October 1, 2010

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Dear Ms. Fine:

Subject: Final Report Entitled “Renewable Electrolytic Nitrogen Fertilizer Production”  
Contract No. R002-006; EERC Fund 9931

Please find enclosed the subject final report and the final report summary.

If you have any questions regarding this report, please contact me by phone at (701) 777-2982 or by e-mail at taulich@undeerc.org.

Best regards,

Ted R. Aulich  
Senior Research Manager

TRA/kmd

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

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

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

| Projected Per-Ton Cost of Ammonia Production via EERC Electrochemical–Thermal Process |
|-----------------------------------------------|-----------------------------------------------|
| Syngas Price\(^1\)                             | $6/MMBtu                                      |
| Electricity Price                             | $0.05/kWh                                     |
| Cost of Electricity\(^2\)                     | $120                                          |
| Cost of Syngas Input                          | $142                                          |
| Capital Cost                                  | $21                                           |
| Operating and Maintenance Cost                | $32                                           |
| Total Cost                                    | $315                                          |

\(^1\) U.S. Department of Energy-published 2010 target price.
\(^2\) Based on electricity consumption of 2400 kWh/ton ammonia produced.

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

Final Report

(for the period of October 24, 2008, through September 30, 2010)

Prepared for:

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2010-EERC-10-01 October 2010
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RENEWABLE ELECTROLYTIC NITROGEN FERTILIZER PRODUCTION

EXECUTIVE SUMMARY

The Energy & Environmental Research Center (EERC)—in partnership with the North Dakota Renewable Energy Council, the North Dakota Corn Utilization Council, and the Minnesota Corn Research and Promotion Council—recently completed a project to optimize the EERC renewable electrolytic ammonia production process as a prerequisite for process commercialization. The process operates at a reaction temperature of 200°–400°C, with inputs of biosyngas, air-extracted nitrogen, and electricity. Project research focused on 1) development of cathode catalysts and electrolytes for improved ammonia production rate and decreased energy consumption, 2) optimization of reaction conditions, and 3) adaptation of the process for scale-up assessment. Cathode catalyst activity for ammonia production was improved through catalyst screening, surface modification, catalyst support development, and reactor engineering. Tests conducted to assess catalyst durability demonstrated the occurrence of no observable catalyst activity decay over 30 days of uninterrupted operation at 350°C. Further catalyst durability assessment is ongoing, as establishment of long-term durability is crucial to assuring commercial viability. To increase ammonia production rate and decrease process energy consumption, an integrated process was developed that combines electrochemical hydrogen extraction from syngas with low-pressure, high-throughput thermal reaction of hydrogen and nitrogen to yield ammonia. The integrated electrochemical–thermal (IET) process was demonstrated and optimized at a 20-watt scale using inputs of electricity and simulated syngas with a composition of 76% H₂ + 2% CO + 2% CH₄ + 20% CO₂. Unlike traditional Haber–Bosch-based ammonia processes that require the use of expensive high-purity hydrogen and operation at high pressure (3000 psi) to achieve economic viability, the IET process can utilize relatively impure hydrogen and works well at 200 psi, the impacts of which are lower capital and operating costs. Based on process optimization results achieved, a preliminary process design was developed and used as the basis for conducting a preliminary economic assessment of the IET process. As shown in the table below, the assessment projects economic competitiveness of the IET process with Haber–Bosch ammonia production based on the market price of ammonia—about $350–400/ton at the time of this writing. Upcoming work is focused on pilot-scale process demonstration via integration of the IET ammonia process with a gasification system or other biosyngas source.

Projected Per-Ton Cost of Ammonia Production via IET Process

<table>
<thead>
<tr>
<th>Syngas Price¹</th>
<th>$6/MMBtu</th>
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<tbody>
<tr>
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</table>

² Based on electricity consumption of 2400 kWh/ton ammonia produced.
RENEWABLE ELECTROLYTIC NITROGEN FERTILIZER PRODUCTION

1.0 INTRODUCTION

Industrial processes for production of ammonia and urea nitrogen-based fertilizers are mainly based on the Haber-Bosch process, which involves the heterogeneous reaction of nitrogen and hydrogen on an iron-based catalyst at high pressure (150–300 atm) and high temperature (400°–500°C) to produce ammonia [1]. The equilibrium conversion of hydrogen gas and nitrogen gas to ammonia in the Haber process is generally only on the order of about 15%. Such low conversion efficiency gives rise to cost-intensive, large-scale chemical plants and costly operating conditions required to commercially produce hundreds to thousands of tons per day of ammonia in an ammonia synthesis plant. Urea is commercially produced via the reaction of carbon dioxide and ammonia to form ammonium carbamate, which is subsequently dehydrated at high pressure (100–200 atm) and a temperature of 180°–185°C into urea. Therefore, it is of industrial interest to develop simplified approaches for the production of nitrogen fertilizers, especially at small to medium scales. A one-step process that can convert carbon sources, nitrogen sources, and/or hydrogen sources to nitrogen fertilizers at decreased pressure and/or temperature has the potential to meet such requirements of small- to medium-scale production of nitrogen fertilizers.

The most obvious advantages of electrochemical processes over the traditional processes mentioned above include 1) decreased process complexity since a one-step process is likely, 2) lower-cost operation since electrochemical reactions can be efficiently run at low temperature and pressure, and 3) decreased reactor system volume and size. The feasibility of using electrochemical processes for ammonia synthesis has been recently demonstrated [2–4]. Most of the electrochemical processes for the synthesis of ammonia reported to date have involved the cathodic reduction of nitrogen gas at the cathode of an electrochemical cell. Both aqueous-based and organic solvent-based electrolyte solutions have been used at ambient temperature and atmospheric pressure. In these liquid electrolyte solution-based investigations the source of hydrogen required for the formation of ammonia is provided by the electrochemical decomposition of water or an organic solvent, such as ethanol, at the anodes of the electrochemical cells.

Initial Energy & Environmental Research Center (EERC) work on electrochemical nitrogen-based fertilizer processes was focused on producing ammonia, urea, and ammonium nitrate from nitric oxide (NO) recovered from coal combustion emissions [5, 6]. High process current efficiency was obtained using NO as a nitrogen source at ambient temperature and atmospheric pressure. However, commercialization of these processes requires the availability of a commercially viable method for recovering NO from utility-scale coal combustion flue gases, and as of today, such a method is not available. In response to the lack of a clear, commercially viable path forward on the NO-based processes, the EERC focused on optimization of electrolytic processes for nitrogen fertilizer production that utilize air-separated elemental nitrogen (N₂) rather than NO as the nitrogen input. A key advantage of these electrolytic processes is that they can directly utilize syngas generated via coal or biomass gasification rather than the high-purity hydrogen required for Haber-Bosch-based processes. The principle of the
EERC renewable ammonia electrolytic process is schemed in Figure 1. Because the electrolytic processes can use a syngas comprising any combination of carbon monoxide and hydrogen, the cost of this “hydrogen-equivalent” input is significantly lower than the cost of the high-purity hydrogen required for the Haber-Bosch process.

2.0 GOALS AND OBJECTIVES

The EERC—in partnership with the North Dakota Renewable Energy Council, the North Dakota Corn Utilization Council, the Minnesota Corn Research and Promotion Council, and the U.S. Department of Agriculture—recently completed a project to optimize the EERC renewable electrolytic ammonia production process. Figure 2 is an overview of how the process would be implemented on a commercial scale. The primary project objectives were to:

- Optimize the ammonia production process using a single 2-watt (W) electrolytic cell.
- Using data acquired during the 2-W work, design and fabricate a 200-W multicell electrolyzer system.
- Optimize the process at a 200-W scale.
- Using data acquired during the 200-W work, develop a preliminary commercial-scale process design and use it as the basis for conducting an economic viability assessment of the electrochemical ammonia process integrated with a biomass gasification process.

Figure 1. Electrochemical ammonia production from N₂ and syngas.
3.0 EXPERIMENTAL

3.1 Electrolysis Cell and Process

A 2-W single electrolysis cell was developed. The cell comprised two high-alumina ceramic tubes separated by a membrane electrode assembly (MEA), as shown in Figure 3. During electrolysis, N₂ gas of 99.99% purity was passed through the cathode chamber. The outlet gas, which is a mixture of reaction products and unreacted N₂, was purged through a solution of 0.5 M sulfuric acid and then vented. Introduced to the anode chamber was high-purity hydrogen or a mixture of water vapor and high-purity carbon monoxide, which was used as a hydrogen resource. All current-controlled or potential-controlled electrolysis was performed using an Autolab general purpose electrochemical system (Ecochemie, Netherlands).

3.2 Evaluation of Cathode Catalysts

It is commonly accepted that the dissociative adsorption of N≡N on catalyst surfaces is the rate-limiting step for both cathodic hydrogenation of N₂ and thermal hydrogenation of N₂. In this research, initial evaluation of cathode catalysts was based on a thermal catalysis approach, which is schemed in Figure 4. During each measurement, 0.1–0.3 g of a powdered catalyst was placed in a continuous-flow microreactor having a volume of 1 mL and secured in place using a Swagelok® in-line filter. A mixture of hydrogen and nitrogen in a desired molar ratio, typically 3:1, was passed through the reactor at gas hourly space velocity (GHSV) = 7200 h⁻¹, and the product ammonia in the outlet gas was captured using a solution of 0.5 M sulfuric acid.
Figure 3. Schematic diagram (left) and image (right) of electrolysis cell.

Figure 4. System for fast evaluation of ammonia production catalysts.
3.3 Analysis of Products

The product ammonia in the outlet gas was captured using a solution of 100 mL 0.5 M sulfuric acid and analyzed by an ammonium ion-selective electrode (Cole-Parmer Instrument Company). Current efficiency was calculated from the ratio of the theoretical charge required for the formation of measured product to the total charge input, assuming the number of electrons transferred to each molecule of ammonia is 3.

4.0 RESULTS AND DISCUSSION

4.1 Development of Ammonia Production Catalysts

4.1.1 Catalyst Activity

At the cathode, the hydrogenation of N\textsubscript{2} is the target reaction, and hydrogen evolution is the main competitive reaction. To achieve high current efficiency of ammonia production, promising catalysts should possess high activity for ammonia formation and high overpotential for hydrogen evolution. Traditionally, an iron-based catalyst with magnetite has been widely used in the industrial process of ammonia synthesis. But the use of this class of catalyst requires critical operating conditions including high pressure and high temperature. Taking into account tendencies to lower the applied pressure and reduce energy consumption, it is of urgent importance to develop new catalyst systems that can work at lower pressure or/and lower temperature at no penalty of reduced activity. Research was focused on development of a non-iron-based catalyst system and included the following activities:

1. Evaluating a range of single elemental and bimetallic non-iron-based catalysts for the ammonia process, and then identifying promising candidates.

2. Investigating high-surface-area metal oxides and carbon materials as electronically conductive supports.

3. Optimizing surface promoters based on alkaline metal salts to improve catalyst activities.

4. Improving catalyst dispersion on supports by developing new application methods and optimizing preparation conditions.

5. Optimizing reaction conditions including temperature, pressure, and reactant inputs.

Figure 5 shows the impact of an improved surface promoter and support. Compared to unsupported catalyst (A), the surface modification of A with promoter (B) increased activity by a factor of about 40. Further substantial increase in activity is achieved by combining efforts: introduction of the promoter and use of catalyst support (C). In one example, (A+B+C1) activity is increased by a factor of around 1540 versus A.
4.1.2 Catalyst Lifetime Study

Catalyst durability was initially evaluated, with results shown in Figure 6. Encouragingly, it was found that no catalyst activity decay was observed over 16 days of uninterrupted operation at 250°C and atmospheric pressure with a molar ratio of $\text{H}_2/\text{N}_2 = 1:3$. Another batch of the same catalyst showed no sign of deactivation after a 28-day test at 350°C and ambient pressure with a molar ratio of 1$\text{H}_2$ to 2$\text{N}_2$ (Figure 7).

As a result of oxygen contamination in a cylinder of what was supposed to be pure hydrogen, it was found that the presence of oxygen deactivates catalyst and shortens its lifetime. Catalyst activity was studied during a 625-hr run at a 1:1 molar ratio of hydrogen to nitrogen in the presence of 300 ppm oxygen, 200 psi pressure, and temperatures of 350°–400°C. The catalyst activity measured at three different temperatures declined to 60% of its original value after 600 hr of continuous operation, as shown in Figure 8. These results indicate the importance of ensuring against oxygen contamination of the reactant gas mixture.

4.2 Electrolyte System Optimization

Three electrolyte systems have been evaluated for the ammonia process: molten salt electrolytes, ceramic-based solid oxide electrolytes, and high-temperature polymer membrane electrolytes. Because there are no suitable solid electrolyte membrane materials available in the appropriate temperature range, initial efforts focused on the evaluation of molten salt-based electrolyte systems, fixed in a ceramic matrix. For the preparation of a thin-film ceramic matrix,
Figure 6. Time dependence of catalyst activity at 250°C and atmospheric pressure with a molar ratio of 1H₂ to 3N₂.

Figure 7. Time dependence of catalyst activity tested with a molar ratio of 1H₂ to 2N₂ at 350°C and ambient pressure.
Catalyst Lifetime Study

Figure 8. Time dependence of catalyst activity at a 1:1 molar ratio of hydrogen to nitrogen in the presence of 300 ppm oxygen at 200 psi pressure and temperatures of 350°, 375°, and 400°C.

we used a tape-casting approach that normally includes a highly dispersed ceramic powder in flowing vehicles and casting of the resulting ceramic paste onto a smooth substrate. Because of the strong corrosivity of molten electrolyte systems, we examined the chemical stability of a couple of ceramic powders in the molten electrolyte system of interest and identified one stable ceramic powder for the preparation of a thin-film matrix. Flexible and uniform ceramic tapes were successfully prepared upon the optimization of the formula and casting procedure. Similarly, we successfully prepared electronically conductive tapes using metallic powders in place of ceramic powders. The ceramic and conductive tapes could be punched or cut into the desired shape for further treatment. Figure 9 shows the images of tape stripes, disks, and patches of conductive elements (dark gray) and ceramic elements (white).

Further treatment of both ceramic and conductive tapes mainly involved the firing of the tapes without deformations by controlling heating rate, firing temperature, and firing atmosphere. Porous electrode discs and porous ceramic discs with good mechanical strength were prepared and evaluated. At the cathode side, we used the porous electrode as a substrate to support newly developed cathode catalysts. At the anode side, the porous electrode prepared via tape casting was directly used as the anode. The porous ceramic tape sandwiched between the cathode and anode was evaluated after the firing treatment and the introduction of electrolyte component. We have examined gas permeability of the MEA based on the change of open-circuit potential (OCP) by introducing H₂ through the anode chamber and O₂ through the cathode chamber. The OCP value is measured at around 1.08 V, very close to the 1.18-V theoretical value under the same conditions. This means that the electrolyte component could satisfactorily fill in all pores of the ceramic matrix, and the MEA has acceptable gas impermeability.
Analogous to the preparation of ceramic electrolyte substrates, thin films of solid oxide electrolytes have also been developed via a tape-casting technique followed by the firing of the tapes. This free-standing thin electrolyte membrane can be “sandwiched” between anode and cathode electrocatalyst layers and evaluated for ammonia formation potential. The biggest challenge associated with the use of solid oxide electrolytes is their operating temperature, normally in the range of 600° to 1000°C, much higher than the normal reaction temperature for the production of ammonia. This temperature range makes the simultaneous decomposition of ammonia back into hydrogen and nitrogen likely, which is undesirable. We have attempted to decrease the operating temperature of the solid oxide electrolytes by decreasing the thickness of the electrolyte thin films. However, the preparation of the thin ceramic film (<10 μm) is extremely challenging, which prevents us from developing a scalable ammonia production process based on solid oxide electrolytes.

Because high-temperature polymer electrolytes have been successfully developed for gas separation and high-temperature fuel cells that can operate on raw hydrogen streams containing high CO levels, the possibility of using high-temperature polymer electrolytes was evaluated in the ammonia process. Figure 6 clearly shows that the evaluated catalyst demonstrates reasonable activity at 250°C. The catalyst was still active at 200°C. This temperature is very close to the operating temperature of high-temperature polymer electrolyte membrane fuel cells (140°–200°C), which makes an ammonia production process based on high-temperature polymer electrolytes very promising because of their low cost and large-scale production potential. Therefore, our process scale-up efforts were focused on an electrolytic ammonia process based on high-temperature electrolyte membranes.
4.3 Process Optimization

Process optimization work has been focused on improving process efficiency and decreasing energy consumption for ammonia production via the following efforts:

- Evaluating nonsupported and supported catalyst systems.
- Examining different electrolyte systems based on molten salts and solid proton conductors.
- Assessing the impact of reaction temperature, reaction pressure, reactant feed rate, and electrolysis mode on process efficiency and energy consumption.

4.3.1 Catalyst Reaction Temperature

For almost every cathode catalyst tested in the temperature range of 200°–500°C, there was a maximum of activity observed somewhere between 350° and 425°C, depending on other variables. Figure 10 is a typical graph of catalyst activity as a function of temperature obtained at a 1:2 molar ratio of hydrogen to nitrogen at atmospheric pressure and a gas space–time velocity (GSTV) of 7200 hr\(^{-1}\) STV.

4.3.2 Gas Composition

In addition to temperature, the ratio of hydrogen to nitrogen also has a big effect on catalyst activity. The nature of the relationship between hydrogen content and temperature is shown in the three-dimensional graph in Figure 11. The reaction rate maximum is located

![Figure 10. Catalyst activity as a function of temperature for a 1:2 molar ratio of H\(_2\):N\(_2\).](image)
between 50% and 67% hydrogen content in a binary mixture with nitrogen; i.e., at H:N molar ratios of 1:1 to 2:1.

### 4.3.3 Pressure Dependence

Generally, pressure helps to increase catalyst activity and ammonia yield. The dependence of ammonia yield on pressure is shown in Figure 12. Yields as high as 18% per single pass can be achieved. As can be seen, sufficiently greater benefit is achieved at pressure values of 200–300 psi. However, systems with different ratios of H₂:N₂, especially at low temperatures, could have a different response to the pressure change, from positive to negative. Thus, at 300°C for a 1H:2N mixture, catalyst activity was almost independent of pressure (Figure 13).

### 4.3.4 Current Efficiency

The current efficiency for ammonia production is a ratio of theoretical charge required for the production of the measured amount of ammonia to the actual charge consumed. At the cathode side, there are two competing electrochemical reactions. The formation of ammonia is the target reaction, and hydrogen evolution is the side reaction. Figure 14 clearly shows that current efficiency is strongly dependent upon current density. At low current density, the calculated current efficiency is as high as 96%. However, the current efficiency is considerably decreased with increasing current density. Therefore, it is important to suppress the side reaction (H₂ evolution) or somehow utilize the side reaction during process optimization. As a result of
Figure 12. Pressure dependence of ammonia yield at a H₂:1N₂ mole ratio with 120 cc/min total gas flow rate (7200 h⁻¹ GSTV) at temperatures of 350°, 375°, and 400°C.

Figure 13. Pressure dependence of ammonia yield at 1H₂:2N₂ mole ratio with 120 cc/min total gas flow rate (7200 h⁻¹ GSTV) at temperatures of 350°, 375°, and 400°C.
the need to utilize evolved molecular hydrogen to achieve maximum current efficiency, our process development strategy was shifted to the development of a two-stage process comprising electrochemical hydrogen purification followed by thermal catalytic ammonia formation from hydrogen and nitrogen. The integrated electrochemical–thermal (IET) process is illustrated in Figure 15.

At a constant current density, it was found that current efficiency for ammonia formation is affected by the choice of electrolyte media. An example is shown in Figure 16. This dependence is understandable because the electrochemical hydrogenation of nitrogen is strongly related to the surface promoters on the catalysts. The cation or anion component of the electrolytes could be adsorbed on the catalyst surface, modifying the catalyst activity. Therefore, it seems that optimization of the electrolyte media is also needed for process optimization.

### 4.3.5 Cell Voltage

The cell voltage for an electrolytic ammonia process is normally determined by cathode overpotential, electrolyte resistance, and anode overpotential. Therefore, it is important to develop a highly active cathode electrocatalyst for decreased cathode overpotential and a highly conductive electrolyte membrane for decreased electrolyte membrane resistance. Figure 17 demonstrates progress in decreasing cell voltage via these two efforts. The cell voltage has been decreased by about 75% during the reporting period.
Figure 15. IET process for ammonia production.

Figure 16. Dependence of ammonia formation current efficiency on electrolyte media (EA, EB, and EC) at constant current density.
4.4 Process Optimization with a 200-W Multistack

4.4.1 Design and Fabrication of a 200-W Multistack

For process optimization, a 200-W electrolyzer stack comprising 10 single cells connected in series and having the capability to produce about 0.5 kg of ammonia per day has been designed and fabricated. The bipolar plate used to connect two adjacent cells is made of graphite and has a five-channel serpentine flow field on each side, as shown in Figure 18. The geometric surface area of the flow field is around 50 cm². The hardware for a fully integrated single cell including two stainless steel end plates, two end flow field plates, and one MEA is depicted in Figure 19. The two end plates, two end flow field plates, nine bipolar plates, and 10 MEAs are used in the construction of the 200-W electrolyzer stack, which is shown in Figure 20.

4.4.2 IET Process

The biggest advantages of the IET process include the abilities to 1) fully utilize the side product, molecular hydrogen, formed during the electrolytic process; 2) maximize the efficiency of the electrolytic process; and 3) use high-temperature polymer electrolytes for process scale-up. Initial work was performed to demonstrate the feasibility of producing high-purity H₂ using a polymer electrolyte-based electrochemical process at ambient pressure by feeding a simulated syngas consisting of 76% H₂ + 2% CO + 2% CH₄ + 20% CO₂ through the anode chamber and pure nitrogen gas through the cathode chamber. The electrochemical hydrogen purification results measured at OCP and under constant-current polarization are
Figure 18. Image of a graphite bipolar plate with a serpentine flow field of 7.1 cm × 7.1 cm in size.

Figure 19. Image of a single unit (20-W) of a 200-W electrolyzer stack.
listed in Table 1. At OCP and 140°C, crossover of hydrogen (and CO, CO₂, and CH₄ gas) through the polymer membrane is too low to be detected by gas chromatography (GC), while at 180°C, slow H₂ crossover occurs. However, as shown in the table, at temperatures of 140°, 160°, and 180°C and a current density of 200 mA/cm², the polymer membrane is impermeable to the gas impurities CO, CO₂, and CH₄. Under constant-current polarizations, only H₂ is detected as an exclusive cathode product, and no CO, CH₄, or CO₂ is found in the cathode gas stream. For the purpose of comparison, pure H₂ (rather than syngas) was fed to the anode side (at 140°C); a similar H₂ recovery was achieved, as shown in the table under the “H₂” column. These results indicate good viability of the IET process for ammonia production since hydrogen produced in the electrochemical unit could be directly utilized in the downstream thermal ammonia reactor. This integration could address the limitation of high current density on current efficiency. In

Table 1. Hydrogen Extraction from Syngas as Function of Temperature

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Current Density/ mA cm²</th>
<th>Cathode Gas Composition Using H₂ or Syngas as Anode Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>140</td>
<td>200</td>
<td>50.6% H₂ + 49.4% N₂</td>
</tr>
<tr>
<td>160</td>
<td>200</td>
<td>51.9% H₂ + 48.1% N₂</td>
</tr>
<tr>
<td>180</td>
<td>200</td>
<td>50.9% H₂ + 49.1% N₂</td>
</tr>
<tr>
<td>180</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

H₂, Syngas
principle, ammonia production could be operated at very high current densities. This is important for large-scale ammonia production directly utilizing syngas.

In process optimization tests, simulated syngas (76% H₂, 2% CO, 2% CH₄, and 20% CO₂) directly from commercially available tanks without external humidification was supplied to the anode side, and high-purity nitrogen (99.99%) was fed to the cathode side to carry produced hydrogen to the thermal unit for ammonia formation. In an electrolysis mode at constant current (200 mA cm⁻²) and a temperature of about 200°C, a cell voltage of about 0.16 V was used to provide hydrogen for the ammonia reaction at a rate of about 86 cc/min. The calculated molar ratio of hydrogen to nitrogen was 2.16. The outlet of the cathode chamber was attached to a tubular thermal reactor heated by a furnace. The thermal reactor, although not required, is used to increase the conversion rate. The temperature in the thermal reactor was set to 400°C. The volume of the catalyst bed in the thermal reactor was about 1 mL, and GSTV was 7200 hr⁻¹. The pressure in the cathode chamber and in the thermal reactor was ambient. The stream of gases from the thermal reactor was passed through a trap filled with phosphoric acid and purged to the atmosphere. Ammonia trapped as phosphate salt was analyzed by the potentiometric method. The rate of ammonia production was 151 mmol hr⁻¹ g⁻¹. For the purpose of comparison, pure hydrogen (99.99%) in place of syngas was fed to the anode side while keeping all other parameters the same. The rate of ammonia production in this case was measured to be 153 mmol hr⁻¹ g⁻¹. The fact that the production rate is not changed by altering the anode feed under constant-current electrolysis strongly indicates the technical feasibility of the IET approach for ammonia production from syngas.

To compare the electrochemical approach with the traditional technology, an experiment was performed by directly feeding the simulated syngas at a rate of 80 sccm to a thermal reactor rather than the electrolyzer at ambient pressure. Nitrogen gas was added at a rate 40 sccm to keep the molar ratio of H₂ to N₂ at 2:1 and the total flow of the gas mixture at 120 sccm. The rate of ammonia production was 9 mmol hr⁻¹ g⁻¹ for the first 3 min and dropped to 6 mmol hr⁻¹ g⁻¹ for the next 2 hr. The significantly lower production rate of ammonia from a syngas in a traditional method (9 vs. 153 mmol hr⁻¹ g⁻¹) indicates catalyst poisoning and that the syngas could not be used directly as the feed.

To further improve the conversion of hydrogen and nitrogen, the stream of unreacted gases after passing through the phosphoric acid trap was recycled back to the thermal reactor using a gas pump operated at a rate such that the total flow of gases through the reactor was 944 standard cubic centimeters per minute (scm). The pressure of gases in the thermal reactor was controlled at 1.5 atm. The initial molar ratio of hydrogen to nitrogen was 2.0. The ratio of added gases after reaching steady state was 3.0. The rate of ammonia production was measured to be 389 mmol hr⁻¹ g⁻¹. The yield of ammonia on a hydrogen basis was close to 100%.

4.4.3 Preliminary Design for an IET Ammonia Process

A preliminary design for an IET ammonia process was developed and is shown in Figure 21. In this process, it is envisioned that air-separated N₂ and biosyngas are fed to the cathode side and anode side, respectively, with the unreacted syngas recycled at the anode side. At the cathode side, the product ammonia, side-product H₂, and unreacted N₂ flow through a
Figure 21. Preliminary design for an IET ammonia process.
downstream thermal reactor where H₂ and N₂ react to thermally produce ammonia. The product ammonia produced electrochemically and thermally is captured inside a chiller, and the unreacted N₂ and H₂ are recycled to the cathode side. All temperatures and pressures are controlled by a computer with temperature and pressure sensors.

5.0 ECONOMIC VIABILITY ASSESSMENT

Preliminary estimates were developed for the cost of producing renewable ammonia via the IET process. This process is conducted at atmospheric pressure and at a temperature range of 200°-400°C and utilizes inputs of molecular nitrogen and biosyngas. Table 2 shows projected total costs of ammonia production via the IET process at project initiation, midway through the project, and at project conclusion. The table shows the dependence of production cost on electricity consumption, and the significant impact of electricity consumption decreases achieved during the project via numerous process improvements. For comparison, at the time of this writing, the wholesale market price of ammonia (Tampa, Florida, basis as per ICIS) was $380/ton.

6.0 CONCLUSIONS

An IET ammonia production process that utilizes electricity, N₂ extracted from air, and syngas produced via biomass gasification was proven technically feasible and has been optimized at the EERC. This feasibility demonstration illustrates the good potential commercial viability of directly utilizing syngas for ammonia production rather than the high-purity hydrogen required for the Haber–Bosch process. Because the IET process can use a syngas comprising any combination of carbon monoxide and hydrogen, the cost of this “hydrogen-equivalent” input is significantly lower than the cost of high-purity hydrogen. Key results of the electrolytic ammonia process development work include:

Table 2. Initial and Current Cost Projections for Per-Ton IET Ammonia Production from N₂ and Biosyngas

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Interim</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syngas Price</td>
<td>$6/MMBtu¹</td>
<td>$6/MMBtu</td>
<td>$6/MMBtu</td>
</tr>
<tr>
<td>Electricity Price</td>
<td>$0.05/kWh</td>
<td>$0.05/kWh</td>
<td>$0.05/kWh</td>
</tr>
<tr>
<td>Cost of Electricity²</td>
<td>$322</td>
<td>$240</td>
<td>$120</td>
</tr>
<tr>
<td>Cost of Syngas Input</td>
<td>$142</td>
<td>$142</td>
<td>$142</td>
</tr>
<tr>
<td>Capital Cost</td>
<td>$21</td>
<td>$21</td>
<td>$21</td>
</tr>
<tr>
<td>O&amp;M Cost</td>
<td>$20</td>
<td>$20</td>
<td>$20</td>
</tr>
<tr>
<td>Cost of N₂</td>
<td>$12</td>
<td>$12</td>
<td>$12</td>
</tr>
<tr>
<td>Total Cost</td>
<td>$517</td>
<td>$435</td>
<td>$315</td>
</tr>
</tbody>
</table>

¹ DOE 2010 target.
² Electricity consumption kWh/ton anhydrous ammonia: 6450 (initial); 4800 (interim); and 2400 kWh/ton (current).
• Development of highly active and durable ammonia catalysts operable at lower
temperature and pressure than required for the Haber–Bosch process.

• Development of an innovative electrolytic ammonia process based on integration of
electrochemical and thermal ammonia reactions, resulting in increased reaction rate and
current efficiency and decreased energy consumption.

• Design and fabrication of 200-W electrolyzer stack capable of producing ammonia
using sygas comprising CO₂, CO, H₂, and CH₄.

• Completion of a preliminary economic assessment indicating commercial viability of
the IET ammonia process.

7.0 REFERENCES

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