

Contract No. R002-006
“Renewable Electrolytic Nitrogen Fertilizer Production”

Submitted by Energy & Environmental Research Center
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PARTICIPANTS

Sponsor	Cost Share
Energy & Environmental Research Center Utilizing National Alternative Fuels Laboratory Program funding	\$104,255
North Dakota Corn Utilization Council & Minnesota Corn Research & Promotion Council	\$100,000
North Dakota Industrial Commission	<u>\$200,000</u>
Total Project Cost	\$404,255

Project Schedule – 12 months

Contract Date – October 21, 2008

Start Date – September 1, 2008

Completion Date – August 31, 2010

Project Deliverables:

Status Report: December 1, 2008 v

Status Report: March 1, 2009 v

Status Report – June 1, 2009 v

Status Report – January 15, 2010 v

Final Report–August 31, 2010 v

OBJECTIVE/STATEMENT OF WORK:

This project will optimize processes for producing nitrogen fertilizers using biomass gasification-derived synthesis gas (biosyngas), nitrogen extracted from air and electricity. Because the processes have been demonstrated to operate with low-cost biosyngas rather than high-cost hydrogen derived from natural gas, they offer the potential for lower-cost and smaller-scale fertilizer production than achievable via the traditional natural gas-based route. Commercialization of the processes would enable regionally produced fertilizer to compete economically with imports and simultaneously develop a new fertilizer production industry.

The Energy & Environmental Research Center has been granted confidentiality for their application and reports with the understanding that a non-confidential version of each report and final report will be made available to the public.

STATUS

December 1, 2008 status report received – During the time period of October 30 – November 30, 2008 the 2-W cell was designed and fabricated, and electrocatalyst evaluation activities

were initiated. This is part of Task 1 which is the process optimization activities to be conducted using an EERC-designed and fabricated 2-W planar electrolyzer with two gas chambers (an anode chamber and a cathode chamber) separated by a membrane electrode assembly (MEA). No Task 2 activities were conducted during this reporting period.

March 1, 2009 status report received – During the time period of December 1, 2008 – February 28, 2009 about 65 different catalyst formulation-catalyst support combinations were evaluated at reaction temperatures ranging from 150°C to 550°C, reaction pressures ranging from ambient to 100 psi, and hydrogen-to-nitrogen ratios ranging from 0.05 to 20. Variations in catalyst design included the use of five different supports, combinations of four metal promoters in different ratios, and combinations of up to five different active metals. The goal was to find the most active catalyst at the lowest possible temperature, pressure, and hydrogen-to-nitrogen ratio. The criterion utilized as the basis for evaluation was catalyst activity expressed as millimoles ammonia produced per hour per gram catalyst (mmol/hr/g). In optimizing the cathode catalyst, EERC researchers developed a catalyst formulation-support combination that provided an activity of 15 mmol/hr/g at 350°C and atmospheric pressure. Based on our status at project initiation (a catalyst with an activity of .31 mmol/hr/g at 350°C), catalyst activity has been improved by a factor of about 50. The best cathode catalysts that emerged from the thermal microreactor screening tests were subsequently evaluated in the 2-W electrolysis cell for confirmation of the screening results. Under Task 2 the design of the 200-W electrolysis system was completed, and fabrication of the system was initiated.

June 1, 2009 status report received – During the time period of March 1 – May 31, 2009 catalyst previously reported has been significantly improved. The compositional ratio of the key metallic components of the catalyst and the temperature, pressure, and other parameters utilized in the catalyst fabrication process were optimized. As result, cathode catalyst activity was improved to 60 millimoles of ammonia produced per hour per gram of catalyst ($\text{mmol hr}^{-1} \text{g}^{-1}$) at 350°C and atmospheric pressure, compared to the 15- $\text{mmol hr}^{-1} \text{g}^{-1}$ activity reported in the previous quarter. To the best of our knowledge this activity level is a record not previously seen in the literature; however, we believe further improvement is achievable. Research is now focused on maintaining high activity at lower temperature—ideally, a temperature of 200° - 250°C—since this temperature range enables use of a wider choice of commercial membrane materials, which would help reduce the capital cost of the electrochemical cell. A catalyst has been developed with a measured activity of 10 $\text{mmol hr}^{-1} \text{g}^{-1}$ at 250°C. This catalyst has undergone endurance testing for over 1 month and shown no sign of a decrease in activity. In regards to Task 2 fabrication of the 200-W electrolysis system is ongoing. It is anticipated that system fabrication will be completed during the next quarter.

No cost extension to December 31, 2009 has been granted.

The EERC has requested a no-cost extension to March 31, 2010 which has been granted with the understanding that an additional status report will be provided by January 15, 2010.

The January 15, 2010 status report has been received. Work has continued on the project with the Task 1 – Process Optimization in a Single 2-W Electrolysis Cell near completion. The activity of the catalysts has been substantially improved, cell voltage and current efficiency has improved and production of ammonia was demonstrated with low energy consumption. Work on Task 2 continues.

A no-cost extension to June 30, 2010 has been granted for filing the final report.

A no-cost extension to August 31, 2010 has been granted for filing the final report.

The Final Report has been submitted and is posted on the Renewable Energy Development Program website. The Final Report Summary states the following:

Purpose of the Project: Purpose is to optimize the Energy & Environmental Research Center (EERC)-developed integrated electrochemical–thermal (IET) ammonia production process as a prerequisite for commercialization. The process operates at a reaction temperature of 200°–400°C, with inputs of biomass gasification- or biogas reformation-derived syngas, air-extracted nitrogen, and electricity. Unlike traditional Haber–Bosch-based ammonia processes that require the use of expensive high-purity hydrogen and operation at high pressure (3000 psi) to achieve economic viability, the IET process can utilize relatively impure hydrogen and works well at 200 psi, the impacts of which are lower capital and operating ammonia production costs.

Work Accomplished: Project accomplishments include 1) development of an improved electrolyte membrane and improved electro- and thermal catalysts that enable higher-efficiency electricity utilization in IET ammonia production, 2) IET process optimization at a 20-watt (W) scale, 3) design and fabrication of a 200-W IET electrolyzer, 4) preliminary design of a 200-W complete IET ammonia production system, and 5) preliminary commercial viability assessment of the IET process.

Project Results: Demonstration of IET process technical viability and projection of IET process commercial viability. Technical viability was demonstrated in long-term 20-W tests conducted using simulated syngas, the results of which demonstrated 1) high (95%) electric current efficiency in hydrogen extraction from syngas, 2) low-pressure (200-psi) formation of ammonia at a 5-times-higher catalyst activity and 10% lower energy input requirement than achievable with Haber–Bosch-based ammonia production, and 3) long-term (at least 26 days) thermal catalyst durability. As shown below, ammonia production via the IET process is projected to cost \$315/ton. Based on comparison to the current price of ammonia—about \$350–\$400/ton at the time of this writing—the IET process appears to be commercially competitive with Haber–Bosch ammonia production from natural gas.

Projected Per-Ton Cost of Ammonia Production via the EERC

Electrochemical–Thermal Process	
Syngas Price ¹	\$6/MMBtu
Electricity Price	\$0.05/kWh
Cost of Electricity ²	\$120
Cost of Syngas Input	\$142
Capital Cost	\$21
Operating and Maintenance Cost	\$32
Total Cost	\$315

¹U.S. Department of Energy-published 2010 target price.

²Based on electricity consumption of 2400 kWh/ton ammonia produced.

Potential Applications of the Project: Commercialization of the IET ammonia process will enable market-competitive production of renewable (and reduced-carbon-footprint) ammonia at smaller scales and more widely distributed production facilities than viable with the current large-scale natural gas-based ammonia production model. Wide-scale implementation of the process in distributed production facilities would enable development of new regionally based fertilizer production and distribution industries. In addition to providing job opportunities, smaller-scale, more distributed ammonia production will help ensure ammonia supply to agricultural communities, which will become increasingly important as ammonia transportation costs increase in response to stricter safety and national security regulations.

This project is now complete.

Updated 11/19/10