

A Review of Ammonia-Based Thermochemical Energy Storage for Concentrating Solar Power

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ABSTRACT | The development of a thermochemical energy storage system based on ammonia, for use with concentrating solar power is discussed in this paper. This is one of a group of storage options for concentrating solar power, some of which are already operating commercially using molten salts. The ammonia storage development has involved prototype solar receiver/reactors operated in conjunction with a 20-m² dish concentrator, as well as closed-loop storage demonstrations. An ongoing computational study deals with the performance of an ammonia receiver for a 489-m² dish concentrator. The ammonia storage system could employ industry-standard ammonia synthesis converters for superheated steam production. A standard 1500 t/day ammonia synthesis reactor would suffice for a 10-MW_e baseload plant with 330 large 489-m² dishes. At this stage, an updated economic assessment of the system would be valuable.

KEYWORDS | Ammonia; concentrating solar power; dish concentrators; energy storage; thermochemical storage

I. INTRODUCTION

This paper discusses the ammonia-based thermochemical storage system which has been developed for use with

concentrating solar power (CSP) systems. As described in several papers within this special issue, CSP systems can provide energy storage fully integrated within the electricity-generating plant—a commercial reality at several CSP plants using molten salt in Spain [1], [2]. Parabolic mirrors in the form of troughs, linear Fresnel, power towers, or dishes are used to concentrate solar radiation to a hot focus. The concentration ratio can be up to 100 for parabolic troughs and linear Fresnel systems, or in excess of 1000 for power towers (central receivers) and dishes—the geometric concentration ratio being the ratio of the area of the receiver aperture to the area of mirror aperture. The heat collected at the focus can be used to produce steam for immediate electricity generation, or alternatively it can be stored prior to electricity generation using molten salt [3], sensible heat storage in solids [4]–[6], phase change salts [7], or thermochemical storage cycles [8].

The thermal approach to energy storage using CSP systems has several potential advantages.

- Because the storage occurs before the conversion of heat to electricity at the turbine/generator set, the difference in overall solar-to-electric conversion efficiency between a system with storage and one without can be close to zero. For example, in commercial molten-salt storage systems, the storage system can have an effective efficiency of 99% [3].
- The actual energy storing components are relatively simple and potentially cost effective.
- Full integration into the system means that some components may actually be reduced in size

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and cost, for example, a system configured for extended/baseload generation would use a smaller and cheaper power block.

Current trends suggest that wind and photovoltaics are leading CSP in lowering generating costs without energy storage. However, the challenging economics of postgeneration electricity storage on a large scale could see dispatchable firming power provided preferentially by CSP plants with storage.

Thermochemical energy storage for CSP is less mature than molten salt and other thermal storage methods, but it has the potential to achieve higher storage densities. Rather than storing heat by increasing the temperature of a substance or changing its physical state, as with other CSP storage methods, thermochemical storage uses a reversible reaction to store energy in chemical bonds. When the reverse reaction is performed, heat is released and used to drive a thermal power cycle (typically a steam turbine and generator). Reactions involving ammonia, hydroxides, carbonates, hydrides, and sulfates have been investigated in the past [8], [9]. Previously, thermochemical storage loops based on methane reforming have received considerable attention [10]–[13]. Investigations continue into methane reforming for solar enhancement of natural gas [14] and hydrogen production [15], [16]. There is also a large field of research into the use of thermochemical processes and CSP for solar fuel production [17]. This includes metal oxide cycles involving iron oxides (ferrites), mixed metal ferrites, zinc, tin, and cerium [18].

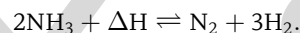
Recent advances in CSP thermochemical storage for electricity grid integration include systems which do not involve the storage of gaseous reaction products. For example, reduction–oxidation reactions with metal oxides are being investigated in a joint project between General

Atomics and the German Aerospace Centre (DLR) [19]. These utilize air at atmospheric pressure for the exothermic oxidation reaction. For cobalt oxide, the heat recovery oxidation reaction occurs at around 850 °C. The decomposition of calcium hydroxide is another thermochemical storage system being developed at DLR which does not involve the storage of gases [20].

The ammonia-based storage system reviewed in this paper involves gas storage at high pressures (10–30 MPa; ~100–300 atmospheres). However, an advantage of ammonia-based storage is that it can leverage the substantial experience of the ammonia synthesis industry. In particular, the ammonia synthesis stage can employ off-the-shelf hardware, with heat and power recovery being a common feature of modern ammonia plants [21], [22].

II. BASIC PRINCIPLES

The ammonia thermochemical energy storage system is based on the reversible dissociation of ammonia



In this storage system, a fixed inventory of ammonia passes alternately between energy-storing (solar dissociation) and energy-releasing (synthesis) reactors, both of which contain a catalyst bed. Coupled with a Rankine power cycle, the energy-releasing reaction could be used to produce baseload power for the grid. At 20 MPa and 300 K, the enthalpy of reaction is 66.8 kJ/mol, equivalent to 1.09 kWh/kg of ammonia, or 2.43 MJ/L, with the corresponding density of 0.6195 kg/L [23].

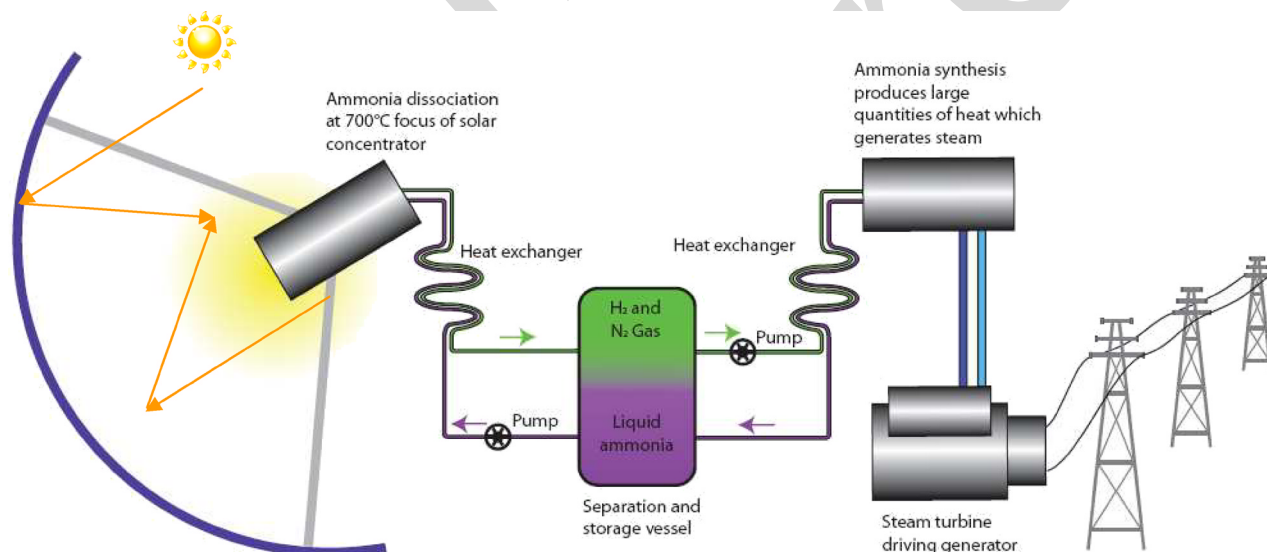


Fig. 1. Ammonia dissociation and storage schematic. (Diagram: T. Wetherell.)

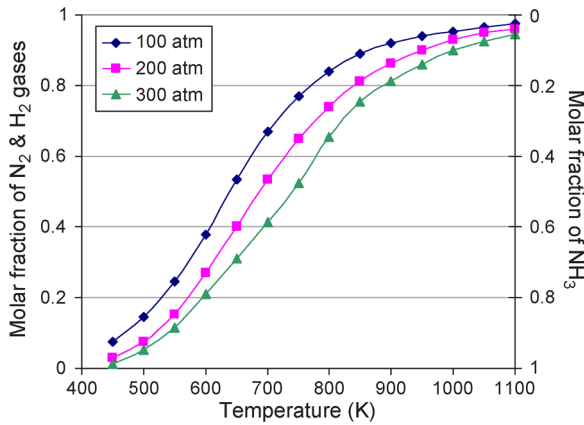


Fig. 2. Equilibrium curves for ammonia. As dissociation takes place, the inventory of working fluid changes composition from 100% ammonia (molar fraction of 0.0 on the left-hand axis and 1.0 on the right-hand axis) to 100% N_2 and H_2 gas (molar fraction of 1.0 on the left-hand axis and 0.0 on the right-hand axis). (Data: O. Williams.)

The basic layout of the system is shown in Fig. 1. A mirrored, two-axis tracking, paraboloidal dish focuses solar radiation into a cavity receiver/reactor through which anhydrous ammonia is pumped. The reactor tubes contain a catalyst which facilitates the dissociation at high temperature of the ammonia into gaseous nitrogen and hydrogen. The gases can then be passed through a standard Haber–Bosch ammonia synthesis reactor at any time, to release heat for the generation of power and replenish the stock of liquid ammonia.

The counterflow heat exchangers shown in Fig. 1 serve to transfer heat from exiting reaction products to the cold incoming reactants. In this way, the transport piping and energy storage volume are all operated at close to ambient temperature, reducing thermal losses from the system.

One advantage of this storage system is that the ammonia dissociation reaction has no possible side reactions, making solar reactors particularly easy to control. Another is that by operating above the ambient temperature saturation pressure of ammonia, the ammonia fraction in storage is present largely as a liquid. Thus, automatic phase separation of ammonia and hydrogen/nitrogen is provided and a common storage volume can be used. In addition, there is over 100 years of industrial experience with the “Haber–Bosch” process to call upon.

The use of a reversible reaction to store energy is governed by the dependency of the thermodynamic equilibrium composition on temperature and pressure. This is shown in Fig. 2 for the ammonia reaction.

Conceptually, if a sample of ammonia were heated slowly (quasi-statically), it would begin to decompose at temperatures of several hundred degrees, with most decomposition taking place where the gradient of the curves is highest, around 700 K at 200 atmospheres (~ 20 MPa) in Fig. 2. Complete dissociation would only be approached

asymptotically at very high temperatures. The amount of energy absorbed at each step would be proportional to the fraction of ammonia split. Reversing the process and withdrawing heat would see ammonia resynthesize, with heat released progressively.

To implement this on an industrial scale, the limitations of reaction kinetics must also be taken into account. Reaction rates are zero at equilibrium by definition; they increase by the degree of departure from equilibrium (and in the direction needed to return the system to equilibrium) and also increase rapidly with temperature in proportion to the well-known Arrhenius factor. Thus, a real system absorbs heat at temperatures higher than the equilibrium curves suggest and then releases it at lower temperatures.

The input temperature for the power cycle is an extremely important issue for all thermal-based energy storage systems, not just thermochemical ones. Electric power generation via a thermal cycle is limited by the second law of thermodynamics—lower temperature thermal inputs reduce the efficiency of power generation. Thus, in designing and examining thermal energy storage systems, it is necessary to consider both “thermal efficiencies” (energy out/energy in) and “second law efficiencies” (potential for work out/potential for work in).

In principle, any of the approaches to solar concentrator design: troughs, dishes, linear Fresnel, or tower/heliostat systems, could be used to drive the dissociation reaction. Troughs and linear Fresnel concentrators are limited to lower operating temperatures because of their lower concentration ratios, but can still operate with reasonable efficiencies up to 400 °C (673.15 K). Based on the equilibrium curves, it can be seen that this would be sufficient to achieve a significant level of ammonia dissociation. Tower or dish systems on the other hand can operate efficiently up to 1000 °C or more and have the potential to drive the reaction to almost complete dissociation and with associated accelerated reaction rates.

Because of the effect of automatic phase separation in the common storage volume, the composition of gases sent to the heat recovery reactor for power production is independent of the degree of dissociation achieved in the solar reactors during energy storage. Thus, the temperature of heat recovery achieved is also independent of the nature of the dissociation process. Such a system would allow decoupling of the temperatures at the solar dissociator and the heat recovery reactor. For example, even if the solar dissociator on a trough was operating at 400 °C, because the unreacted ammonia and the hydrogen and nitrogen product gases separate spontaneously in storage, it would still be possible to produce steam at 520 °C and 10 MPa from the heat released by the synthesis reactor. The system can act as a chemical heat pump in this way. Second law analysis shows that the cost of any heat pumping benefit is seen in increased thermal losses from the heat exchangers.

III. HISTORY OF AMMONIA THERMOCHEMICAL STORAGE

The concept of ammonia-based energy storage for concentrating solar power systems was first proposed by Carden in 1974 at the Australian National University (ANU) [24], [25]. At first, a body of thermodynamic data was established, and this was used for an initial assessment of theoretical limits on thermal efficiency and work production [26], [27]. It was identified that the reaction equilibrium itself as illustrated in Fig. 2 corresponded to an ultimate conversion efficiency limit of 54% at 30 MPa (~ 300 atmospheres). Approaches to remove heat and maintain realistic reaction rates meant that a smaller number would be achieved in reality.

Investigations into the ammonia storage system were also carried out in the late 1970s and early 1980s by a group of researchers at the Colorado State University, Fort Collins. This included engineering design studies, solar receiver design studies [28], and investigations into nickel-on-alumina catalysts [29].

As discussed above the ammonia synthesis stage can employ industry-standard hardware for heat and power recovery, producing superheated steam for electricity generation with a turbine-generator set. However, from a thermodynamic point of view, steam production does not represent an optimum match for the temperature profile produced by the exothermic ammonia synthesis. An alternative concept for electricity generation was proposed by Carden. Termed “direct work output,” in this concept,

rather than using the heat from the synthesis reactor to generate steam, the hot thermochemical product gases themselves (in this case gaseous ammonia) would be fed directly through a turbine [30]. To be realized, this concept would of course involve the development of such a customized turbine.

Further work recovery and exergetic efficiency analyses were conducted [31], [32] with the aid of a 2-D “pseudohomogenous” packed bed reactor computational model [33]. An updated exergetic system analysis was completed by Lovegrove *et al.* in 1999 [34]. This analysis concluded that exergetic efficiencies up to 71% would be possible in the heat recovery reactor, which would translate to overall solar-to-electric conversion efficiencies of around 20%.

Experiments at the ANU were initially conducted with a $1\text{-kW}_{\text{chem}}$ electrically heated dissociation reactor [35], which allowed testing of the aforementioned numerical model for packed bed reactor performance [33]. Calibration tests were first conducted to determine the appropriate activation energy and preexponential factor for the ICI 47-1 nickel catalyst (see Table 1 for catalyst details). After calibration, the numerical model successfully predicted: longitudinal temperature profiles (along the length of the reactor tubes) for both the center of the catalyst bed and the wall of the reactor; the effect of operating temperature on exit reaction extent; and the effect of mass flow rate on exit reaction extent [33]. All of these effects were predicted to within or just outside the bounds of the

Table 1 A Summary of Catalysts Used in Experimental Reactors at the ANU

Reactor type	Reactor Description	Catalyst (compositions in wt%)	Supplier	Temperature range (°C)
Dissociation	$1\text{ kW}_{\text{chem}}$ electrically heated dissociation reactor [35]	47-1 nickel catalyst. 10% Ni, remainder Al_2O_3 support material.	ICI	400-750
Dissociation	$2\text{ kW}_{\text{chem}}$ Mark I solar dissociation reactor for 20 m^2 dish [43],[44] (Fig. 3)	DNK-2R triply-promoted iron-cobalt catalyst. 22-26% Co, 22-26% Fe, 1-2% promoter, remainder Al_2O_3 .	Haldor-Topsøe	400-700
Dissociation	$2\text{ kW}_{\text{chem}}$ Mark II solar dissociation reactor for 20 m^2 dish [45]	DNK-2R triply-promoted iron-cobalt catalyst. 22-26% Co, 22-26% Fe, 1-2% promoter, remainder Al_2O_3 .	Haldor-Topsøe	400-700
Dissociation	$15\text{ kW}_{\text{sol}}$ solar cavity dissociation receiver for 20 m^2 dish with directly irradiated reactor tubes [45],[46] (Fig. 3)	DNK-2R triply-promoted iron-cobalt catalyst. 22-26% Co, 22-26% Fe, 1-2% promoter, remainder Al_2O_3 .	Haldor-Topsøe	400-700
Dissociation	Solar reactor for 2.8 m^2 trough [51] (Fig. 6)	Carbon-supported ruthenium catalyst. 60-99% C, 15-40% alkali carbonate, 7-13% ruthenium oxide, 1-5% barium oxide.	Unknown	300-450
Synthesis	Thin-walled $1\text{ kW}_{\text{chem}}$ synthesis reactor	KM-1 promoted iron catalyst. 94% Fe_3O_4 .	Haldor-Topsøe	360-550
Synthesis	Heavy-walled $1\text{ kW}_{\text{chem}}$ synthesis reactor [58]	KM-1 promoted iron catalyst. 94% Fe_3O_4 .	Haldor-Topsøe	360-550
Synthesis	$10\text{ kW}_{\text{chem}}$ synthesis reactor [46]	S6-10R promoted iron catalyst. Al_2O_3 , K_2O , and CaO promoters, remainder Fe_3O_4 .	ICI/Synetix	350-550

error bars for the experimental results. The variation of exit reaction extent with pressure was also predicted, though these predictions slightly overestimated the bounds of the experimental error bars.

IV. SOLAR RECEIVER REACTORS

Solar receiver designs for ammonia dissociation were initially evaluated theoretically, both by the ANU [36]–[38] and Colorado State University [28].

The ammonia-based system has been considered particularly well suited to dish concentrators because:

- dishes provide a circumferentially homogenous solar flux profile which can facilitate thermochemical reactor design;
- the reaction system is simple and has no complicating side reactions. This means that only simple control systems are necessary, thus the mobile receiver can be maintained at a light weight, and solar transients are easy to handle. Control systems for handling solar transients are described by Petrasch et al. [13], [39].

Development of solar ammonia dissociation has to date been carried out on a single 20-m² paraboloidal dish located at the ANU campus, as shown in Fig. 3. It is envisaged that a large-scale storage system could consist of an array of hundreds of much larger “Big Dishes,” also pioneered at the ANU. The first Big Dish, with mirror aperture area of 400 m² was commissioned in 1994 at the ANU [40], and was followed in 1998 by a dish of the same size in Israel [41]. More recently, the dish has been completely redesigned for reduced-cost mass construction; the first prototype of the new design, which has aperture area of 489 m² was completed at the ANU in 2009 (Fig. 3). The 489-m² dish has a measured peak concentration of 14 100 suns, and a geometric concentration ratio of 2240 for 95% capture [42]. The geometric concentration ratio is the ratio of the mirror aperture to the area of the entrance to the cavity through which the reflected radiation is focused; a high concentration is required to achieve temperatures above 600 °C at which ammonia dissociation

occurs most effectively with iron-based catalysts. To date (mid-2011) the 489-m² dish has been used for high-temperature steam receiver development.

A prototype solar ammonia receiver/reactor, Mark I, was first tested in 1994. This consisted of a single tube-in-tube reactor of 200-mm length machined from a 2-in bar of Inconel alloy 601 [43], [44]. This receiver was mounted in front of a water-cooled shield (which protected instrumentation and cabling) in the focal region of the 20-m² faceted paraboloidal dish. Haldor-Topsoe DNK-2R iron-cobalt catalyst (Table 1) was used in the annular catalyst bed, with temperatures ranging from 400 °C to 700 °C. In 1998, the Mark I reactor was replaced by the Mark II solar reactor (Fig. 3), with identical external geometry, but a thinner annular catalyst bed to increase forced convection heat transfer from the reactor wall to bed [45]. Both of these reactors were significantly undersized for the full 20 m² of dish aperture, as they were only rated for 1.0–2.2-kW_{chem} conversion. However, they served to prove the concept of solar ammonia dissociation.

Several alternative solar ammonia reactor designs were proposed for use within cavity receivers [38], as opposed to the external receiver designs of the Mark I and II reactors. Alternatives included a sodium reflux heat pipe design, a direct absorption design based on a volumetric receiver pressure vessel, and a cavity of directly irradiated catalyst-filled tubes. The latter concept, a cavity of directly irradiated catalyst-filled tubes, was adopted for the design of the 15-kW_{sol} receiver/reactor, as it was a simpler design to implement than either the sodium reflux design or the volumetric reactor with its pressurized window. The sizing of the 15-kW_{sol} receiver/reactor was chosen to better utilize the full 20 m² of dish aperture. This receiver was constructed in mid-1999 [45] and consisted of 20 Inconel-601 reactor tubes, each 500 mm long, arranged in a frustum (truncated cone) inside an insulated cavity receiver, as shown in Figs. 3 and 4. Again, the DNK-2R iron-cobalt catalyst was used in these reactor tubes. The tubes are operated in parallel flow via manifolds. Each of the 20 reactor tubes (Fig. 5) consists of a tube-in-tube, with the catalyst bed in the outer annulus, and a hollow inner



Fig. 3. Left: 20-m² dish concentrator with the Mark II prototype receiver—here the receiver is external to the casing. Center: 20-m² dish concentrator with 15-kW_{chem} ammonia receiver—here the receiver is within the casing. Right: 489-m² dish on sun (test run with steam vented to atmosphere). (Photos: ANU.)

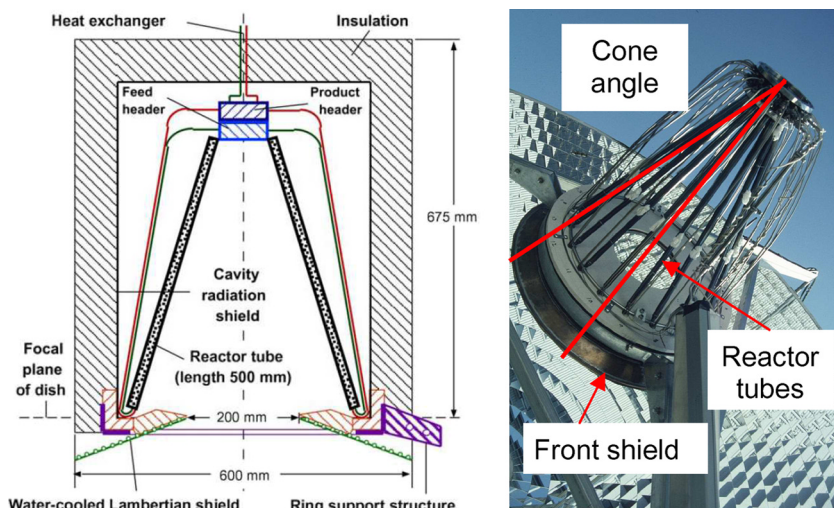


Fig. 4. Prototype 15-kW_{sol} solar dissociation reactor construction. Left: cross-section. Right: insulation removed. (Diagram & photo: ANU.)

tube to allow heat transfer from the exiting product gases to the incoming reactants. The 15-kW_{sol} receiver/reactor has remained intact since its installation, and is still in use. Steady-state on-sun experiments have been carried out with peak reactor tube temperatures ranging from $\sim 590^\circ\text{C}$ to 750°C , and system pressures between 10 and 15 MPa [46].

Recent work has focused on improving ammonia receiver performance and developing a receiver suitable for the 489-m² dish concentrator [47]. These investigations involve cavity receivers containing directly irradiated catalyst-filled tubes, similar to the design of the 15-kW_{sol} receiver/reactor shown in Fig. 4. In order to design improved receivers, investigations into convection losses from cavity receivers have been undertaken [48], [49]. In addition, experimental results show that varying the cone angle (as shown in Fig. 4) of reactor tubes within a cavity

receiver affects the efficiency of energy conversion. The solar-to-chemical efficiency gain in these particular experiments was up to 7% absolute [47]. From this it is apparent that geometric optimizations are worth pursuing since such efficiency gains are achieved with no increase in costs of manufacture for receivers. However, these gains must be balanced against expected reactor lifetime, as packing reactor tubes closer together to increase performance may lead to higher material stresses if higher localized wall temperatures are produced. Work is continuing to develop a computational model that can be directly compared to the experimental results. This can then be applied to develop an ammonia receiver for the second-generation 489-m² dish concentrator.

Investigations into the use of ammonia storage with trough concentrators have also been conducted, both with

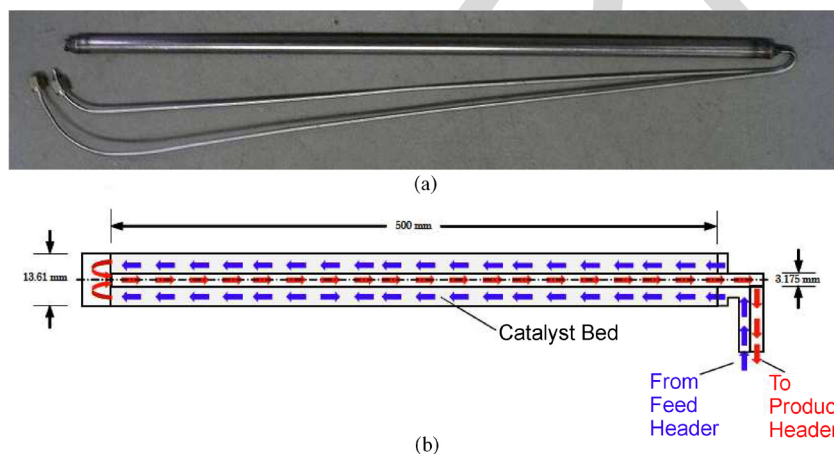


Fig. 5. Individual dissociation reactor tube. (Photo: ANU. Diagram: S. Paitoonsurikarn.)

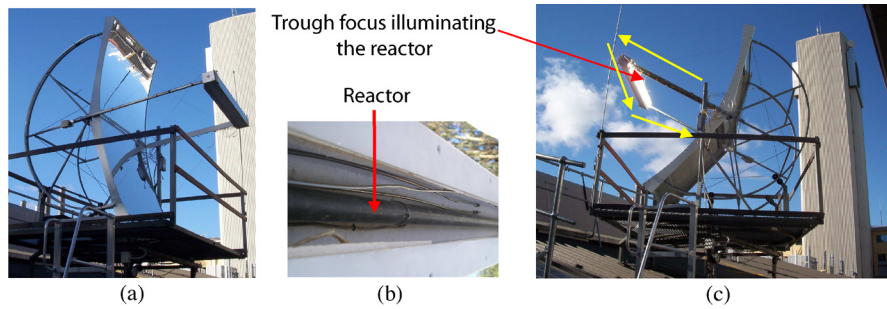


Fig. 6. (a) The 2.8-m² trough concentrator operated at the ANU. (b) A closeup of the cavity receiver showing the ammonia dissociation reactor for the trough. (c) The trough tracking the sun. Yellow arrows indicate the direction of fluid flow. (Photos: ANU.)

computational models and with a 2.8-m² trough concentrator shown in Fig. 6 [46], [50], [51]. A ruthenium-on-carbon catalyst (Table 1) was adopted in these experiments in lieu of the iron-based catalyst, to allow dissociation at lower temperatures achieved with the trough, 400 °C and below. The DNK-2R iron catalyst used with the dish concentrator only shows significant activity at 500 °C and above, and hence was not suitable for use with the trough concentrator. Ultimately, an economic assessment would have to be made on the use of rare metal catalysts such as ruthenium. A summary of the catalysts used in the various experimental reactors at ANU is given in Table 1. The kinetic mechanisms for the synthesis and decomposition of ammonia has been described by various authors for iron-based catalysts [52]–[54] and for ruthenium-based catalysts [55]–[57].

V. CLOSED-LOOP TESTS

In a full-scale thermochemical storage system, the synthesis heat recovery reactor performs the reverse reaction to that occurring in the solar reactor. This reverse reaction releases heat, which is used to drive the power cycle, as illustrated in the right-hand side of Fig. 1. As mentioned above, the ammonia synthesis stage can employ off-the-shelf hardware for heat and power recovery [21], [22], with some converter designs able to produce superheated steam at up to 520 °C and 10 MPa. Nonetheless, three synthesis heat recovery reactors—two 1-kW_{chem} reactors and one 10-kW_{chem} reactor—were constructed at the ANU for the purpose of performing closed-loop storage demonstrations, and also to calibrate a 2-D computational reactor model for synthesis [58]. These reactors are described in Table 1. Results obtained with the computational model were used to investigate the effect of operating parameters on the thermal output from the heat recovery system [22].

A closed-loop demonstration involves both solar dissociation and subsequent synthesis heat recovery. In September 1998, the first closed-loop solar ammonia storage was demonstrated with the 2.2-kW_{chem} Mark II solar receiver/reactor, the 20-m² dish concentrator, and a

1-kW_{chem} heavy-walled synthesis reactor [45]. Further closed-loop storage experiments were conducted with this experimental setup, including a 5-h experimental run in January 1999 [45]. Following the installation of the 15-kW_{sol} receiver, 10-kW_{chem} synthesis reactor, and various improvements to the closed-loop experimental system, the first continuous 24-h run of solar ammonia storage and heat recovery was performed in May 2002.

VI. SYSTEM STUDIES

One of the key motivating factors for the study of the ammonia storage system is the substantial chemical industry engagement with ammonia production via the Haber–Bosch process. There are a range of companies offering synthesis reactors commercially, with typical capacities between 300 and 2000 t/day. High pressures are employed, which referring back to Fig. 2 dictate that synthesis occurs at higher temperatures and this results in higher reaction rates. Typically, a synthesis reactor consists of a large pressure vessel that contains a series of separate catalyst “beds.” Each bed operates as an “adiabatic” reactor with insulated walls. In each bed, or reaction stage, heat is produced by the synthesis reaction. To lower the inlet temperature for the next bed, the reactants can be cooled between each bed, or more low-temperature reactants can be added [22]. As already noted, some such reactors are designed to produce steam at up to 520 °C and 10 MPa, and steam turbines are often incorporated into ammonia plants. The existence of these proven commercial reactor systems facilitates system studies of solar thermal power stations using the technology.

As mentioned above, an exergetic analysis of an ammonia storage system operating at 30 MPa (~300 atmospheres) by Lovegrove et al. [34] concluded that a net solar-to-electric conversion efficiency of 20% was industrially achievable with such a system. Large-scale system challenges such as centralized fluid control have been addressed [59]. In addition, two hypothetical ammonia baseload plants were examined in detail: a 4-MW_e plant [43] and a 10-MW_e plant [60], each with an array of dish

solar concentrators connected to a central power block. The 10-MW_e plant study concluded that a baseload plant of this scale located at Alice Springs in central Australia, with an 80% capacity factor, could be operated with 400 large 400-m² dishes—each converting 308-kW_{th} at design point—and a standard 1500-t/day ammonia synthesis reactor. Taking into account modest economies of scale, such a plant was costed at AUD 157 million (in 1997 Australian Dollars), resulting in a levelized electricity cost (LEC) of AUD 0.24 per kWh. A long-term projection of a LEC was predicted at AUD 0.12–0.15 per kWh. The dishes used in this study were 400-m² dishes, previously developed at the ANU [40], [41], [61]. Substitution with the new 489-m² dishes described above would reduce the number of dishes required to less than 330.

The ammonia-based system as originally conceived by Carden was actually intended to address the need for low-loss energy transport from a field of dishes to a central power block; ideas of the benefit of longer term energy storage came later. The high cost of conventional pressure vessels and the volume of gas storage needed motivated an early investigation of underground storage of gases [62]. Such ideas remain a very long way from commercial reality.

A solution that has been proposed for the purposes of system studies is to employ long lengths of large diameter pressure piping (commonly used by the natural gas industry) as the storage volume. This has the advantage of offering a solution that can be costed based on existing industry practice. The 10-MW_e study, for example, concluded that 162 km of DN-300 pipe (323.9-mm OD, 12.7-mm wall thickness) would provide sufficient energy storage for 24-h baseload operation of the 10-MW_e plant.

The storage volume addressed in this way does become the second most significant contributor to overall system cost—after the solar collector field [60]—and as a consequence, questions remain about the potential economic viability.

VII. CONCLUSION

Through three and a half decades of both experiment and computation, it has been shown that ammonia-based thermochemical energy storage for concentrating solar power

is technically achievable. Development has largely centered on use with dish concentrators, of which a 489-m² prototype is now available.

Technically the system is at a level of development where a multidish pilot scale system could be designed and built with confidence.

On the one hand, an ammonia-based storage system has the benefits of abundant resources (nitrogen and hydrogen gases) and the substantial experience of the ammonia synthesis industry. On the other hand, it is yet to be established conclusively if such a storage system would be economically competitive with other alternatives.

The limits to dispatchability for ammonia-based storage also deserve further investigation. While 24-h baseload operation is clearly technically feasible, conventional industry practice suggests very slow ramp rates for ammonia synthesis reactors, thus limiting the capability to match varying loads. It is possible, however, that innovative approaches could be developed to allow greater flexibility.

Cost estimates have been calculated in the past, including an analysis of piping costs [63] and a more complete analysis of levelized electricity cost for the hypothetical 10-MW_e plant [60]. However, this levelized electricity cost was calculated over a decade ago, and we now find ourselves in a new context in which to evaluate the economic viability of an ammonia storage system. Molten-salt storage for concentrating solar power plants is now commercial, and more information on CSP plant costs is available due to significant industry activity in Spain since 2007, and also in the United States. Thus, a new cost estimate for the technology, including cost-reduction potentials, would be timely.

Somewhat intertwined with new cost estimates is the challenge of high-pressure storage (10–30 MPa; ~100–300 atmospheres). It would also be timely to determine whether such high system pressures could be economic in the long term, and if not whether a less costly alternative exists, for example, storing the product gases in porous “solid state” storage cartridges.

However, regardless of the outcome of such assessments, the receiver and system development produced by this research program will still be of use as other thermochemical storage options approach similar development stages. ■

REFERENCES

- AQ3** [1] S. Relloso and E. Delgado, “Experience with molten salt thermal storage in a commercial parabolic trough plant. Andasol-1 commissioning and operation,” in *Proc. 15th SolarPACES Conf.*, Berlin, Germany, 2009.
- [2] J. Lata, S. Alcalde, D. Fernández, and X. Lekube, “First surrounding field of heliostats in the world for commercial solar power plants—Gemasolar,” in *Proc. 16th SolarPACES Conf.*, Perpignan, France, 2010.
- [3] J. Pacheco, R. Bradshaw, D. Dawson, W. De la Rosa, R. Gilbert, S. Goods,

- M. J. Hale, P. Jacobs, S. Jones, G. Kolb, M. Prairie, H. Reilly, S. Showalter, and L. Vant-Hull, “Final test and evaluation results from the Solar Two Project Solar Thermal Technology Dept., Sandia Nat. Lab., Albuquerque, NM, Tech. Rep. SAND2002-0120. [Online]. Available: http://www.osti.gov/bridge/product.biblio.jsp?osti_id=793226
- [4] N. Siegel, C. Ho, S. Khalsa, and G. Kolb, “Development and evaluation of a prototype solid particle receiver: On-sun testing and model validation,” *ASME J. Solar Energy Eng.*, vol. 132, pp. 021008-1–021008-8, May 2010.
- [5] S. Zunft, M. Hänel, M. Krüger, and V. Dreißigacker, “High-temperature heat storage for air-cooled solar central receiver plants: A design study,” in *Proc. 15th SolarPACES Conf.*, Berlin, Germany, 2009.
- [6] D. Laing, W. Steinmann, R. Tamme, and C. Richter, “Solid media thermal storage for parabolic trough power plants,” *Solar Energy*, vol. 80, no. 10, pp. 1283–1289, Oct. 2006.
- [7] D. Laing, C. Bahl, T. Bauer, D. Lehmann, and W. Steinmann, “Thermal energy storage for direct steam generation,” *Solar Energy*, vol. 85, no. 4, pp. 627–633, Apr. 2011.

- [8] A. Gil A., M. Medrano, I. Martorell, A. Lázaro, P. Dolado, B. Zalba, and L. Cabeza, "State of the art on high temperature thermal energy storage for power generation. Part 1—Concepts, materials and modellization," *Renew. Sustain. Energy Rev.*, vol. 14, pp. 31–55, 2010.
- [9] H. Romero-Paredes, G. Flamant, S. Abanades, P. Charvin, and J. J. Ambriz, "Thermochemical storage of solar energy by means of sulfates: A review," in *Proc. 13th SolarPACES Conf.*, Seville, Spain, 2006.
- [10] M. Levy, R. Levitan, H. Rosin, and R. Rubin, "Solar energy storage via a closed-loop chemical heat pipe," *Solar Energy*, vol. 50, no. 2, pp. 179–189, 1993.
- [11] J. Muir, R. Hogan, R. Skocypec, and R. Buck, "Solar reforming of methane in a direct absorption catalytic reactor on a parabolic dish—Part I: Test and analysis," *Solar Energy*, vol. 52, no. 6, pp. 467–477, 1994.
- [12] A. Wörner and R. Tamme, "CO₂ reforming of methane in a solar driven volumetric receiver-reactor," *Catalysis Today*, vol. 46, pp. 165–174, 1998.
- [13] J. Petrasch and A. Steinfeld, "Dynamics of a solar thermochemical reactor for steam reforming of methane," *Chem. Eng. Sci.*, vol. 62, pp. 4214–4228, 2007.
- [14] R. McNaughton, S. McEvoy, G. Hart, J. Kim, K. Wong, and W. Stein, "Experimental results of solar reforming on the 200 kW SolarGas reactor," in *Proc. 16th SolarPACES Conf.*, Perpignan, France, 2010.
- [15] S. Rodat, S. Abanades, and G. Flamant, "Methane decarbonization in indirect heating solar reactors (10–50 kW) for a CO₂-free production of hydrogen and carbon black," in *Proc. 16th SolarPACES Conf.*, Perpignan, France, 2010.
- [16] N. Gokon, Y. Yamawaki, D. Nakazawa, and T. Kodama, "Ni/MgO-Al₂O₃ and Ni-Mg-O catalyzed SiC foam absorbers for high temperature solar reforming of methane," *Int. J. Hydrogen Energy*, vol. 35, no. 14, pp. 7441–7453, 2010.
- [17] A. Meier, "Task II: Solar chemistry research," International Energy Agency (IEA), Solar Power and Chemical Energy Systems Annual Report 2009, 2009. [Online]. Available: http://www.solarpaces.org/Library/AnnualReports/documents/AnnualReport2009Final_web.pdf
- [18] A. Meier and A. Steinfeld, "Solar thermochemical production of fuels," *Adv. Sci. Technol.*, vol. 74, pp. 303–312, 2010.
- [19] B. Wong, L. Brown, F. Schaubé, R. Tamme, and C. Sattler, "Oxide based thermochemical heat storage," in *Proc. 16th SolarPACES Conf.*, Perpignan, France, 2010.
- [20] F. Schaubé, A. Wörner, and R. Tamme, "High temperature thermochemical heat storage for CSP using gas-solid reactions," in *Proc. 16th SolarPACES Conf.*, Perpignan, France, 2010.
- [21] M. Appl, *Ammonia-Principles and Industrial Practice*. Weinheim, Germany: Wiley-VCH, 1999, pp. 172–173.
- [22] H. Kreetz, K. Lovegrove, and A. Luzzi, "Maximizing thermal power output of an ammonia synthesis reactor for a solar thermochemical energy storage system," *ASME J. Solar Energy Eng.*, vol. 123, pp. 75–82, May 2001.
- [23] M. Zander and W. Thomas, "Some thermodynamic properties of liquid ammonia: PVT data, vapor pressure, and critical temperature," *J. Chem. Eng. Data*, vol. 24, no. 1, pp. 1–2, 1979.
- [24] P. Carden, "A large scale solar plant based on the dissociation and synthesis of ammonia," Dept. Eng. Phys., RSPhyS, Australian Nat. Univ., Canberra A.C.T. Australia, Tech. Rep. EC-TR-8, 1974.
- [25] P. Carden, "Energy coradiation using the reversible ammonia reaction," *Solar Energy*, vol. 19, pp. 365–378, 1977.
- [26] P. Carden and O. Williams, "The efficiencies of thermochemical energy transfer," *Int. J. Energy Res.*, vol. 2, pp. 389–406, 1978.
- [27] O. Williams and P. Carden, "Energy storage efficiency for ammonia/hydrogen-nitrogen thermochemical energy transfer system," *Int. J. Energy Res.*, vol. 3, pp. 29–40, 1979.
- [28] J. Wright and T. Lenz, "Solar energy collection using the reversible ammonia dissociation," in *Proc. 15th Intersoc. Energy Conv. Eng. Conf.*, Fort Collins, CO, 1980, pp. 140–144.
- [29] S. Nandy and T. Lenz, "Observations on the catalytic decomposition of ammonia at high temperatures and pressures," *Amer. Inst. Chem. Eng. J.*, vol. 30, no. 3, pp. 504–507, 1984.
- [30] P. Carden, "Direct work output from thermochemical energy transfer systems," *Int. J. Hydrogen Energy*, vol. 12, pp. 13–22, 1987.
- [31] K. Lovegrove, "Thermodynamic limits on the performance of a solar thermochemical energy storage system," *Int. J. Energy Res.*, vol. 17, pp. 817–829, 1993.
- [32] K. Lovegrove, "Exergetic optimization of a solar thermochemical energy storage system subject to real constraints," *Int. J. Energy Res.*, vol. 17, pp. 831–845, 1993.
- [33] K. Lovegrove, "High pressure ammonia dissociation experiments for solar energy transport and storage," *Int. J. Energy Res.*, vol. 20, pp. 965–978, 1996.
- [34] K. Lovegrove, A. Luzzi, M. McCann, and O. Freitag, "Exergy analysis of ammonia based solar thermochemical power systems," *Solar Energy*, vol. 66, pp. 103–115, 1999.
- [35] O. Williams and P. Carden, "Ammonia dissociation for solar thermochemical absorbers," *Int. J. Energy Res.*, vol. 3, pp. 129–142, 1979.
- [36] O. Williams, "Design and cost analysis for an ammonia-based solar thermochemical cavity absorber," *Solar Energy*, vol. 24, pp. 255–263, 1980.
- [37] O. Williams, "Evaluation of wall temperature difference profiles for heat absorption tubes exposed non-uniformly to solar radiation," *Solar Energy*, vol. 24, pp. 597–600, 1980.
- [38] K. Lovegrove and A. Luzzi, "Endothermic reactors for an ammonia based thermochemical solar energy storage and transport system," *Solar Energy*, vol. 56, no. 4, pp. 361–371, 1996.
- [39] J. Petrasch, P. Osch, and A. Steinfeld, "Dynamics and Control of solar thermochemical reactors," *Chem. Eng. J.*, vol. 145, pp. 362–370, 2009.
- [40] G. Johnston, "Flux mapping the 400 m² 'Big-Dish' at the Australian National University," *ASME J. Solar Energy Eng.*, vol. 117, pp. 290–292, 1995.
- [41] S. Biryukov, "Determining the optical properties of PETAL, the 400 m² parabolic dish at Sede Boquer," *ASME J. Solar Energy Eng.*, vol. 126, pp. 827–832, 2004.
- [42] K. Lovegrove, G. Burgess, and J. Pye, "A new 500 m² paraboloidal dish solar concentrator," *Solar Energy*, vol. 85, no. 4, pp. 620–626, Apr. 2011.
- [43] A. Luzzi and K. Lovegrove, "A solar thermochemical power plant using ammonia as an attractive option for greenhouse gas abatement," *Energy*, vol. 22, no. 2, pp. 317–325, 1997.
- [44] K. Lovegrove, H. Kreetz, and A. Luzzi, "The first ammonia based solar thermochemical energy storage demonstration," *Journal de Physique IV*, vol. 9, pp. 581–586, 1999.
- [45] K. Lovegrove, A. Luzzi, and H. Kreetz, "A solar-driven ammonia-based thermochemical energy storage system," *Solar Energy*, vol. 67, pp. 309–316, 2000.
- [46] K. Lovegrove, A. Luzzi, I. Soldiani, and H. Kreetz, "Developing ammonia based thermochemical energy storage for dish power plants," *Solar Energy*, vol. 76, pp. 331–337, 2004.
- [47] R. Dunn, K. Lovegrove, G. Burgess, and J. Pye, "An experimental study of ammonia receiver geometries for dish concentrators," *ASME J. Solar Energy Eng.*
- [48] S. Paitoonsurkarn, K. Lovegrove, G. Hughes, and J. Pye, "Numerical investigation of natural convection loss from cavity receivers in solar dish applications," *ASME J. Solar Energy Eng.*, vol. 133, no. 2, May 2011.
- [49] T. Taumoeofolau, S. Paitoonsurkarn, G. Hughes, and K. Lovegrove, "Experimental investigation of natural convection heat loss from a model solar concentrator cavity receiver," *ASME J. Solar Energy Eng.*, vol. 126, pp. 801–807, 2004.
- [50] O. Becker, K. Lovegrove, A. Luzzi, and M. Scheffler, "Investigations of solar driven ammonia dissociation in a combined trough dissociation reactor system," in *Proc. 40th Annu. Conf. Australian New Zealand Solar Energy Soc.*, Newcastle, W.A., Australia, Nov. 2002.
- [51] R. Dunn, K. Lovegrove, and G. Burgess, "Baseload solar power for California? Ammonia-based solar energy storage using trough concentrators—A study of heat losses," in *Proc. 45th Annu. Conf. Australian New Zealand Solar Energy Soc.*, Alice Springs, N.T., Australia, Oct. 2–4, 2007.
- [52] M. Temkin and V. M. Pyzhnev, "Kinetics of ammonia synthesis on promoted iron catalysts," *Acta Physicochimica*, vol. 12, pp. 327–356, 1940.
- [53] A. Nielsen, J. Kjaer, and B. Hansen, "Rate equation and mechanism of ammonia synthesis at industrial conditions," *J. Catalysis*, vol. 3, pp. 68–79, 1964.
- [54] B. Fastrup, "Microkinetic analysis of ammonia synthesis based on surface reaction studies of iron catalysts as compared to single-crystal studies," *J. Catalysis*, vol. 168, pp. 235–244, 1997.
- [55] M. Bradford, P. Fanning, and A. Vannice, "Kinetics of NH₃ decomposition over well dispersed Ru," *J. Catalysis*, vol. 172, pp. 479–484, 1997.
- [56] B. Fastrup, "On the interaction of N₂ and H₂ with Ru catalyst surfaces," *Catalysis Lett.*, vol. 48, pp. 111–119, 1997.
- [57] O. Hinrichsen, "Kinetic simulation of ammonia synthesis catalyzed by ruthenium," *Catalysis Today*, vol. 53, pp. 177–188, 1999.
- [58] H. Kreetz and K. Lovegrove, "Theoretical analysis and experimental results of a 1 kW ammonia synthesis reactor for a solar thermochemical energy storage system," *Solar Energy*, vol. 67, pp. 287–296, 2000.

- [59] O. Williams, "Ammonia thermochemical energy transport in a distributed collector solar thermal power plant," *Solar Energy*, vol. 27, no. 3, pp. 205–214, 1981.
- [60] A. Luzzi, K. Lovegrove, E. Filippi, H. Fricker, M. Schmitz-goeb, M. Chandapillai, and S. Kaneff, "Techno-economic analysis of a 10 MW_e solar thermal power plant using ammonia-based thermochemical energy storage," *Solar Energy*, vol. 66, no. 2, pp. 91–101, 1999.
- [61] S. Kaneff, "A 20 dish solar thermal array providing 2.6 MW_e via an existing coal fired steam driven turbogenerator system," in *Proc. Int. Solar Energy Soc. Solar World Congr.*, Jerusalem, Israel, 1999.
- [62] P. Carden and L. Paterson, "Physical, chemical and energy aspects of underground hydrogen storage," *Int. J. Hydrogen Energy*, vol. 4, pp. 559–569, 1979.
- [63] O. Williams, "Thermochemical energy transport costs for a distributed solar power plant," *Solar Energy*, vol. 20, pp. 333–342, 1978.

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