Final Project Report, Project 10749-4.2.2.1 2007-2009

AH Zacher   HM Brown
JE Holladay   DM Santosa
JG Frye   AO Oberg

May 2009

Pacific Northwest
NATIONAL LABORATORY

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AH Zacher   DM Santosa
JG Frye   JL Male
HM Brown   AO Oberg

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Pacific Northwest National Laboratory
Richland, Washington 99352

PNNL IR: PNNL-18407

Project Title: Upgrading of Glycerol to Propylene Glycol

Project Number: 10749-4.2.2.1 part 2 (PNNL project 53231 and PNNL project 56652)

Related Projects: This project continues where 10749-4.2.2.1 2005-2006 (PNNL project 48303) left off after the CRADA between ADM, UOP, and PNNL dissolved at the end of FY06.

Note that the efforts under the first part of 10749-4.2.2.1 2005-2006 (PNNL project 48303) were already reported at the end of FY06 following the dissolution of CRADA 232 in a report entitled "Final Progress Report CRADA 232." This report will focus solely on the activities of the project 2007 -2009.

Project Objective:

The proposed work is to develop an integrated process for the production of propylene glycol from sugar alcohols. PNNL has developed a number of catalysts for the production of propylene glycol from sorbitol. Sorbitol is derived from the hydrogenation of glucose. In order to make these technologies commercially viable, further improvements in the catalyst systems need to be developed. Improvements need to come primarily in the form of increased selectivity to propylene glycol. One of the major co-products from the conversion of sorbitol is glycerol. It is critical that a catalyst system be developed for converting glycerol to propylene glycol in high yields. In addition, other sources of glycerol are available and could be used for the production of propylene glycol. Glycerol is a co-product of bio-diesel production or from the transesterification of fatty acids. The utilization of glycerol from biodiesel production or fatty acid production could provide near-term commercial opportunities for implementation of the technology while the sorbitol conversion to produce propylene glycol is considered a longer term objective.

UOP has substantial interest in providing the engineering and catalyst manufacture for the conversion of glycerol into propylene glycol for use in high purity applications. The processes for biodiesel production and for the transesterification the fatty acids are very similar and it is expected that a single catalyst technology can be developed that will be applicable to both sources of glycerol to produce propylene glycol.

Status:

   1. **Progress toward Statement of Work:**

1.1 Introduction

The final report submitted by PNNL on this project to DOE is abridgments of IP protected internal reports to the partners. Sensitive protected information, such as catalyst compositions, reaction operating conditions, and catalyst characterization information are removed for this shortened non-proprietary version.

The project efforts in tasks 4.2.2.1.A and 4.2.2.1.B were addressed under the previous project final report entitled *"Final Progress Report CRADA 232."*

1.2 Task 4.2.2.1.C Process Economics

The purpose of this task is to develop competitive economics for the process being developed compared to propylene oxide (PO) and other glycerol technologies for at least one target market. To complete the process economic models research at each step in the process will be conducted as listed.

The Milestone for task C is to meet the CCOP/ROI proprietary cost target set by UOP. The metric is an internal number proprietary to UOP. Completion of the CCOP/ROI calculations is a Go/No Go decision point.

Feed preparation

Feed stock costs are often the major cost in products produced from biomass. The cost difference between crude glycerin from a biodiesel facility and purified glycerin is substantial. In this activity we will identify critical impurities that can impact the catalysis. The impurities include, lipid materials (fatty acids and esters); minerals (sodium, chloride, phosphates, and others); and metals (from up-stream process leaching). The critical impurities will be identified as to how they impact catalyst activity, selectivity and life. Scoping work will be completed to assess feed treatment technologies and their ability to remove the critical impurities. The scoping work will involve a variety of techniques identified.

During this task, the following efforts were completed:

UOP and PNNL identified three glycerol feed stocks and determined the impurity profile in the crude feeds. The impurities include, lipid materials (fatty acids and esters); minerals (sodium, chloride, phosphates, and others); and metals (from metal leaching).

During FY07 Q2 PNNL completed an evaluation of seven possible impurities ranging in concentration as high as 4%. These impurities include minerals and organic species such as fatty acids and numerous anions and cations. Some of the impurities were quite damaging to performance, other impurities were benign. From the data an acceptable product impurity profile was being developed. Furthermore, UOP identified potential low cost unit operations to prepare crude glycerol for the catalysis step. UOP, working with its partner, tested these procedures and provided six unique processed-crude glycerol feeds to PNNL.

The crude feeds were evaluated in trickle bed reactors at PNNL. Two of the feeds, in which no processing was done, showed problems during catalysis. Three of the feeds had no deleterious effect on the catalyst step. One crude feed was evaluated in a 300 h run.

Of the pretreated crude feeds evaluated for down-selection, following catalytic processing three of the options were set aside favoring two independent pretreatment options. Both of these options use minimal processing and both have demonstrated acceptable catalytic performance and lifetimes. An actual crude feed which representative of the favored baseline has been processed for 360 hours on one of the downselected catalysts and a slightly cleaner similar feed has also been tested on the other downselected catalyst for 425 hours. Performance was good and stable in both cases.

A second downselected catalyst was brought back from initial screening studies, where it found to be an excellent catalyst with similar performance to the baseline catalyst. This catalyst was advanced as a hedge against potential fluctuations in the catalyst preparation costs that might negatively affect overall process economics between now and when the process is fully commercialized.

In addition to UOP delivering crude feeds to PNNL for evaluation. PNNL obtained six crude glycerol samples from various biodiesel manufactures, primarily in North America, and has delivered those to UOP. Information from these materials is providing data on the composition of crude glycerol from a large cross section of biodiesel manufactures.

During FY07 Q4, additional tests were performed to remove additional pretreatment steps and also to test both baseline catalysts on representative feeds. The crude feeds used in this case were still actual feeds (not simulants) and represented removing additional unit operations. The more crude feeds were processed for a total of nearly 500 hours on one catalyst (20% on "crude" 80% on "more crude" feed.) The more crude feed was also processed for 450 hours on the other catalyst. In both cases, performance appeared good and stable compared to baseline testing with USP grade glycerol.

Finally, some simulants were prepared that represent the crude feed prior to separations for the removal of reaction materials/products from the biodiesel process. This material was processed for conversion of glycerol to PG, but we discovered that after a few days of processing, some of the additional contaminants present in the simulants precipitated on the catalyst. These reaction materials/products were diluted with various amounts of water to determine if the precipitates could be removed to no avail. While it is desirable to operate the process with as crude a feed as possible, additional effort will be required to operate the process with these reaction materials and products still present in the feed.

Commercial catalyst manufacturing

Laboratory produced catalyst developed in this project has achieved catalyst performance criteria around activity, selectivity and life. As part of this activity we will identify suitable manufacturing lines appropriate for large scale production. Preliminary catalyst costing will be analyzed based on the cost of the preferred support, metals (and metal precursors), metal loading

and processing costs. Laboratory activities will assess the robustness of the catalyst formulation. As part of this work a statistical experimental design has been prepared to assess metal loading tolerances. A second design assesses catalyst activation. We have previously shown that proper catalyst activation is paramount. Catalyst activation requires proper reduction (the focus of the second design), passivation and de-passivation conditions.

UOP examined the PNNL baseline catalyst preparation method and modified it to be compatible with industrial scale catalyst manufacturing techniques. UOP prepared several batches of this catalyst which was then delivered to PNNL for validation and found to compare favorably to PNNL laboratory prepared batches.

To further refine the catalyst manufacturing process, an experimental design on catalyst activation was prepared. UOP prepared a set of catalysts for evaluation using various adjustments to the manufacturing technique, many centering on the reduction conditions used during preparation. PNNL tested these catalysts in twelve separate trickle bed test runs each lasting from 50 to 300 h. Catalysts were evaluated under at least two distinct conditions. Several important facts emerged from the study. First, the catalyst was damaged when reduced at the high end of the experimental design (harshest conditions). Minimal damage was done at the high temperature extreme if the reduction time was short. Optimal catalytic performance was not observed at the low temperature reduction extreme, although reduction at "low" temperatures did not cause long-term catalyst damage. The hydrogen concentration was also examined: the high and low extremes were less effective than the center point. Process conditions that one might expect on a commercial scale (relatively high exotherms or water "roll-up" from moisture present on the support) did not have adverse effects. An unexpected pre-conditioning of the catalyst resulted in the highest performing finished catalyst. In addition to reduction, catalyst depassivation was also studied. Depassivation would be required if the catalyst were to be reduced by the vendor, passivated for safe handling and then activated on-site (depassivated).

In addition to the experimental studies described above catalysts were also analyzed by several surface techniques including X-ray diffraction (XRD), X-ray absorption fine structure (XAFS) and X-ray Absorption Near Edge Structure (XANES). These techniques probe the physical and chemical structure of the metal on the support at the atomic level. Work was done by Simon Bare at UOP and at the synchrotron at Argonne National Lab. Simon's data relates directly to the reduction and depassivation of the individual metals making up the catalyst (a mixed-metal system). Information concerning metal-metal interactions was also gleaned. This fundamental work was done as part of the cost share performed by UOP and has provided very valuable information related to optimizing catalyst performance.

UOP continued to scale up the catalyst manufacturing into two pilot batches for use at both UOP and PNNL facilities   As of FY07 Q3, all process testing at PNNL and UOP was performed on catalyst generated using commercial preparation equipment with the exception of targeted testing on catalyst modifications. This included testing of further refinements and example batches. This is further detailed under task D.

Preliminary separation

In FY07 Q3 PNNL has sent additional batches of product solutions to UOP that has been prepared from crude glycerol feedstock. UOP in conjunction with their partner has performed separation tests using different unit operations and/or operating strategies processing the materials obtained from actual catalytic processing at PNNL. UOP is moving forward with scaling up the separations testing.

During FY07 Q4, PNNL transferred responsibility for producing separations feedstocks to the new UOP scale-up reactor system. This represents a major goal in transferring this technology to the commercial partner.

Complete preliminary CCOP/ROI calculations

During FY07 Q3, UOP began an integrated techno-economic model on the overall complete process. This model was calculated using the various pre-treatment and separation options to give an overall ROI/CCOP for this process using data generated at PNNL, UOP, and a UOP partner.

During FY07 Q4, the internal UOP stage-gate review was held to evaluate the techno-economic model on the complete process. It was reported from the internal UOP stage-gate review that the CCOP/ROI passed the stage-gate to go on with continued efforts.

4.2.2.1 Task D: Obtain Commercial Material

In this task the feed pre-treatment technology and catalyst manufacturing technology will be selected as trials of each technology are executed. Task D research builds on the findings of Task C.

Milestones and Decision Points
There are two milestones for task C. The first milestone is selection of the feed pre-treatment technology. The milestone will be complete upon validation in the 30 cc reactor. The metric for the milestone is that there be no loss of activity and that the catalyst performance have >90% selectivity at 90% conversion with the commercial feed. The second milestone for task D is selection of the catalyst manufacturing technology. The milestone will be complete upon validation of the catalyst prepared in the trial manufacture. The catalyst must meet the criteria listed above in regards to performance.

During this task, the following efforts were completed:

Final selection of feed pre-treatment technology

As discussed under Task C, in FY07 Q3 the majority of the pre-treated feeds were tested and two of the pre-treatment options emerged. Both of these minimal processing options, when evaluated using the new techo-economic model appear to have an acceptable overall impact

on the model. As such, both of these feeds went forward as baseline pre-treatment technologies. It was expected that additional data generated from other tasks would further refine the tecno-economic model until one was determined to have an advantage in impact on catalyst performance, economic viability, and/or processing issues.

Trial catalyst manufacture

During FY07 Q3, trial catalyst manufacturing was performed and catalysts were prepared using industrial catalyst preparation methods and equipment. Pilot scale batches were prepared for use in the UOP pilot plant and as a bulk, large batch supply for continued PNNL testing. These batches of catalysts were processed under catalytic conditions and evaluated by both PNNL and UOP at various facilities. The catalysts performed well, and this represented an important success in getting this technology commercialized. All further testing and evaluation has been performed with this commercially prepared batch of catalyst.

However, it was discovered during FY07 Q4 that the primary supplier for the carbon catalyst support used for the baseline catalysts has changed its formulation. Prior evaluations of carbon catalyst supports at PNNL had determined that our baseline carbon support was the foremost with respect to producing a catalyst with sufficient activity and selectivity. PNNL and UOP used industry contacts to try to determine the nature of the carbon support formulation change, but there was not a lot of specific information available besides the supplier press release which was of minimal use.

Through industry contacts, a supposedly representative sample of the new support formulation was obtained and both PNNL and UOP baselined catalysts that were prepared on this new formulation. Initial results were mixed, but it was found that the support did not produce catalysts of equivalent performance. This became a major focus of continued efforts to ensure that the entire program was not hindered by the impact on process economics by the apparent reduction in expected catalyst performance. Results from the PNNL and UOP testing resulted in the discovery that the PNNL laboratory preparation method and the UOP commercially compatible preparation method produced catalysts with different performance profiles on the new support.

At PNNL, a series of tests were performed in the trickle bed reactor using baseline "new support formulation" catalysts that had been prepared using modified methods to restore the lost performance. After a series of 6 trickle bed reactor tests it was found that with some modifications, the support could produce a catalyst on both baseline catalyst pathways of acceptable performance. The final preparations of each baseline catalyst were run on pristine glycerol feed for 500 hours for one and 521 hours for the other with no apparent reduction in performance over time. The modifications would add complexity to the catalyst preparation, and may not produce an exact match to the original support. At UOP testing using their catalyst preparation methods generated different results, indicating that for some catalyst formulations their catalyst preparation method is successful without modification.

Additional samples of the new carbon support formulation were acquired by both PNNL and UOP, and it was found that there were additional differences in the most recent batch of the carbon support, which threw into question the nature of future production from this carbon vendor. In fact, the catalyst preparation modifications discovered at PNNL appeared to actually be detrimental to the catalyst on the newest new support.

After subsequent testing the following conclusions were made: First, the absolute most recent batch of support can be used to make a catalyst with nearly the performance to the original. This would be an acceptable substitute for the original batch, but could use improvement. Second, if the variability in the production during 2007 produced batches from this carbon manufacturer is an indication of future variability, then there may be significant effort to test each batch of support prior to preparing catalyst on it.

Milestones and Decision Points
The Milestones for task D were to "demonstrate >90% selectivity at 90% conversion using vendor pretreated feed" and "demonstration of > 90% selectivity at 90% conversion on commercially manufactured catalyst." In the PNNL reactors, both of these were completed at the same time in multiple experiments using multiple pretreatment options, all on commercially manufactured catalyst obtained from UOP.

In tests F130 and F136 actual feed with the preferred baseline pretreatment method was processed in the PNNL 30cc trickle bed reactors using UOP commercially prepared catalyst (primary baseline catalyst). In F130 initial performance was reported at 93.3% conversion and 91.7% selectivity in the conversion of glycerol to propylene glycol using actual pretreated feed prepared by a partner of UOP, the test had some operational issues and the run was stopped early. A second test was performed in F136 that was stabilized on laboratory prepared feed, but then run on two different feeds made from feed that was again prepared from actual biodiesel derived glycerol that had been pretreated using the baseline treatment option. The feed was processed for 425 hours and demonstrated performance as high as 93% conversion and 92% selectivity to PG, even after an upset where hydrogen flow to the reactor was stopped temporarily.

In tests F142 actual, biodiesel derived glycerol feed that had been pretreated was processed at PNNL using a UOP commercially prepared lot of the secondary baseline catalyst formulation. In this test, the catalyst performed at 90% conversion and 93% selectivity on pretreated feed, and then performed at 91% conversion and 90% selectivity on pretreated actual feed that was slightly more crude.

4.2.2.1 Task E: Demonstration of Commercial Materials

The work in Task E is to prepare to move the technology to the semi-works scale. To do so we will demonstrate the commercial materials and that the technology in larger scale reactors as defined by the commercialization partner and demonstrate that the economics are still competitive with propylene glycol produced from petroleum (propylene oxide) and other glycerol technologies.

In larger scale reactor systems the commercial feed and commercial catalyst will be tested. The purpose of the tests is to provide scale-up data required for the semi-works plant. Catalyst performance will be demonstrated in the larger scale reactors. Key performance indicators will be activity, selectivity and life. The catalyst life target for commercial operation is one year. Catalyst life performance will be extrapolated for large scale-run. During the run product effluent will be collected and accessed for quality. The material will be tested in application uses. Finally, the large scale test will be used to determine operability of the semi-works operation.

The product effluent will be used in experiments to refine the separation design for at least one initial application. EEC (cost) estimates will be determined.

The data generated in the scale-up work will be used to refine CCOP/ROI curves to provide a final technoeconomic analysis of the process.

Milestones and Decision Points
The Milestone in Task E is demonstration of the commercial materials in a continuous operation. The catalyst must meet performance requirement (>90% selectivity at 90% conversion) and show no loss of catalyst activity over a minimum of 300 h. There is a Go/No Go decision point for the project to move to semi-works. The decision point is passing the proprietary metric for the refined CCOP/ROI requirement in the refined CCOP/ROI calculation.

In PNNL testing, as mentioned previously in F136 actual pretreated feed was processed using commercially prepared catalyst at baseline conditions. Conversion ranged between 88% and 93% and selectivity ranged between 90% and 94% over the course of the test. Actual pretreated feed was processed for 425 hours and laboratory prepared feed was processed for about 100 hours as well during this test. On the other baseline catalyst, actual pretreated feed was processed for 360 hours ranging from 88% to 90% conversion and 90% to 94% selectivity.

UOP performed a 4000 hour lifetime test on the baseline catalyst, along with performance evaluation of the process variables. Much of the product from USP grade feedstock was collected and used for separations testing to evaluate purification methods for the final product. Feeds processed on this include USP grade materials as well as actual feeds with pretreatment selected based on PNNL flow reactor testing and screening. Performance requirements of >90% Selectivity at >90% conversion have been exceeded in many of the parameters tested on USP grade feed and on actual feeds with no loss of activity on either feed for the entire 4000 hour run.
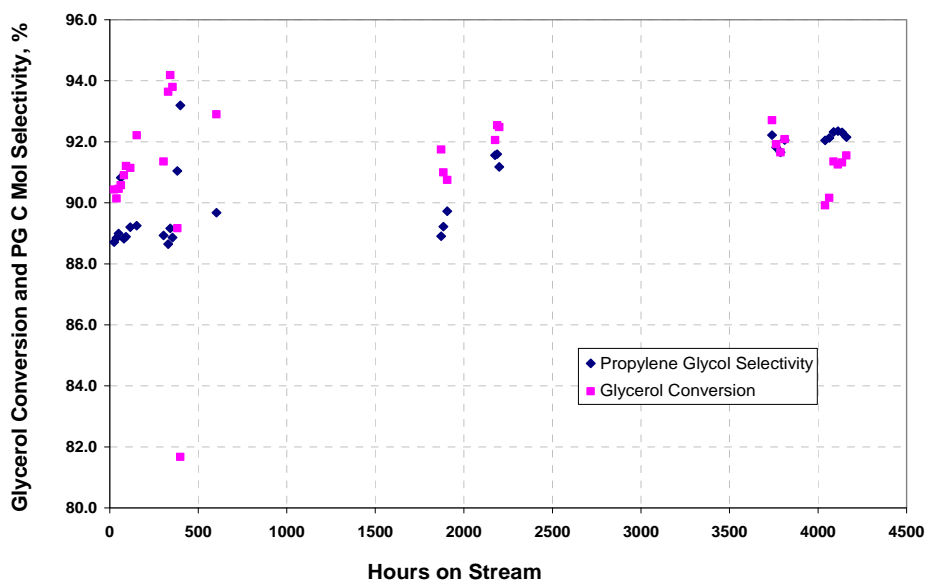
Product from this reactor was processed and separated using the baseline post-processing technology at the UOP partner plant. Samples of these materials were submitted for acceptance testing to evaluate product quality, purity, and to determine if it meets specification potential for a marketable product.

In April 2008 UOP publically announced that the final product from the finished separations process was 99.5% PG with EG concentrations at 180ppm.

4.2.2.1 Task F: Commercialization Support
The purpose of the work is to provide technical support to the commercialization partner during trial scale-up and manufacturing. It is essential that the team that developed the catalyst and reactor technology work with the commercialization team to insure success of the large-scale pilot plant runs planned in FY08.

Milestone: Delivery of FY07 summary Technical Package to partner.
Milestone: Delivery of FY08 summary Technical Package to partner.

As reported during FY08Q3 in task F, the metals loss in the long term testing became an impediment to the commercialization process.

Despite the fact that the performance in both conversion and selectivity for the long term, pilot scale testing at UOP was very stable over the entire 4000 hours, later analysis of the metals on the spent catalyst found that a significant percentage of the metals were missing. It was decided at a mid-gate review in FY08Q3 that the revised process economics would no longer meet the target. A focused effort was performed at UOP and PNNL at this point to understand, isolate, and control the metals loss, but by the end of FY08Q4 the UOP commercialization effort was fully wound-down. By early in the project, UOP had generously vastly exceeded cost share expenses, so the remaining PNNL focus for this task

was shifted towards additional efforts to isolate and neutralize the observed metals loss from the catalyst.

During this task, the following efforts were completed:

Technology package milestones
At the end of FY07 a technology package detailing all of the PNNL efforts was completed for transfer to UOP. At the end of the FY08/09 efforts a second technology package was completed for transfer to UOP.

Support Replacement Efforts
Changes by the carbon support supplier have replaced our baseline support with a new material that does not perform as well for use in this reaction. Evaluation of a sample of new support was performed at UOP and PNNL which verified that catalysts made with the new support have a reduced performance when compared to the previous baseline. Additionally, UOP and PNNL catalyst preparation methods resulted in different performance on the new support.

PNNL developed a modified preparation method that appears to restore some of the activity lost through use of the newly manufactured carbon material. UOP performed new reactor tests of both baseline and modified catalyst preparation techniques. These were performed and evaluated on the slightly larger scale system to evaluate use of the newly manufactured support material. Efforts were mostly positive, but indicated that some work still needs to be performed to modify catalyst manufacturing on the new support to provide good performance on both catalyst systems. PNNL also determined that some process condition changes could improve performance on some of the preparations.

Metals Loss Testing
As mentioned in the summary, metal loss discovered during operations contributed to the wind-down of commercialization efforts. After the surprising discovery of metals loss from the catalyst in the pilot-scale 4000 hour test, a number of archived spent catalysts were collected from previous lab scale tests with as long hours on stream from both PNNL and UOP efforts. It was found that a number of catalysts demonstrated significant metals loss, while a number of them demonstrated minimal loss.

To address the issue, UOP and PNNL personnel evaluated the various potential causes of metals loss throughout the process. A list of potential mechanisms were detailed that could result in metals loss and where compared for consistency against observed behavior. A prioritized list of experiments was created to test each of the potential mechanisms and to determine what focus is needed to improve the metals recovery from a spent catalyst charge.

UOP performed a series of tests where the baseline catalyst was loaded and subjected to all reactor operations except for the actual processing of glycerol feed. In all tests, it was demonstrated that these procedures caused metals loss on the catalyst, and it was concluded that this loss came from the techniques used in post process rinsing of the catalyst.

UOP performed a second round of flow reactor tests on multiple catalysts using modified operating procedures, and found that 7 of the 9 tests resulted in little-to-no metals loss even after processing feed for 2 to 4 days. 2 of the 9 tests did, however, demonstrate significant metals loss, putting into question our ability to reliably control loss.

PNNL performed a set of batch and flow reactor tests to evaluate specific potential metals loss mechanisms. These tests were grouped into evaluation of the initial induction period and post processing rinsing.

PNNL batch testing was performed by batch extraction of a catalyst under reaction conditions with the exception of the glycerol feed for 11 days. This demonstrated between 10% and -1% (gain) of metals on the catalyst, with almost negligible metals detected in the effluent. Additional tests were performed to determine if this was due to redeposition of the metals in the reactor or if it was variability in the ICP analysis.

In PNNL flow reactor testing, catalysts were subjected to reduction and a post-run rinse to examine the effects of rinsing the catalyst with oxygenated water with and without the presence of hydrogen. Using super-oxygenated water to accelerate the observed effect, it was found that extraction of metals from the catalyst can be performed even in the presence of hydrogen at reaction conditions. This demonstrated that the exposure of oxygen laced feed could indeed result in metals loss.

The extent and severity of metals loss under normally saturated oxygenated water rinse, as used at the end of most of the archival tests that demonstrated metals loss, is unknown. ICP of the catalyst demonstrated significant metals loss on all catalysts. However, the damaged catalysts also demonstrated reduced glycerol conversion after the rinse. This also suggests that post-run rinse may be the mechanism, as performance data prior to rinsing during normal testing did not decline during operations as a general rule, even when the spent catalyst demonstrated metals loss. In addition, metals were detected in the effluent, but not at the levels consistent with the analyzed loss from the catalyst.

Additionally, a literature search was performed on the catalytic metals in oxidized form and it was found that the presence of caustic can increase the stability of some of the catalytic metals in the current baseline catalysts in oxidized form. This lends more confidence to the ideal that while processing the caustic glycerol feed, the catalyst may be somewhat protected from this mechanism.

In summary, the metals loss task was mostly finished by FY09Q1. We believe that the primary metals loss mechanism is centered on the post-operational treatment of the catalyst, as it is in harmony with all indications that catalyst performance did not suffer even on the tests where the greatest metals were lost. However, the second set of flow reactor tests at UOP appeared to indicate that we did not have full control to prevent this mechanism. Finally, this does not also preclude an additional processing based mechanism that could be responsible for the 1% to 5% metals loss detected in 100+ hour flow reactor tests where rigorous post catalyst treatment procedures were followed.

4.2.2.1 Task G: Reactor Configuration

The primary focus was modifying the operating strategy of the combinatorial screening system to correlate to the empirical results generated in the research batch and flow reactor systems. This would also have a large impact in the support of this project and any other OBP programs current and future relying on the Combi system. This would overcome a large hurdle in the confidence of data generated in the catalyst screening process, and shorten the catalyst discovery process. Success in this task would have major cross cutting impact on multiple programs that support OBP.

A second focus will be testing new reactor configurations. This work will be carried out only if the CCOP/ROI sensitivity analysis curves indicate the potential impact is significant. Alternative reactor configurations including Taylor flow and bubble column will be examined against the baseline trickle-bed reactor. The outcome of this task could be broadly enabling to support OBP-programs that also use similar reactor processes.

Milestone: Obtain performance correlation of 75% between combinatorial catalyst performance and 300cc batch performance or 30cc flow reactor performance.

During this task, the following efforts were completed:

Empirical Verification of the Combinatorial Testing System

Summary: A good correlation was successfully established between the flow reactor and combi systems once significant changes were made in many unit operations. A large amount of process variability was eliminated, resulting in much greater confidence for this project and any OBP project that will use the system from this point forward.

This effort was performed at PNNL with UOP providing expert guidance and advice. The plan was to develop an empirical correlation between results generated in the PNNL 30cc trickle bed reactor and results generated from combinatorial (combi) system.

This required a major baselining of the unit operations in the combinatorial system, an activity that has not been done on this scale in the history of the system at PNNL. This effort was required to normalize performance of the combi system such that error generated in the preparation, handling, and operation are minimized such that real correlations can be made in reaction performance between the combi and the bench scale. The effort was temporarily halted midway to accommodate the complete shutdown and move of the combinatorial system to the new BSEL facility.

Extensive data mining was done on the historical combi database, while paying specific detail to the reactions involving glycerol to propylene glycol or similar reactions. Significant variability was been found between similar reaction plates, and to a lesser extent, within single reaction plates.

During this task, all unit operations of the combi system were broken down into discrete components and tested individually. Modifications were implemented as needed and tested.

As part of this effort, the PNNL Combi team met with the research team of the vendor of this Combi unit and identified areas that may affect the correlation between the flow and combi system.

Many operations were found to be working as intended, but it was important to prove that each system was reliable and repeatable. This included tests that showed that the HOSS Reactor temperature and performance was stable across the entire plate with insignificant variation with vial location ±0.7°C. Catalytic performance variation within a single reactor plate's vials also appeared negligible.

However, many systems were found to have issues and required modifications:

1) Support/Catalyst weighing robot: Issues were found in the solids weighing learning logic that resulted in the first 3 samples of each solid having gross variation. Delivery logic was adjusted to correct this reducing the standard deviation of delivery on a 10mg sample from ±5mg to ±1.5mg.

2) Liquids handling robot: Delivery logic designed to increase the speed of delivery caused variations in the liquid delivery accuracy. Delivery logic was adjusted to correct this reducing the standard deviation of delivery down to ±0.6 μL.

3) Reactor Membrane: Standard reactor membrane used to keep process liquids sealed in each vial but allow gas transport between the headspace was found to be unsuitable. The suggested membrane allowed liquid loss from the reaction vial. A Teflon membrane with pinhole perforations was used in its place which provided excellent process liquid retention and suitable gas transport from the headspace. This resulted in surprisingly consistent mass balances ranging between 96.9% and 99.3%.

4) Liquid/Catalyst Loading: Liquid catalyst loadings were originally based on convenience. Tests determined a more suitable reactor loading for optimal results for this catalyst.

5) Stirring: The HOSS reactor, due to modifications designed to improve safety, was found to not adequately stir the vials. A stainless steel ball was added to each vial as a stirring aid and was found to improve the expected performance.

6) Gas metering: Original hydrogen metering equipment was found to have significant variations. Mass flow controllers and check valves were replaced which yielded much more reproducible metering.

7) Analytical: Fast column analytical was found to have significant resolution issues with this product matrix. A different column and procedure was put in place that increased analysis time from 6 minutes to 12 minutes per sample, but yielded excellent separation between EG and PG as well as glycerol and lactic acid that formerly co-eluted.
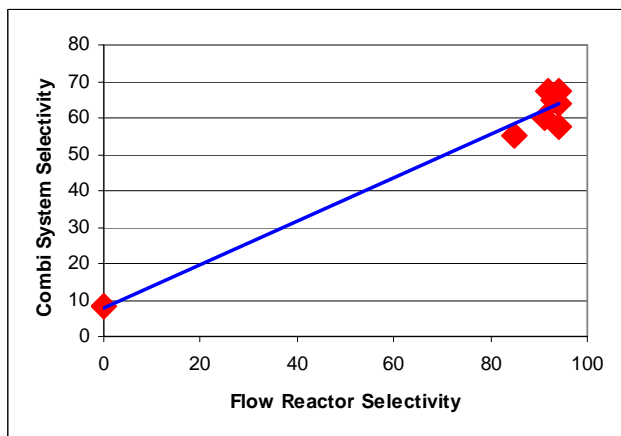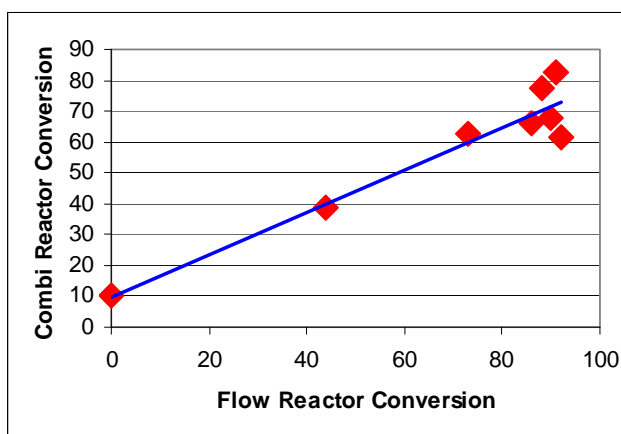
8) Catalyst Prep Robot: Analysis of the catalyst preparation robot indicated that it was stirring the support very poorly during loading, potentially resulting in non-uniform catalyst
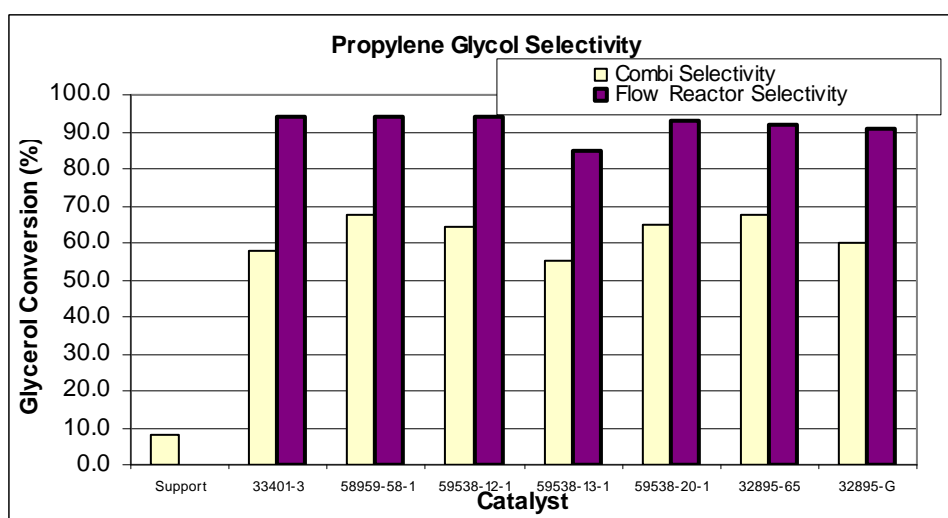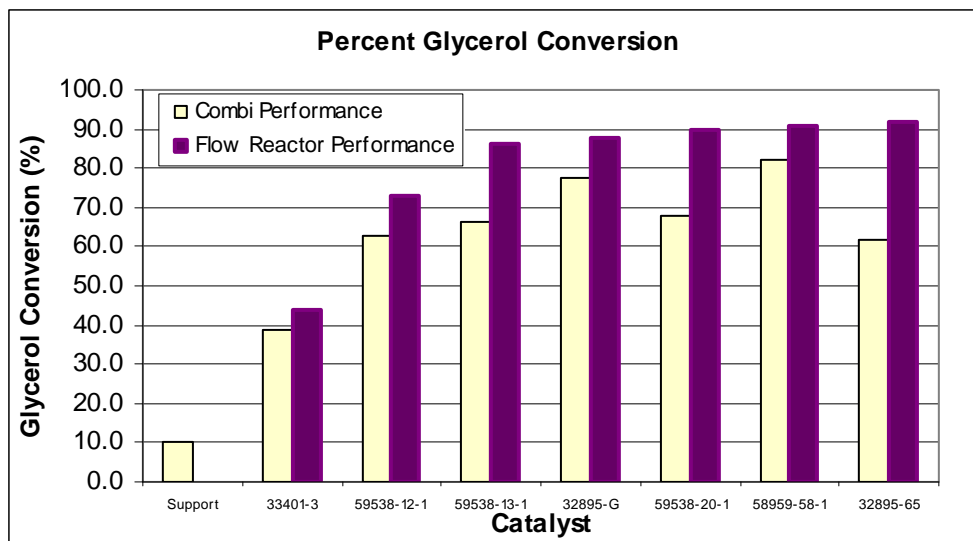
preparation. The shaker table was modified to firmly affix the catalyst vials to the rack allowing the shaking energy to be transferred to stirring the catalyst instead of lifting the vial, resulting in uniform churning of the support during catalyst impregnation.

9) Reaction Strategy: It was found that the temperature and gas addition strategy used when starting a reaction was insufficient. The procedures used were modified to include hydrogen pressurization prior to heat up of the reactor resulting in better performance correlation.

10) Catalyst Reduction Strategy: Current procedures for reducing catalyst prepared in the Combi system were found to have significant differences from laboratory prepped catalysts. The strategy was corrected to match the standard methods used in the lab to manually prepare catalysts.

Efforts culminated in the completion of the correlation between the flow reactor system and the Combi system through modifications and enhancements in the Combi system. The final conversion correlation gave an R^2 value of 0.918 which exceeds the value of 0.75 given for this task. The selectivity correlation had an R^2 value of 0.966; however the available selectivity baseline data available was distinctly bimodal which may tend to yield an exaggerated R^2 value.

Percent Glycerol Conversion

Combi Performance
Flow Reactor Performance

Glycerol Conversion (%) — Catalyst: Support, 33401-3, 59538-12-1, 59538-13-1, 32895-G, 59538-20-1, 58959-58-1, 32895-65

Propylene Glycol Selectivity

Combi Selectivity
Flow Reactor Selectivity

Glycerol Conversion (%) — Catalyst: Support, 33401-3, 58959-58-1, 59538-12-1, 59538-13-1, 59538-20-1, 32895-65, 32895-G

This effort represents a major success for this project and for OBP. All projects in OBP that use the combi system for catalyst and reaction screening from this point onward will benefit from a system that has been vetted and improved. The confidence in the results generated from this system will be greatly improved, and lead to a shortening of the discovery period in future projects. The detailed results from this effort will be scrubbed of proprietary data and kept in a separate document in order to be used as a resource for future projects that use the combi system.

Task H: Advanced separations and catalyst technology

The objective of the partner is to engage advanced separation technology or feed conditioning technology. The goal is to lower separations cost and will be used to direct PNNL second generation catalyst and process research to prevent the formation of specifically identified impurities.

PNNL focus will be on process and catalyst improvements that would reduce the separation requirements and feedstock conditioning. Significant cost improvements may be made by working on tolerance to impurities in the feed (thus reducing feed preparation costs), reducing byproduct inventory (reducing separation costs), or reducing the total metal loading of the catalyst thus reducing catalyst cost. The focus of our research as related to this task will be dictated by economic sensitivity analysis by UOP. If UOP determines that catalyst cost is not significant to the overall economics, then work on reducing the overall metal will be refocused.

Milestone: Use partner techno-economic model to determine research direction
Milestone: Lower processing costs by 20% by a combination of catalyst and separation technology improvements: <u>Developed catalyst to potentially reduce catalyst manufacturing cost by 90%.</u>
Go/No go: improvement of ROI achieved (number internal to UOP)

During this task, the following efforts were completed:

<u>Integrated Separations/Reactor Concept</u>

UOP working with a partner spent considerable effort to refine the separations process. This resulted in the ability to reliably produce a purified PG stream that met their internally set targets. There was also significant amounts of work performed at UOP and its partner to look at pretreatment options with regards to increasing the feed concentration of glycerol that the reactor could tolerate, as well as determining which pretreatments steps could be deleted or retained.

Two novel process operating strategies were developed by PNNL to reduce process operating costs either by combining separations unit operations into the catalytic reactor bed and/or adjusting the operating strategy of the catalytic reactor bed.

This first strategy of combining separations with the catalytic reactor was tested in a scoping study to evaluate the efficacy of the process. Using one of the vendor prepared baseline catalyst that had been evaluated using the standard conditions prior to being subjected to the combined unit operation.

After evaluating a narrow range of selected conditions, the best performance of the new concept appeared about 5 percentage points lower in selectivity and 29 percentage points lower in conversion in initial testing compared to the baseline. Unfortunately, the catalyst tested was an experimental catalyst for the new carbon support testing and its baseline condition conversion when tested under the normal configuration was only 77% instead of the normal catalyst conversion of >90%.

However, the modified reactor had a significant effect in reducing the amount of water diluent headed to the standard separations train. The effluent coming from the baseline reactor configuration test contained 22.7% propylene glycol and the effluent from the reactor

when it was in modified configuration contained nearly 56.7% propylene glycol before heading to the distillation separations. The process also significantly reduced the amount of water added to the feed, which has consistently been a target set by UOP early in the process. However, there was not the expected improvement in the selectivity to desired products. An invention report was filed.

New Catalyst Development

UOP determined that the escalating costs of the catalytic metals were becoming a growing concern and had a terminal impact on the process economics. This concern was further escalated by the possibility of metals loss from the catalyst adding an even larger impact due the lower metals recovery credit.

For this reason, PNNL focus for this task was primarily on new catalyst technology research to generate catalysts that would alleviate these concerns. This work was performed in conjunction with work in Task I due to the similar shared goals. The same pool of ideas for the development of new catalysts for glycerol conversion could also be evaluated for conversion of inexpensive sugars in Task I.

Based on literature search and expert analysis, a number of catalyst matrices were developed that were screened on the Combi system. These matrices were prepared in part to target the favoring of the primary reaction over side reactions responsible for the majority of the byproducts in the reaction. This is particularly important to target the side reactions responsible for the production of ethylene glycol as it has significant impact on product purity and market use.

Experimental matrices were developed to address the following:

1) Replacement of key metals in the baseline catalyst formulations.
2) Evaluate dispersion modifiers in preparation of catalysts.
3) Examine doping agents that may enhance certain key steps in the glycerol to PG reaction.

Initial tests of these plates were performed as per the screening protocols for glycerol to propylene glycol verified under Task G. Two primary candidates were identified that had nearly equivalent performance to the combi-prepared version of the #2 baseline catalyst. There were also a limited number of catalyst compositions that approached but did not meet the baseline catalyst performance on the combi system.

The two primary new catalyst formulations were prepared on the newest batch of the carbon support using PNNL insipient wetness techniques so they could be tested in the flow reactor. During the preparation, one of the PNNL catalyst experts suggested that the preparation for second catalyst should be performed in a different manner than was prescribed by the combinatorial testing. Thus a third catalyst was also prepared using this expert's method.

The flow reactor results were not encouraging for the first two catalysts generated from the combi work. The first catalyst reported 92% selectivity but only 16% conversion. While the

selectivity looked good, at this low conversion analytical variability puts significant doubt into the true selectivity number. The second catalyst reported nearly no activity and was almost completely dead.

However, the third catalyst which was made by modifying the preparation of the second (dead) catalysts preparation gave very encouraging results. The overall selectivity to propylene glycol came to 89% with conversion of glycerol at 50%. This selectivity is very close to the baseline catalyst, however the new catalyst has about half of the activity.

While the activity of this catalyst is not a match to the baseline catalyst, the high selectivity is encouraging. By metals content alone this catalyst is about 0.4% of the price of the metals on the #1 baseline catalyst and 1.1% of the metals price of the #2 baseline catalyst. However, the cost of carbon and catalyst preparation becomes dominant on this new catalyst. When factoring in carbon and finishing costs, the new catalyst is approximately 10% of the finished cost of the #1 baseline catalyst and 25% of the finished cost of the #2 baseline catalyst. Additionally, if this catalyst lost metal, the total value of the catalytic metals lost would be negligible to the process.

Note that this catalyst is completely unoptimized and was discovered in the final part of the project. Some optimization may be able to bring the catalyst performance up to close part of the gap between this and the baseline catalysts. An invention report was filed.

In summary, we were unable to calculate a techno-economic analysis by the time this data was generated, but it is clear that this catalyst would do the following:

1) Reactor size and catalyst charge would increase to account for the lower activity.
2) Catalyst production costs would decrease greatly, by 75% to 90%.
3) Metals loss would be irrelevant, as the recovery value of this catalyst is negligible.

4.2.2.1 Task I: Catalyst for new product slate
The focus of this task was to expand the feedstock slate to inexpensive sugars, including C5 and C6 sugars using novel catalyst systems. Starting from C5 sugar our goal is to hit 70% of the theoretical selectivity to C3 products.

A second focus would be on catalyst systems that operate at neutral pH. These next generation catalysts could offer lower processing costs (no need for neutralization) as well as the potential for lower amounts of base induced byproducts. Success in both of these areas could lead to reducing processing costs by 20% to 50%. Our initial goal is to hit 70% selectivity under no/low-base conditions.

Go/No Go: Initial target of 70% of the theoretical selectivity to C3 products: Met using a novel catalyst system detailed below, from xylitol 92% of theoretical maximum selectivity to C3 products (75% to PG alone).

During this task, the following efforts were completed:

Neutral pH Testing

One of the first questions that needed to be answered was the role and longevity of base on the catalyst, particularly as it is thought to be a co-catalyst and not appreciably consumed in the primary reaction, as it is in secondary and byproduct reactions.

Catalyst testing in the PNNL flow reactor included examining the baseline catalyst system under various pH conditions and experimenting with momentary pulsing of the base. Various other techniques were evaluated, and none of them appeared to enable the catalyst system under no-base conditions.

Previously, a novel catalyst was identified during the first part of Project 10749-4.2.2.1 during Task A&B efforts that generated good selectivity under potentially neutral conditions. Particularly important, some key byproducts were not present in the effluent from this test. The test was performed in a PNNL flow reactor where a novel catalyst was subjected to standard baseline feed but at elevated base concentrations. Conversion was at 98% (partly due to the high base) and selectivity was 92%. The base in the feed was reduced to 0% and the reactor was held for 90 hours to ensure that all of the base had left the catalyst. The final conversion had dropped to 13%, but with an unusually high PG selectivity of 99%. Many of the usual byproducts were nearly undetectable on the analysis. This was an excellent result for no-base conditions, but unfortunately on a novel catalyst that was composed of metals that may not find wide industry acceptance.

During the renewed efforts under Task I, an archived sample of unused catalyst was not available for this testing, so a new catalyst preparation had to be performed. The new catalyst was ultimately different; as the original support used for this novel catalyst was an older support that was no longer available. This catalyst was loaded into the reactor and evaluated under various conditions, but the results from the first experiment could not be repeated with the new catalyst. It has been speculated that the properties of the new support may have interfered with the interaction among the catalytic metals that shut down byproduct pathways. This will require future research to develop.

In addition, tests were performed on additives to the catalyst preparation to enable no-base feed processing on the baseline catalyst. A series of tests were performed on this modified method that resulted in opening byproduct pathways rather than shutting them down. This may be a function of the baseline catalyst composition, as it had been demonstrated as particularly sensitive to changes in the apparent support chemistry as mentioned during the support replacement task. The additives to the preparation designed to enhance no-base processing likely interfered with the interaction among the catalytic metals. However, the additives enhanced the conversion of the baseline catalyst under no-base conditions, indicating that it may be appropriate for other metal matrices.

Alternative Feeds and Products

Research at PNNL was performed in order to expand this process to additional feeds and/or additional products which may benefit the goals of DOE-OBP.

New Catalysts for Conversion of Polyols

Efforts in Task H were performed in conjunction with this task to also develop new catalysts that could potentially be advantageous not just for glycerol to propylene glycol conversion, but also applied to inexpensive C5 and C6 sugars and sugar alcohols. The 3 new catalyst formulations discussed in Task H were also evaluated for use on C5 polyols that can be extracted from biomass rich in arabinoxylan demonstrated under prior work at PNNL.

Results were similar to the glycerol evaluation in that the first two combi selected catalysts had mediocre performance. However, the expert modified catalyst resulted in 93% conversion of xylitol. It also had carbon molar selectivity to desired products of 45% to PG, 29% to EG, and 10% of the carbon going to glycerol. As it is a C5 compound, perfect selectivity for xylitol it 1 mole of C3 and 1 mole of C2 per mole of xylitol. Thus, the theoretical maximum selectivity to PG would be 60% and the theoretical maximum for a perfect split would be 40% of the carbon going to EG.

For this run, we achieved 92% theoretical selectivity to desired C3 (PG + glycerol) and 72% theoretical selectivity to C2 (EG). Separating out the PG alone, we achieved 75% of theoretical selectivity just to PG. This passed the milestone and appears to be a good catalyst for both glycerol and xylitol conversion. An invention report was filed.

Fuel 1

In a flow reactor test at PNNL, a series of conditions were tested that unexpectedly produced a fuel like material from glycerol. The process used aqueous phase glycerol, but produced a 2 phase product containing an aqueous and hydrocarbon phases. The hydrocarbon phase was analyzed to discover a number of compounds with properties similar to fuel. Unfortunately, the process was not selective to a single compound. While this is outside the intent of the project, these results may have broader implications as a renewable fuel if other feedstocks can be processed with this chemistry. An invention report was filed.

Fuel 2

In a separate set of flow reactor tests, a novel catalyst was used to process C3, C5, and C6 polyols. It was noted that the product contained an unusually high amount of mixed of mono-alcohols. Further adjustments to the reaction conditions indicated that as much as 50% selectivity to mono-alcohols could be achieved using this novel catalyst with certain feedstocks. Again, this may have broader implications if other feeds can be used to produce mixed alcohols with this chemistry. An invention report was filed.

Novel Compound

A novel catalyst was identified by PNNL in advanced catalyst screening under this task that enabled interesting chemistry when processing polyols. The catalyst was placed in a batch reactor at PNNL and changes were made to the operating conditions and feedstock with the intent to produce a very unique compound. The intended compound is largely unaddressed in literature.

The conversion of feed was approximately 75% while the selectivity to the intended product was approximately 16%. The analytical for determining the existence and concentration of this material was involved as no supplier for this compound could be found. The analytical was based on calculating the expected GC/MS fragmentation patterns and we have a reasonable confidence that we produced what we intended.

The test was a single proof of principle experiment and was wholly unoptimized. This is an interesting and significant discovery as this is the only 1-step route to produce this chemical outside of complex organic synthesis. The current market is completely unknown for this compound as it is neither commercially available nor can it even be purchased. An invention report was filed and we are evaluating if protection should be pursued. Until a determination of the novelty of the compound can be made, even the name of the compound will not be discussed publically.

Intellectual Property:

The following inventions have been discovered under this project:

15824-E "Advanced Preparation method for Hydrogenation Catalysts"
15945-E "Process for the production of propylene glycol from glycerol"
16289-E "Catalytic Process for the Conversion of Biomass Derived Feedstocks to Mixed Alcohol Products"
16291-E "Process for the conversion of glycerol into mixed higher carbon alcohols, ketones, and others"
16356-E "New Catalyst Compositions (Re replacements) for Glycerol Conversion to Polyols"
16361-E "Production of XXXXXXXXXXXXX" [Name of novel compound redacted, Task I]

Publications / Presentations:

PNNL Industrial Conference, "UOP's Collaborations with PNNL Efforts in conversion of biodiesel glycerin and pyrolitic lignin" March 2007, presentation, UOP.

Catalysis Club of Philadelphia Spring Symposium "Aqueous Phase Catalytic Upgrading of Biomass to Address Fuels and Chemicals" 14 May 2007, presentation, PNNL.

North American Catalysis Society, 20th North American Meeting "New Catalysts for the Hydrogenation of Glycerol and Sugar Alcohols" 16 June 2007, poster, PNNL.

Organic Reactions Catalysis Society 22nd Conference on the Catalysis of Organic Reactions "New Catalysts for the Hydrogenolysis of Glycerol and Sugar Alcohols" 2008, paper, PNNL.

World Congress on Industrial Biotechnology & Bioprocessing, "Highly Selective Catalytic Conversion of Glycerin to Propylene Glycol" 30 April, 2008, presentation, UOP.

Joint Northwest & Rocky Mountain Regional Meeting of the American Chemical Society "Catalyst for the Hydrogenation of Glycerol to Propylene Glycol" 17 June 2008, presentation, PNNL.