2015 Project Abstract
For the Period Ending June 30, 2019

PROJECT TITLE: Renewable and Sustainable Fertilizers Produced Locally
PROJECT MANAGER: Alon McCormick
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: 2015

APPROPRIATION AMOUNT: $1,000,000
AMOUNT SPENT: $994,638
AMOUNT REMAINING: $5,362

Sound bite of Project Outcomes and Results
We can reduce the environmental impact of Minnesota farms, and provide practical assistance to them as well, by producing ammonia locally with renewable wind energy. This project demonstrated a new UMN technology that can make this economically feasible for Minnesota corn and small grain farms and coops. It also explored another technology that may find use in hydroponics.

Overall Project Outcome and Results
Activity 1 demonstrated that UMN absorbent technology can pave the way to making ammonia sustainably for the farm, using renewable energy and with producing no greenhouse gas emission. This would reduce the environmental impact of Minnesota farms while also providing relief from stringent seasonal demand for ammonia. Numerous engineering and technoeconomic analysis publications and presentations - assisted also by the US Department of Energy ARPA-E - laid the foundation to develop intellectual property and seek potential future partners. For Minnesota farms, it is next most promising to focus on designing a single integrated reactor-separator module, safer and more efficient than to date, able to produce cheaper ammonia at the farm scale. We will next to seek support to pursue this direction to benefit the Minnesota environment.

Activity 2 explored plasma-generated ammonia and nitrates, showing potential for use in hydroponic irrigation streams providing on-demand fertilizer.

Activity 3 technoeconomic and policy analysis examined appropriate siting and planning of distributed ammonia production for the Minnesota agriculture, establishing important case studies that frame the challenge for the future. Data used was from WCROC's existing wind-to-ammonia facility, demonstrating nationally and internationally the important of this nation-leading benchmark, and drawing interest in possible use of WCROC for a future US Department of Energy demonstration.

Activity 4 explored the question of whether hydrochar might be used to help prevent runoff of ammonia and nitrates from fields (in partnership with Prof. Ken Valentas' project).

Project Results Use and Dissemination
Engineering publications that laid the foundation for intellectual property development.
Presentations at major meetings (national and international ammonia and fertilizer meetings) and state, national and international meetings arranged with the UMN Office of Technology Commercialization, to pursue contacts and plans with prospective partners.

Workshops with possible Minnesota stakeholders convened by co-PI Steve Kelley (formerly UMN Humphrey School of Public Affairs; now, though, Minnesota Commerce Commissioner) to learn and address needs of farmers and local utilities.
News features and science outreach to help get the message out and stimulate further inquiries and discussion
Website logging progress and literature resources as they grow from the team's work: (https://wcroc.cfans.umn.edu/research-programs/renewable-energy/ammonia)

Environment and Natural Resources Trust Fund (ENRTF) M.L. 2015 Work Plan Final Report

Date of Report: July 1, 2019

Final Report

Date of Work Plan Approval: June 11, 2015

Project Completion Date: June 30, 2019

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Project Manager: Alon McCormick

Organization: University of Minnesota

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Location: Statewide, especially Morris

Total ENRTF Project Budget: $1,000,000

ENRTF Appropriation:	**$1,000,000**
Amount Spent:	**$994,638**
Balance:	**$5,362**

Legal Citation: M.L. 2015, Chp. 76, Sec. 2, Subd. 07a
M.L. 2017, Chp. 96, Sec. 2, Subd. 18

Appropriation Language:
$1,000,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota for the Morris West Central Research and Outreach Center and Twin Cities Campus to develop and demonstrate new technologies aimed at enabling renewable and sustainable production of ammonia for fertilizer in a localized manner. This appropriation is subject to the requirements in Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2018, by which time the project must be completed and final products delivered.
Carryforward (b) The availability of the appropriations for the following projects are extended to June 30, 2019: (2) Laws 2015, chapter 76, section 2, subdivision 7, paragraph (a), Renewable and Sustainable Fertilizers Produced Locally.

I. PROJECT TITLE: Renewable and Sustainable Fertilizers Produced Locally

II. PROJECT STATEMENT:
Humankind is faced with a grand challenge – to feed the world while sustaining the environment. Conventional production of nitrogen fertilizer has many environmental drawbacks – using natural gas as reactant, emitting greenhouse gases, relying on energy-intensive chemical plants and distribution network. We are developing new technologies to improve the environment – enabling production of fertilizer with zero carbon footprint, using only water and air as reactants, using wind or solar energy, and using small inexpensive facilities that can be near the farm.

The ultimate goal is to make renewable and sustainable fertilizer technologies realistic for Minnesota companies and farmers. We will bring new technologies from our labs to the demonstration scale to reduce the capital and energy requirements for sustainable fertilizer production, and we will provide engineering and economic models to design and implement local, environmentally-benign fertilizer production. Activity 1 will lower capital cost by eliminating the first key engineering constraint – the need to perform expensive energy-intensive high pressure recycle operations. Activity 2 will use novel plasma chemistry to eliminate the need for high pressure. Activity 3 will bring these together, integrating demonstration results of these three cutting edge technologies with rigorous economic analysis to project true sustainability and environmental impact, using state of the art engineering and economic modeling as well as analysis of how policy trends will affect these. Activity 4 will explore prospects for developing time-release ammonia.

The United Nations projects world population of 10.9 billion by 2050, and feeding the world only using conventional fertilizer production and distribution will have disastrous environmental impact. Environmentally benign fertilizer technology will reduce the carbon footprint of agriculture – both in Minnesota and around the world. Moreover, farms benefit from locally produce fertilizer to supplement conventional supplies when they are pinched by distribution or price constraints.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of January 1, 2016:
In Activity 1, we have identified the need to improve the efficiency of ammonia absorption, and we have begun pursuing these improvements, in order to make more efficient, low capital, small-scale, distributed designs of Haber-Bosch synthesis plants possible. Current emphasis is on improving the absorber capacity and the number of absorption/desorption cycles achievable. We have also improved the design of our lab-scale reactor/absorber system. In Activity 2, we have improved the efficiency of the lab-scale plasma process (alternative to Haber-Bosch), both by improving the catalyst used and by implementing an adsorption and recycle system design. In Activity 3 we have advanced the analysis of the performance of the current pilot plant in Morris, we have made improvements to that pilot plant to improve the quality of future data, and we have begun techno-economic analysis and supply chain analysis, with account of the influence of policy and cost volatility.

Project Status as of July 1, 2016:
All Activities are accomplishing currently scheduled outcomes and are showing progress toward upcoming-scheduled outcomes. For Activity 1, scale-up principles have been established to optimize the absorbent-enhanced reactor using ammonia absorption packed columns, and integration of an ammonia-absorption packed column with the Haber Bosch reactor in the lab has demonstrated the potential for reducing reactor pressure. For Activity 2, high performance catalyst systems and sorption systems have been tested under NTP conditions, and there has been progress toward a potentially improved non-thermal plasma (NTP) reactor configuration, but new developments in plasma technology will be explored in the coming year in seeking to

improve ammonia synthesis efficiency. For Activity 3, techno-economic evaluation, policy analysis, and feasibility assessment of the current pilot plant technology has led to a current manuscript in press, with economics-of-scale analysis up to county-level. Moreover, the team's productivity in dissemination and outreach has increased significantly in this project status period.

Amendment Request (01/01/2017):
We are requesting a no-cost extension of this project through a fourth year (to June 30, 2019). We are currently in contract negotiations for a potential significant award from ARPA-E (the Advanced Research Projects office of the U.S. Department of Energy) for a related project that would require more time (than the current ENRTF/LCCMR end date) but that would significantly increase the impact and scope of this ENRTF/LCCMR project. This is further described in the updates for Activities 1 and 3 below, with corresponding changes proposed for the outcome dates. There are also changes to the Activity 2 outcome dates to take advantage of recent developments in plasma technology – described more in that section.
Amendment Approved: May 30, 2017

Project Status as of January 1, 2017:
Progress made in Activity 1 includes substantial analysis of the integration of the ammonia absorption packed bed with the reactor in the lab, significant progress in reducing reactor pressure, and significant progress toward the outcome of design principles for future realization of absorbent-enhancement with the pilot plant in Morris MN; but delayed progress toward the integration of ammonia absorption and reactor in a single vessel. Progress made in Activity 2 includes further progress in the design of high performance catalytic reactor to use with non-thermal-plasma synthesis. Progress made in Activity 3 includes substantial progress in the pilot plant test runs in Morris to establish benchmarks for techno-economic analysis, and progress is being made toward evaluating demand and facilitating policy discussion. Modeling and optimization of the absorbent-enhanced reactor approach awaits completion of the tasks of Activity 1; but we hope that will be accelerated, and broadened, with new leveraging opportunities.

Project Status as of July 1, 2017:
Progress has been made on all scheduled outcomes, but the approval of the amendment request on May 30 also permits us to amplify the impact ENRTF resources with a new (distinct but related) grant from ARPA-E that will start soon. A recent Technology Forum has given us a good start at making connections with potential stakeholders for the new technologies being explored. Key achievements in each activity have led to new publications, with new papers also in progress. The partnership with Valentas (Activity 4) is now yielding useful data that will help us better understand the scope for possible use of hydrochars.

Amendment Request (01/01/2018):
We are requesting two types of minor amendment. First, a reallocation of the small "Experimental Supplies" budget from Activity 3 to Activity 1 to better reflect the connection of this budget with absorption-related work. Second, some changes in Activity 1 and Activity 3 outcome dates to better align with the amendment approved May 30,2017.

Progress has been made on all scheduled outcomes. The new ARPA-E grant (focused on absorption enhancement moving toward scales of production for local energy storage and liquid fuel and hydrogen transport to urban centers) is allowing expansion of our scope in a way that enhances our ENRTF outcomes. Publications are proceeding, and we expect more discussion with potential industry partners and/or advisors in the coming grant period.
Amendment Approved by LCCMR 3/1/2018.

Project Status as of July 1, 2018:
Progress has been made on all scheduled outcomes. With Activity 1, the new ARPA-E grant (focused on absorption enhancement moving toward scales of production for local energy storage and liquid fuel and

hydrogen transport to urban centers) is allowing expansion of our scope in a way that enhances our ENRTF outcomes. With the extra support, more absorbent materials have been tested and a new prototype system is being assembled to demonstrate and test at WCROC the absorption enhanced approach of Activity 1; meanwhile, the WCROC facility is being prepared to operate the prototype. The other outcomes of the ENRTF/LCCMR funding are also being pursued and accomplished, and discussion with potential industry partners and/or advisors is now accelerating.

In Activities 2 and 3 as well, publications are proceeding and outcomes are being accomplished. In Activity 2, publications mark the progress of new reactor design concepts. In Activity 3, a new publication, invited presentation, and a policy-centered workshop mark progress in understanding techno-economic aspects of distributed ammonia production for fertilizer use.

Project Status as of January 1, 2019:
All outcomes for this date have been achieved to a large degree; work is still in process on some, as we enter the last time six months of the extension year. With the help of a leveraging project from ARPA-E, we have been able to achieve somewhat more than we originally hoped in Activity 1. Activity 2 and 3 outcomes are on target, showing achieving much as hoped.

Amendment Request (01/01/2019)
In Activities 1-3, we are able to save on supplies, travel, and publishing cost budget items. Generally, we wish to make minor adjustments to remove almost any further expenses in these budget items, in order to concentrate remaining resources in supporting personnel to maximize our achievements in the remaining outcomes. The exception in Activity 3 is the need to cover a new expense in "Professional/Technical/Service Contracts" for the refurbishing and maintenance of our electrolyzer and its two power units (due to ongoing use in part due to Activity 3), and also the need to hold some "Supplies" funds for needed pilot plant supplies (for instance, replacements for materials and safety items to continue runs through the remainder of the project).
Amendment Approved by LCCMR 3/8/2019.

Overall Project Outcomes and Results:

Activity 1 demonstrated that UMN absorbent technology can pave the way to making ammonia sustainably for the farm, using renewable energy and with producing no greenhouse gas emission. This would reduce the environmental impact of Minnesota farms while also providing relief from stringent seasonal demand for ammonia. Numerous engineering and technoeconomic analysis publications and presentations - assisted also by the US Department of Energy ARPA-E - laid the foundation to develop intellectual property and seek potential future partners. For Minnesota farms, it is next most promising to focus on designing a single integrated reactor-separator module, safer and more efficient than to date, able to produce cheaper ammonia at the farm scale. We will next to seek support to pursue this direction to benefit the Minnesota environment.

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Activity 4 explored the question of whether hydrochar might be used to help prevent runoff of ammonia and nitrates from fields (in partnership with Prof. Ken Valentas' project).

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: *Improve efficiency for absorbent-enhanced ammonia synthesis*

Description:

In the last decade we have already demonstrated the promise of farm-scale environmentally-benign ammonia synthesis in a unique UMN facility – the Renewable Hydrogen and Ammonia Pilot Plant facility at WCROC in Morris – using wind energy, getting reactant nitrogen from air and hydrogen from water, nourishing 300 acres of cornfield. But as elegant as this process is, economies of scale and cost of production remain serious limitations for practical widespread use of the technology.

First, the existing conventional reactor achieves only partial conversion of raw materials, requiring capital- and energy-intensive separation and recycle of the unreacted reactant mixture; the engineering of this is feasible only with economy of scale in massive ammonia plants. When the nitrogen and hydrogen are combined over the catalyst at high pressure and temperature, the reaction is still incomplete: the unreacted gases must still be separated and recycled. While such a process will work, the need for the recycle means that the process is just a scaled down version of the current one. Because the economies of scale of the large plants are lost, the locally made ammonia will be more expensive. We will work toward ways to reduce this expense, eliminating the need for conventional separation and recycle by using high temperature absorption of the ammonia.

The second key limitation is the high pressure typically required of the state-of-the-art process. We intend to perform the separation of ammonia sufficiently well that lower pressures can provide adequate reaction rate. Our analysis of the catalyzed kinetics suggests that if we can remove ammonia efficiently enough with the absorbent, the suppression of equilibrium limitations may be sufficient to allow us to get respectable rates at much lower pressure. Rather than the 80 atm typical in current state-of-the-art reactors, we need to reduce the pressure by an order of magnitude and still achieve acceptable rates. This would be a breakthrough, reducing hazard and cost enormously. We will endeavor to partner with companies (preferably MN companies) to realize this implementation and also to enable practical realization well beyond the Morris pilot plant.

We will improve the process in three ways.

Task 1: Better absorption

We want to absorb the ammonia more quickly and at lower pressure. Making the absorption faster will need more absorbent ground into much smaller particles following well-established methods. Running at low pressure should be possible according to published data for ammonia synthesis. Doing so will make the process equipment cheaper and safer. We aim to complete this improvement in the first year, boosted by the preceding work funded by the University of Minnesota MNDrive effort.

Task 2: Reduce need for temperature control

Our second improvement is to run both reaction and absorption at the same high temperature. At present, the absorption is carried out at lower temperature. We estimate learning how to absorb hotter will take a year, and again will reduce the cost and complexity of the equipment. Along with that effort, we will work with stakeholders to find a partner to design an implementation with the Morris pilot plant facility.

Task 3: Simplify reactor/absorber

Our third improvement will be to attempt running reaction and absorption simultaneously, in the same container. Since past efforts to do this have worked poorly, we expect this goal will be hard to achieve. Still, when all three improvements are realized, we will be close to a successful process that might be practical to implement in new, small facilities. In the same timeframe, we hope to have the first implementation well on the way in Morris, and this will provide Activity 3 investigators the chance to check and advance their models for future implementations.

Once the lab studies are successful, research efforts at the WCROC Pilot Plan will be extended to operate the system to duplicate the operational parameters of the lab system. Operating conditions to duplicate would include similar gas pressures, temperatures, and molar ratio of gases. This activity will provide a baseline for the conventional technology of the pilot plant, which can then be compared to the performance with new technology used in the lab and which can be implemented in the future with the pilot plant. The control and data acquisition systems will be enhanced in the WCROC pilot plan to achieve the desired comparisons.

Summary Budget Information for Activity 1:	**ENRTF Budget:**	**$408,920**
	Amount Spent:	**$408,885**
	Balance:	**$ 35**

Outcome	Completion Date
1. Scale-up principles to optimize the absorbent-enhanced reactor using ammonia absorption packed columns	January 1, 2016
2. Integration of ammonia absorption packed bed with reactor in the lab, progress in reducing reactor pressure.	July 1, 2016
3. Integration of ammonia absorption and reactor in a single vessel.	July 1, 2018
4. Design principles for future realization of absorbent-enhancement with the pilot plant in Morris MN; seek industrial partners.	July 1, 2018
5. Adaptation of laboratory absorbent-enhanced reactor in a simplified vessel with pressure swing operation, for use in distributed production.	January 1, 2019
6. Establish baseline operating parameters in the pilot plant consistent with optimized absorbent-enhanced reactor operation. Pursue implementation opportunities.	July 1, 2019

Activity Status as of January 1, 2016:

Packed bed absorption of ammonia
Current experiments seek ways to increase the $MgCl_2$ absorbent capacity and lifetime, and to make separation easier (other inorganic salt absorbents are also being explored). Although the absorbents have a high capacity under ideal conditions, realistically we have only been able to access a small fraction of this capacity. We believe this is because the absorption process creates a skin on the surface of the particle where the ammonia is absorbed, leaving the interior of the particle unreacted. This reduces both the total absorption capacity of the magnesium chloride and the "cycle lifetime" (number of absorption/desorption cycles achievable), due to ammonia becoming “trapped” in the center of the particle (it can be removed, but not without difficulty). Now we have supported the magnesium chloride on porous alumina. This increases the effective capacity of the absorbent due to a higher surface area to volume ratio, and also increases the cycle lifetime because the ammonia can be more easily removed from inside the absorbent particles. Moreover, while the unsupported $MgCl_2$ can see capacity reductions repeated absorption-desorption cycles, the supported $MgCl_2$ shows a much better retention of capacity. We have also designed a microscopy cell that we hope will enable us to visualize, understand, and learn to solve problems posed by the changes in microstructure (with continued absorption-desorption cycles) that are responsible for the capacity loss.

Improving the reactor/absorber test apparatus
We have improved the reliability and ease of use of our labscale reactor/absorber test apparatus - reducing leakage problems, improving instrumentation and data logging, improving the catalyst bed packing, and providing more effective process gas circulation. These improvements have enabled us to characterize catalyst activity at wider ranges of temperature and pressure than before; this has enabled us to test our hypothesis and

quantify our expectation that the reactor/absorber system can perform better with improved absorption, perhaps enabling successful operation at pressures much lower than conventionally used.

Activity Status as of July 1, 2016:

- Ammonia separation using absorption near reactor temperature

We have made progress in the design of column absorbers that can very effectively remove ammonia from the process stream. A technical manuscript is in preparation to describe how to ensure reproducible and effective column performance over many cycles.

- Progress toward lower pressure synthesis using absorption

Ammonia is normally made at high pressure to overcome gas phase reaction equilibrium limitations. If the product ammonia can be removed effectively enough, these equilibrium limitations can be circumvented. We have made progress on demonstrating this principle; a technical manuscript has been prepared and submitted, and is under review for publication.

- Moreover, analysis of the steady state operation of the Renewable Ammonia Pilot Plant continues to inform the Activity 1 project team regarding the challenges of small production facilities and the benefit of new absorption technology. A technical manuscript has been published.

Activity Status as of January 1, 2017:

Progress made in Activity 1 includes:

- substantial analysis of the integration of the ammonia absorption packed bed with the reactor in the lab,
- significant progress in reducing reactor pressure, and
- significant progress toward the outcome of design principles for future realization of absorbent-enhancement with the pilot plant in Morris MN. However, progress toward the integration of ammonia absorption and reactor in a single vessel has been delayed to allow for firmer design principles and to allow for a new opportunity presented with a possible related project (currently in contract negotiation).

One of our key outcomes is the publication of the paper “Ammonia Synthesis at Reduced Pressure via Reactive Separation” (Ind. Eng. Chem. Res. 2016, 55 (33), 8922). Excerpting from the abstract of the paper: “Ammonia is normally made at high temperature and pressure using a promoted iron catalyst. High temperatures are needed to get fast kinetics; the high pressure is used to ensure high conversion. Alternatively, ammonia can be made at high temperature but lower pressure if the product ammonia is rapidly separated. Here, we have systematically studied the effect of temperature and pressure on the rates of reaction. We then have qualitatively investigated the absorptive separation of ammonia using calcium chloride in a reaction−separation process. Rapid separation reduces the constraint of reversible reaction and enables us to obtain appropriate reaction rates at relatively lower pressure. The effect of different operating conditions - reaction temperature, pressure, absorption temperature, and gas transport - on production rates is carefully measured, and this elucidates the potential and the limits of this type of low-pressure ammonia synthesis.”

Activity Status as of July 1, 2017:

Progress on several fronts, leading toward the goal of small scale absorbent-enhanced integrated synthesis of ammonia:

- Started obtaining ammonia absorption isotherms at different temperatures, to better understanding the interactions of ammonia and absorbent at different temperatures and pressures than has been available in the literature to date

- Significant improvement in the physical and chemical design of absorbent materials, for improved capacity and cleaner ammonia separation (restricting the amount of ammonia that the catalyst is exposed to)
- Significant progress breaking ground on a novel effort leading to a staged ammonia absorption using pistons that can combine pressure swing with incremental flow
- Beginning progress has been made to understand the molecular mechanism of absorption, from the limited microstructure information and breakthrough curves. This enables substantial progress in the analysis of the integration of the ammonia absorption packed bed with the reactor in the lab

Activity Status as of January 1, 2018:
This work in the last research period has had three major efforts.

The first, was an exploration of a possibility that could augment the absorber columns we have been working with so far. The idea, called a "molecular gate," is a means of simply and completely separating ammonia from nitrogen and hydrogen; it could augment the absorption separation in a way that would prevent even small amounts of ammonia from returning to the reactor. It could potentially further reduce the cost of wind-generated ammonia manufacture. This "molecular gate" idea uses an oscillating form of conventional pressure swing adsorption, but with an electronically driven collection of valves like those described in the literature. {G.E. Keller and C.H. Kuo, US Patent 4354859, Enhanced gas separation by selective adsorption, October 19, 1982; R.T. Yang, Gas Separation by Adsorption Processes, Butterworths, Boston, 1987. p225.} (We already successfully use PSA to separate air, providing the nitrogen used in the small-scale Haber Bosch process already operating in Morris, MN.) However, when we tried to extend this to the ammonia separation, we had a variety of problems, centering on the attack by ammonia on seals and fittings in the process. Because we have enjoyed advances (described below) in the absorption process using improved solid calcium and magnesium halides absorbents, we have abandoned the "molecular gate" research effort for now.

The second research achievement focuses on improvement of the absorption separation of ammonia *into* (not onto) solid salts like calcium chloride. As we have described before, this method of absorption operates at temperatures much closer to those of ammonia synthesis than either PSA or condensation, and so allows a simpler process. However, absorption is also often said to be much slower than conventional condensation of ammonia, so we needed to address that concern explicitly in this research period. With the materials that we are developing, we have found that the process can be fast enough to be practical, and we are extending this research. This aspect of the project is augmented by leverage with a new project (related, but with a different production target and context) supported by the Department of Energy. This work has produced a new publication and a new submitted paper in this research period. Quoting from the abstract of the new paper:

> To reduce the production cost, we replace the conventional ammonia condensation with a selective absorber containing metal halides, e.g., calcium chloride, operating at near synthesis temperatures. With this reaction-absorption process, ammonia can be synthesized at 20 bar from air, water, and wind-generated electricity, with rates comparable to the conventional process running at 150−300 bar. In our reaction-absorption process, the rate of ammonia synthesis is now controlled not by the chemical reaction but largely by the pump used to recycle the unreacted gases. The results suggest an alternative route to distributed ammonia manufacture which can locally supply nitrogen fertilizer and also a method to capture stranded wind energy as a carbon-neutral liquid fuel.
> {ACS Sustainable Chem. Eng. 2018, 6, 827−834; DOI: 10.1021/acssuschemeng.7b03159}

The third research achievement addresses the goal of outcome 3. That outcome is delayed a bit as we had to work on the absorbent material (described above), but is now being undertaken in earnest using a Parr reactor system enabled by the combined support with the Department of Energy.

Activity Status as of July 1, 2018:
Activity 1 work continues to be facilitated and leveraged with additional support from the Department of Energy (in related work, but directed toward the different constraints of production of ammonia as a renewable fuel or hydrogen carrier). We continue to make progress in the following areas with our absorbent-enhanced approach. Detailed descriptions are in the publications disclosed in the last report, as well as one currently submitted, and others in preparation.

CURRENT PROGRESS
Synthesizing ammonia at lower pressure, with the following advantages:
- Lower capital required
- Safer
- Lower energy cost

Stabilizing the absorbent material performance
- Support on an inert
- Effective with $MgCl_2$ and $CaCl_2$, two cheap, non-toxic salts
- Salts work well with silica and zeolite supports; less well with alumina, diatomaceous earth

Measure rates and other key parameters
- Mechanism now understood; basis of current submitted paper and future work
- Developing improved design

New prototype designed, currently being fabricated
- Will be tested on TC campus
- Preparations underway in Morris to operate new prototype next to existing skid

CURRENT CHALLENGES
Improve the absorbent
- Tune chemistry and cycling process, as pressures and support altered
- Identify formulation and operation giving highest net production rate

Combine synthesis reaction and product absorption in one vessel for robust simple system
- Key parameters identified and measured
- Experiments being planned

More sharply identify market for outcome, identifying prospective partners

Activity Status as of January 1, 2019:

In concert with our complementary-scope project with ARPA-E, we have:
1. explored a wider range of stable absorbent options,
2. made progress on a proof of concept single vessel reactor (paper in preparation; relevant to Activity 1 Outcome 5)
3. developed a mathematical model that we feel will assist in improving the proof of concept (accepted 1/1/2019 pending minor revisions; relevant to Activity 1 Outcome 4). Excerpting from the abstract of that paper:

    "Ammonia is made from hydrogen and nitrogen over a catalyst operating at high temperature and pressure. More ammonia can be produced by changing how the ammonia synthesized is separated, i.e., by replacing the current condensation of ammonia with absorption in salts like magnesium chloride. This paper uses the concept of resistances in series in conjunction with experiments of absorption and a well-established theory of reaction to identify conditions where the rate of ammonia synthesis can be increased.”

Final Report Summary:

The absorbent-enhanced synthesis effort for fertilizer was assisted by a related, larger scale, effort funded by ARPA-E to pursue synthesis for energy applications. This accelerated effort led to intellectual property development, described at the University of Minnesota Office of Technology Commercialization website, in the page for Technology #20180113.

We have found a variety of absorbents that work, including magnesium bromide and nickel chloride. Magnesium chloride is the best for many synthesis conditions. These absorbents are more stable if they are prepared with supports of inert material like silica, or if they are diluted with an excess of inert material. In either case, we project the lifetime of the absorbent may be years. We find that the performance is stable over at least one hundred cycles of uptake/release, so they may enable a safe and robust way to make ammonia on the farm using hydrogen and nitrogen from water and air. The environmental benefit, and potential economic benefit, could be enormous.

We now project that we can make ammonia more effectively using an absorbent than using traditional condensation at the farm scale, while still using conventional catalysis. This new technology can allow production of ammonia at lower pressures, which makes small scale farm production realistic. If we find a way to pursue this goal, this grant from LCCMR will have helped seed a revolution in the environmentally sustainable production of agriculture’s key chemical, and the production of intellectual property toward that end.

For single farm use, one of the most interesting results was a demonstration of the promise for a single vessel integrated synthesis unit. Further work was proposed to LCCMR in that direction in Summer 2019; though not supported ~~supported~~ at this time, we will seek other means to make progress for carbon-free ammonia for Minnesota farms.

ACTIVITY 2: ***Low pressure ammonia synthesis using non-thermal-plasma***
Description: The second technology developed by our team is Non-Thermal Plasma (NTP) Assisted Catalysis, which is an alternative synthesis method to high temperature and pressure method for ammonia production. A catalytic non-thermal plasma reactor can produce ammonia at much lower temperatures and pressures than the conventional Haber-Bosch ammonia synthesis process.

Non-thermal plasma (NTP) assisted catalysis is highly scalable and portable and can be conducted in temperatures and pressures much lower than those used in traditional catalytic reactions. Therefore the NTP method would enable synthesis of ammonia from renewable hydrogen in scales and conditions achievable on farms and renewable hydrogen production sites. Furthermore, the conversion and energy efficiency of NTP assisted ammonia synthesis can be significantly improved through optimizing synthesis catalysts, ammonia absorbers-catalysts, nitrogen and hydrogen recycling, and temperature control. The techno-economic feasibility and environmental impacts of the technology can be adequately evaluated on a pilot demonstration NTP based ammonia production system. The goal of this activity is to develop, demonstrate, and evaluate a novel NTP based technology for production of ammonia locally and sustainably.

One postdoctoral research fellow (1 FTE) will be employed to conduct the work outlined in this section. Tasks 1 and 3 will leverage the outcome from an MNDrive funded project (2 years). The focus of the present activity is to develop and optimize ammonia absorption process and system, integrate individual processes, and develop a pilot scale facility for testing, evaluation, and demonstration.

Task 1: Selection and testing of catalyst systems for low temperature ammonia synthesis
A project funded by MNDrive will be focused on development of catalyst system for low temperature ammonia synthesis. The outcome will be leveraged by the present LCCMR project. The catalyst systems with acceptable performance in terms of conversion and energy efficiency will be selected for the study and will be tested together with the ammonia absorption process and new NTP reactors under different operational conditions.

Task 2: Development of ammonia absorption systems for use in the NTP system
Improvement of the equilibrium reaction yield of ammonia synthesis at low temperature and low pressure requires separation and removal of ammonia from the reactor during reaction. Several alkaline earth metal halides and zeolites have been found to have ammonia absorption capacity. Use of ammonia absorbents for separation of ammonia during synthesis, especially at low pressure has not been extensively studied. The sorption and desorption behaviors of ammonia absorbents at low temperature and low pressure are not well documented. Furthermore, the possible role of absorbents as synthesis catalysts in NTP assisted catalysis has not been investigated.

Our preliminary study showed that ammonia absorption using $MgCl_2$ and zeolite as absorbents were quite fast and effective. The data suggests that the role of the adsorbent in the new ammonia synthesis system is two-fold: to achieve complete adsorption of the ammonia formed in the catalytic NTP reactor and to facilitate further synthesis of ammonia on the absorbent surface with the remaining active radicals generated in the NTP discharge process. The objective of this experiment is to study the sorption and desorption behaviors and additional synthesis activity of alkaline earth metal halides ($MgCl_2$, $CaCl_2$, $CaBr_2$, $SrCl_2$, and $SrBr_2$) and zeolites in our NTP assisted ammonia synthesis process. The ratio of absorbent to flow rate, absorption temperature and pressure, and placement of absorbents will be studied. Effective desorption methods and efficient desorption scheme will be developed.

Task 3: NTP reactor development and process optimization
This effort will leverage the outcome from the MNDrive funded project. A new NTP reactor will be designed based on the best configuration developed from the MNDrive project. This reactor will be used to further study and optimize the catalyst and absorbent systems. It will serve as the prototype modular unit for the pilot scale facility.

Task 4: Process and system integration and pilot facility development and testing
With the knowledge and understanding generated through Tasks 1-3, we will integrate individual processes into the circulation system. Key components of the facility will include reaction gas feeding, NTP reactor with catalysts, ammonia absorption, ammonia desorption, unreacted gas recycling, flow rate control, temperature control, and product storage. The pilot facility will be built with ability to control and monitor temperature and pressure and provide easy access to sampling.

After the pilot facility is assembled, we will carry out extensive intermittent and continuous operations to test the performance and stability of the facility. Operational conditions including temperature, feeding gas flow rate, and circulation flow rate, will be optimized. Mass and energy balancing will be carried out to determine the conversion and energy efficiency.

Task 5: Technology demonstration
After Task 4 is completed, we will move to demonstrate pilot facility in partnership with LCCMR. At least five demonstrations will be made to stakeholders including state agencies, private investors, academic researchers, and the public. Demonstration events will be broadly publicized through various channels and media. The demonstration events will be one of our major findings dissemination efforts.

Summary Budget Information for Activity 2: **ENRTF Budget: $192,963**

Amount Spent: $192,795
Balance: $ 168

Outcome	Completion Date
1. High performance catalyst systems will be selected from leveraging research activities and tested under NTP conditions.	January 1, 2016
2. Efficient ammonia absorption systems will be developed and evaluated.	January 1, 2016
3. New NTP reactor will be developed and used for process optimization	July 1, 2018
4. Processes will be integrated and a pilot scale facility will be designed, fabricated, and tested.	January 1, 2019
5. The entire technology will be demonstrated to stakeholders	July 1, 2019

Activity Status as of January 1, 2016:

Catalyst development
Several Ru based catalysts with different supports and promoters were developed. The supports included carbon multiwalled nanotubes, MCM-41, and mesoporous activated carbon; and promoters were Cs, K, and Ba. These new support materials have higher surface area and porosity than those used in previous work. So far, tests results showed that catalyst Ru loading of 10% performed the best. The results of the three support materials showed that carbon nanotubes and MCM-41 work much better than the previously used alumina-supported catalysts. The energy efficiency obtained with carbon nanotubes may be twice that using alumina.

Sorbent evaluation
To evaluate sorbent performance, we designed a system to implement recirculating flow, incorporating also a cooling device to cool the recycle gas flowing into the catalyst-assisted NTP (nonthermal plasma) ammonia synthesis system. Experimental results so far show that this cooling is very effective in maintaining low temperature and system stability to allow comparison of sorbents with the plasma reactor. Compared to other sorbents tested ($MgCl_2$ and Amberlyst 15), the adsorbent Molecular Sieve 13X shows the highest capacity under the conditions of the NTP system. After reaction was terminated, ammonia can be desorbed from this adsorbent. We are now studying effect of the adsorption/recycle on overall ammonia productivity of the NTP system.

Reactor design
A new NTP reactor design has also being pursued; the objective of this design is to make the catalyst loading process easier and more convenient, compared with our current reactor configuration (which consists of a quartz tube and a stainless steel tube placed coaxially).

Activity Status as of July 1, 2016:

- A new perpendicular-configuration reactor (with catalyst oriented perpendicular to gas flow) was fabricated and tested. In the new reactor, the potential advantage is that the gas reactants could fully contact the catalyst. However, this reactor, thus far, is unable to produce stable discharge.
- Copper mesh and porous carbon electrodes were tested on the perpendicular reactor. The copper mesh electrodes yield point discharge, while the porous carbon electrodes generated unstable corona discharge.
- The parallel-configuration coaxial reactor (with catalyst oriented parallel to gas flow) still exceeds the perpendicular-configuration reactor in performance.

Activity Status as of January 1, 2017:

The Ruan group:

- intensively characterized the Ru-promoter catalyst supported on mesoporous structures.
- coordinated with an industrial partner (Plasma Technics Inc.) that manufactures the inverter and transformer and tested system performance at high frequency, greater than 20,000 Hz.
- found that the high frequency favors the ammonia synthesis, increasing synthesis efficiency (using the same catalyst) from 1 g/kWh to 1.7 g/kWh.
- found that at high frequencies, less current is needed to produce the same amount of ammonia, owing to a resonance effect.

It is expected that a publication on this new technology, along with details of the new reactor design, will be pursued in the coming report period.

Activity Status as of July 1, 2017:

The Ruan group:

- Performed additional characterizations (AFM, XPS & XRD) on the Ru-promoter catalyst supported on mesoporous structures.
- Found that for the mesoporous catalyst, 50 vol% of N_2 in the feed gas yields the greatest energy efficiency (previously 75 vol% for MgO and aluminum-based catalysts).
- Designed a new dielectric layer made by the perforated quartz plate that enhance the performance of the perpendicular reactor. This system will be manufactured and tested in the next report period.

Activity Status as of January 1, 2018:

A new "plasma gas liquid" system was developed that used gaseous nitrogen plasma and liquid water to synthesize ammonia. The highlight of this system was an in-situ plasma gas liquid reaction using a spray-type plasma jet. This new system circumvented the use of hydrogen, which could greatly lower the capital cost and safety concerns of the process. This system was able to co-synthesize nitrate and nitrite in the liquid, which was more suitable for producing ammonia-based fertilizers. One of the largest limitations for the gas-gas plasma synthesis was the decomposition of ammonia. For this new system, the ammonia could be immediately absorbed in the liquid after being produced. The current 2-L plasma gas liquid ammonia production system was able to generate and 2.5 µmol·min-1, 15.1 µmol·min-1, 40.3 µmol·min-1, of ammonium, nitrate and nitrite, which outperformed the previous literature with an ex-situ system with a regular plasma generator.

Also, recent work resulted in a new publication. Quoting from the abstract:

> The non-thermal plasma (NTP) allows the synthesis of ammonia, one of the major hydrogen carriers, at a lower temperature and pressure than the traditional Haber-Bosch process. In this study, we report the synthesis of ammonia using NTP, and a Ru-based, multifunctional catalytic system deposited on mesoporous Si-MCM-41. Various surface characterization methods were used to analyze the catalyst. For the ammonia synthesis results, we determined that the synthesis efficiency increased in the high frequency zone (>20,000 Hz). The effects of different experimental parameters were studied and the highest ammonia synthesis efficiency achieved was 1.7 g/kWh at 5000 V and 26,000 Hz. Results were analyzed in the context of several synergetic effects including the plasma forming mechanism, discharge effects of the catalysts, plasma shielding effects of the mesoporous structure, and other plasma-catalyst interactions. Lastly, a new concept of a two-step non-thermal plasma ammonia synthesis method was also proposed.

{ International Journal of Hydrogen Energy, 42(30), 19056-19066, 2017.}

Activity Status as of July 1, 2018:
Two new papers have been published (see dissemination section). Progress highlights include:

- The new “plasma gas-liquid” system was developed and optimized in terms of temperature control, constant mixing, and gas/liquid sampling.
- UV irradiation was added to the “plasma gas-liquid” system. The irradiation energy could help excite the water, release more hydrogen and enhance the ammonium synthesis.
- The effects of various controlled parameters mentioned above were studied and analyzed.

The near-term objective is to keep optimizing the system with possible new reactor configurations and different plasma discharge options. For the "plasma gas-liquid" system, the ultimate goal is to develop an instant, on-demand nitrogen fixation, which will generate nitrogen-rich solutions either on-site or in the field for direct on-demand cropland application. At the same time, we will examine the possibility of improving the ammonia absorption system we previously developed in 2016, combining it with the plasma synthesis system we developed in 2017. We believe that this can help reduce the dissociation of ammonia (back-reaction) in the plasma region.

Activity Status as of January 1, 2019:

One new paper has been published (see dissemination section).
Progress highlights include:

- One recent literature showed MgO, beyond being a catalyst in N_2 and H_2 “plasma gas-gas system”, could form the important intermediate Mg_3N_2 to facilitate ammonia production. We explored and found that $MgCl_2$ has better performance of forming Mg_3N_2, and can absorb ammonia to reduce back reactions. This was a combination of the previously absorption system developed in 2016 and the gas phase synthesis system developed in 2017.
- We worked with the power supply manufacture of the “plasma gas-gas” system and make electrical enhancements and improved the plasma energy efficiency to produce ammonia.
- Nitrogen products from the “plasma gas-liquid” system was tested and used as the sole nitrogen fertilizer source for hydroponic vegetable growth.
- The “plasma gas-liquid” system was used to treat diluted anaerobic digestion wastewater and was tested for hydroponic vegetable growth to provide additional nitrogen source and disinfect microorganisms.
- The above two hydroponic growth systems showed better growth than untreated diluted anaerobic digestion wastewater, but not as good as the commercial hydroponic recipe.

Future Plans
We will keep working on improving both the plasma energy efficiency and total energy efficiency in both the “gas-liquid” and “gas-gas” systems.

For the "plasma gas-liquid" system, we are one step closer to the building an instant, on-demand, and on-site nitrogen fixation for cropland application, since it is proved that the fixed nitrogen products can be directly used for hydroponic fertilizers. The next step is to optimize the composition of and increase more nitrate and ammonium in the product mixture. We will do so by exploring the different reactor structures, possibly using our patented concentrated high intensity electric field (CHIEF) system to generate plasma inside the water.

Final Report Summary:

- As mentioned in previous progress reports, we explored a different reactor structure using our patented concentrated high intensity electric field (CHIEF) system to generate plasma inside the water, where the water could act as both reactant and sorbent for the synthesized nitrogen products.
- By generating nitrogen plasma inside the flowing water, we increased the nitrate concentration within the nitrogen products, from 26 mol% to 55 mol%.
- We explored the effects of various parameters ~~include~~ including input power, conductivity, etc. The above activities have led to a paper submitted to the Journal of Physics D: Applied Physics.
- We tested the continuous flowing hydroponic growth of vegetables with plasma-treated water, DI water + ammonium nitrate as nitrogen source, plasma treated wastewater, and wastewater. Compared with our tests in the previous report, now the system is operated with circulating water, and with a three-fold~~-~~ larger flow rate.
- The scaled-up and flowing hydroponic showed that plasma-fixed nitrogen can be utilized by lettuce, and can be used for producing on-demand nitrogen fertilizer.
- To conclude this project, we performed a thorough investigation on the plasma-related nitrogen fixation studies that emerged in the recent years (including our work), to identify possibilities to improve efficiency of generating sustainable nitrogen fertilizers for local industries and farms. This work has recently been published in ChemSusChem.

ACTIVITY 3: ***Integration, modeling, planning for various economic and policy scenarios***
Description: Research will be pursued at the Morris pilot plant facility analyzing ongoing dynamics and economics of the state-of-the-art existing pilot plant. This will inform modeling and economic research, better enabling judgment of implementation opportunities with the cutting-edge technologies of Activities 1 and 2. The information will be integrated into engineering modeling and economic analysis to help design optimal solutions responsive to a variety of business models and scenarios. Policy, economic, and business model options will be examined that affect the interaction of distributed ammonia producing sites with the electric grid, that relate to ammonia pollution that may affect distributed ammonia fertilizer production or create incentives for innovation in ammonia application methods, and that affect how distributed ammonia production may relate to distributed hydrogen production. (e.g., with increasing fertilizer value, fluctuating energy values, distance from infrastructure, policy incentives and regulations in place). This multidisciplinary technology will involve a wide variety of expertise.

Current efforts are focused on the pilot plant being operated as close as possible to “commercial” operation in order to obtain consistent data. The production data from the pilot plant will be inputted into the spreadsheet model to refine the economic evaluation. In the coming year we shall also study opportunities to improve conversion efficiencies at appropriate scale economies capable of utilizing stranded wind power in corn producing areas in smaller scale anhydrous ammonia production facilities. The use of absorbents to enhance the efficiency of catalysts is expected to favor development of smaller scale ammonia production facilities. At this time, there seems to be interest in building smaller scale, and more widely distributed anhydrous ammonia facilities in the U.S., in part encouraged by the lower prices of natural gas.

Activities under this track with the LCCMR project will focus on systems level analysis and evaluation of the different technologies. The goal is to optimize the different designs, explore possible synergies between them, and determine the economic and policy environment that will enable the proposed distribute production paradigm to be successful.

Task 1: Process simulation, design and optimization
We will develop first principles process models for the different production technologies, which will be used to determine optimal operating conditions to minimize the cost of production of ammonia, minimize the amount of byproducts (and hence, the environmental impact), and maximize energy efficiency. For the

absorbent-enhanced ammonia synthesis, we will evaluate the range of temperatures and pressures that will allow on one hand sufficiently high conversion, but also low energy requirements. We will also evaluate the performance of alternative absorbent materials. These tasks are too expensive and time consuming to determine experimentally, but can be performed easily through modeling and simulation. Similarly, for the non-thermal plasma-based process, we will examine the interplay between the energy requirements of the plasma reactor and its performance. Close interaction with the experimental effort will allow obtaining the necessary data for model validation in these efforts. Simulation studies will also allow us to address process modifications to overcome performance bottlenecks, as well as scale up issues.

Task 2: Advanced use of pilot plant operation and analysis

The WCROC pilot plant will be operated in a series of test runs to determine optimized operating conditions. The test runs will mimic scenarios developed through the techno-economic modeling studies. Operating pressures, temperatures, molar ratios, and other process variables will be refined to determine the optimal technical and economic parameters. Inputs such as hydrogen, nitrogen, and water will be determined and the resulting anhydrous ammonia output will be measured. To achieve optimum performance, power units within the hydrogen production system will be refurbished and tested prior to the test runs. An enhanced Supervisory Control and Data Acquisition System (SCADA) will replace the current software and hardware to allow safe and efficient test runs. Software will be added to a data historian to store key information during the test runs. Data from the pilot plant and the wind turbine are essential for use in evaluating policy, economic, and business model scenarios.

Task 3: Enterprise-level analysis and evaluation: impact of economic and policy considerations

The proposed research promotes a new paradigm of distributed production of fertilizers with reduced environmental impact. Successful deployment of such facilities will depend both on the technical feasibility of the underlying technologies (addressed in the previous tasks), but also on the broader economic, business and policy environment. Some of the questions that we will address in this task are:

a. What is the optimal scale-down strategy to optimize the overall, industry-level performance at a regional scale? In other words, what is the optimal capacity, location and technology of choice for these distributed facilities that will optimize the overall supply chain?
b. What is the optimal way to integrate these distributed facilities in the current fertilizer production infrastructure? One could envision that even if conventional fertilizer supplies are still used, such facilities can provide important flexibility and resilience in mitigating price increases or demand peaks. What is the business opportunity in this context?
c. How can the tradeoffs between cost and environmental impact be assessed in a broader policy context?

Summary Budget Information for Activity 3: **ENRTF Budget: $398,117**
Amount Spent: $392,958
Balance: $ 5,159

Outcomes	**Completion Date**
1. Conduct techno-economic evaluation, policy analysis, and feasibility assessment of the current Morris pilot plant	July 1, 2016
2. Economics-of-scale analysis showing the Morris pilot plant conventional technology at a range of scales, up to county-level	July 1, 2016
3. Preliminary modeling and optimization of absorbent-enhanced ammonia synthesis	July 1, 2017
4. Estimated demand for renewable low-carbon ammonia for organic and advanced biofuel production in Minnesota and the Upper Midwest	January 1, 2017
5. Policy discussion of statewide implementation of revenue-neutral carbon tax applied to fossil-energy-derived ammonia, incentivizing renewable low-carbon ammonia	July 1, 2018
6. Complete first phase of pilot plant test runs	January 1, 2019

7. Techno-economic analysis and feasibility assessment of novel technology - absorbent-enhanced ammonia synthesis	January 1, 2019
8. Techno-economic analysis of distributed ammonia production in Minnesota using multiple technologies	July 1, 2019
9. Revision of capital cost of Morris-technology units (at various scales) using absorbent-enhanced synthesis (reducing capital cost)	July 1, 2019
10. Formulate a development and commercialization strategy: Investigation of interest of venture capitalists and coops in renewable fertilizer in Minnesota; Report opinions of coop bankers for financing multiple distributed ammonia production units; Report opinions of international parties interested in this MN-based technology around the world.	July 1, 2019
11. Economic analysis of distributed ammonia production in Minnesota using alternative hydrogen and power sources (cf. those used in Morris)	July 1, 2019

Activity Status as of January 1, 2016:

Advanced use of pilot plant operation and analysis

Since the initiation of the project on July 1st, staff at the WCROC have been preparing for a series of test runs to determine optimized operating conditions. In order to achieve optimum performance within the hydrogen production system, power units have been refurbished and are being tested under production scenarios. In addition, a bid has been accepted from Matrix to enhance the Supervisory Control and Data Acquisition System (SCADA). The bid includes replacing the current software and hardware to allow safe and efficient test runs. Software will be added to a data historian to store key information during the test runs. These upgrades will be performed in early 2016. Also, other key maintenance (University-funded) has been performed this past Fall on compressors and other pilot plant components in preparation for the test runs.

Analysis of the data available to-date provides a benchmark for the performance of the current small-scale ammonia synthesis pilot plant in Morris, powered by wind energy (but with otherwise conventional Haber-Bosch technology). The wind energy drives the pressure swing absorption of air to make nitrogen and the electrolysis of water to make hydrogen; these are combined in the small-scale continuous Haber process to synthesize ammonia. Analysis of steady state runs achieved this year at the pilot plant shows a rate controlled by three resistances: catalytic reaction, ammonia separation by condensation, and unreacted gas being recycled. Measured catalytic reaction rates in the pilot plant are consistent with separate experiments of chemical kinetics and with published reaction mechanisms. The ammonia condensation rates predicted are comparable with literature correlations. These rate constants successfully predict the measured production rate in the plant; more importantly, they will allow us to assess potential improvements in efficiency with the current technology, and prospects for improvements with the new technologies of Activities 1 and 2.

Techno-economic analysis and ammonia supply chain research

Initial effort has focused on i) techno-economic analysis of the Morris plant, with the goal of developing production cost estimates, and ii) developing a supply chain model for introducing distributed ammonia production in Minnesota. The current research in the Daoutidis group adds detailed analysis to previous work done by Tiffany and Reese addressing production economics, transportation and greenhouse gas reduction. Policy drivers like future carbon taxes and the volatility of costs of ammonia, renewable ammonia plant costs, and transportation costs are now entering the analysis. The analytical framework developed should prove useful for further analysis as the research team advances efforts to enhance catalyst efficiency and reduce capital cost of renewable ammonia production facilities.

Activity Status as of July 1, 2016:

- The recent study published by the Daoutidis group offers additional insight, extending earlier techno-economic modeling and scale-up analysis of the pilot facility at the WCROC-Morris by Tiffany and Reese. They analyzed numerous Midwest locations for renewable ammonia production using wind with the objective of minimizing costs of production and transportation from plant locations to sites of crop production. They considered how distributed renewable ammonia production would compete with existing production capacity in the Midwest (ND, IA, and KS) as well as Gulf Coast and Oklahoma production sites. Using optimization algorithms they were able to compare and select from numerous production possibilities. They learned for instance that under base case assumptions a single new renewable plant could be built to supply 27% of Minnesota ammonia that would be optimally located at Dexter, MN, with favorable proximity to substantial developed wind resources.

- When considering the sensitivity of their solution to a potential carbon tax as low as $35 per metric ton, the optimized solution would drive the establishment of three renewable plants. With a carbon tax of $55 per metric ton, the optimized solution has the greatest impact on the solution of overall regional carbon emissions. The implication of this sensitivity study is that policy efforts can make a huge difference in improving the competitiveness of renewable ammonia plants.
- Despite much lower natural gas prices and low crop prices, the market prices for anhydrous ammonia and the other forms of fertilizer using this source of nitrogen have remained quite high.
- A new aspect of Activity 3 investigations involves consideration of new constraints and motives presented by the work of colleague Will Northrup in Mechanical Engineering, in his exploration of adding anhydrous ammonia to diesel fuel in combustion.
- Analysis of the operation of the existing plant in Morris uncovered the operational importance of preferred molar ratios of nitrogen and hydrogen in the synthesis process. The pilot plant long-term production data of the summer of 2014 continue to be scrutinized with the aid of improved instrumentation and interpretation.

Activity Status as of January 1, 2017:

Activity 3 progress has been aided with leveraged investment by the University of Minnesota MNDrive program.

A key outcome was attained (in conjunction with Activity 1) with the benchmark analysis of some of our key pilot plant runs, resulting in the publication “Performance of a Small-Scale Haber Process” (Reese et al., Ind. Eng. Chem. Res. 2016, 55 (13), 3742). Quoting from the abstract of that paper: “This work identifies a benchmark for the performance of a small-scale ammonia synthesis plant powered by wind energy. The energy used is stranded, far from urban centers but near locations of fertilizer demand. The wind energy drives the pressure swing absorption of air to make nitrogen and the electrolysis of water to make hydrogen. These are combined in the small-scale continuous Haber process to synthesize ammonia. The analysis of runs of the small plant presented in this article permits an assessment of how the current production rate is controlled by three resistances: catalytic reaction, ammonia separation by condensation, and recycling of unreacted gas. The measured catalytic reaction rates are consistent with separate experiments on chemical kinetics and with published reaction mechanisms. The condensation rates predicted are comparable with literature correlations. These rate constants now supply a rigorous strategy for optimizing this scaled-down, distributed ammonia plant. Moreover, this method of analysis is recommended for future small-scale, distributed manufacturing plants.”

Further pilot plant runs are necessary to complete our techno-economic analysis, but we have made some progress toward that outcome. From Doug Tiffany:

- On July 11, 2016 Stephen Rose, Research Scientist of Humphrey School of Public Affairs met with Ed Cussler, Alon McCormick and Doug Tiffany. The goal of the meeting was to discuss temporal price data of electricity across the Midwest Independent System Operator (MISO)) region in order to gain an understanding of opportunities to operate small scale, distributed ammonia plants. Stephen Rose reported on his access and work to study the MISO data with respect to some work he was doing in the Humphrey Institute. Dr. Cussler had a number of questions about costs of wind energy, so Doug Tiffany made a presentation based on previous wind energy research he had conducted. This may initiate a new collaboration and possible publication in the future.

- Additional economic analysis was conducted by Doug Tiffany in August to segregate the ammonia production into three separate businesses: hydrogen production, nitrogen production, and ammonia synthesis. This analysis was based upon the capital costs and operation of the pilot plant standing at WCROC-Morris and offers insight into the production costs, and energy usage of each of these three key stages of ammonia production. These conclusions were reported to Dr. Cussler for a paper he was writing and the rest of the research team. Having segregated enterprises should be very helpful when analyzing technologies that increase efficiency of catalysts in the ammonia production process. The team is discussing these issues with Doug Tiffany to see if Institute on the Environment seminar might be constructed, possibly leading to publication.
- In December 2016 at our team meeting we laid the groundwork for the first technology symposium, now planned to be convened by Steve Kelley with the collaboration of the UMN Office of Technology Commercialization in Spring 2017.

From the Daoutidis group's techno-economic analysis of the current technology and market situation in the Upper Midwest:

- Further analysis of the ammonia supply chain showed that hydrogen production, with its high energy cost and current inability to provide the same economies of scale as the other units, will provide one of the largest barriers for scaling up the current pilot ammonia plant. Overall, we found that for the current type of plant to be economically competitive with conventional ammonia at a scale of 10,000 t/y (one plant providing ammonia for about an entire MN county), one of the following would need to occur: ammonia costs of $1414/t, a carbon tax of $408/t, or a reduction in capital cost of 55% (e.g., such as might be achieved with advanced technology such as absorbent-integration). When the plant becomes larger scale, these numbers become significantly less prohibitive: a 100,000 t/y plant requires ammonia costs of $860/t, a carbon tax of $64/t, or a 22% reduction of capital costs.
- A comparative study between the ammonia supply chains of Minnesota and Iowa showed that, because of its larger wind potential and larger ammonia demand, renewable plants are closer to being economical in Iowa than in Minnesota. This is purely an argument of scale: Iowa has larger existing wind farms which allowed for larger renewable ammonia plants in the analysis. A study of the operation of renewable ammonia plants in different power markets showed that renewable ammonia plants can be effectively regulated to provide grid friendly operation (~~i.e~~i.e. reduced short term load variability with day ahead power exchange commitments) for a small (~1%) increase in operating costs.
- We also showed that by optimally scheduling plant set points, the renewable ammonia system can leverage its flexibility to take advantage of temporal changes in electricity prices. This framework further allowed for the analysis of plant operating cost as a function of various unit capacities, which will allow us to further refine our supply chain optimization by varying the exact configuration of unit sizes (such as electrolyzers installed and wind capacity vs. ammonia capacity).

Activity Status as of July 1, 2017:

Activity 3 progress has been aided with leveraged investment by the University of Minnesota MNDrive program.

Reese and coworkers:

Significant progress has been made in the operation of the WCROC pilot plant in a series of test runs to determine optimized operating conditions. The test runs mimic scenarios developed through the techno-economic modeling studies. The first phase of pilot plant testing has been completed and data is being analyzed. The research protocol was designed to evaluate the effect of varying the molar ratio of the hydrogen and nitrogen supplied to the ammonia production skid. The intent is to find optimum operating parameters as a bench mark for testing new production technologies. Initial energy consumption results from baseline testing of the pilot plant have shown that approximately 10.3 kWh of electricity are consumed to produce 1 lb. of anhydrous ammonia and, of this total, 61% is attributed to hydrogen production, 9% to nitrogen production, and 30% to the ammonia production process. Economic analysis is also in progress using the molar ratio test run data set.

Daoutidis and coworkers:

- We have further developed our algorithm for optimally scheduling renewable ammonia plant set points and obtained results that highlight the importance of operating the plant intermittently (i.e. changing production levels over time instead of maintaining a single constant production level). Our preliminary results indicate that using scheduling to take advantage of the inherent storage and flexibility within the ammonia system can reduce operating costs by 2% when power costs are constant. Savings become much more significant when considering time-varying power costs, as this value increases to 27%.
- Furthermore, we established that the variability over time of the amount of power purchased from the grid can be reduced, thus mitigating stress on the power grid, by considering a novel market structure which requires day-ahead power exchange commitments and imposes penalties for violating these commitments. Results showed that the variability of the power purchased can be reduced by 50% for a less than 1% increase in operating costs. This is significantly less than the cost increases found in studies of other systems where this market structure was applied, again due to the inherent flexibility in the ammonia system.
- We have applied our scheduling algorithm to different locations with different hourly wind speeds obtained from the National Renewable Energy Laboratory database. We have found that location has a strong effect on operating cost, with costs varying as much as 35% for the same plant design at different locations. We have identified that this cost difference is strongly correlated with the capacity factor (i.e. the fraction of installed wind power that is actually generated over the course of the year) at each location. We have used the capacity factor to collapse operating costs for different locations, installed wind capacities, and installed ammonia capacities onto a single plot with very good correlation. We intend to use these results to refine our supply chain optimization in the near future.

Tiffany and collaborators:

Production log data from the West Central Research and Outreach Center-Morris pilot ammonia was sent to Doug Tiffany in mid-May for further analysis of energy usage for each of the production steps during production cycles with alternative molar ratios of hydrogen to nitrogen. The installed instrumentation has been improved since earlier productions runs in 2014 and 2015. The data has more resolution than in the past and is now summarized by minutes of the day and for various production cycles of two or more hours. In some cases higher energy requirements were observed than recorded in earlier production runs. The analysis of this data continues; LCCMR specifically supports analysis of the optimum feed ratio.

Kelley and collaborators:

The project team made progress on the commercialization front through hosting a technology forum on February 22, 2017. A facilitated discussion after presentations by the project team members led to insights about the economic and technological issues facing the technology. Among other questions, the discussion pointed to consideration of a production subsidy as a policy alternative to be considered. This is further described in the Dissemination section. Moreover, with leveraging support, Kelley is also addressing safety policy issues.

Activity Status as of January 1, 2018:

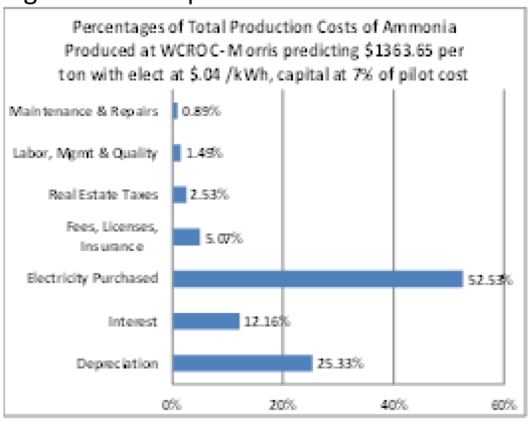
Activity 3 progress has been aided with leveraged investment by the University of Minnesota MNDrive program.

Reese and coworkers

Activities at the pilot plant during this period centered on troubleshooting a faulty electric heater necessary for ammonia production. A research trial to determine optimum pressure parameters was in progress when the electric heater began to fail. Efforts were made to repair the heater but eventually testing revealed the failure required the design, procurement, and installation of a new heater. The heater is currently being fabricated and is expected to be installed at the WCROC Renewable Hydrogen and Ammonia Pilot in mid-February.

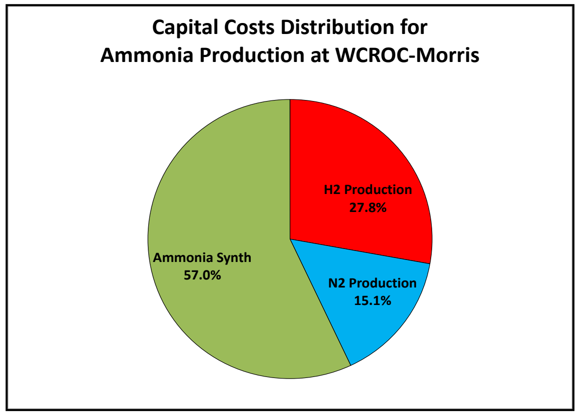
During this period, production data from previous pilot plant test runs was used to refine an economic analysis. Initial economic results are shown in Figures 1 through 4 (part of a poster presentation at the NH3 Fuel Conference and AIChE meeting, November 2017).

Figure 1. Total production costs



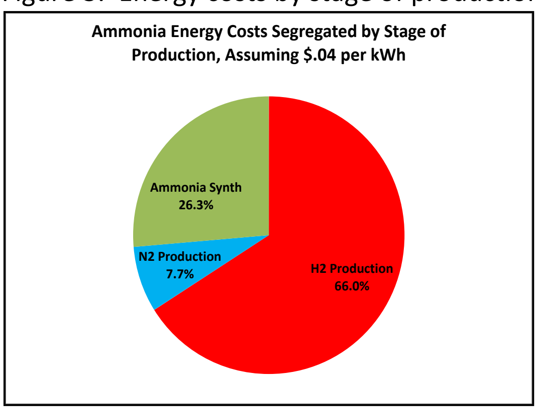
Tiffany, Reese, & Marquart (2017)

Figure 2. Capital cost distribution



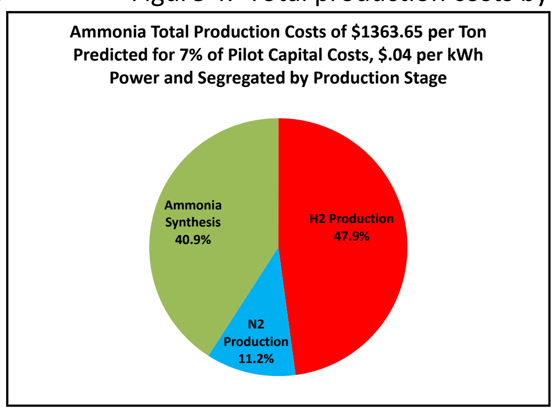
Tiffany, Reese, & Marquart (2017)

Figure 3. Energy costs by stage of production



Tiffany, Reese, & Marquart (2017)

Figure 4. Total production costs by stage of production



Tiffany, Reese, & Marquart (2017)

The total cost of producing ammonia using wind energy within the pilot plant was estimated at $1,363.65 per ton of ammonia. Even though more expensive than conventional ammonia prices, this result is promising for these reasons:

1. The pilot plant is not optimized and future plants will most likely be optimized, larger, and more efficient.
2. As a baseline, the cost of production is in a range in which technology improvements can possibly make ammonia production from wind energy cost competitive.
3. The ammonia produced is near carbon-zero.

<u>Daoutidis and coworkers</u>

- Our recent efforts have been to use our optimal scheduling algorithm on hypothetical renewable ammonia plants of various sizes and at various locations in order to determine key design parameters impacting operating cost.

- Our analysis determined that the “effective” wind to ammonia ratio; that is, the size of installed wind turbines multiplied by a location-dependent capacity factor (the percent of possible wind power that is actually being produced) divided by the size of the installed ammonia plant has the best correlation with operating cost.
- Our analysis also determined that a lack of hydrogen or nitrogen production ability will add to the operating cost, but diminishing returns are seen as more production ability is added. Hydrogen production has a greater effect on the cost than nitrogen production.
- We developed simple correlations between operating cost and design parameters which allow us to easily implement these results into longer term planning decisions and, for example, analyze the tradeoffs between capital and operating costs.

Also, new paper has been published based on previous work; quoting from the abstract:

> Ammonia is a critical chemical to fertilize plants and feed the world. Recently, a first of its kind renewable ammonia plant has been built in Morris, MN, powered by wind energy. A broader deployment of such renewable plants will require careful selection of location and unit sizing to keep costs low and optimize the entire ammonia supply chain. In this paper, a 48-h receding horizon optimization problem is developed to optimally schedule unit set points for the system in order to minimize annual operating costs. This optimization formulation is then used to examine how the optimal operating cost depends on the key design parameters of location and unit size. Using the results obtained, simple correlations are developed which capture the dependence of operating costs on ratios of unit capacities, properly scaled to remove the dependence on location.
> {Chem. Eng. Res. Des. (2017), https://doi.org/10.1016/j.cherd.2017.10.010}

Tiffany

Additional production runs were completed with the pilot plant equipment at WCROC-Morris in October and November of 2016 to measure usage of electrical power at the key production stages of hydrogen production, nitrogen production, and ammonia synthesis. While production trials were completed in previous years, there is an ongoing need to validate the metrics of production at various production settings. Trials completed in 2016 were conducted with improved instrumentation called E-gauge and with data loggers. The protocol was to operate the pilot plant twenty-four hours a day to test durability of equipment and stability of the reactions under conditions approaching industrial situations. Eleven days of continuous operations occurred from October 10 through October 20 as well as nine days from October 27 through November 4.

Trials of the past revealed that molar ratios, the proportion of hydrogen molecules matched to nitrogen molecules are an importance parameter in reducing energy requirements at the ammonia synthesis stage. Chemical stoichiometry suggests that three moles of hydrogen are needed react with one mole of nitrogen in ammonia production. Molar ratios of 3.15, 3.2, 3.3, 3.45, 3.6 and 3.75 were tested in production trials, in all cases overloading hydrogen. Analysis of the production trials revealed that the molar ration of 3.45 to 1 resulted in substantially lower amounts of energy required per unit of ammonia produced.

Data collection using E-gauge has caused the research team to revise their thinking about the amount of energy used in each of the three stages of production. Significantly higher electrical energy requirements were recorded for each of the three stages of production.

Importance and Impact

Across the literature of ammonia production, the findings presented from this study at WCROC-Morris are among the few available to the public. This is an example of basic research being conducted on this grant that supports the efforts of researchers worldwide to go forward and try to refine the process and improve the economics of production of ammonia.

The higher energy usage figures were incorporated into the techno-economic analysis and resulted in modeled costs of production that rose from $941.38 per ton of anhydrous ammonia to $1363.65 when using electricity costing $.04 per kWh and capital costs based on a plant scaled up to commercial size, costing 7% of the cost of the pilot plant per ton of ammonia capacity. This finding makes greater the need to reduce capital costs in order to lower costs of production. The efforts to utilize absorbent technologies to improve catalyst efficiency, reduce or eliminate the need for recycle of unreacted gases and reduce capital costs are even more important.

Activity Status as of July 1, 2018:

Reese and coworkers:
Work at the WCROC Wind-to-Ammonia facility has been leveraged with the new Department of Energy effort. We are preparing the facility to connect to and run tests on a new prototype absorbent-enhanced reaction system (described in Activity 1). The operation of the existing skid required installation of a new heater – this has been commissioned and tested, and operation is back up to normal capacity.

Daoutidis and coworkers:
We have recently submitted a paper to the AIChE Journal entitled: "Scheduling-informed optimal design of systems with time-varying operation: A wind-powered case study". In this paper, we develop a decision-making tool that determines the optimal sizes of an ammonia reactor, hydrogen and nitrogen storage tanks, and a battery in a system that produces renewable ammonia, given available wind capacity, power load data, and ammonia demand. We use optimal scheduling, a method that allows us to make decisions about how to operate such a system, to develop correlations with design variables that help inform our design optimization problem. Such a tool could be important to farmers and coops that are potentially interested in building a renewable ammonia system as it would allow them to build a system that gives them the highest potential for profit.

Tiffany:

Doug Tiffany presented a seminar February 20, 2018 at Massey University in New Zealand. It was a multi-departmental seminar including thirteen faculty and graduate students, including soil scientists, agronomists, forage experts and chemical engineers. Doug described our University of Minnesota project to produce renewable anhydrous ammonia using wind energy and water. He reports that the audience had strong interest in our project and were complimentary of our efforts because New Zealand farmers face higher cost inputs for fertilizer and fuel. New Zealand agricultural producers are more advanced than those of the U.S. in calculating the carbon footprint of their agricultural production, which is heavily focused on value-added production, export markets, and sustainability. Doug predicts we shall have New Zealand visitors coming to West Central Research and Outreach Center-Morris in the future to see the operation of our U of M pilot plant. Doug notes that New Zealand would be an excellent place to produce renewable ammonia because it has limited natural gas to make ammonia and 80% renewable electricity from hydro and wind on their grid. New Zealand producers are eager to produce low carbon milk, milk products, meat and other food and agricultural exports for foreign markets seeking low carbon goods.

Kelley leading:

On the afternoon of June 11, 2018, Steve Kelley convened a Policy discussion on statewide implementation of revenue-neutral carbon tax applied to fossil-energy-derived ammonia, incentivizing renewable low-carbon ammonia. The meeting was held at the Learning and Environment Center on the St. Paul Campus. In attendance were key investigators on the LCCMR grant projects involving production of renewable ammonia as well as statewide leaders of organizations interested in supporting biofuels, renewable energy and low carbon agricultural production. Presentations were made by: Ed Cussler (CEMS), Douglas Tiffany (Biosystems), Andrew Allman (graduate student with Prodromos Daoutidis, CEMS), Michael Reese (WCROC-Morris), and Steve Kelley (Humphrey School of Public Affairs). Among the invited guests were staff members of the Minnesota Department of Agriculture, Minnesota Corn Producers, Fresh Energy, the Minnesota Farmers Union and the

Minnesota Farm Bureau. Following the presentations, Kelley facilitated a discussion of the policy implications of the engineering and economic research. The role of state incentive payments in the establishment of the ethanol industry and for bio-based material production in Minnesota and the possibility of incentives for renewable ammonia production were discussed. The discussion identified some additional research questions. Participants also agreed that it was useful to be aware of the progress of the research and pilot projects and were interested in additional discussion as development of the technology for distributed production of renewable ammonia moves forward.

Activity Status as of January 1, 2019:

Daoutidis
(Relevant to Activity 3 Outcome 7)
We have recently submitted three papers, two of which have been accepted, that have made progress towards the goals of ENRTF/LCCMR Activity 3 (some work also supported by the leveraging project with ARPA-E).
The first, in chronological order, has been accepted by *Processes* and is entitled: "Modeling and optimal design of absorbent enhanced ammonia synthesis". In this paper, we develop a mathematical model for the absorbent-enhanced ammonia synthesis process. We also develop a mathematical optimization framework which is used to minimize the net present cost of installing and operating the process by deciding the best unit designs and process operating conditions. This framework is easily adaptable to any ammonia production scale and any feedstock or utility costs. In this paper, the optimal design framework was used to minimize the net present cost of the process at ammonia production scales of 800 to 80,000 t/y under the assumption that stranded wind energy, valued at $0.03/kWh, is available to power the process. A capital cost correlation was then fit to the capital cost results at these different scales. This correlation can be used for economic feasibility studies of small-scale, wind-powered ammonia production using this new process. It is also used in the subsequent works reported herein.

The second paper, accepted by *Industrial and Engineering Chemistry Research*, is entitled: "Exploring the benefits of modular renewable-powered ammonia production: A supply chain optimization study". In this paper, we develop a supply chain optimization framework which can be used to determine the optimal location and scale of renewable-powered, absorbent enhanced ammonia production. We simultaneously consider the possibility of modular manufacture of these processes and incorporate this into our optimization model. This construction approach can be advantageous for the distributed ammonia production paradigm envisioned by ENRTF/LCCMR because cost savings are achieved simply the manufacture of a higher number of fixed-sized ammonia production units, even when these units are not located in the same geographic location. In this paper, we perform optimization-based economic feasibility studies for ammonia supply in Minnesota and Iowa over a range of conventional ammonia prices. We consider both continuously-sized and modular installation options. We determined that (i) the absorbent enhanced process is installed at lower conventional prices of ammonia than the scaled-down conventional production technology and (ii) modular manufacturing provides further economic benefit as compared to its continuous counterpart. This supply chain optimization tool could also be used to investigate the economic effects of state-wide or regional policy such as a carbon tax or renewable production incentive.

The third paper, submitted to *Chemical Engineering Processing: Process Intensification*, is entitled: "A novel system for ammonia-based sustainable energy and agriculture: Concept and design optimization". In this paper, we propose a novel conceptual design for a farm-scale system which uses renewable energy to (i) to produce ammonia both as fertilizer and as fuel for tractors and grain drying, (ii) to meet local electrical power demand and (iii) to provide predictable, consistent power export to the grid. The collocation of agriculture and energy systems exploits synergies to allow for economic viability, specifically time-varying chemical production as well as the potential of ammonia (via gensets) and hydrogen (via fuel cells) as energy storage media. We also develop a model for integrated optimization of the design and operation of the sustainable energy and agriculture system. This optimization tool minimizes the annual net present cost of the system by determining the optimal selection and size of units (e.g. electrolysis, ammonia synthesis, chemical storage, fuel cells, etc…) from a list of candidates as well as the optimal production rates and chemical storage inventories for each hour of an operating horizon which is chosen to account for both the short- and long-term variability of renewable energy. We also perform a case study on the implementation of this sustainable energy and agriculture system using real-world data from the West Central Research and Outreach Center (WCROC) in Morris, MN. The annual net present cost is approximately $60,000, which corresponds to an emissions reduction cost of $13.80/tonCO2. The ABSEA optimal design uses both hydrogen and ammonia, but not a battery, for energy storage, illustrating their efficacy in this synergistic application. This work demonstrates the conceptual initial promise of farm-scale ammonia and energy production, and the above-described optimization model can easily be adapted to demand different scenarios or to include more and different candidate process units.

<u>WCROC</u>

(Relevant to Activity 3 Outcome 6)
A third replication was run with varying pressures on the U of MN Wind to Ammonia Pilot Plant. During this trial which took place from August through October 2018, the ammonia skid was operated at a range of pressures to determine baseline production rates. Data is being analyzed and will be included in the final report.

Final Report Summary:

<u>Daoutidis and coworkers:</u>

Relevant to Activity 3, Outcome 8: We revised our paper to submitted *Chemical Engineering Processing: Process Intensification* entitled "A novel system for ammonia-based sustainable energy and agriculture: Concept and design optimization. This paper has now been accepted and is published (see the dissemination section). A key result reported in the revised and published version of this paper is quantification of the benefits of afforded by collocating agriculture and energy systems. We considered two "less integrated" scenarios: (i) steady-state chemical production, and (ii) batteries only for energy storage. In these scenarios, the net present cost of the system was 755% and 1990% higher respectively. This demonstrates the necessity of integrated solutions for small-scale, distributed ammonia production as well as the quantitative decision-making capabilities to design and operate these integrated systems.

Relevant to Activity 3, Outcome 9: We are continuously revising our capital cost estimates for the absorbent enhanced ammonia production process by (i) leveraging feedback from both ARPA-E project managers and information from potential industrial collaborators about improvement of process configurations and (ii) incorporating new results from absorbent experiments. We are also developing a model of a conventional (condenser-based) ammonia production process which will be used to allow for a consistent comparison between the two processes. We will use optimization capabilities to minimize net present cost (capital and operating costs) over a range of production scales and a variety of scenarios for electricity availability and policy.

Relevant to Activity 3, Outcome 11: We have expanded the concept and model of a sustainable agriculture-energy system originally proposed in the *Chemical Engineering Processing: Process Intensification* to include potential utilization of biomass to generate additional hydrogen or electrical power. We performed a case study for the West Central Research and Outreach Center (WCROC) where corncobs were used to supplement wind power. Biomass-fed gensets and small-scale biomass-to-hydrogen based on gasification were included as candidate technologies. The utilization of biomass reduced the net present cost of the system by $18,500 (25% or $4.70/tonCO2 avoided). All biomass was used for power generation, possibly due to the current high cost of small-scale biomass-to-hydrogen technologies. This shows the complementary nature of wind and biomass, which are both inherently present in a Minnesota agricultural setting. This modeling and optimization case study was published under the title "Concept and Design Optimization of a Novel Ammonia-Based System for Food-Energy-Water Sustainability" in the Proceedings of the 9th International Conference on Computer-Aided Process Design, a world-class systems engineering research conference which occurs once every five years.

Reese and coworkers:

(Relevant to Activity 3 Outcome 6)
A third replication was run with varying pressures on the U of MN Wind to Ammonia Pilot Plant. During this trial which took place from August through October 2018, the ammonia skid was operated at a range of pressures to determine baseline production rates. For optimum ammonia production rates and energy consumption in the U of MN Wind-to-Ammonia Pilot Plant, results indicate the ideal operating pressure is between 1300 and 1500 PSI of H_2. Under the current configuration, it was not possible to test higher pressures. Higher pressures were anticipated to yield better results. However, the highest pressure treatment (1500 PSI H_2) resulted in slightly higher numerical energy consumption values than the next lowest pressure treatment (1400 PSI H_2). This may be attributed to the difference in ambient temperature conditions during the test as well as other experimental error. The results also indicates that hydrogen production is the greatest energy consumer at an average of 64.4%, nitrogen production is the lowest at 8.2%, and the electrical energy consumption required to operate the ammonia production skid is 27.3% of the total. These results indicate that there is some improvement to be made within the ammonia production skid. However, most of the energy consumption is a result of hydrogen production which is not addressed in this research project. The project team has subsequently participated in research with the world's largest hydrogen electrolyzer manufacturing company, Nel dba Proton On-site to study possible methods in which to lower the cost of hydrogen production.

Table 1. Impact of operating pressure on ammonia production and energy consumption

H_2 and N_2 Pressure (PSI)[1]	NH_3 Production Rate (lb/hr)	H_2 Production kWh/h	N_2 Production kWh/h	NH_3 Production kWh/h	Total Plant kWh/h	Total kWh / lb of NH_3
1500/1400	8.60	48.68	6.70	21.40	80.38	9.35
1400/1300	8.48	48.67	6.22	21.04	78.68	9.27
1300/1200	8.37	52.60	6.12	21.45	82.70	9.88
1200/1100	7.98	51.72	6.51	20.79	81.94	10.26
1100/1000	7.22	46.81	6.16	20.70	76.85	10.65

[1] The molar ratio was set at 3.2 moles of hydrogen to 1.0 moles of nitrogen. Differential pressure was required to provide adequate hydrogen into the system.

(Relevant to Activity 3 Outcome 10)

Recent efforts are guided in part by a key stakeholders meeting last Summer. An agricultural-related ammonia production meeting was held on June 11, 2018 from 3:00 to 4:30 pm at the Learning and Environment Center on the St. Paul Campus. In attendance were key investigators on the LCCMR grant projects involving production of renewable ammonia as well as statewide leaders of organizations interested in supporting biofuels, renewable energy and low carbon agricultural production. Presentations were made by: Dr. Cussler (CEMS), Douglas Tiffany (Biosystems), Andrew Allman (CEMS), Michael Reese (WCROC-Morris), Steve Kelley (then, Humphrey School of Public Affairs). Among the invited guests were staff members of the Minnesota Department of Agriculture, Minnesota Corn Producers, Fresh Energy, the Minnesota Farmers Union and the Minnesota Farm Bureau. Following the presentations, Mr. Kelley facilitated a discussion of the policy implications of the engineering and economic research. The role of state incentive payments in the establishment of the ethanol industry and for bio-based material production in Minnesota and the possibility of incentives for renewable ammonia production were discussed. The discussion identified some additional research questions. Participants also agreed that it was useful to be aware of the progress of the research and pilot projects and were interested in additional discussion as development of the technology for distributed production of renewable moved forward. One of the key comments came from Gary Wertish, President, Minnesota Farmers Union. He indicated that the *next step should be the establishment of a large-scale pilot plant that could deploy the best technologies available in an optimized and integrated package*. This type of pilot plant would give farmers and cooperatives the confidence needed to pursue similar businesses across the state. On a related note, the US Department of Energy ARPA-E REFUEL program is developing plans for a potential large-scale ammonia production facility using wind energy. The target scale has been tentatively identified as 1000 kg per day which will be consist with the annual consumption of many agricultural input cooperatives across the state. Our team hopes to leverage the results from this LCCMR funded project to be competitive in soliciting this new pilot plant for Minnesota. As for business interests in this technology, we have maintained a spreadsheet detailing contacts and interviews with multiple state, national, and international companies and their interest in the ammonia production technologies.

ACTIVITY 4: *Exploring the capture of ammonia with hydrochar for time-release field application*
Description: The third technology will explore a cutting-edge use of hydrochar, a material derived from biomass that acts as a soil amendment, to facilitate time-release field distribution of ammonia. The technology for production of this material has been developed so far by Prof. Ken Valentas in the University of Minnesota Biotechnology Institute, and he will be exploring its use in agriculture with separate support. As we near deployment of new local ammonia production, and as he establishes more knowledge of the behavior of hydrochar, we will partner to explore how much it can further enhance the viability of local ammonia production and distribution and impart time-release capabilities. Hydrochar is a porous carbonaceous material from the hydrothermal carbonization of biomass (which can be food processing waste, fermenter residue, manure, etc.) This material promises to provide superior economics and soil amendment properties. We will be able to help assess the potential for holding ammonia for targeted, low-runoff, time-release delivery to fields. We judge that we can evaluate this alternative using one graduate student for a six-month period after the Valentas team has further developed and characterized the performance of these materials.

Summary Budget Information for Activity 4: **ENRTF Budget: $ 0**
(partnership with Valentas project)

Amount Spent: $ 0
Balance: $ 0

Outcome	Completion Date
1. Ammonia sorption characteristics on hydrochar	July 1, 2017
2. Ammonia release characteristics with hydrochar	July 1, 2018

Activity Status as of January 1, 2016:
Prof. Valentas has participated in research review meetings, updating us about his progress with hydrochar research. We are beginning discussions to formulate details of an experimental plan to explore how hydrochar materials may further enhance the viability of local ammonia production and possibly impart time-release capabilities.

Activity Status as of July 1, 2016:

Valentas' group has begun to set up experiments (co-located in the lab with Activity 1 work, to better enable collaboration and shared resources). They will measure ammonia absorption both with a hydrochar that has been post-treated with nitric acid and also with a hydrochar that serves as a composite matrix for absorbent magnesium chloride.

Activity Status as of January 1, 2017:
Progress toward measuring ammonia sorption characteristics continues.

Activity Status as of July 1, 2017:
The performance of several modified hydrochars was evaluated by measuring a breakthrough capacity with a fixed bed adsorption column. The ratio of the mass of ammonia removed to the mass of hydrochar in the column is calculated and reported as the ammonia sorption capacity with units of mg NH_3/g char.
Nitric acid treatment of corn stover based hydrochar can increase ammonia absorption capacity from 1 mg NH_3/g char for untreated hydrochar to absorption as high as 20mg NH_3/g char for char treated with 3 molar nitric acid for 1 hour at 900C. This is consistent with literature values and is thought to be due to the increase in carboxylic acid groups on the char from nitric acid treatment. However, evolution of NO_2 gas was observed during the treatments, which is a harmful pollutant. The production of NO_2 during nitric acid treatment is a serious concern and must be considered as a cost for the increase is sorption capacity.

Hydrochars produced from corn stover were subjected to metal chloride ($MgCl_2$) treatment during the HTC process (in situ). This resulted in an ammonia absorption capacity of 6.6 mg NH_3/g char as compared to 1 mg NH_3/g char for untreated corn stover char. Results from Boehm titration experiments found an increased amount of carboxylic acid surface groups on the in situ $MgCl_2$ treated hydrochar which could account for the increase in ammonia sorption capacity. Based on some limited desorption test results it appears that most of the adsorbed ammonia is strongly held by the hydrochar and not readily released.

A hydrochar made from corn ethanol fermentation residue (CDS, condensed distillers solubles) was loaded with 6.7 mg NH_3/ g char and subsequently analyzed for N, P, K to assess value as a fertilizer. It appears that the ammonia is tightly bound by the char and only 1.3 mg NH_3/ g char is readily available for potential plant growth. However, the char could be used as a soil amendment to improve soil quality and would also provide a small amount of nitrogen. Hydrochar breaks down in a several weeks in soil and improves soil microbial health.

Activity Status as of January 1, 2018:

The results obtained with CDS (condensed distillers solubles) in the last period raised questions as to why this material should perform as well as the corn stover modified with MgCl2. It was postulated that this could be due to the presence of lipids (corn oil) in the CDS and that these are hydrolyzed to fatty acids that are incorporated into the hydrochar during hydrothermal carbonization resulting in carboxylic acid groups being added to the char. To test this hypothesis corn oil was added to corn stover and the mixture was processed by ~~hydothermal~~hydrothermal carbonization. The result was ammonia sorption of 6 mg ammonia/gram char while the corn stover char without corn oil sorbed only about 1.3 mg ammonia/gram char. This hydrochar material produced from corn stover and oil addition has the potential to be utilized as an effective and low- cost ammonia sorbent and a soil amendment with slow release ammonia capability.

In addition to the specific application of this technology toward ammonia sorption, the discovery of a method to utilize hydrothermal carbonization to produce hydrochars with high a concentration of carboxylic acid surface groups may be valuable in other situations.

Activity Status as of July 1, 2018:
Complete.

Activity Status as of January 1, 2019:
Complete

Final Report Summary: Professor Valentas' work on ammonia absorbing hydrochar led to the pursuit of intellectual property in a non-fertilizer application, described at the University of Minnesota Office of Technology Commercialization website, under Technology # 20180070.

V. DISSEMINATION:

Description: We will arrange regular workshops and conferences with stakeholders; with an enabling project currently supported by the University, we have already begun this series by convening a meeting this month in conjunction with the Minnesota Renewable Energy Roundtable forum. This meeting, facilitated by Steve Kelley, explored the strengths, weaknesses, opportunities, and threats regarding the proposed research and technology development. We had representatives from renewable energy and agricultural businesses, non-profits, Minnesota Department of Agriculture, commodity organizations and government staff. At the end of each grant year, we plan to hold further stakeholder meetings to help assess progress toward achieving research milestones. The names of participants and the meeting minutes will be submitted with our reports.

We will also present the results of our work at regional conferences. We aim to submit invention disclosures with the University and pursue partnerships with companies that can facilitate the deployment of our new technologies, both at Morris and beyond. Finally, we intend to pursue academic publication resulting from this research.

Status as of January 1, 2016:

A conference with stakeholders is being planned for 2016.

Recent presentations about past research (prior to the LCCMR project) and describing current directions have been at the NH3 Fuel Association meeting at Argonne National Labs in September, 2015 (invited presentation); at the American Institute of Chemical Engineering meeting in Salt Lake City in November, 2015; and at the workshop described below. Papers are also in preparation for scientific and engineering journals and conferences.

Responding to an invitation made to our group from workshop organizers, Doug Tiffany was sponsored by the National Science Foundation (NSF) to participate in a three-day workshop in Dublin, Ireland in October, 2015. Organizers included NSF, Eirgrid (Ireland and Northern Ireland power utility) and the NSF-funded FREEDM Systems Center (based at North Carolina State University). The goal of the workshop was to plan future research toward energy systems that are low carbon and highly renewable. The workshop was largely organizational, meant to identify key research topics that guide progress toward greater production of renewable energy. A prime research need identified, particularly relevant to Minnesota, is to address the situation created by production of "stranded" renewable energy, at rates that can at times exceed the capacity to transport and use the power. These needs can be addressed by sustainable, distributed production of ammonia (whether for agriculture, for excess energy storage (as hydrogen carrier and/or for ammonia combustion), or both). Interest in our work in Minnesota is also likely because of our analysis of incentives in the future to guide and influence the demand for and the use of wind energy for distributed, carbon-free production of ammonia.

Status as of July 1, 2016:

Activity 1

- Outreach - 3 undergraduate researchers assisting (academic experiences).

- One manuscript submitted and under review for publication.
- One manuscript in preparation for submission.
- Published: Reese, Marquart, Malmali, Wagner, Buchanan, McCormick, and Cussler, "Performance of a Small-Scale Haber Process", Industrial Engineering and Chemistry Research, 2016, 55, 3742-3750. DOI: 10.1021/acs.iecr.5b04909.
- Poster presentation with archival extended abstract, associated with McCormick-led chemical engineering student design projects of Spring 2016: Malmali, Wagner, Reese, Cussler, McCormick, "Undergraduate Design Project Ideas in Sustainability: Rethinking Ammonia Synthesis," Paper #15283, Poster presentation at the American Society for Engineering Education, Annual Meeting, New Orleans, June 2016.
- Invited presentation, Ed Cussler, "A Sustainable Chemical Industry May Imply Dispersed Manufacturing," University of Washington, May 2016.
- Invited presentation, Ed Cussler, "Distributed Ammonia Synthesis", 5th International Symposium on Energy Challenges, Inverness, Scotland, July 2016.

Activity 2
Published: Peng, Li, Cheng, Deng, Chen, and Ruan, "Atmospheric Pressure Ammonia Synthesis Using Non-thermal Plasma Assisted Catalysis," Plasma Chemistry and Plasma Processes (published online June 2016), DOI: 10.1007/s11090-016-9713-6.

Activity 3
- Reese - Presentation to U of MN Dean of Extension Bev Durgan on Greening Ag Energy Initiatives including renewable ammonia. March 23, 2016. U of MN West Central Research and Outreach Center
- Reese - Interview with Elizabeth Dunbar on Net-Zero Dairy and efforts to lower carbon footprint of dairy production including use of renewable ammonia. March 30, 2016. U of MN West Central Research and Outreach Center. News story ran on May 31, 2016. (http://www.mprnews.org/story/2016/05/31/dairy-energy-use)
- Daoutidis - Conference talk, "Ammonia supply chains: a new framework for renewable generation" 15 June, 2016, ESCAPE-26:26th European Symposium on Computer-Aided Process Engineering conference, Slovenia.
- Daoutidis - Paper in press: "Optimal design of synergistic distributed renewable fuel and power systems", Renewable Energy.
- Daoutidis - Poster presentation at a research outreach event at Cargill R&D facility, Plymouth, MN, on methods and results for renewable ammonia supply chain research.
- Daoutidis - An undergraduate student was engaged in research this past semester.

Status as of January 1, 2017:

Activity 1:
Publications submitted and published
(1) Wagner, K.; Zhu, M.; Malmali, M.; Smith, C.; McCormick, A.; Cussler, E. L. Ammonia Selective Absorbents for Small Scale Ammonia Synthesis. AIChE J. 2016 - submitted.
(2) Cussler, E. L.; McCormick, A.; Reese, M.; Malmali M.; "Ammonia Synthesis at Low Pressure," Journal of Visual Experiments, (2016), - submitted.
(3) Malmali, M.; Wei, Y.; McCormick, A.; Cussler, E. L. Ammonia Synthesis at Reduced Pressure via Reactive Separation. Ind. Eng. Chem. Res. 2016, 55 (33), 8922 – published.

Presentations (travel supported by our leveraging UMN MNDrive grant, not by ENRTF/LCCMR):
(1) Cussler, E. L., "Distributed Ammonia Synthesis," AIChE Academy webinar, December 2016.
(2) Malmali, M.; Wei, Y.; McCormick, A.; Cussler, E. L. "Viability of Low Pressure Ammonia Synthesis via Reactive Separation," 2016 Annual AIChE Meeting, San Francisco, CA, November 2016.

(3) Malmali, M.; Reese, M.; Marquart, C.; Buchanan, E.; Wagner, K.; McCormick, A.; Cussler, E. L. "Small-Scale Distributed Ammonia Produced: Analysis of Pilot Plant Runs and Routes to Improve the Economics of Scale," 2016 Annual AIChE Meeting, San Francisco, CA, November 2016.
(4) Malmali, M.; Reese, M.; McCormick, A.; Cussler, E. L. "Small-Scale Low Pressure Ammonia Synthesis," 2016 NH3 Fuel Conference, Los Angeles, CA, September 2016.

Proposals for further, related work submitted:

- Currently under contract negotiation: ARPA-E DE-FOA-0001562: Renewable Energy to Fuels through Utilization of Energy-Dense Liquids (REFUEL program) –in partnership with a national laboratory and a small company, September 2016. As of January 2017, this proposal was selected for contract negotiation for a partnership of UMN, a national laboratory, and an electrolyzer company partner, to meet the requirement of the program to build and test as a benchmark, for a significant duration, a prototype at a scale selected by ARPA-E and with techno-economic analysis for potential fuel use. If selected and awarded, this grant could leverage (with distinct but complementary scope) Year 3 of the ENRTF/LCCMR grant; leverage and expansion of the impact of the ENRTF grant might be attained with a no-cost extension to a 4th year of the ENRTF/LCCMR project.
- Not awarded: DE-FOA-0001569: Sustainable Ammonia Synthesis; "Multifunctional porous catalyst/absorbent for ammonia" - (concept paper submitted to Department of Energy, but not accepted); PI: Alon McCormick, Co-PIs: Ed Cussler, Paul Dauenhauer
- Not awarded: DE-FOA-0001569: Sustainable Ammonia Synthesis - novel catalytic approach - (full proposal submitted, but not awarded); PI: Paul Dauenhauer, Co-PIs: Ed Cussler, Alon McCormick

Our Research in News:
Ammonia Energy Newsletter, "University of Minnesota's Ammonia Program". November 2016. Available at: http://www.ammoniaenergy.org/university-of-minnesotas-ammonia-program/

Three undergraduate researchers from the Chemical Engineering and Materials Science Department (2 with stipends from the Dreyfus Foundation (via grant to Ed Cussler), one with stipend from the UMN Undergraduate Research Opportunities Program).

Visiting professor, Dr. Ming Zhu, Nanjing University of Technology (primarily self-funded with small stipend from our leveraging support from UMN-MNDrive).

Activity 2

The Ruan group coordinated with an industrial partner (Plasma Technics Inc.) that manufactures the inverter and transformer and tested system performance at high frequency, greater than 20,000 Hz. The promising technology development suggests an opportunity to expand the impact of the ENRTF investment with a no-cost extension.

Activity 3

In this period, Doug Tiffany responded to a requests for information about capacity, costs, and operation lessons gleaned from our Morris pilot plant studies, from two corporate entities that may become future partners or sources of collaboration toward publication: ITM Company of Sheffield, Great Britain (which has built electrolyzers for hydrogen (cf. those we use in Morris from Proton-Onsite)), and Agriculture Canada, based in Manitoba (contemplating use of hydro-power or a mix of wind and hydro-power).

In December, Steve Kelley updated the team on plans to coordinate with the UMN Office of Technology Commercialization to host a technology forum for potential stakeholders in Minnesota and the Upper Midwest. We anticipate the first such event this year in the coming report period.

From the Daoutidis group,

- A presentation entitled "A supply chain optimization framework for distributed renewable ammonia" was presented at the 2016 AIChE Annual Meeting, 11/16/16, San Francisco, CA
- A presentation entitled "Optimal scheduling of renewable ammonia production under time sensitive electricity pricing" was presented at the 2016 AIChE Annual Meeting, 11/15/16, San Francisco, CA
- A conference proceedings paper entitled "Distributed chemicals and energy production with regulated energy exchange" was accepted for the Foundations of Computer-Aided Process Operations (FOCAPO) 2017 conference, Tucson AZ, and a poster will be presented for this on 1/9/17.

Status as of July 1, 2017:

Involving all Activities:

Not funded by LCCMR directly, but related to this project, was the hosting of a Green Ammonia Technology Forum in February 2017 at the McNamara Center of the University. It offered a slate of speakers to discuss various aspects of the project with an audience of LCCMR staff, angel investors and corporate finance specialists for new technologies. Alon McCormick, Doug Tiffany, Andrew Allman (with Prodromos Daoutidis), and Steve Kelley all made presentations and participated in discussions with this audience of about 30. The project team was able to receive feedback on potential next steps. As a result, potential policy implications were subsequently studied and a second technology forum geared to an agricultural audience is being planned. As one follow-up, an initial meeting will be held with representatives of the Minnesota Corn Research and Promotion Council on July 13th at the West Central Research and Outreach Center in Morris.

Activity 1

Published:
Wagner, K.; Zhu, M.; Malmali, M.; Smith, C.; McCormick, A.; Cussler, E. L. Ammonia Selective Absorbents for Small Scale Ammonia Synthesis. AIChE Journal, 63:7 (2017) 3058-3068.

Accepted and in press:
Cussler, E. L.; McCormick, A. V.; Reese, M.; Malmali, M. – "Ammonia Synthesis at Low Pressure", Journal of Visual Experiments, (2017).

Submitted: One additional paper.

Several presentations accepted at upcoming meetings of the American Chemical Society and of the American Institute of Chemical Engineers (including a topical conference with the Ammonia Fuel Association.)

Outreach and education:
Six undergraduate students participating, some with leveraged support from the Dreyfus Foundation (via grant to Cussler), UMN UROP program (Undergraduate Research Opportunities Program)

Activity 2

Accepted for publication: Peng, Cheng, Hatzenbeller, Addy, Zhou, Schiappacasse, Chen, Zhang, Anderson, Liu, Chen, and Ruan, "Ru-based multifunctional mesoporous catalyst for low-pressure and non-thermal plasma synthesis of ammonia", International Journal of Hydrogen Energy, (Expected to be published in July 2017)

Activity 3

Reese and coworkers:

A summer undergraduate intern is working on analyzing the molar ratio test run data from the pilot plant, with results being presented to a Native American student engineering conference which will be held later this year.

Several guests toured the ammonia pilot plant in Morris including the head of a Danish company. Follow-up conversations are in progress relating to possible future collaborations. A representative from a Nebraska ammonia producer also toured the pilot plant in June. Finally, as part of the 2017 Midwest Farm Energy Conference hosted on June 13 and 14th, approximately 70 participants were presented information about the project and a subset of the people toured the pilot plant.

Daoutidis and coworkers:

- A peer reviewed journal article entitled “A framework for ammonia supply chain optimization incorporating conventional and renewable generation” has been accepted for publication in AIChE Journal.

Tiffany and collaborators:

On March 23, 2017, Doug Tiffany presented a televised lecture in the Frontiers on the Environment series sponsored by the Institute on the Environment. The presentation was entitled, “Replacing Agriculture’s Most Energy Intensive Input with Wind, Water and Intellect.” The lecture was presented on the Minneapolis campus (Walter Library) and webcast live to other campuses and to all registrants. It is now available at the following URL: https://www.youtube.com/watch?v=ahYeNHTBClI

Submitted to the 2017 AIChE Conference and the Ammonia Fuel Conference (coordinated meeting this year) in Minneapolis, October 2017: Doug Tiffany, “Economic Analysis of Ammonia Production Using Renewable Energy”.

Kelley and coworkers:

The Technology Forum held on February 22, 2017 was video recorded. We plan to edit portions of the presentations into a short policy-oriented video and post it to a Humphrey School website in order to make information about the project and the technology more accessible to Minnesotans and other current and future stakeholders.

Status as of January 1, 2018:

Activity 1

Published:

Malmali, Mahdi; Reese, Michael; McCormick, Alon; Cussler, Edward, Converting Wind Energy to Ammonia at Lower Pressure, ACS Sustainable Chemistry & Engineering , (2017), DOI: 10.1021/acssuschemeng.7b03159

Cussler, E., McCormick, A., Reese, M., Malmali, M. Ammonia Synthesis at Low Pressure. J. Vis. Exp. (126), e55691, doi:10.3791/55691 (2017).

Mahdi Malmali, Alon McCormick, Edward L. Cussler, Joshua Prince, Mike Reese, Lower Pressure Ammonia Synthesis, NH3 FUEL CONFERENCE 2017 , Minneapolis, MN, USA (2017), presentation pdf posted at https://nh3fuelassociation.org/2017/10/01/lower-pressure-ammonia-synthesis/

Submitted: One additional paper.

Several presentations presented at the American Chemical Society and of the American Institute of Chemical Engineers (including a topical conference with the Ammonia Fuel Association.)

Ed Cussler – department seminar at University of California, Berkeley, November 2017.

Outreach and education:
Three undergraduate students participating, some with leveraged support from the Dreyfus Foundation (via grant to Cussler), UMN UROP program (Undergraduate Research Opportunities Program)

Activity 2

Peng, P., Cheng, Y., Hatzenbeller, R., Addy, M., Zhou, N., Schiappacasse, C., ... & Ruan, R. (2017). Ru-based multifunctional mesoporous catalyst for low-pressure and non-thermal plasma synthesis of ammonia. International Journal of Hydrogen Energy, 42(30), 19056-19066

-Accepted for publication:
Peng, P., Chen, P.; Schiappacasse, C.; Zhou, N.; Anderson, E.;… & Ruan, R., "A review on the non-thermal plasma-assisted ammonia synthesis technologies", Journal of Cleaner Production, (Expected to be published early 2018)

Submitted: One additional paper on the new plasma gas liquid ammonia synthesis system.

Peng, P.; Schiappacasse, C.; Zhou, N.; Cheng, Y.; Hatzenbeller, R.; Chen, P.; and Ruan, R.,"Atmospheric-Pressure Synthesis of Ammonia Using Non-Thermal Plasma with the Assistance of Ru-Based Multifunctional Catalyst", NH3 Fuel Conference at the ~~The~~ American Institute of Chemical Engineers (AICHE) Annual Meeting, Minneapolis, Minnesota, USA, November 2017; presentation posted at https://nh3fuelassociation.org/2017/10/01/atmospheric-pressure-synthesis-of-ammonia-using-non-thermal-plasma/

Presentations also at:
The American Society of Agricultural and Biological Engineers (ASABE) Annual International Meeting, Spokane, WA, USA., July 2017

University of Minnesota Department of Bioproducts and Biosystems Engineering annual research showcase, St. Paul, Minnesota, USA, October, 2017

Activity 3

Reese and coworkers:
On July 13th, staff and board members from the Minnesota Corn Growers Association toured the pilot plant, learned about progress on new technologies, and discussed potential policy.

On August 17th, a panel presentation regarding the pilot plant was given to the attendees of the ARPA-E REFUEL Kickoff Conference in Denver, CO. Approximately 100 people including researchers, industry, and US Department of Energy representatives attended the event.

On August 29th, Minnesota Public Utilities Commissioner John Tuma visited the pilot plant along with a delegation from the University's Energy Transition Lab. Commissioner Tuma is interested in energy storage and possible options to store renewable electric generation. One of the inherent disadvantages to wind and solar electric generation systems is that the power production does not always match the electric load or demand. Finding methods to storage wind and solar PV for periods of higher demand is paramount to increased development of renewable electric generation. There are many options for storing power such as batteries, compressed air, hydrogen production, and pumped hydro. However, most of these options tend to be too expensive. As shown in a presentation by Grigorii Soloveichik of the US Department of Energy [posted at https://nh3fuelassociation.org/2017/10/01/future-of-ammonia-production-improvement-of-haber-bosch-process-or-electrochemical-synthesis/}, using ammonia for energy storage appears to be more economical, and have the added advantage of long term storage, transportability, and market flexibility (e.g., use as nitrogen fertilizer).

On October 3rd, the WCROC hosted a delegation from the state of North Rhine Westphalia (NRW), Germany. Minnesota participates in a Climate Smart Cities exchange with NRW. The group toured the pilot plant and learned about the University's efforts to develop absorbent enhanced ammonia production.

On November 2nd, a renewable energy presentation including wind to ammonia was delivered at the Rural Renewable Energy Discussion in Kasson, MN. The event was organized by Minnesota Senator David Senjum and was attended by approximately 60 people from the south east Minnesota region.

On November 3rd, the West Central Research and Outreach Center hosted program leaders from the US Department of Energy ARPA-E REFUEL program (Washington DC), researchers from Siemens (Germany and UK), and IHI Corporation (Japan). The guests toured the Renewable Hydrogen and Ammonia Pilot Plant and discussed research efforts with the research team.

On November 29th, Professor Ed Cussler and Mike Reese delivered a presentation regarding the absorbent enhanced ammonia production to the University of Minnesota's Business Advisory Council.

On December 6th, approximately 60 people participated in the Stevens County Energy Dialogue seminar and learned about ammonia production using wind energy.

Daoutidis and coworkers:

- "Optimal scheduling for wind-powered ammonia generation: Effects of key design parameters" was accepted and is in press in the journal *Chemical Engineering Research and Design.* {Chem. Eng. Res. Des. (2017), https://doi.org/10.1016/j.cherd.2017.10.010}
- A presentation entitled "Scheduling of wind-powered ammonia plants: Determination of key design parameters" was given on 2 November 2016 in Minneapolis, MN at the AIChE Annual Meeting.

Tiffany and collaborators:

Doug Tiffany prepared a poster entitled, " Economics of Ammonia Using Renewable Energy" for the AICHE Conference and at a separate session of the Ammonia as a Fuel Conference, both held on November 1, 2017. The poster is shown on the following page and touches on the motivations for renewable ammonia, the percentages of the modeled cost of production at 7% capital costs of the WCROC-Morris pilot facility using $.04 per kWh electricity. The poster also notes lessons learned and contrasts capital costs, energy costs, and total production costs for ammonia production based on the latest pilot trials of $1,363.65 per ton, which is about double that of prevailing prices.

Kelley and coworkers:

Though not focused exclusively on this project, a special project by Steve Kelley expanded his expertise in advising our project through his participation in a delegation visit to Germany. This and other activities led to his moderating this Humphrey Forum at the Humphrey School of Public Affairs: "The Renewable Energy Transition Is a Revolution," a forum with energy policy leaders on September 11, 2017. It featured one of Europe's recognized clean energy analysts - Gerard Reid, founder and co-partner, Alexa Capital LLC, Berlin. It also featured Dr. Sam Mukasa, Dean, College of Science & Engineering, U of MN; Ellen Anderson, Executive Director, Energy Transition Lab, U of MN; and Laureen Ross McCalib, Manager, Resource Planning & Regulatory Affairs, Great River Energy.

Status as of July 1, 2018:

Activity 1

Published:
Better Absorbents for Ammonia Separation
Mahdi Malmali, Giang Le, Jennifer Hendrickson, Joshua Prince, Alon V. McCormick, and E. L. Cussler
ACS Sustainable Chemistry & Engineering 2018 6 (5), 6536-6546
DOI: 10.1021/acssuschemeng.7b04684

Invited presentations:
Ed Cussler seminars at:
Rice University 18January 2018
Brown University 30January 2018

Invited participation:
ARPA-E Summit meeting, Washington DC, March 2018

One additional paper (Smith, McCormick and Cussler) submitted for publication on the mechanism and optimization of absorption and regeneration. Other papers also in preparation.

Activity 2

Published:
Peng ~~Peng~~, Paul Chen, Charles Schiappacasse, Nan Zhou, Erik Anderson, Dongjie Chen, Juer Liu, Yanling Cheng, Raymond Hatzenbeller, Min Addy, Yaning Zhang, Yuhuan Liu, Roger Ruan
"A review on the nonthermal plasma-assisted ammonia synthesis technologies"
Journal of Cleaner Production, 177, 597-609, 2018.
DOI: 10.1016/j.jclepro.2017.12.229

Peng ~~Peng~~, Paul Chen, Min Addy, Yanling Cheng, Yaning Zhang, Erik Anderson, Nan Zhou, Charles Schiappacasse, Raymond Hatzenbeller, Liangliang Fan, Shiyu Liu, Dongjie Chen, Juer Liu, Yuhuan Liuc and Roger Ruan,
"In situ plasma-assistedatmospheric nitrogen fixation using water and spray-type jet plasma".
Chemical Communications, 54(23),2886-2889, 2018.
DOI: 10.1039/C8CC00697K

Activity 3 (for details, see Activity 3 status)

Steve Kelley arranged a Technology Forum Summit addressing Outcome 5 of Activity 3, June 11, 2018.
An additional manuscript by Allman and Daoutidis was submitted for publication.
Doug Tiffany - invited seminar at Massey University, February 2018, in New Zealand.

Status as of January 1, 2019:

Activity 1
Cussler McCormick and coworkers
ACS Sustainable Chemistry and Engineering - paper accepted 1/1/2019 pending minor revisions.
Optimizing the Conditions for Ammonia Production Using Absorption, Collin Smith, Alon V. McCormick , and E. L. Cussler, ACS Sustainable Chem. Eng., DOI: 10.1021/acssuschemeng.8b05395

AIChE conference and NH3 Fuel Association meeting, November 2018, Pittsburgh PA. "Ammonia Absorption and Desorption in Ammines" Collin Smith, Mahdi Malmali, Chen-Yu Liu, Alon McCormick, E L Cussler*

Activity 2
Ruan and coworkers

Journal publication
Peng, P., Chen, P., Addy, M., Cheng, Y., Anderson, E., Zhou, N., ... & Ruan, R. (2019). Atmospheric plasma-assisted ammonia synthesis enhanced via synergistic catalytic absorption. ACS Sustainable Chemistry & Engineering. 2019 7 (1), 100-104 DOI: 10.1021/acssuschemeng.8b03887
Poster presentation
Peng P. et al. "Sustainable water-based nitrogen fixation using non-thermal plasma (NTP) under atmospheric pressure" at the 2018 Bioproducts and Biosystems Engineering (BBE) Showcase, St. Paul, MN. October 25th, 2018
Oral presentation
Peng P. et al. "Current Situation of Non-Thermal Plasma (NTP) Ammonia Synthesis and Its Potential to Build a Sustainable Nitrogen Fixation Industry" at the 2019 IAFOR International Conference on Sustainability, Energy & the Environment, Honolulu, HI. January 4th, 2019

Activity 3
Daoutidis and coworkers
Modeling and optimal design of absorbent enhanced ammonia synthesis
Matthew J. Palys, Alon V. McCormick, E. L. Cussler and Prodromos Daoutidis
Processes 2018 6 (7), 91. DOI: 10.3390/pr6070091

Exploring the benefits of modular renewable-powered ammonia production: A supply chain optimization study
Matthew J. Palys, Andrew Allman, Prodromos Daoutidis
Industrial and Engineering Chemistry Research 2018 6 (5), 6536-6546. DOI: 10.1021/acs.iecr.8b04189

A novel system for ammonia-based sustainable energy and agriculture: Concept and design optimization
Matthew J. Palys, Anatoliy Kuznetsov, Joel Tallaksen, Michael Reese and Prodromos Daoutidis
Chemical Engineering Processing: Process Intensification (Submitted)

Final Report Summary:

Activity 1:

Though some of the following have been reported in previous updates, together these publications tell the story of how the science and engineering have evolved; they are not mere academic papers - rather, they form the foundation of the intellectual property developed with the help of this grant.

- Mahdi Malmali, Michael Reese, Alon V. McCormick, and E.L. Cussler, “Converting Wind Energy to Ammonia at Lower Pressure,” ACS Sustainable Chem. Engr. 6, 827-834 (2018).
- Mahdi Malmali, Giang Le, Jennifer Hendrickson, Joshua Prince, Alon McCormick, and E. L. Cussler, “Better Absorbents for Ammonia Separation,” ACS Sustainable Chem. Engr. 6, 6536-6546 (2018).
- Matthew J. Palys , Alon McCormick and E.L. Cussler , and Prodromos Daoutidis , “Modeling and Optimal Design of Absorbent Enhanced Ammonia Synthesis,” Processes 6, 91-98 (2018).
- Collin Smith, Mahdi Malmali, Chen-Yu Liu, Alon V. McCormick, and E. L. Cussler, “Rates of Ammonia Absorption and Release in Calcium Chloride,” ACS Sustainable Chem. Eng.(2018) 6, 9, 11827-11835. DOI: 10.1021/acssuschemeng.8b02108
- Collin Smith, Alon V. McCormick and E. L. Cussler “Optimizing the Conditions for Ammonia Production Using Absorption” ACS Sustainable Chem. Eng., 7,4019–4029 (2019). DOI: 10.1021/acssuschemeng.8b05395
- Deepak K. Ojha, Matthew J. Kale, Alon V. McCormick, Michael Reese, Paul Dauenhauer, and E. L. Cussler, “Isothermal Ammonia Synthesis and Separation: Integrated Catalysis and Metal Salt Absorption,” ACS Sustainable Chem. Eng., (submitted)

Ed Cussler gave a presentation at the NH3 Event conference in Rotterdam, The Netherlands, in June 2019 to tell this story and help continue discussions with possible implementation partners.

Further aspects can be seen at our absorption-enhanced ammonia webpage, https://wcroc.cfans.umn.edu/research-programs/renewable-energy/ammonia

Activity 2:
Published:
Peng, P. , Schiappacasse, C. , Zhou, N. , Addy, M. , Cheng, Y. , Zhang, Y. , Ding, K. , Wang, Y. , Chen, P. and Ruan, R. (2019), Sustainable Non‐Thermal Plasma‐Assisted Nitrogen Fixation—Synergistic Catalysis. *ChemSusChem*. In press. doi:10.1002/cssc.201901211

Submitted:
Peng, Peng; Schiappacasse, Charles; Zhou, Nan; Addy, Min; Cheng, Yanling; Zhang, Yaning; Anderson, Erik; Chen, Dongjie; Liu, Yuhuan; Chen, Paul; Ruan, Roger, “Plasma in situ gas-liquid nitrogen fixation using concentrated high-intensity electric field”, Journal of Physics D: Applied Physics

Activity 3:
Daoutidis group:
Journal Publications
A novel system for ammonia-based sustainable energy and agriculture: Concept and design optimization, Matthew J. Palys, Anatoliy Kuznetsov, Joel Tallaksen, Michael Reese and Prodromos Daoutidis, Chemical Engineering Processing: Process Intensification 2019 140, 11-21. DOI: 10.1016/j.cep.2019.04.005

Conference Proceedings
Concept and design optimization for a novel system for ammonia-based food-energy-water sustainability, Matthew J. Palys, Andrew Allman, Anatoliy Kuznetsov, and Prodromos Daoutidis
Proceedings of the 9th International Conference on Foundations of Computer-Aided Process Design, July 14th to 18th, 2019, Copper Mountain, Colorado, USA. DOI: 10.1016/B978-0-12-818597-1.50011-4

Poster Presentation

Concept and design optimization for a novel system for ammonia-based food-energy-water sustainability, Matthew J. Palys, Andrew Allman, Anatoliy Kuznetsov, and Prodromos Daoutidis, presented at the 9th International Conference on Foundation of Computer-Aided Process Design on July 17th (Awarded 1 of 6 "Best Contribution Awards" from 125 posters)

Oral Presentation
Innovations in Ammonia: The Minnesota Story, Prodromos Daoutidis, Fertilizers Europe Annual Meeting, June 24th to 28th, 2019, Athens, Greece

Reese and coworkers:

Greening Agricultural Energy. Reese, M. 2018. Poster. Minnesota Corn Growers Reception. Bell Museum, St. Paul, MN.

Ammonia Production from Wind Energy Gaining Momentum. Reese, M. 2018. WCROC Newsletter. February, 2018 (Re-printed in Stevens County Times)

The Haber-Bosch Process (in production). In July 2019, the production company for PBS Nova filmed a segment at the WCROC Wind to Ammonia Pilot Plant in Morris. Professor Ed Cussler and Michael Reese participated in the segment.

VI. PROJECT BUDGET SUMMARY:
A. ENRTF Budget Overview:

Budget Category	$ Amount	Overview Explanation
Personnel:	**$904,000 total personnel**	
Research assistants: *(supervised by Senior personnel, in specific activities, as shown below)*	*About $712,000 subtotal for research assistant personnel*	The 5 (FIVE) research assistants will address the workplan goals under the supervision of the senior personnel. Supervision of the research assistants (graduate students, postdoctoral associates or equivalent, and an assistant scientist) are described below with the supervising senior personnel.
Senior personnel: *McCormick, project manager, and also senior personnel responsibilities as described below -*	*About $192,000 subtotal for senior personnel**	The role of the 8 Senior Personnel includes: • Provide intellectual conception, leadership, perspective and drive; set tone and direction of project;

Cussler, *with Dauenhauer and McCormick* *(and with Project Partner Schmidt) supervising one postdoctoral associate in Activity 1* *Reese supervising one assistant scientist at the Morris pilot plant, supporting Activities 1 and 3* *Ruan supervising one postdoctoral associate in Activity 2* *Daoutidis supervising one graduate student in Activity 3* *Daoutidis and McCormick supervising partial effort of one additional graduate student bridging Activities 1 and 3* *Tiffany supervising one graduate student in Activity 3* *Kelley supporting Activity 3 and also conducting outreach, policy, and stakeholder communications for all Activities*	**30,025 McCormick total, 0.04 FTE for 3 years* **$16,243 Cussler total, 0.02 FTE for 3 years* **$12,171 Dauenhauer total, 0.02 FTE for 3 years* **Reese effort cost-shared (see other funding)* **$13,252 Ruan total, 0.02 FTE for 3 years* **$18,135 Daoutidis total, 0.02 FTE for 3 years* **$79,413 Tiffany total, 0.25 FTE for 3 years* **$22,662 Kelley total, 0.04 FTE for 3 years*	• Advise, direct, supervise, and review performance of research assistants; • Coordinate with other senior personnel and project partners to review project progress and goals; • Arrange, conduct, and review efforts at stakeholder engagement, dissemination, publication, and outreach; • Conduct research reviews both internally and with stakeholders
Professional/Technical/Service Contracts:	$39,000	The maintenance and servicing of the pilot plant equipment and software is fundamental to the progress of this project.
Equipment/Tools/Supplies:	$54,600	The technical work at the pilot plant and the research activities in the laboratories require supplies to be safe and effective. The funding requested may only partially meet the need.
Capital Expenditures over $5,000:	$0	
Fee Title Acquisition:	$0	
Easement Acquisition:	$0	
Professional Services for Acquisition:	$0	
Printing:	$100	This includes partial support for the costs of reporting, outreach, conference preparation, and publication efforts. The funding requested may only partially meet the need.
Travel Expenses in MN:	$2300	Travel for collaboration and outreach in Morris, the Twin Cities, and further throughout the state. The funding requested may only partially meet the need.
Other:	$0	
TOTAL ENRTF BUDGET:	**$1,000,000**	

Explanation of Use of Classified Staff: NA

Explanation of Capital Expenditures Greater Than $5,000:

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: *ABOUT 4.27 FTE TOTAL*
Five research assistants over three years, leveraged with other funding.

a. 2 postdoctoral associates or equivalent (each averaging 87.5% FTE appointment over the grant period)
b. 1 graduate student (averaging 83.3% of graduate research assistant effort over the grant period; note that graduate student research assistants can be appointed only at 50% FTE, so this averages 41.7% FTE over the grant period.)
c. 1 additional shared graduate student at average 55% graduate research assistant effort over the grant period - so averaging 27.5% FTE over the grant period.
d. 1 assistant scientist (pilot plant engineer) at 100 % FTE over the grant period.

In addition, 6 senior personnel are appointed for 1-2 weeks for salary each year - *totaling* 0.16 FTE over the grant period. Finally, one senior personnel is appointed 0.25 FTE over the grant period.

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 0.06 FTE

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			
University of Minnesota MNDRIVE program	$250,000	$250,000	Concurrent with year 1 of the proposed LCCMR project, leveraging and advancing the workplan objectives
0.04 FTE cost share for Senior Personnel Mike Reese over 3 years	> ca. $11,000	ca. $11,000	
ARPA-E REFUEL project, US Department of Energy		ca. $1.3 million	Direct costs for a distinct but synergistic project, 2017-present, to fabricate operate and analyze prototype using UMN absorbent technology for ammonia energy storage applications.
State			
	$	$	
TOTAL OTHER FUNDS:		**$ 1.5 million**	

VII. PROJECT STRATEGY:

A. Project Partners:

Professor Lanny Schmidt
Professor Ken Valentas (also conducting a related LCCMR project on hydrochar)
Participants in our stakeholder meetings (see dissemination and outreach plans)

B. Project Impact and Long-term Strategy:
The proposed work is aligned with previous environmental grant work (the origin of this team) and the UMN WCROC strategic plan to reduce fossil energy dependence and carbon footprint in production agriculture. The ultimate goal is demonstration for economic and engineering modeling allowing commercial implementation.

Its environmental benefits in agriculture can be huge, and the economic potential for green business development with this technology in Minnesota is substantial.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	$ Amount
Concurrent with LCCMR Year 1: UMN MNDrive project, year 2	July 2015-June 2016	$250,000
UMN MNDrive project, year 1	July 2014-June 2015	$250,000
UMN Initiative for Renewable Energy and the Environment (IREE) Competitive Large Grant Program, plus matches to two MDRPC grants (see below)	March 2011 - Nov 2014	$513,000
Two grants for Economic Evaluation of Local Ammonia Production from the Minnesota Corn Research and Promotion Council	March 2008 - Nov 2014	$141,600
MN State Bond to plan and construct Renewable Hydrogen and Ammonia Plant	July 2007 - Oct 2013	$2,500,000
UMN College of Food Agriculture and Natural Resource Sciences Match to MN State Bond	July 2007 - Oct 2013	$430,000
ENRTF Wind to Hydrogen Demonstration (final report 2010)	July 2005 - June 2010	$800,000

VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS:
NOT APPLICABLE

IX. VISUAL COMPONENT or MAP(S):
See accompanying file: "LCCMR Graphic - Renewable and Sustainable Fertilizers FINAL 10-7-14.pdf"

X. RESEARCH ADDENDUM:
See accompanying file

XI. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted no later than January 1, 2016; July 1, 2016; January 1, 2017; July 1, 2017; January 1, 2018; July 1, 2018; and January 1, 2019. A final report and associated products will be submitted between June 30 and August 15, 2019.

Environment and Natural Resources Trust Fund
FINAL M.L. 2015 Project Budget
Project Title: Renewable and Sustainable Fertilizers Produced Locally
Legal Citation: M.L. 2015, Chp. 76, Sec. 2, Subd. 07a
Project Manager: Alon McCormick
Organization: University of Minnesota
M.L. 2015 ENRTF Appropriation: $1,000,000
Project Length and Completion Date: 4 Years, June 30, 2019
Date of Report: 7/1/2019

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget 03/08/2019	Amount Spent	Activity 1 Balance	Activity 2 Budget 03/08/2019	Amount Spent	Activity 2 Balance	Revised Activity 3 Budget 03/08/2019	Amount Spent	Activity 3 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	*Improve efficiency for absorbent-enhanced*			*Low pressure ammonia synthesis using non-*			*Integration, modeling, planning for various*				
Personnel (Wages and Benefits)	$381,748	$381,748	$0	$185,716	$185,715	$1	$336,889	$331,730	$5,159	$904,353	$5,160
PI McCormick $30,025 (74.8% salary, 25.2% benefits) at .04 FTE for 3 years - PI and project manager											
PI Cussler $16,243 (74.8% salary, 25.2% benefits) at .02 FTE for 3 years											
PI Daoutidis $18,135 (74.8% salary, 25.2% benefits) at .02 FTE for 3 years											
PI Dauenhauer $12,171 (74.8% salary, 25.2% benefits) at .02 FTE for 3 years											
PI Kelley $22,662 (74.8% salary, 25.2% benefits) at .04 FTE for 3 years- outreach/discussions with stakeholders and policymakers											
PI Reese $0 (no cost to LCCMR grant, 4% cost share effort) - ROC research and outreach											
PI Ruan $13,252 (74.8% salary, 25.2% benefits) at .02 FTE for 3 years											
PI Tiffany $79,413 (74.8% salary, 25.2% benefits) at .25 FTE for 3 years											
2 Postdoctoral Associates or equiv. $311,577 (81.7% salary, 18.3% benefits) Position 1 (Cussler lead advisor) at 50% FTE in year 1, then 100% FTE in years 2 and 3 (Activity 1). Position 2 (Ruan lead advisor) at 75% FTE in year 1, then 100% FTE in years 2 and 3 (Activity 2).											
2 Graduate Student Research Assistants $215,998 (61.5% salary, 38.5% benefits (including tuition)) Note maximum FTE appointment for an individual graduate student is 50%. Position 1 (Daoutidis lead advisor): 25% FTE (50% graduate student effort) in year 1, and 50% FTE (100% graduate student effort) in years 2 and 3. Activity 3. Position 2 (Daoutidis/McCormick advisors, shared student, partial appointment): 16.5% FTE (33% graduate student effort) in year 1, 33% FTE (66% graduate student effort) in years 2 and 3. Effort split between Activities 1 and 3 (funds allocated to Activity 1).											
Assistant scientist $170,417 (78.5% salary, 21.5% benefits) (Reese primary supervisor) 100% FTE each year for 3 years. Effort and funds split between Activities 1 and 3.											
Professional/Technical/Service Contracts											
Matrix Tech for programming offsite and onsite, including travel lodging and meals							$14,276	$14,276	$0	$14,276	$0
Refurbish test and maintain electrolyzer and power units							$24,776	$24,776	$0	$24,776	$0
Equipment/Tools/Supplies									$0		
Pilot plant Supplies - Matrix Software Update for SCADA System (control system for the pilot plant)							$9,001	$9,001	$0	$9,001	$0
Pilot plant Supplies - Matrix Software Update for Data Historian (data acquisition system for the pilot plant)							$3,935	$3,935	$0	$3,935	$0
Hardware upgrade for SCADA System and Data Historian (essential for operation and analysis of the pilot plant performance)							$1,320	$1,320	$0	$1,320	$0
General pilot plant supplies - including safety goggles, gas masks, chemical gloves, chemical suits, chemical boots, gas mask cartridges, water prefilters and filters for the deionized water system, chiller system coolant, calibration gases for safety sensors, and leak detection spray bottles							$6,137	$6,137	$0	$6,137	$0
Experimental supplies for laboratory research assistants (apportioned by number of lab-intensive research assistants) : Chemicals, lab analysis, safety and laboratory needs for the chemical-intensive research assistants. Includes: cylinders of nitrogen, hydrogen, and ammonia; magnesium chloride; stainless steel tubing, Swagelok fittings, high pressure/temperature ceramic fittings, thermocouples, gas syringes for chromatograph, chromatograph replacement parts, leak detection fluid and supplies, gloves, emergency gas mask; catalysts, supports, and promoters; zeolite adsorbents; reagents such as ethanol, methyl red, and sulfuric acid; porous ceramic and quartz tubes for NTP reactor; electrodes, minor power supplies; temperature guages, pressure guages, flowmeters, and monitoring equipment; carrier gases (argon, helium) and liquid nitrogen for chromatography; sieves for particle sizing; sample containers	$26,551	$26,516	$35	$7,247	$7,080	$167	$0	$0	$0	$33,798	$202
Printing											
Reporting, grant administration, conference organization, outreach, and publication (partial funding - apportioned by number of senior personnel)	$109	$109	$0	$0	$0	$0	$0	$0	$0	$109	$0
Travel expenses in Minnesota											
In-state travel between Morris and Twin Cities for full-day research collaboration and outreach elsewhere in the state (partial funding, apportioned by number of senior personnel) Roughly monthly visits, ca. $300 for 2 person overnight Morris to TC, ca. $100/person for TC to Morris.	$512	$512	$0	$0	$0	$0	$1,783	$1,783	$0	$2,295	$0
COLUMN TOTAL	**$408,920**	**$408,885**	**$35**	**$192,963**	**$192,795**	**$168**	**$398,117**	**$392,958**	**$5,159**	**$1,000,000**	**$5,362**