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Final Scientific / Technical Report

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Cost-Sharing Partners:	NA
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Final Scientific/Technical Report

1.
DOE Award number: DE-FG36-04GO14238
Name of recipient: Iowa State University
Project title: Center for Catalysis at Iowa State University
Name of Project Director: Dr. George A. Kraus
Consortium members: Drs. Lin, Jane, Larock, Verkade, Angelici, Woo, Pohl, Reilly, Nikolau.

2. No distribution limitations.

3. Executive Summary

The overall objective of this proposal is to enable Iowa State University to establish a Center that enjoys world-class stature and enhances the economy through the transfer of innovation from the laboratory to the marketplace. The funds were used to support experimental proposals from interdisciplinary research teams in areas related to catalysis and green chemistry.

Taken as a whole, the science we accomplished will improve the economy and will significantly increase the visibility of the Center for Catalysis. Specifically, we are involved in the following economic development activities that have resulted from research projects funded by this grant:

1. We are discussing licensing opportunities for the Lin biodiesel catalyst with Rohm and Haas, West Central Cooperative, and Grace Davison.
2. We have been contacted by Huntsman, Concurrent Technologies Corporation, Grain Processing Corporation, and Twin Rivers Technologies about the technology for the transformation of glycerol to 1,3-propanediol.
3. We have discussed technology transfer opportunities for the catalyst that transforms biodiesel into a hydroxy ester with Huntsman and with Global Watch Service.
4. We have been contacted by Mohr Davidow Ventures about starting up a small business centered around catalyst synthesis.

Specific focus areas included:
- Catalytic conversion of renewable natural resources to industrial materials
- Development of new catalysts for the oxidation or reduction of commodity chemicals
- Use of enzymes and microorganisms in biocatalysis
- Development of new, environmentally friendly reactions of industrial importance

These focus areas intersect with barriers from the MYTP draft document. Specifically, section 2.4.3.1 Processing and Conversion has a list of bulleted items under Improved Chemical Conversions that includes new hydrogenation catalysts, milder oxidation catalysts, new catalysts for dehydration and selective bond cleavage catalysts. Specifically, the four sections are:

1. Catalyst development (7.4.12.A)
2. Conversion of glycerol (7.4.12.B)
3. Conversion of biodiesel (7.4.12.C)
4. Glucose from starch (7.4.12.D)

All funded projects are part of a soybean or corn biorefinery. Two funded projects that have made significant progress toward goals of the MYTP draft document are:

1. Catalysts to convert feedstocks with high fatty acid content to biodiesel. This research was performed by Drs. Kraus, Lin, and Verkade. Currently, biodiesel is prepared using homogeneous base catalysis. However, as producers look for feedstocks other than soybean oil, such as waste restaurant oils and rendered animal fats, they have observed a large amount of free fatty acids contained in the feedstocks. Free fatty acids cannot be converted into biodiesel using homogeneous base-mediated processes. The CCAT catalyst system offers a cooperative catalytic system that performs both esterification (of free fatty acids) and transesterification (of soybean oil) in one-pot. This allows the biodiesel producers to use the aforementioned cheap feedstocks without any pretreatment. In addition, the catalyst system is heterogeneous and has been shown by the researchers to be highly recyclable and reusable.

2. Conversion of Glycerol into 1,3-Propanediol. This research was performed by Drs. Lin and Kraus. Although markets currently exist for glycerin, concern is mounting that the price of glycerin may plummet to $.05 - $.10 per pound if future production exceeds demand. Developing a system to make high value chemicals such as 1,3-propanediol from the glycerin stream will add value for biodiesel producers who implement the new technology. Given that both DuPont and Shell chemicals have announced the commercialization of two new PDO-based polymers, a rapid increase of market demand for PDO is very likely.

4. Comparison of actual accomplishments with goals and objectives

From our progress reports, the four areas are:

1. Catalyst development (7.4.12.A)
2. Conversion of glycerol (7.4.12.B)
3. Conversion of biodiesel (7.4.12.C)
4. Glucose from starch (7.4.12.D)

1. Catalyst development: This area had mixed success. The overall goal of this area was to discover catalysts that convert bio-based starting materials into value added products of use to the chemical and biofuels industries.

Drs. Angelici and Woo discovered a catalyst to convert biodiesel into a terminal hydroxy ester. Although this research has been performed on a multi-gram scale and must be scaled up to a kilogram scale, such hydroxy esters are key monomers in the polymer industry. Representatives from Huntsman have requested a sample of the hydroxy ester to be evaluated by their scientists.

Drs. Angelici and Woo identified a catalyst to convert natural unsaturated fatty acids into a five-membered ring lactone, a useful chemical building block for the specialty chemicals industry. This transformation utilized Nafion, a solid acid catalyst, and has been conducted on a multi-gram scale. Researchers will submit a proposal to the USDA National Research Initiatives program in 2007 for further support.

Drs. Larock and Armstrong led a catalyst project designed to use chiral natural materials to produce chiral building blocks for the polymer industry. Unfortunately, their research gave products with an enantiomeric excess of less than 20%. This project focused on the use of palladium catalysts and chiral ionic liquids to make chiral building blocks. This project will not be continued.

2. Conversion of glycerol: This project had a breakthrough. The overall goal of this area was to demonstrate on a laboratory scale that glycerol could be economically converted into a higher value industrial product.

The Iowa State ionic hydrogenation reaction for the preparation of 1,3-propanediol used a silane, catalytic quantities of an acid and glycerol. It was conducted without a solvent. The optimal temperature was around 80 °C. This process has already been disclosed to the Iowa State Research Foundation and is being patented. We have been contacted by Huntsman, Concurrent Technologies Corporation, Grain Processing Corporation, and Twin Rivers Technologies about this technology. This technology could in principle be used to convert higher molecular weight polyols into diols. A full proposal describing this technology was submitted with Grain Processing Corporation and West Central Cooperative to the USDA/DOE program in 2006.

3. Conversion of biodiesel: This project has also had a breakthrough. The overall goal of this area was to identify a cost-effective heterogeneous catalyst that would convert a variety of feedstocks to biodiesel.

Two heterogeneous catalysts were discovered that efficiently converted soybean oil into biodiesel. Both catalysts were also tested with poultry fat provided by West Central Cooperative with good results. We are discussing licensing opportunities for the Lin biodiesel catalyst with Rohm and Haas, West Central Cooperative, and Grace Davison.

4. Glucose from starch: This project has been successful. The overall goal of this area was to improve the yield of the transformation of starch into glucose.

Dr. Jane used a combination of isoamylase and glucoamylase and a substrate of liquefied starch, to convert starch into glucose in an improved yield (99.1% for this project versus 96% for the industrial process). The glucose produced by the Jane technology also contained a much lower quantity of resistant oligosaccharides, such as panose and isomaltose, which give a bitter taste. Therefore, the hydrolysate does not require further purification using an ion-exchange column. Both the increased yield and the removal of the need for ion exchange reduce the production costs of glucose.

Because of the industrial importance of this transformation, Jane filed a disclosure with the Iowa State Research Foundation that is the basis for a patent.

5. Summary of Project activities.

1. Catalyst development (7.4.12.A)

Technical or economic target or objective: The goal of this project is to convert monounsaturated fatty acid methyl esters in biodiesel fuel into monomers that could be transformed into polymers for use as plastics or lubricants. Di- and tri-unsaturated esters can be hydrogenated to give a biodiesel that contains nearly 90% monounsaturated fatty acid methyl esters. It is this enriched monounsaturated biodiesel that is the ultimate feedstock for the desired conversions of this project. These monounsaturated fatty acid methyl esters exist as a complex mixture of different isomers in which the double bond is located in various positions along the 18-carbon atom chain. For this material to be useful in the polymer industry, all of these isomers must be converted into one product containing a functional group at the terminal carbon atom.

Milestones established:

1. Convert fatty acid methyl esters into a single hydroxy ester.

Accomplishments to date

The Iowa State researchers have found that the catalytic hydroboration of methyl oleate with a catalytic amount of $[Ir(COE)_2Cl]_2$ produces the terminal borane in 45% yield. Considering the unfavorable thermodynamics of the isomerization step, it is remarkable that a 45% yield is achieved. The success of this strategy suggests that other functionalizations of complex mixtures of olefins can be achieved.

Future plans and partners – Representatives from Huntsman have requested a sample of the hydroxy ester to be evaluated by their scientists. A proposal will be submitted to the USDA, NSF or DOE to expand the scope of this technology.

Market and customers - biodiesel producers, polymer industry

Production costs - economic analysis awaits scale up to a kilogram scale.

Competitive Advantage - The catalytic reaction afforded a 45% isolated yield. This work demonstrates the feasibility of a single catalyst performing two reactions in tandem.

Competing technology - None

2. Conversion of glycerol (7.4.12.B)

Technical or economic target or objective: explore the technical and economic feasibility of using ionic hydrogenation to convert glycerin from biodiesel production into 1,3-propanediol (PDO). PDO is a component of Sorona, a DuPont product.

Milestones established:

1. Optimize the conversion of glycerin with respect to silane, acid, solvent, and temperature.
2. Scale up optimized reaction to a kilogram scale.

Accomplishments to date

The Iowa State ionic hydrogenation reaction for the preparation of 1,3-propanediol used a silane, acid (catalytic amounts) and glycerol. It was conducted without a solvent, with the optimal temperature around 80 °C. A disclosure was filed with the Iowa State Research Foundation which is the basis for a patent. Preliminary results obtained by the

Kraus and Lin group showed that reduction of glycerol *on a multi-gram scale* using the Lin silane produces *only* 1,3-propanediol in 75% yield and *no* products such as 1-propanol or 2-propanol. Since the acid component is catalytic (5 mole percent was used), the most crucial reagent is the silane.

Future plans and partners – We have established a partnership with West Central Cooperative and with Grain Processing Corporation. West Central Cooperative manufactures 12 million gallons of biodiesel annually, and will supply the glycerin. Grain Processing Corporation will provide pilot plant facilities.

Customers – biodiesel manufacturers and other glycerol producers

Production costs - Recent developments of fermentation procedures for conversion of cornstarch to PDO provide a renewable source to meet the market demand. However, the typical cost of such fermentation processes is still expensive and uneconomical for mass production. Therefore, the current price of PDO is around $.80 per pound. We estimate the cost of our reagents (glycerol, acid, silane) at a total of $.20 per pound.

Evaluation of the market - For every gallon of biodiesel produced, there is one pound of glycerin produced. The expected expansion in the number of biodiesel production plants is expected to produce an additional one billion pounds of glycerin per year. The current amount of glycerin produced from non-biodiesel sources is 557 million pounds. Although markets currently exist for glycerin, the price of glycerin may plummet to $.05 - $.10 per pound if future production exceeds demand. Developing a system to make high value chemicals such as PDO from the glycerin stream will add value for biodiesel producers who implement the new technology. Since DuPont and Shell Chemical have announced the commercialization of two new PDO-based polymers, an increase of market demand for PDO is very likely.

Competitive Advantage - Our technology is a one-step process that does not require a solvent and does not require enzymes.

Competing technology - Several PDO plants have recently been built that will increase American manufacturing capacity. The 75,000 MTPY Shell Chemical PDO plant completed in Louisiana uses fossil fuel as the feedstock while the 45,000 MPTY Tate and Lyle plant built in Tennessee will use cornstarch fermentation to produce PDO. While the cornstarch fermentation process affords the manufacture of PDO from a renewable resource, it is fraught with problems including low yield and poor economics.

3. Conversion of biodiesel (7.4.12.C)

Technical or economic target or objective: The objective is to design an environmentally friendly heterogeneous catalyst for the synthesis of biodiesel from feedstocks such as soybean oil, animal fats and restaurant oils. Animal fats and restaurant oils are lower in cost than soybean oil.

Milestones established

1. synthesize a series of materials with both *general acids* and various *organic bases*.
2. Identify optimal catalysts for biodiesel generation from soybean oil.
3. functionalize the exterior surface of the materials with catalytic groups for the esterification of free fatty acids.
4. Identify optimal catalysts for biodiesel generation from poultry fat.

5. Determine turnover numbers and recyclability of optimal catalysts.

Accomplishments to date

Several catalyst systems have been synthesized. Two catalysts have emerged as the most promising. These two catalysts convert soybean oil into biodiesel in quantitative yield. Both catalysts were tested with poultry fat provided by West Central Cooperative with successful results.

Future plans and partners: We are discussing licensing opportunities for the Lin biodiesel catalyst with Rohm and Haas, West Central Cooperative, and Grace Davison.

Customers – biodiesel industry

Range of production costs - Based on a recent communication with West Central Cooperative, the cost of the currently used homogeneous catalyst (NaOMe) is $0.25 per pound. Our best catalyst to date has a cost of approximately $0.30 per pound. The recyclability of our catalyst is over 20 cycles. The catalyst can also be regenerated. Therefore, the effective cost of our catalyst will be significantly less than that of the homogeneous catalyst.

Market dynamics – Based on a continuing evaluation of the patent literature, other heterogeneous catalysts are being developed by industry and academic labs. Esterfip-H™ employs heterogeneous catalyst technology to convert triglycerides into biodiesel.

Competitive Advantage - Currently, biodiesel is prepared using homogeneous base catalysis. However, as producers look for feedstocks other than soybean oil, such as waste restaurant oils and rendered animal fats, they have observed a large amount of free fatty acids contained in the feedstocks. Free fatty acids cannot be converted into biodiesel using homogeneous base-mediated processes. Our cooperative catalysts perform both esterification of free fatty acids and transesterification of soybean oil in a one-pot fashion. This will allow the biodiesel producers to use the aforementioned cheap feedstocks without any pretreatment. In addition, the catalyst system is heterogeneous and is recyclable and reusable.

4. Glucose from starch (7.4.12.D)

Technical or economic target or objective: About 80% of corn used in the food and other industries in the US requires enzyme hydrolysis of starch to produce glucose. The production of glucose from starch is a two-step enzyme catalyzed process involving a liquefaction, hydrolysis of starch to maltodextrin using thermostable amylase, and a saccharification, conversion of liquefied starch to glucose using glucoamylase. In an effort to increase the glucose yield, a debranching enzyme was employed in conjunction with glucoamylase to hydrolyze more efficiently the branched-chain oligosaccharides.

Milestones established:

1. Compare *Pseudomonas* isoamylase with *Bacillus* pullulanase as a debranching enzyme in the production of glucose from maltodextrin following the standard procedures used in the wet-milling industry.

Accomplishments to date

The Iowa State starch scientists used a combination of isoamylase and glucoamylase and a substrate of liquefied starch, to produce glucose in a much improved yield (99.1%). The product also contained smaller amounts of resistant oligosaccharides, such as panose and isomaltose, which give bitter taste.

Future plans and partners – Dr. Jane has established collaborations with Hayashibara International Company and Tate & Lyle.
Market and customers: ethanol producers
Production costs - This process reduces the production cost of glucose.
Competitive Advantage: The hydrolysate does not require further purification using an ion-exchange column, which reduces production costs of glucose.
Competing technology - the existing industrial process.

6. Products developed under the award

Publications

1. Ghebreyessus, K. Y. ; Angelici, R. J. *Organometallics* **2006**, *25*, 3040-3044.

2. S. Huh, H.-T. Chen, J. W. Wiench, M. Pruski, V. S. Y. Lin, *Angew. Chem., Int. Ed.* **2005**, *44*, 1826.

The Lin biodiesel research has attracted many interests in the scientific community as well as in industry. Several magazines and general newspapers, such as Des Moines Register, Wired, Biodiesel America, United Press International, Hindu (India), Iran Daily (Iran), Engineer Online (London, UK) and Science Daily have published stories on the developments of his catalysts for biodiesel production.

Inventions

1. An IP disclosure has been filed through Iowa State University Research Foundation (ISURF) on the improved transformation of starch to glucose (Dr. Jane).
2. An additional IP disclosure will be filed through ISURF on the biodiesel catalysts (Dr. Lin).

Conclusions

Both chemical catalysis and bio-catalysis were used to address scientific problems of direct relevance to the Department of Energy. New catalysts for the efficient conversion of inexpensive bio-based feedstocks into value-added products were discovered. A bio-catalyst that enhanced the transformation of starch into glucose was discovered. Over 25 undergraduate students, graduate students and postdoctorals were trained. Almost all of the projects initiated through this funding will be continued either through grant proposals to federal agencies or through technology transfer to industry.