AMMONIA – THE OTHER HYDROGEN

Rebecca Dunn, Keith Lovegrove
Solar Thermal Group
Department of Engineering
Australian National University
rebecca.dunn@anu.edu.au, keith.lovegrove@anu.edu.au

ABSTRACT

This paper reviews many aspects of the use of ammonia as a renewable fuel, including the properties of the fuel itself, and current developments in the field. Most notable among the properties of ammonia is the high energy density. Current developments in the field of ammonia fuel use include advances in solid state ammonia synthesis, direct ammonia fuel-cells, combustion characterisation of ammonia-powered Internal Combustion engines and on-vehicle storage innovations with metal ammines. In addition, commercial projects are currently underway in the US to utilise hydroelectric power from Niagara Falls and wind power in the mid-west to produce ammonia.

The ANU Solar Thermal Group is in the process of commercialising a baseload electricity generation process involving an ammonia-dissociation-based storage system. The synergies possible between this process and ammonia production lead to a comparison between the use of concentrating solar thermal energy to produce ammonia as an alternative to using this same energy to generate baseload electricity via the aforementioned process. The solar-to-end-product efficiency was found to be 15% for the production of ammonia fuel, and 26% for the generation of baseload electricity.

INTRODUCTION

A future energy economy based on hydrogen that is derived from splitting water using renewable energy is a much discussed element of a truly ecologically sustainable society. A range of technology solutions have been presented that address the various technical challenges. Implementing technical solutions in an economically feasible manner is possibly the greatest challenge. If electrolysis of water using renewable electricity is chosen as the method of production, then extra capital cost and energy losses must be added to the already challenging task of producing renewable electricity at least cost. The next challenge is the storage and transport of an element that is naturally gaseous and has an extremely low temperature for liquification. High pressure vessels, cryogenic tanks and metal hydride banks are all technically possible options, once again at a cost. Each of these would also require a major global shift in the nature of energy infrastructure.

An alternative approach to the storage and transport issue is to combine hydrogen into a compound that preserves the energy value but is easier to transport as a liquid. Methanol is one option, ammonia is another.

The Australian National University has worked for many years on a solar thermochemical energy storage system based on the reversible dissociation of ammonia, since it was first proposed by Carden (1974). In this concept a fixed inventory of ammonia is alternately dissociated and re-synthesised to provide energy transport and storage for solar thermal power generation. When the concept was first introduced it was recognised that as well as producing dispatchable electric power, the potential existed for building an oversized ammonia synthesis block and with the addition of renewable hydrogen production and air separation, to provide a net export of ammonia.

This paper briefly reviews the solar ammonia work and then looks in depth at the properties of ammonia as a fuel and current developments in the field. A preliminary assessment is then reported of the viability of producing ammonia in conjunction with the ammonia-dissociation-based solar thermal storage method.

AMMONIA-BASED SOLAR ENERGY STORAGE

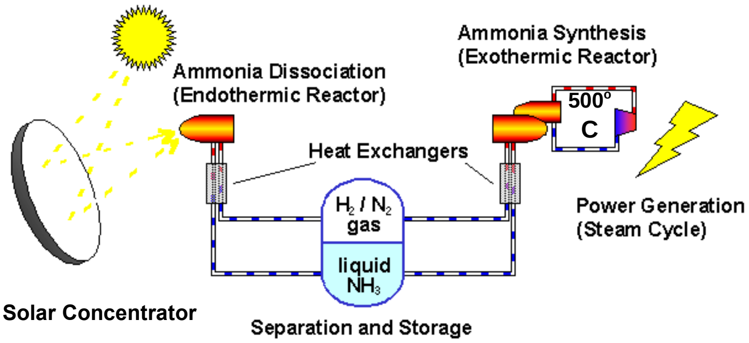

Fig. 1: An overview of energy storage using the dissociation of ammonia.

The concept of solar energy storage using the reversible dissociation of ammonia is illustrated in Fig. 1. A fixed inventory of reactants passes alternately between energy-storing and energy-releasing reactors with provision for ambient temperature storage of reactants in between. These reactors are packed bed catalytic units which use standard commercial catalyst materials. Counter-flow heat exchangers transfer heat between in-going and out-going reactants at each reactor, so that the ambient temperature storage is achieved with minimal thermal loss. In addition, there is almost 100 years of industrial experience with the "Haber Bosch" process for ammonia synthesis to call upon.

The dissociation reaction is endothermic, and proceeds according to Equation (1).

$$NH_3 + \Delta H \rightleftharpoons \frac{1}{2} N_2 + \frac{3}{2} H_2 \tag{1}$$

In a thermochemical storage system, the whole system operates at the high pressures that are needed for effective ammonia synthesis. At 20MPa, 20°C, the enthalpy of reaction is 66.8kJ/mol.

Successful ammonia dissociation experiments have been carried out using a $20m^2$ paraboloidal dish concentrator (Lovegrove *et al.* 2004). ANU's ammonia technology has been licenced to Wizard Power Pty Ltd (www.wizardpower.com.au), who have secured support via the Australian Federal

Government's "Advanced Energy Storage Technology" program, to demonstrate the technology with an array of 500m^2 Big Dish concentrators, similar to the 400m^2 prototype dishes also shown in Figure 2. The possibility of operating the system with lower concentration parabolic concentrators has also been investigated Fig. 2: The Big Dish prototype. (Dunn *et al*. 2007).

AMMONIA AS A FUEL

The oxidation of ammonia proceeds according to Equation 2. The only products of the complete oxidation of ammonia are water and nitrogen gas. At standard conditions (25°C, 1atm), the enthalpy of combustion is 317kJ/mol.

$$NH_3 + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2O + 317kJ \tag{2}$$

At 25°C, the saturation pressure of ammonia is 6.7 bar, around the same as propane which is commonly used in LPG powered cars and for portable gas cookers. Zamfirescu and Dincer (2008), have carried out an extensive review of the use of ammonia as a fuel. In order for ammonia to be competitive as a fuel, it needs to be stored at moderate pressures, and have an energy density when stored that compares favourably to other fuels, including hydrogen. Table 1, reproduced from that study, compares key energy storage performance criteria for ammonia to a range of other fuel options. The energy density of ammonia is three times higher than that for hydrogen stored at similar pressures, and slightly higher than that for Compressed Natural Gas (CNG) stored at 25 times the pressure. The study by Zamfirescu and Dincer found the current specific energetic cost (US$/GJ) for ammonia – albeit produced with hydrogen from methane reforming – to be under half the current specific energetic cost for petrol, and one third the cost for CNG. Therefore, if ammonia could be produced renewably at twice or three times the price of producing it with hydrogen from methane reforming, consumers would be no worse off than for buying petrol or CNG. Options for using ammonia to produce electric power or drive transport include both direct combustion and oxidisation in fuel cells. Figure 3 illustrates the range of possible approaches that can be followed, with assessments of possible conversion efficiencies from Zamfirescu and Dincer.

Fuel & storage mechanism	P (bar)	Density (kg/m^3)	HHV (MJ/kg)	Energy density (GJ/m^3)	Cost ($/m^3)	Cost ($/GJ)
Petrol (C_8H_{18}) – liquid tank	1	736	46.7	34.4	1000	29.1
CNG (CH_4) – tubular tanks in safety foam	250	188	55.5	10.4	400	38.3
LPG (C_3H_8) – pressurized tank	14	388	48.9	19.0	542	28.5
Methanol (CH_3OH) – liquid tank	1	749	15.2	11.4	693	60.9
Hydrogen (H_2) – metal hydrides	14	25	142	3.6	125	35.2
Ammonia (NH_3) - pressurized tank	10	603	22.5	13.6	181	13.3
Ammonia (NH_3) – metal amines	1	610	17.1	10.4	183	17.5

Tab. 1: A comparison of ammonia with other fuels. HHV designates the high heating value of the fuel. Adapted from Zamfirescu and Dincer (2008).

They claim that the most efficient use of ammonia is to thermally decompose it into H_2 and N_2 gases, feed the hydrogen into a high efficiency H_2 fuel-cell, expand the hot nitrogen for work recovery, and at the same time exploit the cooling effect of this expansion. This gives an efficiency of 46%, closely followed by 44% efficiencies for direct ammonia fuel-cells, and the combustion of pure ammonia in Internal Combustion

(IC) engines. This latter efficiency is of particular importance, because ammonia can be used as a fuel with very little modification to existing vehicles.

In the case of combustion in an internal combustion engine, some fraction of the ammonia may be only partially oxidised, forming nitric oxide. This can be avoided by reducing the combustion temperature, and using a catalytic converter.

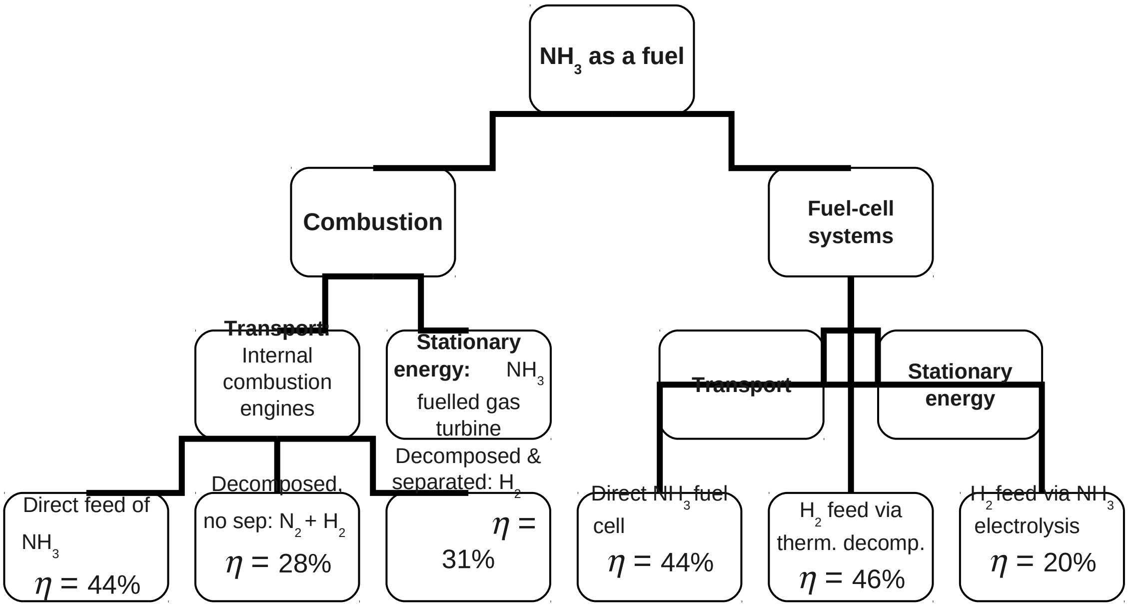

Fig. 3: Energy uses of ammonia. Adapted from Zamfirescu and Dincer (2008).

STATUS OF AMMONIA FUEL RESEARCH AND DEVELOPMENT

Current Research

Use of Ammonia in Internal Combustion Engines

In order to fuel an internal combustion engine directly with ammonia, the engine must have special control features to overcome the low flame speed and narrow flammable range compared with hydrocarbon fuels. Fortunately, these control issues can easily be addressed with cheap electronics. Alternatively, if it is first decomposed, ammonia can be used to fuel regular spark ignition engines as the resulting mixture of hydrogen, nitrogen, ammonia and air has combustion characteristics similar to petrol (Zamfirescu and Dincer 2008). However, this operation comes at the expense of a reduction in efficiency from 44% for an engine modified to run directly on ammonia to 28%, as indicated in Figure 3.

Several studies have been performed with both regular spark ignition (petrol) and compression ignition (diesel) engines. Kong (2008) has obtained virtually identical power versus load curves for a diesel engine operating with a mix of 5% diesel and 95% ammonia. Ammonia has an auto-ignition temperature of 651°C – compared to 225°C for diesel – and hence will not self-ignite except at very high compression ratios (50:1). Therefore approximately 5% of a fuel with lower self-ignition temperatures, which could be biofuel, must be added for combustion in diesel engines.

Hollinger (2008) reports on 1000 hours of operation of a spark ignition engine running on a mix of ammonia and propane. The engine has been used in an agricultural pumping application. He concludes that the fuel mix for starting and stopping, equivalence ratio and spark timing must be well controlled for efficient operation.

The Energy and Gasdynamic Systems Lab at the University of Florida, is investigating the use of ammonia to power modified gas turbines for electricity production (Lear 2007). While further research is necessary in this field, the use of ammonia in similar machines could solve the carbon emissions problems of aircraft.

Storage of Ammonia

As noted in preceding discussions, ammonia can be stored as a liquid at room temperature in tanks at pressures of only 10 bar. However, for safer on-vehicle storage that eliminates the dangers of caustic exposure in the event of a collision, “solid state” storage cartridges are being developed, in which the ammonia is absorbed in porous metal ammine complexes containing magnesium chloride or calcium chloride – $Mg(NH_3)_6Cl_2$ or $Ca(NH_3)_8Cl_2$. These cartridges then release the ammonia slowly when heated to 350ºC. The Danish firm Amminex are pursuing this technology.

Metal ammine cartridges have volumetric capacities comparable with liquid ammonia, however, two drawbacks of the metal ammine cartridge are the “charging” time required to fill cartridges, and the power usage required (as heat) in order to release the ammonia. The latter effectively reduces the high heating value of the ammonia from 22.5MJ/kg to 17.1MJ/kg, as shown in Table 1. The charging time required for vehicular cartridges is several hours, which would necessitate a system of cartridge exchange at refueling stations.

Ammonia Production

As noted above, the industrial method of ammonia production is the Haber-Bosch process. As an alternative to the Haber-Bosch synthesis process, Solid State Ammonia Synthesis (SSAS) can be used to synthesis ammonia electrolytically, according to Equation (3). SSAS uses 7,000-8,000kWh electricity per ton of ammonia produced, compared to the 12,000kWh/ton of electricity required to produce H_2 from the electrolysis of water, and then perform Haber-Bosch synthesis of ammonia.

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2O \rightarrow NH_3 + \tfrac{3}{4}O_2 \tag{3}$$

This solid state synthesis is illustrated in Figure 4. Water (steam) is decomposed at the anode. The oxygen atoms combine to form molecules (O_2), and exit the cell, while the hydrogen atoms are adsorbed by the anode and their electrons are stripped. The electrons travel around the electrical circuit, driven by the electromotive force from the power supply. The positive hydrogen ions, migrate across the solid state (ceramic) electrolyte to the cathode. Here they combine with nitrogen atoms and electrons to form ammonia molecules (Ganley *et al*. 2007).

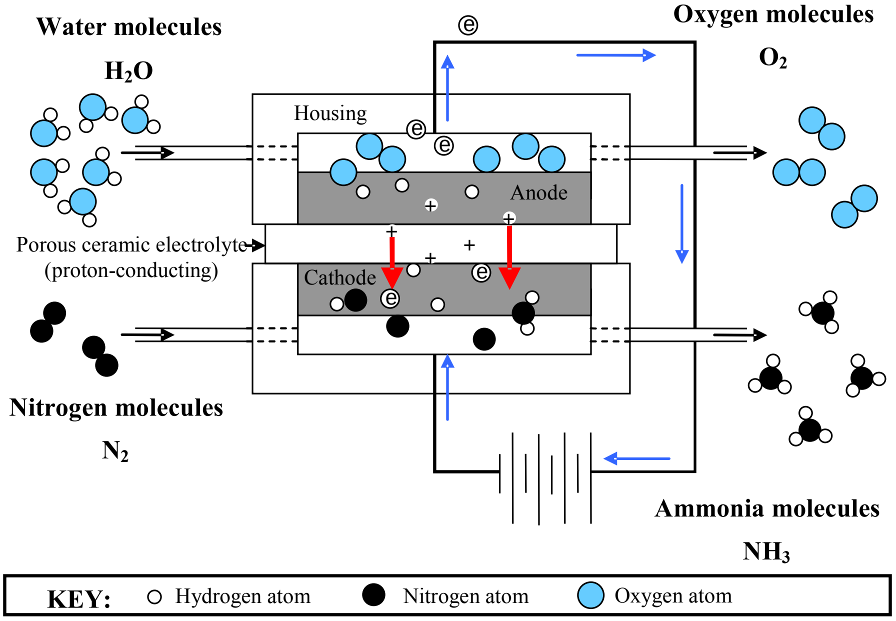

Fig. 4: Solid state ammonia synthesis. Adapted from Ganley *et al.* (2008).

Sammes *et al.* (2008) have developed planar “button cell” prototypes to perform solid state ammonia synthesis. These cells were operated at temperatures of 550°C, and produced ammonia at a rate of 3.4×10^{-10} moles per square centimetre of anode surface area, per second for an applied potential of 2.5V. This performance is expected to improve with the development of microtubular cells, rather than planar cells.

Fuel-Cells

Ammonia can be fed directly into some commercial fuel-cells, including alkaline fuel-cells, which operate at temperatures of 80 to 150°C, and solid oxide fuel cells, which operate at higher temperatures around 800°C. Investigation of Intermediate Temperature Direct Ammonia Fuel-Cells (IT-DAFC) is a developing field. These operate using the same process illustrated in Figure 4, but in reverse. Fuel cells that can operate at intermediate temperatures have two advantages. If they operate above around 300°C, precious metal catalysts are not necessary. And if they operate below 500°C, steel internals may be used. Ganley *et al.* (2008) have reported power densities of 52mW/cm^2 for prototype planar cells operated at 450°C at a current density of 96mA/cm^2. Improvements are expected with the introduction of tubular geometry, and modifications to the catalyst and electrolyte.

Current Projects

Niagara Falls Ammonia Project

Rauhauser *et al.* (2008) report on plans for an ammonia production facility using hydroelectric power from the existing Niagara Falls generation facility. The proposed facility will run continuously consuming 45MW_e to produce 24 tons of hydrogen, and from this, 136 tons of ammonia per day and 7.6MW heat. The nitrogen required for the ammonia production will be supplied using an on-site air separation unit. With a plan to use off-the-shelf technology, the estimated plant cost is US$150 million. The plant is expected to produce 50,000 tons of ammonia per year, which currently sells at approximately US$1,000 per ton wholesale. Aside from paying-off the debt from construction of the plant, the hydroelectricity must also be purchased from the New

York Power Authority. The cost of this electricity will lie in the range of 2.2 to 6.3c/kWh.

It is predicted that economics will be improved by the utilisation of the waste heat created at the facility. The most likely options are to use the waste heat in nearby greenhouses over winter and dry wood pellets with the heat during summer. An additional revenue stream available is from the by-product of medical grade oxygen.

Ammonia from Wind Power

In the upper mid-west of the United States, a large wind resource coincides geographically with a large consumption of ammonia-based fertilizers, in addition to the overall potential for use of ammonia as a fuel. A company called Freedom Fertilizer has been established in Iowa to use "stranded wind" to power the production of hydrogen and subsequent synthesis of ammonia (Gruhn and Sackett 2008). Their goal is to produce cost-competitive ammonia in locations where it is not economically feasible to connect the wind power to the grid. In the US, the agricultural industry is becoming increasingly concerned about the predicted rise in the price of imported, fossil-fuel-derived ammonia, and is keen to have a local supply with known capital costs.

One possible concern with the use of ammonia as a fuel is the possibility of rises in food prices due to competition between fuel and as a fertilizer use. However, such a scenario is less likely than the effect of bioethanol on corn prices, due to the secondary rather than primary influence of ammonia on the price of food.

A group from the University of Minnesota is also investigating the production of ammonia from wind. Their approach involves producing the ammonia in batches, which allows the ammonia to be absorbed from the reactor by porous MgCl salts, and yields higher equilibrium conversions (Huberty 2008).

BASELOAD SOLAR POWER WITH NET PRODUCTION OF AMMONIA

If a baseload solar thermal power plant was to be configured to also produce a net output of ammonia fuel, this would require some of the solar concentrators to be dedicated to producing hydrogen.

Hydrogen production via the hybrid sulfuric acid cycle

It is possible to produce steam with the solar concentrators, generate electricity from this steam, and use electrolyzers to produce hydrogen. However, this process produces has a heat-to-hydrogen conversion efficiency of ~30%. Thermochemical cycles, on the other hand, are predicted to have heat-to-hydrogen efficiencies of up to 45% (Kolb *et al.* 2007). One of the most studied thermochemical processes for the production of hydrogen is the hybrid sulfuric acid cycle. This process uses heat from the solar concentrator to thermally decompose sulfuric acid, with a catalyst aiding the reduction of sulfur trioxide.

$$H_2SO_4 \rightarrow H_2O + SO_3 \xrightarrow{catalyst} H_2O + SO_2 + \tfrac{1}{2}O_2 \qquad (4)$$

The process is "hybrid" because it uses an electrolyzer to perform the following hydrogen-producing reaction, and reform the sulfuric acid so the cycle may begin again.

$$2H_2O + SO_2 \rightarrow H_2 + H_2SO_4 \qquad (5)$$

For further details on the hybrid sulfuric acid cycle, refer to Kolb *et al.* (2007), and Schmitz *et al.* (2008).

Combining baseload power and ammonia production

Given one peak hour of operation of a 500m^2 Big Dish, the available solar energy could be used in two ways. Firstly, the solar energy could be used to dissociate ammonia for baseload electricity production. Alternatively, it could be used to produce hydrogen via thermochemical means, and from this, synthesise ammonia for export from the plant as a fuel. A solar thermal power plant could be configured using a combination of dishes dissociating ammonia, and dishes producing hydrogen. In this way, the plant could produce both baseload electricity and ammonia fuel. The hydrogen, along with nitrogen from an air separation unit would be fed into the ammonia synthesis reactor shown in Figure 1 such that more ammonia would be produced than that required for dissociation.

Table 2 compares the system efficiencies of ammonia fuel production and baseload power generation, using efficiency predictions from Lovegrove *et al.* (2004) for ammonia dissociation and from Schmitz *et al.* (2008) for hydrogen production via the hybrid sulfuric acid cycle. Importantly, Schmitz *et al.* included the use of electricity in the electrolyzers that perform Equation (5) in their overall efficiency calculation.

Schmitz *et al.* (2008) performed their study using a central receiver tower as the concentrator. However, Big Dish concentrators are capable of achieving higher concentration ratios than central receiver towers, and hence it in this comparison it has been assumed that Big Dish concentrators could replace the central receiver tower, with an equivalent hydrogen production per unit of thermal energy available at the receiver. This comparison has neglected the energy required for nitrogen separation via an air separation unit, as it is expected to be quite low compared to other energy uses in the process.

The comparison in Table 2 shows that using Big Dish solar concentrators to produce ammonia for use as a fuel reduces the solar-to-end-product efficiency to almost half of that achievable with baseload electricity produced via ammonia dissociation. However, there is a certain degree of value-adding when producing a fuel, compared to baseload electricity, and hence the ultimate decision whether to proceed with ammonia fuel production would be made based on economics. In addition, if the direct conversion of nitrogen and water to ammonia and oxygen could be performed thermochemcially – as per the electrolytic reaction for solid state ammonia synthesis – this could provide a more viable and more direct source of ammonia synthesis than the option outlined in Table 2. It has already been identified that a heat source, such as a solar thermal concentrator, will improve the efficiency of SSAS (Ganley *et al*. 2008).

	NH_3 production (H_2 via hybrid sulfuric acid cycle)	NH_3 dissociation for baseload electricity
Available solar energy: 1 peak hr, 500m^2 dish (kWh)	500	500
Thermal efficiency of Big Dish concentrator & receiver	0.80	–
H_2 production efficiency[b] (kg/kWh th)	5.022 E-3	–
H_2 production per peak hour of operation (kg)	2.01	–
H_2 production per peak hour of operation (mol)	0.996 E+3	–
NH_3 production per peak hour of operation (mol) (According to Eq (1) & assuming 100% conversion.)	0.664 E+3	–
NH_3 production per peak hour of operation (kg)	11.3	–
Electricity production from NH_3 synthesis heat (kWh)	4.4	–

(66.8kJmol^{-1} x rankine efficiency / 3600s/h)		
High Heating Value (HHV) of NH_3 at 10 bar [c] (kJ/mol)	383	–
HHV of NH_3 per peak hour operation (kJ at 10 bar [c])	2.543 E+5	–
HHV of NH_3 per peak hour operation (kWh equiv.)	70.6	–
NH_3 dissociation efficiency, solar-to-chemical [a]	–	0.75
Rankine cycle efficiency, electricity production	–	0.35
Energy content of end product (kWh equivalent)	75.0 (NH_3 fuel + electricity from synthesis heat)	131.3
Solar-to-end-product efficiency (energy available from fuel or electricity produced)	15%	26%

[a] Lovegrove *et al*. (2004). [b] Schmitz *et al*. (2008). [c] For on-vehicle storage in a pressurized tank.

Tab.2: A comparison of ammonia fuel production, and baseload power generation.

CONCLUSIONS

From the properties of ammonia, and the developments in its production, storage, and use in internal combustion engines and fuel-cells, it can be concluded that ammonia holds much promise as a renewable fuel. Moreover, the business community is beginning to embrace this potential as commercial projects such as the Niagara Falls Ammonia Project and wind-to-ammonia projects develop.

Given the reduction in system efficiency, if a decision were made purely on energetic grounds, Big Dish concentrators would not be used to generate hydrogen for ammonia synthesis in preference to generating baseload electricity via ammonia dissociation. However, a levelised energy cost comparison should be performed for each option, due to the value-adding nature of fuel production. In addition, a process that warrants investigation is the direct thermochemical conversion of nitrogen and water to ammonia and oxygen.

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BRIEF BIOGRAPHY OF PRESENTER

Rebecca Dunn is a first-year PhD student with the Solar Thermal Group at the ANU.