high-performance liquid chromatography (HPLC) pump and the condensable product was collected in a high pressure vessel after a high pressure condenser. A fed-batch reactor system using the same PARR reactors was also designed and was used for testing. Using the continuous-flow reactor system under the conditions of 220°C, 1:1 water-to-glycerol mass ratio and 30 mL/min feeding rate, liquid product was successfully collected in the receiver vessel. However, analysis of the liquid product showed small amounts of methanol and ethanol were produced. Further investigation revealed that the major component in the liquid product was water, which is hypothesized as the result of reformation reactions such as water-gas shift reaction. Using the fed-batch system, a slight improvement in the ethanol yield, approx. 3.5%mol, was observed.

In summary, the continuous-flow reactor converted from the batch reactor vessels was not able to produce alcohols with high yields as expected. Having a relatively large head space in the reactor may have caused the reaction to favor gaseous products. Despite the less favorable results of process efficiency and alcohol yields from this study, it is still strongly recommended to further investigate the applicability of a continuous-flow reactor system for this process using a different design such as the tubular reactor that is under pre-experimental testing by this research team.

DESCRIPTION OF PROBLEM

Background

Biodiesel is a well-known alternative fuel to the fossil-based diesel. It can be produced from the reaction of plant oil and/or animal fat with an alcohol, such as methanol, through a chemical process called transesterification. Biodiesel greatly reduces the net carbon emission to the atmosphere since plant oil comes from renewable biomass. However, biodiesel is still not completely an all biomass-based fuel. Currently, the majority of methanol used in biodiesel industry is still derived from petroleum. With this current practice in biodiesel production, the biodiesel's potential to be a greenhouse-free fuel is not fully achieved. There are possible sources of renewable and biomass-based alcohols, such as ethanol from corn starch. Another potential source of biomass-based alcohol can come from glycerol, the by-product of biodiesel production. Glycerol, also named glycerin, is a polyhydric alcohol. It is the major by-product of biodiesel production that for every ten million pounds of biodiesel produced, approximately one million pounds of crude glycerol is co-produced. With the exponential expansion of the biodiesel industry in the past decade, the production of crude glycerol from the biodiesel industry has flooded the market. This surplus of glycerol not only affected the biodiesel industry but also other industries that produces and co-produces glycerol, such as the soap industry. Therefore, a technology that converts glycerol to valuable products and alcohols is highly desirable to make the biodiesel industry more sustainable by utilizing its byproduct glycerol on-site and to further improve the renewability of biodiesel, and its positive impact to the environment by using alcohols produced from renewable resources.

Thermochemical conversion of glycerol to monohydric alcohols is a process to potentially increase the value of crude glycerol and produce alcohols needed by the biodiesel industry. Thermochemical conversion uses heat to breakdown compounds into simpler compounds. Monohydric alcohols are organic compounds that have only one hydroxyl group. Glycerol, on the other hand, is a three carbon compound with each carbon containing a hydroxyl group. Breaking the carbon-to-carbon bonds or removing one or two of the hydroxyl groups in glycerol will produce monohydric alcohols such as methanol and ethanol. These alcohols can be used as feedstock for biodiesel production and will reduce the dependence on petroleum-based alcohols.

The results from our previous research entitled “Thermal Processing of Low-Grade Glycerol to Alcohols for Biodiesel Production,” funded by the National Institute for Advanced Transportation Technology (NIATT), showed that glycerol was converted to monohydric alcohols at temperatures above 300°C and more than an hour of reaction. Meanwhile, other products were also produced. The yield of the targeted monohydric alcohols produced was low even if there was a high percentage of glycerol that had been converted. The low yield of alcohols was due to the complexity of reactions of glycerol decomposition during the thermochemical process.

In order to address this issue, the research group attempted to improve the conversion efficiency to the desired products by exploring different metal-based catalysts. Conventional thermochemical conversions involve high temperature in order to break the chemical bonds, which also favors further decomposition of the desired products to unwanted compounds like char. Catalysts have the capability to decrease the energy required by a chemical reaction by lowering the activation energy of the reaction. Another important role that catalysts play is its selectivity of breaking chemical bonds in order to produce the desired products. Our second stage research, also funded by NIATT, focused on applying metal catalysts to improve the selectivity of the desired alcohol products. This research showed that the ethanol yield was largely improved with the addition of the Raney nickel catalyst. Among other liquid products, up to 11.37% mol of ethanol yield was achieved at optimum condition of 1.82:1 water-to-glycerol molar feed ratio, 223°C reaction temperature and 45 min reaction time.

The process used to study the catalytic thermochemical conversion of glycerol to alcohols was operated in a batch mode. With this type of system, the reactants and catalysts are placed in the reactor at the start of the process and the products are collected after the reaction. The disadvantage of this setup is the extended heating and cooling time before and after the reaction. Extending heating and cooling times result in unwanted reactions occurring prior to the designed reaction conditions and results in the products being further decomposed. Similar to the pyrolysis of biomass, more char is produced and less alcohol is formed if the liquid products cannot be collected immediately. This is the reason why most of the studies on biomass pyrolysis were conducted using semi-continuous or continuous reactor systems rather than in a batch mode. Another advantage of a continuous process is its better productivity per unit reactor volume

compared to that of batch processes. Productivity is increased in a continuous-flow reactor system since the heating and cooling periods are eliminated and products are collected continuously. Therefore, it is worthwhile to conduct a study on catalytic conversion of glycerol to valuable products in a continuous-flow reactor system, which is also a necessary step of technology development.

Objective

The goal of this project was to improve the process efficiency of glycerol conversion in a continuous, catalytic reactor system. The specific objectives are (1) to determine the applicability of thermochemical conversion of glycerol to primary alcohols in a continuous-flow system and (2) to conduct an investigation on the effects of process parameters.

These objectives were in accordance with Goal 2 of the NIATT's Strategic Plan: *“improve the quality and economic viability of biofuels and reduce the environmental impacts and improve the fuel economy and safety of motorized vehicles (including cars, transit vehicles, and recreational vehicles) to protect the nature and built environment.”* This project directly addressed Strategy 2.3 of Goal 2 of the *Strategic Plan*, namely, *“develop new biofuels production methods and techniques for reducing biofuels emissions.”*

METHODOLOGY AND RESULTS

Development of a continuous reactor system

Although there are numerous designs for continuous reactor systems in chemical, food and petroleum industries, the basic designs still follow the principles of either a continuous stirred tank reactor (CSTR) or plug flow reactor (PFR). A CSTR uses an agitated vessel with constant inflow of the reactants and outflow of the products, while a PFR forces the reactants to flow continuously to a tubular reactor. In PFR, products are formed as the reactants travels in the tube then the products are collected at the end of the tube. PFRs typically require less reactor volume than CSTRs but better mixing can be achieved in the latter. For this research project, a CSTR was developed by converting from the existing 300 mL PARR bench scale batch reactor system. The 300 mL PARR 4560 Pressure Reactor System, which was available at the Biofuels Research Laboratory of the Department of Biological and Agricultural Engineering (BAE) at the University of Idaho, was modified to a CSTR. A HPLC pump was installed to achieve a continuous flow. Aqueous glycerol was pumped to the reactor system continuously to the reactor and the condensable liquid product was collected to another pressure vessel (Figs. 1 & 2). A high pressure condenser, purchased from PARR Instruments (Moline, IL), was installed between the reactor vessel and the receiver vessel. A new water pipe system was installed in the reactor chamber to supply cooling water to the condenser, reactor, and the reactor's agitation system and pressure transducer. A ball valve was also installed to switch on and off the cooling water for the condenser (Fig. 3). Another reason for having a valve is to make it easy to change to different reactor configurations, such as from the batch reactor, with which the condenser was not used, and to the continuous reactor. Preliminary tests using water and nitrogen gas was conducted to test for possible water and gas leaks. These preliminary tests also provided information about the system operation for refining the operating and safety procedures.

A fed-batch reactor system was also set up for use to examine the effect of a different reactor configuration on the yield of alcohols. To re-configure the existing batch reactor to a fed-batch reactor, a feeder was installed. The feeder used was an all-purpose pressure vessel reactor with specifications similar to those of the batch reactor but without the agitator assembly, pressure transducer and cooling system. This feeder can deliver 100 mL of pure glycerol to the reactor for

a fraction of a minute by using a pressurized gas (Fig. 2). Such a configuration has been used in the previous research projects.



Figure 1: The modified continuous-flow reactor system (shown in the picture is PhD student Randy Maglinao).



Figure 2: Pressure feeder and reactor setup.

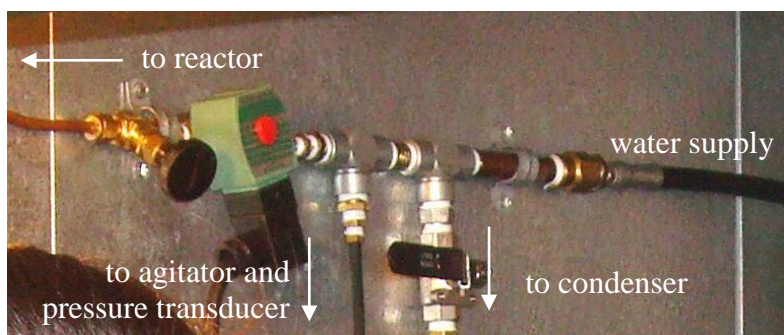


Figure 3: Water piping system to supply cooling water to the continuous reactor system.

Application of the catalyst in continuous-flow reactor system

The application of metal catalyst to the thermochemical conversion process of glycerol is different for a batch system and continuous-flow system. In a batch mode, reactants and the catalyst are placed in the reactor at the same time, and the products are collected along with the catalyst after the reaction. In a CSTR, heterogeneous catalysts are typically pre-loaded into the reactor and retained by a retaining mechanism. In this study, the solid catalyst in powder form was placed inside the reactor at the beginning of each experiment, and remained in liquid phase

under adequate agitation. The alcohol products formed in the liquid phase vaporize into the headspace under the operating condition (220~240°C) and are directed to the receiver vessel after condensing.

Conversion of glycerol to alcohols using the continuous-flow reactor system

Preliminary tests without the catalyst were conducted to provide reference based data on how thermochemical conversion takes place in the continuous reactor. Pure glycerol and aqueous glycerol (50% w/w) was fed at 5 mL/min continuously to the reactor which was set at 300°C. Bio-oil was collected in the receiver vessel and catalyst and solid char, if any, accumulated in the reactor vessel. At the equilibrium, the reaction temperature ranged from 150° to 180°C, due to the presence of water and operated under atmospheric pressure. In both treatments, less than 0.5%wt. of total alcohols (methanol and ethanol) were collected in the receiver vessel. It was also observed that the temperature of the receiver vessel increased from 20° to 40°C during the reaction. This temperature increase indicated that the condenser was not able to cool down the condensable products to room temperature, and the alcohols, especially methanol, may have escaped without condensation. Thus a colder cooling media is necessary to efficiently condense and collect alcohols.

Based on the results of the preliminary tests, a cold circulating bath, also available at the Biofuels Research Laboratory in BAE, was used to circulate cold ethanol, the cooling media at -10°C, to the condenser. Table 1 summarizes the results of the condensable products collected in the experiments with the Raney-nickel catalyst. A feed of 1:1 water-to-glycerol mass ratio and a feed flow rate of 30 mL/min were used in all of the treatments. The reactor vessel was pre-heated to 250°C before reactants were introduced from the feeder. In each treatment, the reactor ran continuously for one hour. The liquid product was sampled every 10 minutes. The reactor pressure in treatment CF1 was maintained at atmospheric pressure, while the reactor pressure in treatment CF2 was regulated at a higher pressure (200 psi) by the gas exit valve. In all of the treatments, liquid product was successfully collected in the receiver vessel under the continuous-flow operating mode, but gas chromatograph analysis of the liquid product showed only small amounts of methanol and ethanol were produced in treatment CF2 (Table 1), and not at all in treatment CF1. Further analysis of the product revealed that a major component of it is water. It is hypothesized that the liquid product collected is the result of reformation reactions like water-

gas shift reaction which produces hydrogen and carbon dioxide. This was confirmed as gaseous products were observed in treatment CF2. Separate tests on the catalytic thermochemical conversion of glycerol using the batch system, showed that the gaseous products contain hydrogen and carbon dioxide with carbon dioxide as the dominant component. The gaseous products were analyzed using Draeger gas detection tubes (Fig. 4). Since the same reactions happened in the batch reactor and the continuous reactor, the gaseous products observed in treatment CF2 was likely to contain hydrogen and carbon dioxide which were produced through a water-gas shift reaction. The only difference that occurred in the continuous reactor was the reaction equilibrium may have shifted towards producing more gaseous products because the gases formed in the head space of the reactor was constantly siphoned out, condensed and collected at the receiver vessel. Unlike in the batch reactor, the gases stayed in the reactor vessel and inhibited producing more gaseous products. Another source of the water in the liquid product using the continuous reactor is from the reactant itself because aqueous glycerol was used as the feed. This was more evident in treatment CF1 in which most of the water in the feed evaporated immediately in the reactor and did not participate in the reaction, in which the reactor was operated at atmospheric pressure.

Table 1: Alcohol Mass Percentages in the Liquid Product from Catalytic Thermochemical Processing of Glycerol Using the Continuous Flow Reactor System

RUN	Reaction Temp.	Reducing gas	Make-up nitrogen	Methanol (%wt)	Ethanol (%wt)	Water content (%wt)
CF1	150 °C	None	14 psi	ND	ND	72.4
CF2	220 °C	None	200 psi	0.354	0.580	58.1

Note: ND – not detected



Figure 4: Undergraduate student Sonam Sherpa analyzing the gaseous products using Draeger gas detection tubes.

Using the fed-batch system similar results were obtained. Up to 3.5% mol ethanol yield was observed (Table 2). To have the right reaction temperature, the reactor with the catalyst was preheated 30~60°C higher than the desired reaction temperature right before feeding the reactants. After the aqueous glycerol was fed to the preheated reactor, the temperature was monitored and controlled until it stabilized at the desired reaction temperature, and maintained for the duration of the experiments.

Table 2: Alcohol Yields from Catalytic Thermochemical Processing of Glycerol Using the Fed-Batch Reactor System

RUN	Reaction Temp.	Water to Glycerol Ratio	Reaction Time (min)	Methanol (%mol)	Ethanol (%mol)
FED1	220 °C	1:1	15	0.368	0.561
FED2	220 °C	7:3	15	0.539	0.528
FED3	240 °C	1:1	45	0.577	3.580
FED4	200 °C	7:3	45	0.671	0.697

In both the fed-batch and continuous reactor systems, more ethanol was produced at higher temperatures (Tables 1 & 2). One possible reason is that glycerol is converted to ethanol through a series of reaction steps. Based on literature and previous batch experiments using a Raney-nickel catalyst, glycerol undergoes hydrogenolysis with hydrogen to propylene glycol then at higher temperatures propylene glycol undergoes further hydrogenolysis to form ethanol. In this project, hydrogen was not added to the reactor but it was produced *in situ* in the reactor.

Propylene glycol was not collected in the receiving vessel along with the methanol and ethanol since propylene glycol has a boiling point of 188°C at 1 atm and higher at higher pressures.

The reaction pressure also affected the yield of ethanol. At higher reaction pressures, more ethanol was produced from both continuous and fed-batch reactors. The highest yield of ethanol was observed in the fed-batch in which the reactor was allowed to build up pressure. In the continuous reactor, increasing the pressure prevented the immediate evaporation of water which is essential in the conversion of glycerol to ethanol. Water inhibits dehydration reaction such as the formation of acrolein, aldehydes, and ketones from glycerol. Water also helps maintain a uniform temperature inside the reactor and prevent hot spots that could lead to the formation of char.

SUMMARY

The continuous-flow reactor used in this study was not able to produce alcohols at high yields due to its design. It was planned that methanol and ethanol produced during the reaction would immediately escape into the head space of the reactor, then condense through the condenser, and collect in the receiving vessel. Although *in situ* hydrogen production, which is needed by the reactions to produce methanol and ethanol, worked well in the batch reactor system; it did not happen simultaneously in the continuous reactor. The hydrogen produced in the reactor was immediately vented out which prevented it from reacting with glycerol to form alcohols.

Adjusting the gas exhaust valve, which restricts the gases to flow out to the vent, produced some ethanol but still not as well as that in the batch reactor. Although the fed-batch completely prevented *in situ* hydrogen escaping from the reactor, preheating the reactor higher than the desired reaction temperature might have deactivated some of the catalyst. Because of these reasons, no further investigation was conducted using these reactor set-ups. However, even though the continuous-flow reactor did not demonstrate improved efficiency and alcohol yield, it is still recommended to investigate the applicability of a continuous-flow reactor system for this process using a different design such as a tubular reactor. A tubular reactor will allow complete mixture of glycerol, hydrogen and water to produce alcohol as it goes to the reactor tube. This will permit hydrogen to react with glycerol to form methanol and ethanol as it goes to the reactor tube. Unlike in the continuous reactor tested in this project, the alcohols, residual glycerol, water, hydrogen and other products produced during the reaction will come out at the same time at the end of the reactor all at once. Further separation is needed to collect the alcohol products.

APPENDIX: STUDENT INVOLVEMENT

A graduate student and two undergraduate students participated in conducting this research project. Randy Maglinao, a graduate student of Biological and Agricultural Engineering at University of Idaho, was in charge of managing, designing and conducting the experiments, and drafted this report. He also directly supervised two undergraduate students, Sonam Sherpa and Sushant Kshetri, who assisted him in data collection and experimental operations.

As a graduate student, the research project gave Randy Maglinao the opportunity to integrate his education in chemistry, engineering, and biology to scientific research in bioenergy and biorefinery. The project also provided assistance in his pursuance of a doctoral degree in Biological and Agricultural Engineering. The experiences acquired from this research project are preparing him for his professional career growth as scientist and engineer in this field. Supervising undergraduate students in conducting the experiments helped him to acquire management skills that will be beneficial for his future occupation as a research scientist, faculty, or a project leader in the field of biological and agricultural engineering. It also gave him the opportunity to learn the skills to plan and execute experiments and other tasks for the purpose of completing a project and achieving its goals in a specified time period. This research has provided him the experience of holding lectures in class and writing technical papers and presenting it through oral and poster presentations in professional technical conferences.

Sonam Sherpa and Sushant Kshetri, undergraduate students of Chemical Engineering and Material Science at University of Idaho, learned the proper techniques and methods in handling chemicals and conducting experiments in a laboratory. They became skilled in using common laboratory equipment for both qualitative and quantitative analysis that would be beneficial in their studies and senior design/research projects. This research project also provided them the knowledge of the applications of the theories that they learned in their classes like chemical reactions, thermodynamics, and chemical structures to real-world problems in bioenergy and biorefinery.