

# Idaho Incubation Fund Program

## Final Report Form

**Proposal No.** IF13-005  
**Name:** B. Brian He  
**Name of Institution:** University of Idaho  
**Project Title:** Advancing glycerol conversion technology for commercialization for sustainable biodiesel industry

### Information to be reported in your final report is as follows

1. Provide a summary of overall project accomplishments to include goals/milestones met, any barriers encountered, and how the barriers were overcome

The technology that was proposed to develop in this research is to produce valuable alcohols, such as 1,2-propanediol (or 1,2-PDO; also called propylene glycol), from glycerol (the byproduct from biodiesel industry) via catalytic thermochemical conversion process with *in situ* hydrogen generation. The objective of this project was set to further develop such a system to improve the process efficiency in a continuous-flow operation. From process engineering aspect, the research focused on evaluating the schemes of process operation, and catalyst implementation. It was also to evaluate other process parameters, such as the processing cost and energy requirement from scale-up point of view.

(1) To develop the process from previously a batch-mode operation to a continuous-flow operation, the key challenge is the means of catalyst application. In batch operations, the catalyst used was an a slurry form. Under vigorous agitation, the fine particles of metal-based catalyst suspend in the liquid phase and uniformly contact with the reactants to provide active sites for reaction. Therefore, the first step of this project is to implement the catalyst application from the suspended slurry form to a shaped, heterogeneous catalyst form so that the catalyst is ably retained in the reactor system for long term operations. A pelletized nickel catalyst was purchased from the BASF Company and tested in batch mode for its activity and then applied in a continuous-flow reactor system.

Experimental results of batch-mode testing showed that the activity of BASF pelletized nickel catalyst is similar to or slightly better than that of fine particle Rainey nickel catalysts. Increased reaction time led to a higher glycerol conversion and a higher targeted product yield under both temperatures tested (211°C & 230°C); however, there was no significantly observed increases in 1,2-PDO selectivity (Table 1).

Once activated in batch with heated hydrogen, the pelletized catalyst was charged into the continuous-flow reactor with special retaining cages for testing under various operating conditions. It was observed that glycerol conversion rates reached 55-66% level while the yield of 1,2-PDO was 25-28% at approx. 10 hours of residence time. Glycerol conversion increased to 76-77% when the residence time was extended three times longer. However, the yield of 1,2-PDO remained at similar level, implying the increased occurrence of undesired side reactions (Fig. 1).

Table 1 BASF Nickel catalyst tested in batch mode.

Conditions	Conversion (%)	Selectivity / Yield (mol%)			
		Propanol	Hydroxy Acetone	1,2-PDO	Ethylene Glycol
230/ 5.6	62.31	0.80/ 0.50	6.35/ 3.96	35.58/ 22.18	2.31/ 1.44
230/ 12	91.41	1.19/ 1.10	2.77/ 2.53	31.72/ 28.99	1.55/ 1.41
211/ 5.6	44.47	-	7.87/ 3.50	35.09/ 15.60	2.71/ 1.21
211/ 12	75.22	0.45/ 0.35	3.70/ 2.79	39.08/ 29.39	2.27/ 1.70

Conditions: reactants = 100 g, glycerol conc. = 60 wt%, catalyst (5g), pressure = 300 psia, agitation = 500 rpm

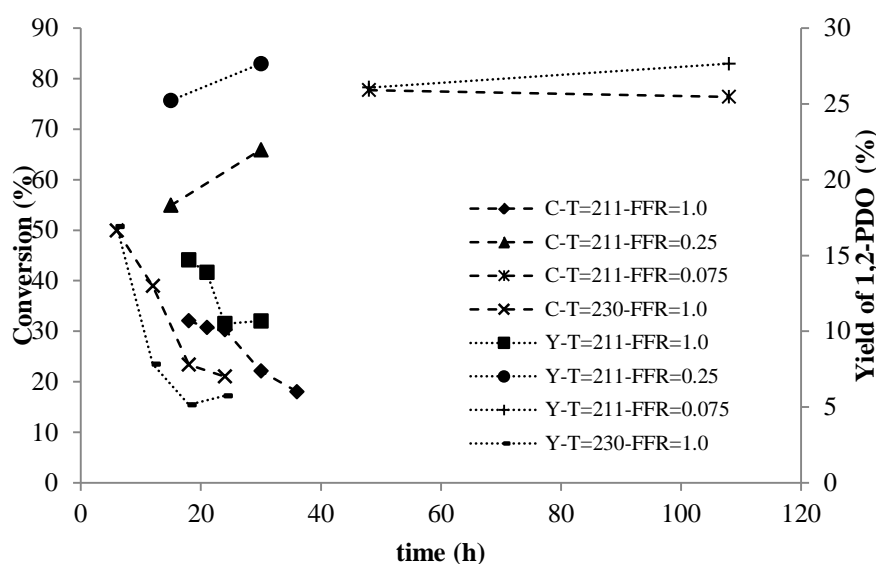


Figure 1 Experimental results of continuous production of 1,2-PDO on BASF Ni catalyst.

Operation of the continuous-flow reactor system for an extended period of time, however, led to significant decreases in reactant conversion rate and product yield, as shown in Fig. 2.

After 32 to 37 days of continuous operation, the glycerol conversion rate decreased to the level of 12-16% and the product selectivity to 7 mol%. This dramatic change might be caused by the deactivation of the catalyst due to the impurities in the product. Observation revealed that there was dark, varnish-like substance in the product and on the surface of the reactor, especially at higher operating temperature. This varnish-like substance may also deposit on the catalyst particles, cover the active sites and block the channels for reactant/product diffusion.

The testing was continued into July and part of Aug 2013 after the project's official termination (June 30, 2013). Due to the time constraint for such a long term testing, further experiments were not conducted. However, it is our expectation to continue testing the system for its long term operability and the catalyst on its deactivation and potential causes.

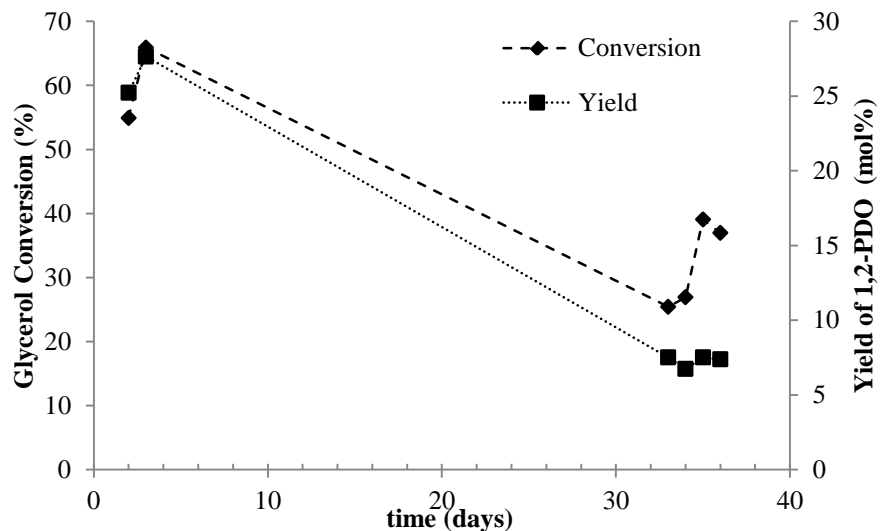


Figure 2 Experimental results on catalyst stability at 211 °C and flow rate of 0.25 mL min<sup>-1</sup>.

(2)

A dual-catalyst continuous-flow system of thermochemical processing of glycerol was also evaluated. The purpose of this part of the research was to explore the process by utilizing different catalysts to optimize the overall process efficiency.

The experiments were carried out using a bench-scale two-stage tubular reactor with BASF Cu and Ni catalysts in series. The reaction temperature, reaction pressure and liquid hourly space velocity (LHSV) were varied to determine their effects on the conversion of glycerol to 1,2-PDO (the targeted product) and hydroxyacetone (the intermediate compound of the process). Experimental results confirmed the production of hydroxyacetone and 1,2-PDO in the system. Up to 20.13% and 6.34% wt of hydroxyacetone and 1,2-PDO were produced in the liquid stream, respectively. Reaction temperature, reaction pressure and LHSV affected the production of hydroxyacetone and 1,2-PDO. It was found in continuous operations that BASF Cu disintegrated into clay-like substance after 15 h and blocked the liquid flow. When crude-glycerol was used as the feedstock, the flow was stopped even earlier (in 7 hours). The main reason for the clog was due to the impurities present in the crude glycerol. Despite BASF Cu catalyst's instability for this process, the performance of BASF Ni catalyst remained consistent throughout the experiments.

As designed, significant amount of hydroxyacetone was produced under the conditions in the continuous-flow processing. In fact, the production rate of hydroxyacetone was higher than 1,2-PDO in the dual-catalyst system. This was likely caused by the incomplete conversion of the intermediate hydroxyacetone under the BASF Cu catalyst in Column I to 1,2-PDO under the BASF Ni catalyst in Column II. In other words, the conversion of hydroxyacetone to 1,2-PDO in Column II was much slower than the production of hydroxyacetone in Column I.

Analytical analysis of the product mixture has revealed that numerous unknown compounds have showed in the GC spectrum thus side-reactions have occurred in a significant level during continuous processing. This phenomenon was not as significant in the previous batch processing system. This was unexpected and believed one of the possible causes of the low

1,2-PDO conversion rate. Another possible explanation for the incomplete conversion of hydroxyacetone might be the reduced hydrogen presence in the system. Unlike in the batch system where hydrogen produced *in situ* builds up during the reaction course to assist the conversion, hydrogen generated in the continuous system was withdrawn with other gaseous product during the operation. The continuous withdrawal limits the availability of hydrogen for hydroxyacetone conversion to 1,2-PDO. Meanwhile, the undesired side reactions that do not require hydrogen take place vigorously and consume the reactant. Thus, the production of 1,2-PDO was depressed.

Table 2. Hydroxyacetone and 1,2-PDO concentrations at different reaction temperatures and pressures in the dual-catalyst system.

RUN	Reaction Conditions			Concentration, % wt			
	Temperature, K		Pressure, atm	Hydroxyacetone		1,2-PDO	
	Column I	Column II		Column I	Column II	Column I	Column II
1	483	484	4.4	13.10	8.41	4.20	6.34
2	523	484	4.4	14.20	8.16	4.82	4.92
3	523	503	4.4	20.13	1.23	4.98	-N.D.-
4	483	484	21.4	-N.D.-	-N.D.-	-N.D.-	-N.D.-
5	523	503	21.4	3.36	-N.D.-	2.57	-N.D.-
6	523	573	21.4	3.54	-N.D.-	3.05	-N.D.-

Other operating parameters, including liquid hourly space velocity, reaction temperature and reaction pressure, influenced the production of hydroxyacetone and 1,2-PDO in the dual-catalyst continuous-flow process. More 1,2-PDO was produced at milder reaction temperatures, which is in concurrence with the observations from batch reactor system.

Although the BASF Cu catalyst showed consistent activity towards converting glycerol to hydroxyacetone and partially to 1,2-PDO, the catalyst disintegrated and eventually clogged the system. Using crude glycerol, viscous sludge and foam blocked the column during continuous operation only after eight hours of continuous operation. It suggests that impurities, such as soap, may cause the problem and should be avoided or minimized.

In summary, the hydro-thermochemical processing of glycerol has the potential in bringing new markets for biodiesel producers in a continuous-flow operation. Glycerol is an ideal feedstock for this process but further work needs to be done to improve the catalyst's stability under long term continuous-flow operation and to optimize the parameters to increase 1,2-PDO yield.

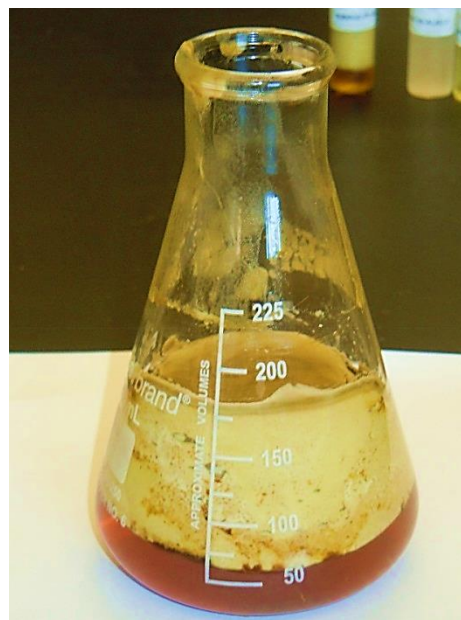


Figure 3. Product collected from Column II after 17 hours of continuous operation using crude glycerol as feedstock.

(3)

The third task of the project was to conduct a process analysis and conceptual design. This task is not quite accomplished by the time of this report being drafted. The major reason of this is the inconclusive experimental results which lead to more research questions than conclusions. Conceptual design and process analysis could be performed with reliable data on valid process parameters and appropriate means of catalyst implementation, which require continued research

## 2. Describe the current state of the technology and related product/service

As the primary goal of this project, realization of 1,2-propanediol production from glycerol via catalytic thermochemical conversion process was conducted and conformed. Testing of pelletized nickel catalyst in continuous-flow system for long period of time and dual Ni-Cu catalyst system also showed promising results. As a necessary step for technology development, this project has made a progress. New findings were unveiled as well as additional challenges.

The ultimate goal of this research is to develop a technology that has industrial application. Although a patent has been filed to protect the principle of the technology supported by the project, we felt that the technology is still immature and further investigation is needed before a commercialization is taken into consideration.

## 3. List the number of faculty and student participants as a result of funding

One faculty member and two student researchers (one undergraduate and one graduate) were funded as a result of this funding.

Two other undergraduate students, who were not funded by this project, also participated the project activities.

## 4. What are the potential economic benefits

Despite the challenges encountered, we still believe that this project addressed a need from biodiesel producers for value-added utilization of the surplus crude glycerol byproduct. Given the significantly increased production of biodiesel, the byproduct glycerol will also continue to increase. Once this technology is further developed and matured after the challenges are overcome, significant economic benefits will be shown. However, at this stage, we can't provide a quantitative analysis on the potential economic benefits.

## 5. Description future plans for project continuation or expansion

The PI's future plan on this technology, additional to overcome the challenges unveiled from this project, is to explore the process scale-up to a pilot facility to further investigate the engineering aspects of the technology, including scale-up effects, equipment requirement and operation, and engineering economy. Possibility of external funding and/or industrial partnership will be actively explored and sought.

6. Please provide a final expenditure report (attached) and include any comments here

Final expenditure reports are attached with this technical report to show the actual spending, including one from the collaboration institution.

The expenditure largely followed the funds requested in the proposal and complied with the spending policies according to the SBOE GAP grants. One minor change (and a positive one) within the funding scope was to include an undergraduate student in the project, which was not initially included in the proposal.

7. List invention disclosures, patent, copyright and PVP applications filed, technology licenses/options signed, start-up businesses created, and industry involvement

Invention patent was filed on the technology of this project during the project period: US patent application: A 61,609,971. 03/11/ 2013. Catalytic Conversion of Glycerol to Alcohols.

8. Any other pertinent information

n/a

**FINAL EXPENDITURE REPORT**

<b>A. FACULTY AND STAFF</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>B. Brian He / Associate Professor</i>	\$8,556	\$8,022.00
<b>B. VISITING PROFESSORS</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>n/a</i>		
<b>C. POST DOCTORAL ASSOCIATES/OTHER PROFESSIONALS</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>n/a</i>		
<b>D. GRADUATE/UNDERGRADUATE STUDENTS</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>Russel Menchavez / Graduate Research Assistant (GRA)</i>	\$10,920	\$8,120.00
<i>Sharon Strom/ Undergraduate Research Assistant (URA)</i>	\$0	\$2,316.00
<b>E. FRINGE BENEFITS</b>		
Rate of Fringe (%)	\$ Amount Requested	Actual \$ Spent
<i>23% for PI (summer), 3% for GRA (the average of 1%AY &amp; 9% summer), 1% for URA</i>	\$2,292	\$2,218.95
<b>PERSONNEL SUBTOTAL:</b>	\$21,768	\$20,676.95
<b>F. EQUIPMENT: (List each item with a cost in excess of \$1000)</b>		
Item/Description	\$ Amount Requested	Actual \$ Spent
<i>1. n/a</i>		
2.		
3.		
4.		
<b>EQUIPMENT SUBTOTAL:</b>	\$0	\$0.00
<b>G. TRAVEL</b>		
Description	\$ Amount Requested	Actual \$ Spent
<i>1. The PI &amp; GRA had a travel to the collaborator's site (BioEnergy Center, Montana State University-Northern, Havre, Montana) on collaborative visits and meeting.</i>	\$1,500	\$1,550.12
2.		
3.		
<b>TRAVEL SUBTOTAL:</b>	\$1,500	\$1,550.12

<b>H. PARTICIPANT SUPPORT COSTS:</b>			
Description		\$ Amount Requested	Actual \$ Spent
<b>PARTICIPANT SUPPORT COSTS SUBTOTAL:</b>			
<b>I. OTHER DIRECT COSTS:</b>			
Description		\$ Amount Requested	Actual \$ Spent
<i>1. Materials and supplies</i>		<i>\$4,074</i>	<i>\$5,804.26</i>
<i>2. Sub-contract for collaboration</i>		<i>\$18,000</i>	<i>\$17,938.67</i>
<i>3. Student support (tuitions &amp; fees)</i>		<i>\$4,654</i>	<i>\$4,030.00</i>
<b>OTHER DIRECT COSTS SUBTOTAL:</b>		<b>\$26,728</b>	<b>\$27,772.93</b>
<b>TOTAL COSTS (Add Subtotals):</b>		<b>\$50,000</b>	<b>\$50,000.00</b>
<b>TOTAL AMOUNT REQUESTED:</b>			<b>\$50,000</b>
<b>TOTAL AMOUNT SPENT:</b>			<b>\$50,000.00</b>



**FINAL EXPENDITURE REPORT**  
(Montana State University-Northern; collaboration institution/sub-award)

<b>A. FACULTY AND STAFF</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>Randy Maglinao/Post Doctoral Research Associate –the Bio-Energy Center through the US EDA grant provided the compensation for this research project</i>	<i>\$0.00</i>	<i>\$0.00</i>
<b>B. VISITING PROFESSORS</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>n/a</i>		
<b>C. POST DOCTORAL ASSOCIATES/OTHER PROFESSIONALS</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>n/a</i>		
<b>D. GRADUATE/UNDERGRADUATE STUDENTS</b>		
Name/Title	\$ Amount Requested	Actual \$ Spent
<i>n/a</i>		
<b>E. FRINGE BENEFITS</b>		
Rate of Fringe (%)	\$ Amount Requested	Actual \$ Spent
<i>n/a</i>		
<b>PERSONNEL SUBTOTAL:</b>	<i>\$0.00</i>	<i>\$0.00</i>
<b>F. EQUIPMENT: (List each item with a cost in excess of \$1000)</b>		
Item/Description	\$ Amount Requested	Actual \$ Spent
1. <i>n/a</i>		
2.		
3.		
4.		
<b>EQUIPMENT SUBTOTAL:</b>	<i>\$0.00</i>	<i>\$0.00</i>
<b>G. TRAVEL</b>		
Description	\$ Amount Requested	Actual \$ Spent
1. <i>n/a</i>		
2.		
3		
<b>TRAVEL SUBTOTAL:</b>	<i>\$0.00</i>	<i>\$0.00</i>

<b>H. PARTICIPANT SUPPORT COSTS:</b>			
Description		\$ Amount Requested	Actual \$ Spent
1. <i>n/a</i>			
2.			
3.			
<b>PARTICIPANT SUPPORT COSTS SUBTOTAL:</b>			
<b>I. OTHER DIRECT COSTS:</b>			
Description		\$ Amount Requested	Actual \$ Spent
1. <i>Reagents and catalysts</i>		\$3,000.00	\$2,938.67
2. <i>Continuous reactor testing fee</i>		\$5,000.00	\$5,000.00
3. <i>GC/MS analysis fees</i>		\$10,000.00	\$10,000.00
<b>OTHER DIRECT COSTS SUBTOTAL:</b>		<b>\$18,000.00</b>	<b>\$17,938.67</b>
<b>TOTAL COSTS (Add Subtotals):</b>		<b>\$18,000.00</b>	<b>\$17,938.67</b>
<b>TOTAL AMOUNT REQUESTED:</b>			<b>\$18,000.00</b>
<b>TOTAL AMOUNT SPENT:</b>			<b>\$17,938.67</b>