Final Report

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Recipient: Iowa Corn Promotion Board

Project Title: Continuous Isosorbide Production from Sorbitol using Solid Acid Catalysis

Project Number: PNNL project 47233

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Consortium:

Iowa Corn Promotion Board (ICPB)
Pacific Northwest National Laboratory (PNNL)
New Jersey Institute of Technology (NJIT)
General Electric Global Research (GE)

Director and Principle Investigators:

Rodney Williamson, ICPB, (515-225-9242) rwilliamson@iowacorn.org
Johnathan Holladay, PNNL, (509-375-2025) john.hollady@pnl.gov
Michael Jaffe, NJIT, (973-596-6497) jaffe@adm.njit.edu
Dan Brunelle, GE, (518-387-6605) brunelle@crd.ge.com

Executive Summary

The Iowa Corn Promotion Board is the principal contracting entity for this grant funded by the US Department of Agriculture and managed by the US Department of Energy. The Iowa Corn Promotion Board subcontracted with General Electric Global Research, Pacific Northwest National Lab and New Jersey Institute of Technology to conduct research in this project. The Iowa Corn Promotion Board also contracted with Monsanto EnviroChem, Inc. (MECS) to conduct the economic engineering assessment of the technology. The Iowa Corn Promotion Board and General Electric provided cost share for the project. The purpose of this diverse collaboration was to integrate both the conversion and the polymer applications into one project and increase the likelihood of success. This project has led to additional collaborations with other polymer companies.

This project had two primary goals: (1) develop a renewable route to isosorbide for commercialization that is economically competitive with all known existing production technologies and (2) working with industry to develop new applications for isosorbide and thus add further value to corn and reduce the risk in the effort toward commercialization.

How research adds to understanding of the area investigated. Under the program a novel process for the production of isosorbide was developed, and evaluated. The new process utilized solid catalyst and integrated water removal and product recovery in a novel way. The process had some challenges and has been amended for continuous operation. Nevertheless the research has shed light on key issues including catalyst life and regeneration, heavies formation, water removal, and product separation. In addition, key findings were developed in applying isosorbide into novel polymers and materials. New Jersey Institute of Technology developed new applications for isosorbide based chemistries in epoxy resins, UV stabilizers and plasticizers. General Electric developed a new application for using isosorbide based chemistry into polyesters. All of these applications combined represent a significant volume of materials for isosorbide.

Technical effectiveness and economic feasibility. Corn-derived glucose is the raw material for the production of isosorbide via sorbitol. Sorbitol is commercially produced today by four companies at a level of about 1.2 billion pounds annually. New interest in the use of sorbitol as a feedstock to produce isosorbide has been driven by recent discoveries of co-polymerizing isosorbide in a variety of polymers. The production of isosorbide in high yields has recently been described in an international patent application filed by DuPont. The inherent challenge with the described technology is the use of solvents associated with the process. In addition, the patent describes the use of both homogeneous acid catalysts as well as heterogeneous catalysts. The results are substantially better with the homogenous catalysts systems with respect to yields.

Production cost for isosorbide has been determined from engineering models developed. The cost has been calculated as a function of production size. Based on this, appropriate polymer applications have been determined and developed. In the near term isosorbide will be developed for potential customers to test in their applications.

How otherwise benefits the public.

There are a number of ways the public will benefit from this work. First the displacement of petroleum derived monomers with isosorbide provides a new example of how high value and high volume products can be produced using renewable resources in a sustainable manner. The products themselves have value not achieved at the same price with petroleum derived materials. The value to farmers in the Midwest and rural parts of the United States as new uses are developed for corn and other starch-rich crops. Finally, there is significant value to the DOE and USDA, who funded this work, in empowering biorefineries with the choice of a new product that we believe will develop into a significant market as polymer applications are increased and the cost of production is decreased.

Accomplishments versus goals and objectives

ICPB had an earlier award from EERE-OIT for the production of isosorbide (PNNL project 41719, "Continuous Isosorbide Production from Sorbitol Using Solid Acid Catalysts"). The ICPB-PNNL team made significant headway toward developing an economically viable process for the production of isosorbide culminating in four patent applications. We applied for further funding, which was awarded through the USDA and managed through DOE's Golden Field office. The additional award, $300k for process research and $400k for polymer research, funded the work in this report which included (1) further process improvements to meet the demand for large-scale polymer applications; (2) development of new solid acid catalysts to reduce waste generation and further improve process economics; and (3) development of new polymers and applications to provide a diversified customer base for the corn wet mill producer of isosorbide and reduce the risk of start-up production. This project had two primary goals: first develop a renewable route to isosorbide for commercialization that is economically competitive with all existing production technologies and second working with industry to develop new applications for isosorbide and adding additional value to corn and reducing the risk in the effort toward commercialization.

The original statement of work contained four decision points as shown:

DOE-DP1	Define the options for a continuous process (6 mo from start)
DOE-DP2	Determine best conditions for solid acid regeneration (8 mo from start)
DOE-DP3	Develop co-catalyst for high purity process (1 year from start)
DOE-DP4	Determine economic options (14 months from start)

Amy Manheim, at that time with DOE-EERE-OBP, worked with the researchers to redefine the decision points. The amended decision points are shown below.

GO-DP1	Integrate solid acid into process (1 year from start)
GO-DP2	Integrate water removal options into final process (1 year from start)
GO-DP3	Integrate polymer reduction technique into final process (1 year from start)
GO-DP4	Isosorbide recovery/ purification (18 mo from start)
GO-DP5	Polymer application development (2 years from start)
GO-DP6	Process engineering –integrate process developments (2 years from start)
GO-DP7	Small scale pilot plant (2 years from start)

The remainder of this section will discuss, at high level, accomplishments versus the two sets of decision points and the overarching goals listed in the introduction portion of this section.

DOE-DP1 called for providing further definition of the continuous process.

Work completed at PNNL:
During the course of research PNNL discovered that isosorbide could be prepared in fairly high purity directly from the reactor. This was novel and unexpected since under other processes a darkly colored product was produced which contained dehydration byproducts (2,5-anhydroiditol and 2,5-anhydromannitol), and oligomeric color bodies. The process was quite unique to anything presented in the literature including our own early work. Process options and definition were pursued during the first six months of research. This culminated in intellectual property captured in the form of an invention report. Best of all the process was perfectly aligned to answer issues in the other decision points listed.

DOE-DP2 and GO-DP1 are related decision points which involve incorporating solid acids into the process.

Work completed at PNNL:
Current processes favor the use of mineral acids. In general solid acids have lower activity and fouling problems. The problems inherent with solid acids and how to overcome such problems is part of intellectual property currently being sought and hence will not be discussed in further detail at this time. However, we can state a new process developed in this study provided a unique way to incorporate solid acids into the process. The solid acids can be quite simple and inexpensive. Approximately 100 distinct experiments were completed on developing and testing solid acids for the process. Some of the acids were commercially available others were produced by impregnating various materials with various acidic media. Separate experiments were completed to determine the lifetime of the acids and techniques for their regeneration to qualify for completion of this objective. In our regeneration experiments we found certain techniques destroyed the catalyst but other techniques were affective in regeneration. Tests were also done to determine the frequency of regeneration.

DOE-DP3 had to do with the use of co-catalysts for high purity process.

Work completed at PNNL:
The discovery made during this milestone negated the need for the co-catalysts that we envisioned needing. For this reason tasks associated with this decision point were not pursued. However, preliminary proof-of-principle data was developed for co-catalyst in the DOE-OIT program. Findings from that program are part of the subject inventions in the various patent applications filed.

GO-DP2 deals with water removal methods in the process.

Work completed at PNNL:
The catalytic reduction of glucose to sorbitol is done under aqueous conditions. Sorbitol is produced at about 30% concentration in water. Before shipping sorbitol is often concentrated to

70% and most often sold in this form. However, solid or crystalline sorbitol is also sold commercially. Solid sorbitol melts in the range of 100 to 110 ºC dependent on moisture content. The bottom line is that numerous options exist for water removal as one can start from dilute (30 wt%) somewhat concentrated (70 wt%) or sorbitol as a melt (100 wt%). Water removal was an integral part of the process developed in this work. Water removal and the impact water has on catalysis in this chemistry are part of the intellectual property that is under current review and unfortunately cannot be discussed in further detail at this time. However, we can clearly state that water removal options were incorporated into the process and this decision point accomplished.

GO-DP3 deals with incorporating polymer reduction techniques into the process.

Work completed at PNNL:
Oligomer and polymer formation is an inherent problem with the production of isosorbide. Desired reactions occur intra-molecularly. Such reactions form the cyclic ethers required in the isosorbide structure. Inter-molecular dehydrations can also occur to produce oligomeric and polymeric material. The polymeric material is often associated with color bodies in the reaction. We have done work to determine the source of polymer formation. Possible precursors include sorbitol, isosoribide, intermediates (1,4-sorbitan), by-products (2,5-anhydrosugars) or various degradation products such as olefins or carbonyl containing materials. Initial data appeared to indicate that the novel process developed in DOE-DP1 had a built in method for limiting oligomer formation and in some instances causing some oligomeric materials to partially revert back to desired products. The polymer reduction technique, inherent in the process, was not as effective as we initially thought. Measurable amounts of oligomeric-polymeric material were still produced and would be a hindrance in later research.

GO-DP4 deals with product recovery and purification.

Work completed by ICPB at PNNL and MATRIC:
This step was the primary responsibility of ICPB with feedback and input from PNNL. The process method developed as part of DOE-DP1 had a unique product recovery component and produced isosorbide from the reactor in a form of higher purity than previous methods. This automatically lends itself to simplified purification. MATRIC devised a system to integrate recovery with the reactor. This recovery concept was tested at PNNL. In addition, two purification schemes were tested as part of the DOE-OIT project. That data was made available to this project.

This project will continue on with Iowa Corn Promotion Board contracting with Mid Atlantic Technology and Research Innovation Center (MATRIC). MATRIC will continue to develop an integrated system and work to scale-up the initial technology developed at PNNL. The objective with MATRIC is to develop a commercially viable process that can be scaled to larger volumes. In addition ICPB plans to have MATRIC produce small quantities of isosorbide for companies to test in their products. Samples of isosorbide will be distributed for further evaluation and testing by companies.

GO-DP5 Polymer application development (2 years from start).

Work completed at NJIT.
Work completed at NJIT has identified several areas of isosorbide based chemistries that are of commercial interest within the current polymer industry. This work has been reported to the ICPB and has elicited interest at a number of commercial polymer producers. Based on internal and external review in 2005, the following areas were identified for scale-up to kilogram synthesis and development in 2006:

- Epoxy resins based on the isosorbide diglycidyl ether and a variety of related compounds including the bis Na alkoxide salt, crosslinking agents containing isosorbide, itaconic acid or other renewable building block chemistries
- Low molar mass UV stabilizers based on ferulic acid derivatives of isosorbide and related compounds
- Low molar mass plasticizers for PVC, PLA and other polymers of commercial interest based on an isosorbide core

In all cases chemistry and efficacy had been demonstrated at scales of up to 100 grams. Future work in 2006 is focused on developing the above identified areas, specifically:

- Completing existing provisional patent applications as full patent applications
- Scaling chemistries to the 1 kilo scale such that:
  - Material is available for in-house and partner testing
  - Initial estimates of process economics can be defined
- Producing relevant specification sheets that are comparisons against compounds currently in commercial usage to allow:
  - Estimation of value in use
  - Identification and commercial partnering with established companies

Experience with isosorbide chemistry, itaconic acid chemistry and related compounds, review of the available literature as well as discussions with companies active or interested in isosorbide research has led to the identification of several new areas for exploration.

Milestones and priorities have been reviewed at least quarterly with agreed to changes added to this statement of work as amendments. All development aspects of the program are tied to well defined milestones as shown below.

Milestones at NJIT:

Technology Development	Milestone	Deliverable	Target Date
UV Stabilizer	Complete Patent	File Application	15Jan
	Kilo for test	Assay	1Mar
	Economic data	Yield profile	1Sept
	Initial spec sheet	Use data	1May
	Revised Spec sheet	Use data	1Sept
Plasticizer	Complete Patent	File Application	1Feb
	Kilo for test	Assay	1Apr
	Economic data	Yield profile	1Oct
	Spec sheet PVC	Use data	1June
	Spec sheet PLA	Use data	1Sept
	Spec sheet other	Use data	1Feb07
Epoxy	Complete Patent	File Application	1Mar

DiNaSalt	Kilo for test Economic data Initial spec sheet	Assay Yield profile Use data	1June 1Sept 1Sept
Diglycidyl ether	Kilo for test Economic data	Assay Yield profile	1Apr 1Aug
Epoxy Resin	Complete Patent Kilo for test,phthal Kilo for test, renew Economic data Spec sheet, phthal Spec sheet renew	File Application Assay Assay Yield profile(s) Use data Use data	1May 1May 15June 15Dec 1Sept 1Nov

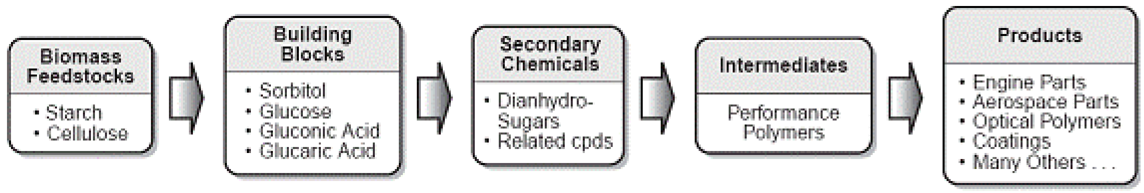
Milestones have been met for the technology development areas of Epoxy resins, plasticizers for PVC and UV stabilizers. Four patent applications have been completed and filed and several additional areas for patent review have been identified. Kilo quantities of representative compounds have been produced and reaction details required for economic evaluation are available. Initial specification sheets have been prepared and shared with interested companies and publicly through presentations (M. Jaffe et al.) at the Corn Utilization and Technology Conference held June 5-7, 2006 and the 10th Annual Green Chemistry and Engineering Conference held June 26-30, 2006. During the summer, a new chemical synthesis laboratory, with improved hoods (one walk-in hood and one bench top hood) and storage facilities was supplied to the program by NJIT, adding significantly to MDCL recourses. This laboratory has now been fully renovated and work is in progress. An NJIT chemistry professor, Sanjay Malhotra, and his post-doc have joined the program to augment the chemistry effort.

It has been shown that isosorbide based epoxy resins have mechanical properties similar to bis-phenol A based epoxies when cured and stored dry. It has also been established that in an epoxy network, isosorbide retains its highly hydroscopic character, leading to a broad range of controllable moisture pickup through choice of curing agent and other components of the epoxy resin system. This novel behavior suggests that a family of isosorbide based epoxy systems, ranging from stable adhesives to a new class of hydrogels can be developed. Commercial input will be important to defining the next step in epoxy performance.

Isosorbide based bis cyclo-aliphatic ethers and fatty acid esters have been synthesized and shown to be both proprietary and of similar effectiveness to DOP in plasticizing PVC. As in the case of the epoxy studies, this work opens the opportunity to develop specific systems with highly controlled plasticizer performance characteristics. Isosorbide has been shown to be an effective nucleus for plasticizers; target polymers other than PVC would require different substitution strategies.

The isosorbide bis ferulate UV stabilizer has been shown to be attractive in its UV absorption profile, absorbing both UVA and UVB. An NJIT chemistry faculty member, Dr. Sanjay Malhotra has joined the program and we share a post-doc with skill in organic and biological synthesis.

Work completed at GE.
As part of GE's analysis of alternative feedstocks for the petrochemical industry, isosorbide stands out as a monomer readily available from corn with a promising price. Starch and cellulose can be converted to glucose and sorbitol, which in tern can be dehydrated to isosorbide, a dianhydrosugar having two hydroxyl groups in a rigid conformation. GE's goal was to find out if isosorbide could lead to useful polyesters.



Polyester resins are used worldwide in a variety of applications, from electronics, food-handling systems, and automotive parts to medical devices. The economic impact of utilizing renewable monomers in large volume of polyester thermoplastics could be predicted to be high.

Following earlier studies on the incorporation of isosorbide into poly(ethylene terephthalate) carried out by DuPont, GE's work concerned copolymers with several other polyesters. Several poly(ester-co-isosorbide) compositions were synthesized using standard melt polymerization techniques, their thermal properties were characterized using DSC, and thermal stabilities were studied by TGA and melt rheology. The isothermal crystallization kinetics were thoroughly studied using DSC. Some preliminary mini-dynatup tests were also performed on the polymer films. Demonstration of scalability was shown by carrying out reactions in resin kettles at 500g scale.

DOE-DP4 and GO-DP6 deal with process economics and engineering.

Work completed by ICPB at EnviroChem
PNNL data was fed to ICPB, who as part of their cost share, worked with an EnviroChem (an engineering company) to develop process economics and engineering. A number of scenarios were evaluated to determine which was the most cost effective in capital and operating cost. This should allow us to define the optimal process design from the reactor through recovery and purification and to compare the process developed under DOE-OIT with the process developed under this work.

GO-DP7 has to do with moving the process to small-scale pilot operation.

Work completed by ICPB at MATRIC:
ICPB is currently under negotiations with MATRIC to produce isosorbide process on a continuous small-scale operation. This work will be used to develop engineering data for scale-up and provide material for customers and further polymer research.

Summary of Project Activities

Our original hypothesis was that incremental improvements were possible to improve the economics of isosorbide production through incorporating solid acid catalysts, optimizing water removal from sorbitol, reducing the amount of oligomeric and polymeric by-products formed and potentially using a co-catalyst to reduce byproducts. These components could be integrated with recovery and purification schemes developed with process engineering models which would bring each component together for the low cost production of isosorbide. At the same time that process work was going on, isosorbide polymer application research was taking place. This integrated approach would lower the risk of industry accepting isosorbide as a monomer into polymer and fiber applications. A small-scale pilot facility will produce sufficient isosorbide supply for industry to test feasibility and product quality.

The original hypothesis was sound. New polymers have been produced that show promising applications in several fields. On the production side, work is going forth as well. Problems were encountered in the process developed under this work. The exact nature of the problem will not be provided in this report. The challenges that arose postponed the advent of small-scale piloting resulting in a departure of the initial work plan. However, we have closely examined the issues raised and have developed a path forward. An amended process has been developed that addresses water content, polymer reduction techniques, and product recovery and purification. A demonstration of the amended process, under continuous conditions, is planned. The process will be used to provide material to clients and build isosorbide demand.

Products Developed

Under this program a novel process for the production of isosorbide was developed and evaluated. The novel process converts corn based sorbitol into isosorbide using a solid catalyst with integrated water removal and product recovery. In addition the work under this program has identified several novel products based on isosorbide chemistries. These market applications include: epoxy resins, UV stabilizers, plasticizers and polyesters. These market applications have commercial interest within the current polymer industry.

Six inventions and four patent applications have been written as a result of this project. When the patent applications are published, additional data will be published. Strong networks have been forged between ICPB, industry and academia. The Iowa Corn Promotion Board had discussion with 17 different polymer and materials companies that may have an interest in isosorbide.

Two presentations were made by M. Jaffe at NJIT. The first publication was at the Corn Utilization and Technology Conference held June 5-7, 2006 in Dallas, Texas. The other technical presentation was given at the 10th Annual Green Chemistry and Engineering Conference held June 26-30, 2006 in Washington, D.C. The title of Dr Jaffe's presentation was *Corn (Sugars) Based Polymer Chemistries for the Polymer Industry*. Additional publications are on hold until intellectual property has been adequately captured.