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CSIRO Hydrogen to Ammonia R&D Project – 2018 / RND002

Final Public Report

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Low Emissions Technologies Program, Energy Business Unit

Contents

Figures

Acknowledgments

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Executive summary

The major objective of this R&D project was to demonstrate the conversion of hydrogen to ammonia at significantly lower pressures compared to the conventional Haber-Bosch (H-B) process that requires pressures in excess of 150 bar. Orica and GRDC (Grains Research and Development Corporation) were the other project partners. Orica is a major ammonia producer in Australia, and have contributed to the designing of the ammonia synthesis reactors and flow sheeting of the process; and GRDC have contributed in providing funds to the project as well as in producing reports on the viability of using farm based biomass for ammonia production. The scope of work in this final period of the project was to construct and operate a prototype reactor system capable of producing a kilogram of ammonia per day. The ammonia production demonstration rig has been built capable of operation at 30-50 bar pressure, 450^{o}C temperature and producing 1 kg/day ammonia in CSIRO's Centre for Hybrid Energy Systems (CHES). This report provides the details of the rig constructed for the production of ammonia and its operation. The demonstration rig has been operated for more than 200 hours of accumulated period, and for more than 24 hours continuous operation. The hydrogen to ammonia conversion rates, volume% of ammonia in the product stream and ammonia production rates were continuously monitored during the rig operation. The hydrogen to ammonia conversion rates and Vol% ammonia in the product stream were respectively achieved up to 14.5% and 7.5 Vol% at 30 bar pressure. These values are very encouraging when compared to those achieved by Haber-Bosch process at above 150 bar pressures in a single pass through the catalyst bed, thus clearly demonstrating the merits of this technology. The production rate of ammonia achieved by the rig operation at 30 bar pressure were up to 400g/day. These values are lower than the originally designed reactor capacity of 1 kg/day and is due to the reduced volume of the membrane reactor that was essential to overcome the reactor sealing challenges. The ammonia production rates were though found to be very stable over the time period, and somewhat improving with the duration of operation.

A substantial IP has been generated during this reporting period in the form of publication of a provisional, invention disclosure report on a new hybrid reactor ammonia production concept, and know-how in several other areas (Reactor design concepts, reactor materials and designs, ammonia capture and gas recycling strategies).

The other additional areas of work during this reporting period were: the preliminary costing of the pilot scale facility and ammonia production costs based on this technology; participation of the project team in the GRDC / BRII challenge initiative on biomass to hydrogen / ammonia (This involvement is still continuing with two SMEs currently building proof of concept plants based on respectively gasification and biohydrogen production process).

CSIRO team is currently in discussions with existing industrial partners Orica and GRDC, and an investor company. A proposal was prepared and submitted to the partners. There is in principle agreement now to continue the technology development work for another 6 months, while a strategy is being developed on the technology commercialisation.

This project area has been presented / discussed during this period at three more international events / conferences and one local event as part of the knowledge sharing activity.

1 Introduction

1.1 Rationale

Currently most of the ammonia is globally produced by sourcing hydrogen from Natural Gas (NG) and making this hydrogen react with nitrogen in the presence of a catalyst in a Haber-Bosch reactor at around 450^{o}C and pressures in excess of 150 bar. The major aim of the proposed work was to develop an alternative technology that can produce ammonia at much lower pressures (~30 bar) by sourcing hydrogen directly from a PEM electrolyser and scale-up the technology to build a prototype capable of producing ammonia with the only inputs being water, air and solar PV. In the conventional ammonia synthesis Haber-Bosch reactor hydrogen to ammonia conversion rates of around 15% are achieved at pressures above 150 bar, in a single pass and with multiple passes the reactor is able to achieve over 90% hydrogen to ammonia conversion. In the previous project (2014-2016) in collaboration with Orica, a membrane-based process was developed to convert hydrogen to ammonia. The technology was developed to TRL 3, with ammonia synthesis rates of up to 10^{-6} mol cm^{-2} s^{-1} and hydrogen conversion rates of up to 4% at pressures much lower than used in the conventional H-B reactor. The technology was demonstrated in the lab by sourcing hydrogen directly from a PEM electrolysis cell.

1.2 Objectives

The main objective of the work in this project was to enhance hydrogen conversion rates from 4% to 15% at pressures up to 35 bar (current capability of PEM electrolysers to produce hydrogen) and scale-up the technology to build a prototype unit capable of producing ammonia with hydrogen sourced from a gas cylinder or an electrolyser. This work involved the development of catalyst, modifications to catalyst/membrane interfacial structures, reactor design optimisation for the process conditions and scale-up of the reactor to showcase the commercial viability of the technology by building a prototype that produces ammonia at a kilogram scale per day.

1.3 Thermodynamics

Ammonia is conventionally produced by Haber-Bosch process by making hydrogen sourced from NG and nitrogen react in the presence of an iron-based catalyst. The ammonia synthesis process can be represented by the following reaction:

$$N_2 + 3H_2 = 2NH_3 \qquad \Delta H = -46 \text{ kJ mol}^{-1}$$

The exothermic nature of the reaction and decrease in entropy indicates that the ammonia synthesis is favoured at lower temperatures and high pressures. However due to the slow kinetics of the reaction, the synthesis process is carried out at high temperatures (400-500^{o}C) and high pressures (in excess of 150 bar). There are worldwide efforts to lower the pressure required for the ammonia synthesis to make it a less energy and capex intensive process and to be able to produce ammonia at distributed scale (few tonnes/day), as compared to the existing centralised plants that produce over 1000 tonnes of ammonia per day. However, lowering the pressure also lowers the amount of ammonia produced in the product stream due to the decrease in equilibrium content[1] as seen in **Error! Reference source not found.**. For example, at 450°C the equilibrium ammonia content is around 22% at 150 bar compared to only 6.5% at 30 bar.

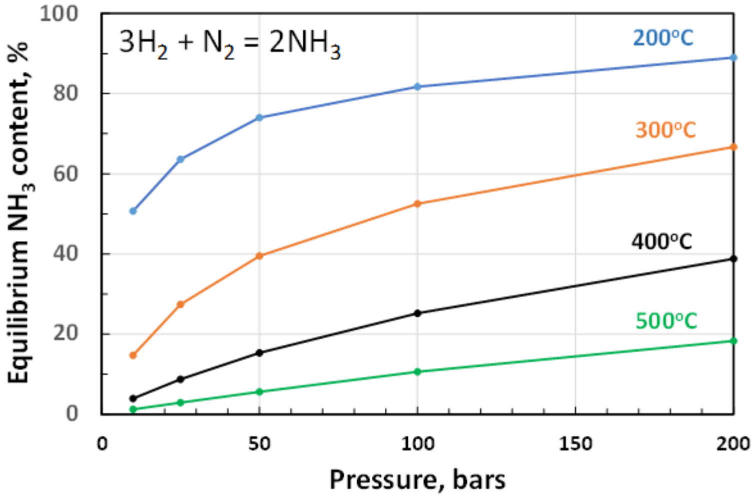

Figure 1 The equilibrium content of ammonia as a function of temperature and pressure

We are here proposing a new concept that allows the achievement of ammonia concentrations above the equilibrium value, thus making the ammonia synthesis process occur at lower pressures.

[1] The maximum volume % of the product (i.e. ammonia) achievable under certain process conditions (i.e. temperature and pressure).

2 Milestone activities description and progress

2.1 Technology demonstration rigs

2.1.1 Gas Supply System

The demonstration rigs were constructed in the Centre for Hybrid Energy Systems (CHES) in Victoria. For the purpose of the demonstration, gases connected to the rig are Nitrogen (N_2) and Hydrogen (H_2)/Nitrogen (N_2) gas mix. However, during the catalyst conditioning stages, pure H_2 was made available to the rig. The H_2/N_2 Gas mix and N_2 gases were supplied from the gas cylinders at this stage, but facilities are being built to use hydrogen in future from an electrolyser powered by solar PV panels on the CHES building.

2.1.2 Overall Rig layout

The overall rig consists of 4 cabinets.

Cabinet 1 houses the instrument controls consisting mainly of gas flow control panel and readouts (manufactured by Bronkhorst), reactor temperature controllers, datalogger and a computer. *Cabinet 2* houses the gas analyser and the calibration gas for the calibration of the gas analyser as required at regular intervals. *Cabinets 3 &4 house* the dual reactor arrangement for the ammonia production. Except for the cabinet 1, all others are connected to dedicated exhaust ducting system for the appropriate dilution and subsequent disposal of the gases to the atmosphere after the capture of ammonia.

2.1.3 Exhaust and ammonia disposal system

The main extraction duct is in the middle of the Laboratory. All 3 cabinets are connected to this main exhaust system. All gases from the reactors are passed through an ammonia scrubber then diluted by sufficient mixing with once through air, and the safe levels are exhausted into the atmosphere above the plant room which resides directly above the laboratory.

2.1.4 Laboratory safety system

The overarching laboratory safety system monitors parameters in rigs and the laboratory. If any unsafe conditions/levels are reached in the laboratory, the safety system shuts down power to rigs, gases at source and activates alarms and warnings. The power and alarms latch on until safe conditions are manually acknowledged and reset.

2.1.5 Rig Safety triggers

The cabinets that house the two reactors have their own individual safety triggers that also communicate unsafe conditions to the Laboratory safety panel. These triggers also actively take internal action to prevent escalation.

2.1.6 Reactors

The reactors were designed to be able to operate at temperatures up to 500°C and pressure in the 30-50 bar range, and capable of handling gas flow rates to produce ammonia at a production rate of 1kg/day.

2.2 Demonstration rig operation and results

The demonstration rig was operated for 165 hours of accumulated time with gas flow rates through the reactors in the range 1.2 to 1.5L/min, and for 25.5 hours continuously with gas flow rate 7.75L/min. The reactors were operated at pressures varying from around 15 to 30 bar and temperature maintained close to 450°C.

Following observations were made from the operation at lower flow rates (1.2 to 1.5L/min).

- The vol% ammonia in the product stream increased with increase in pressure from 15 to 30 bar. These values were reasonably stable over the time period for particular process parameters. The peak values of ammonia vol% achieved at 30 bar pressure after 120h operation were in the 7.0 – 7.5 vol% range. This value is higher than the equilibrium value of 6.5 vol% ammonia that can be achieved under the process conditions in a Haber-Bosch reactor. This clearly demonstrates the merits of the new concept proposed in this project.
- The hydrogen to ammonia conversion rates were also a function of the reactor pressure. Again these values were reasonably stable under particular process conditions, but continued to improve with time. The peak values of conversion achieved at 30 bar were in the 13.5-14.5% range. These values are extremely high, and again demonstrates the benefits of the current approach of ammonia synthesis.
- The ammonia production rates were a function of the reactor pressure. Again these values were reasonably stable under particular process conditions, but continued to improve with time. The peak values of ammonia production rate achieved at 30 bar pressure were in the 105-112 g/day range during 165 hours of operation.

After 165 hours of operation of the rig, the total gas flow rates were increased to 7.75L/min, and the rig was operated for another 25.5 hours at this gas flow rate. The temperature and pressure in the reactors were maintained respectively close to 450°C and 30 bar. Following observations were made from the results obtained.

- The vol% ammonia in the product stream was reasonably stable for a significant part of the operation, though showing a steady increase with time at later stages of the operation. The peak values of ammonia vol% achieved was 5.2 vol%. This value is lower than the equilibrium value of 6.5 vol% ammonia that can be achieved under the process conditions in a H-B reactor. These lower values seem to be due to the high gas hourly space velocities (GHSV)[2] through the reactors. Note that the volume of one of the reactors had to be reduced to less than 1/10th due to sealing issues, and this contributed to extremely high GHSV through the reactor.

- The hydrogen to ammonia conversion rates were reasonably stable and continued to improve with time. The peak values of conversion achieved were close to 10.5%. These values are again reasonably high considering a single pass of gases.
- The ammonia production rates were reasonably stable and continued to improve with time. The peak values of ammonia production rate achieved were close to 0.4 kg/day.

The demonstration rig was operated for a total period of over 200 hours, producing close to 1 kg of ammonia during this period. The ammonia production rates in the last 25.5h operation increased from 0.3kg/day to 0.4kg/day by the end of operation. In order to realise the full potential of the technology, one of the reactors will require redesigning so it can be operated at higher gas flow rates as per the original design parameters of the reactor to achieve more than 1 kg/day target.

[2] GHSV – Gas Hourly Space Velocity (units expressed as per hour) is the term used for the industrial reactors and is a measure of the volume of the reactor able to be utilised for the reaction.

3 Additional work

The main focus of the R&D work was on the completion of the project milstones, however some additional work, crucial for the successful outcome of this project was carried out and is described below.

3.1 Preliminary costing of pilot scale facility and ammonia production costs

A preliminary designing and costing analysis of a pilot scale plant based on the developed technology with hydrogen sourced from an electrolyser powered by solar PV were carried out to explore the technical and economic viability of this technology for commercialisation. The staff from Orica (engineers) and CSIRO (flow sheeting, techno-economic analysis etc.) worked on this together. The techno-economic analysis was performed under certain assumptions. The preliminary plant capital cost and ammonia production costs were determined as a function of pilot plant size.

The results showed that a 10 tonnes/day ammonia production pilot scale facility (Includes the electrolyser capital and operating costs but not of solar PV facility) will cost around $15M with ammonia production costs of around $650/tonne. Assuming lower costs of the materials used in the reactors, reduced the cost of the pilot plant to $11.5M with a ammonia production cost of around $550/tonne.

3.2 Other initiatives in support of the current project

Hydrogen from farm waste (Biomass):

GRDC is one of the partners in this project. GRDC had applied for funding via the Business Research and Innovation Initiative (BRII) (Department of Industry, Innovation & Services) to seek innovative solutions (in the form of feasibility studies) from SMEs. The solutions would be addressing the challenge of obtaining hydrogen from farm waste (biomass) in order to feed the ammonia production technology that we are working on. This application by GRDC was successful.

GRDC worked with BRII in selecting 4 SMEs to do the feasibility study. Each SME received approximately $100,000 over 3 months to conduct the study. At the conclusion of these studies, all SMEs were asked to apply for further funding ($1M for over 18 months) from BRII for constructing a prototype hydrogen production pilot for the production of ammonia. The challenge is to use farm based biomass to produce hydrogen of following specifications, for the ammonia production:

- Hydrogen will need to be of high purity (>99.9%).
- Impurities (Sulphur, arsenic and chlorine containing compounds) <1ppm total.
- CO, CO_2, H_2O and any other oxygen containing compounds <10ppm total.

- Pressure will need to be in excess of 30 bar.
- Hydrogen production in excess of 200 kg/day.

Two SMEs were selected to work on the pilot scale demonstration, and have received $1M each. CSIRO staff (S Giddey and San Hla) have been supporting and providing advisory role to GRDC and BRII on this journey for two years by regularly attending meetings / discussions, and scrutinising the SME applications for moving to next rounds, including the monitoring of the progess of the projects. The SMEs selected and currently involved in the pilot scale demonstration are as follows.

- HydGene Renewables - On-farm biohydrogen production from excess crop residues – straw waste.
- Wildfire Energy Pty Ltd - Grain Crop Residues to Hydrogen using the Moving Injection Horizontal Gasification (MIHG) Process

The above projects are under way now.

4 Way forward and future work

CSIRO team is currently in discussion with existing industrial partners Orica and GRDC, and an investor company. The investor company is a specialist climate change investment and advisory firm, accelerating the transition to a net zero, nature positive future. CSIRO has prepared a proposal for further technology development leading to pilot scale demonstration of the technology, and this was shared with Orica, GRDC and the investor company. The discussions are still continuing on developing the best path forward (i.e. through the formation of a company etc.) to take this technology to commercialisation scale. While this is being finalised, GRDC has agreed to fund further R&D work on this project for another 6 months.

5 IP / know-how and knowledge sharing

Patents granted, PCT (Patent Cooperation Treaty), Invention disclosures and know-how:

- Processes utilising selectively permeable membranes; US patent 9895652, now also granted in Europe, Australia, Japan, South Korea, China.
- Application published now on "Ruthenium promoter catalyst compositions" filed in March 2020 - US 2021/0395101 A1.
- Prepared an invention disclosure report on "ammonia synthesis to produce ammonia contents above equilibrium contents";.
- Know-how under consideration for patenting in future: Reactor concepts, materials and designs, ammonia capture and gas recycling strategies.

Conferences / Forums where the project was discussed:

1. Invited talk - Austrade CSIRO Japan H_2 Webinar 12 March 2021, Ammonia as a energy carrier – production and utilisation technologies, Sarb Giddey and David Harris
2. Invited talk - Australian-French Workshop on Hydrogen, 22-23rd Sept 2021, CSIRO research activities on hydrogen and ammonia production, Sarb Giddey
3. Invited talk - Presentation made to Fortescue Future Industries, 29th June 2021, Electrochemical synthesis of ammonia – global technology status, Sarb Giddey
4. Invited talk - Green Ammonia International Conference, 14th Sept 2021, Organised by Korea Institute of Energy Research (KIER), Australian initiatives on green ammonia, Sarb Giddey

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