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Developing ammonia based thermochemical energy storage for dish power plants

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Abstract

The Solar Thermal Group at the Australian National University has completed an experimental solar-driven ammonia-based closed-loop thermochemical energy storage system. The system uses a cavity receiver containing 20 reactor tubes filled with iron based catalyst material, which collects the radiation from a 20 m^2 dish solar concentrator. Reliable operation over a range of conditions including cloud transients has been demonstrated. Parallel theoretical investigations have established that maximising the potential for electrical power production from ammonia synthesis reactors, can largely be achieved through appropriate choice of average operating temperature in standard reactors. The possibility of operating the ammonia based system using trough concentrators has also been investigated theoretically, and the preliminary results indicate encouraging energy storage efficiencies in the region of 53%.

1. Introduction

Concentrating solar thermal technologies offer a promising method for the large scale use of solar energy. There are three main solar thermal concentrator technologies; central receivers, parabolic troughs and paraboloidal dishes. All have been successfully demonstrated on a multi-megawatt scale. Of the three, parabolic troughs contribute the greatest share of installed capacity, with 354 MW_e of natural gas assisted power plants operating for up to 15 years on a fully commercial basis in Southern California (Pilkington Solar, 1996, www.kjcsolar.com). The Australian National University (ANU) has developed a paraboloidal dish concentrator design which promises to be cost effective for large scale solar thermal power systems (Kaneff, 1999) (see Fig. 1).

Solar thermal technologies via thermochemical conversion paths offer the prospect of systems with inherent energy storage for continuous (24 h) generation of electricity. This issue will be increasingly significant as the world moves towards a truly renewable energy based economy. This natural advantage combined with overcoming the "economy of scale" hurdle should see a rapid increase in the adoption of solar thermal power technology in the coming decades.

Ammonia is a pungent smelling gas which is used in the production of fertilizers and cleaning agents among other applications. Production of ammonia is one of the world's largest chemical process industries, with in excess of 125 million tonnes produced annually (Appl, 1999). In a modern ammonia plant the exothermic reaction heat from ammonia synthesis converters is routinely converted to superheated steam suitable for electric power generation in conventional Rankine cycle systems.

The Solar Thermal Group at the Australian National University (ANU) has been working for over two decades on a system for dissociating ammonia with concentrated solar energy so that the products can be stored and recycled through a conventional ammonia synthesis converter to achieve 24 h power production (Carden, 1977, 1987; Lovegrove and Luzzi, 1996; Luzzi and Lovegrove, 1997).

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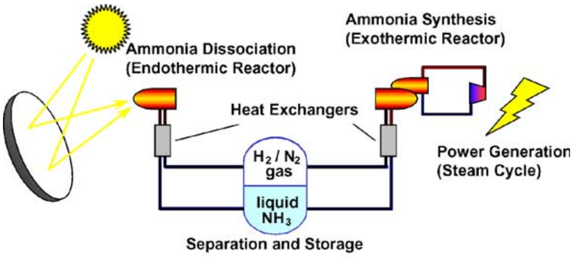
Fig. 1. ANU's 400 m^2 solar concentrator.

A detailed study of a hypothetical 10 MW_e baseload power plant in central Australia, has indicated that Levelised Electricity costs less that AUS \$0.15/kW h are potentially achievable, on par with that from a steam based system without storage (Luzzi et al., 1999). Previously, the team reported on the successful testing of a world first closed loop system that operated at a solar input level of 1 kW (Lovegrove et al., 1999). This paper reports on the scale up to accept the full (≈15 kW) input from the ANU's 20 m^2 dish system. The possibility of operating with trough concentrators is also examined.

2. The concept

The concept is illustrated in Fig. 2. 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. Counterflow 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.



$$NH_3 + DH \rightleftharpoons 1/2N_2 + 3/2H_2$$

Fig. 2. Closed loop thermochemical storage of solar energy using ammonia.

Use of the ammonia reaction, has a number of distinct advantages over alternative reactions. There are no possible side reactions, making solar reactors particularly easy to control. The endothermic reaction operates at temperatures well suited to solar concentrators. 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 almost 100 years of industrial experience with the "Haber Bosch" process to call upon.

A solar thermal power station based on the concept would consist of multiple-dish solar concentrator units (Kaneff, 1999) joined to a central plant by an array of high-pressure gas pipelines as shown in Fig. 3. The pipeline array is of large diameter and has extra parallel sections sufficient to provide the storage volume needed to operate the plant on a 24 h basis. The central plant contains a standard ammonia synthesis reactor, which incorporates heat exchangers/boilers to recover the exothermic reaction heat for superheated steam production. The power block itself is a standard steam Rankine cycle system. The central plant also contains various other system control components. These include circulation pumps and separator units, which reduce the amount of ammonia vapour present in the feed-gas to the heat recovery reactor, by chilling it and capturing the condensed liquid ammonia.

3. Solar driven closed loop experiments

The ANU group is currently experimenting with a solar driven closed-loop system operating on a 20 m^2 paraboloidal dish concentrator. This is a scaled up version of a pilot system that was first tested in September 1998 (Lovegrove et al., 1999). Fig. 4 illustrates the design of the solar reactor. Twenty 0.5 m long Inconel tubes are positioned in a conical arrangement around the cavity receiver aperture. At the apex, the tubes are tied to disk shaped inlet and outlet manifolds. The tubes are filled with a triply-promoted iron-cobalt catalyst ('DNK-2R' by Haldor Topsøe).

This reactor has been operated at pressures up to 20 MPa and tube surface temperatures up to 750 °C, under conditions of both uniform and intermittent insolation.

Fig. 5 shows the receiver reactor in operation. It has initially been operated with a water cooled shield sur-

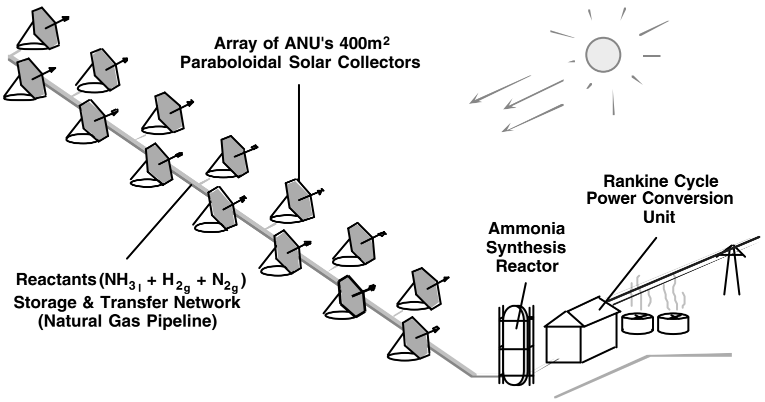


Fig. 3. Solar thermal power station using thermochemical energy storage.

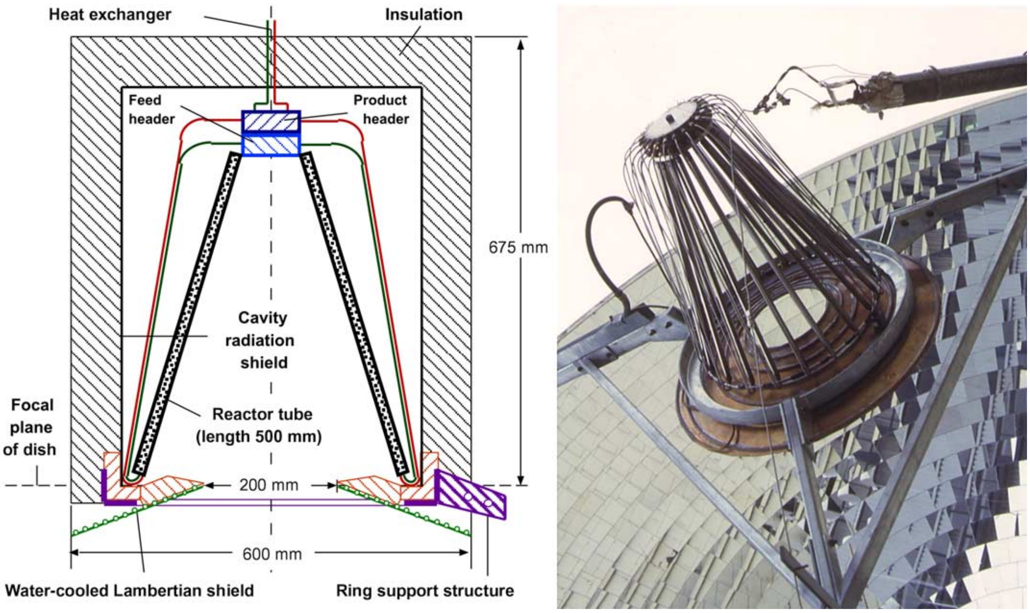


Fig. 4. Design of the cavity receiver with 15 kW$_{sol}$ solar ammonia dissociation reactor and its assembly on ANU's 20 m^2 dish without insulation fitted.

rounding the aperture as a precaution against dish misalignment. This shield has the side effect of acting as a heat sink from the receiver and draws away between 30% and 40% of the collected energy, depending on the operating reactor temperature. Measurements of thermal losses from radiation, convection and conduction from the cavity have varied between 18% and 27% of collected radiation during low solar angle winter operation. Fig. 6 shows the energy balance of a representative steady state experiment conducted at peak reaction temperature of 593 °C and pressure of 15 MPa. So the potential thermal efficiency of the current design for the reactants is estimated at 75%. The water cooled shield has now been replaced with an un-cooled version and tests with this arrangement are continuing.

Fig. 7 shows representative polar plots of reactor tube peak temperatures around the receiver. The average temperature in each case is determined by the flow rate chosen. There is a tube to tube variation of the order of 50 °C, which is acceptable for maintaining reasonable output from each tube, without any tube exceeding the design operating temperature. There are some obviously repeatable features in the distribution. Particular "hot" tubes are most likely explained by variations in the packing of the catalyst beds. The overall offset in the distribution has been found to vary

Fig. 5. 15 kW_{sol} ammonia dissociation receiver reactor in operation on the ANU 20 m^2 dish.

with the adjustment of the tracking alignment however some internal convective effects are also expected to be contributors.

The heat recovery reactor is constructed from a bundle of nineteen tubes, each of these similar in design to a previous 1 kW_{chem} synthesis reactor extensively investigated (Kreetz and Lovegrove, 2000). The design and the partially completed assembly are shown in Fig. 8. As with the solar reactor, the tubes are operated in parallel flow via manifolds. 'Synetix' ('S6-10') iron based catalyst is used.

Fig. 9 shows the experimentally measured and numerically modelled internal and external temperatures obtained from a single reactor tube fitted with internal thermocouples. Internal temperatures were hotter than the walls, confirming that the reaction was producing heat. The wall temperatures up to 475 °C also confirmed that synthesis reactors can recover heat at temperatures useful for electric power generation.

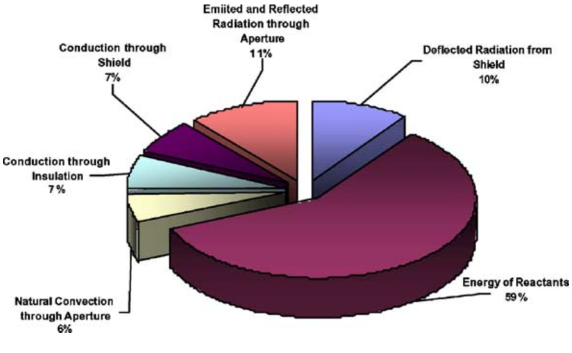


Fig. 6. Energy balance of a steady state experiment at peak reaction temperature of 593 °C and pressure of 15 MPa.

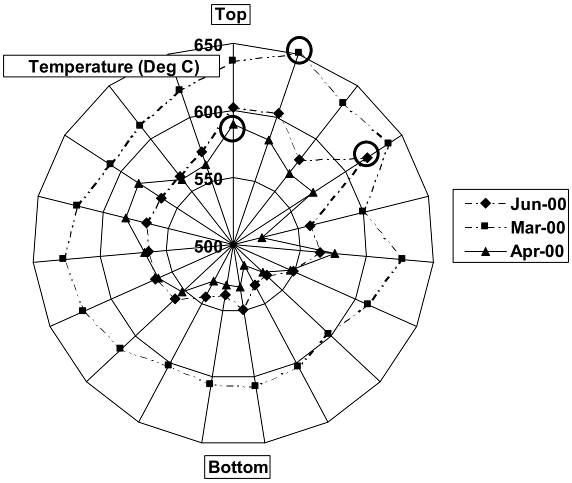


Fig. 7. Temperature distribution around the receiver/reactor.

4. Theoretical investigations

4.1. Optimisation of heat recovery

A thermochemical approach to energy storage inherently works towards the minimisation of thermal losses. However a fundamental issue is the extent to which the recovered energy will be at a lower temperature than the energy input process, with the associated implications for production of work (electrical power). The experimental results achieved with the small synthesis reactor, together with investigation of the performance of industry standard units, confirms that heat recovery at temperatures suitable for superheated steam production for electrical power generation, can readily be achieved. The possibility that the performance of synthesis reactors for electrical power generation, could be improved over those designed for maximum ammonia production is worth investigating.

This issue has been examined using a two dimensional reactor model (Kreetz and Lovegrove, 2000) to examine the performance of tubular reactors built to the same geometry as the experimental unit. Specifically, the heat and exergy recovered from the reactor, has been examined assuming that the temperature profile in the reactor wall is linear. The slope and average value of reactor wall temperature have been varied to determine an optimum operating point. Fig. 10 illustrates the selection of wall temperature profile for maximum thermal

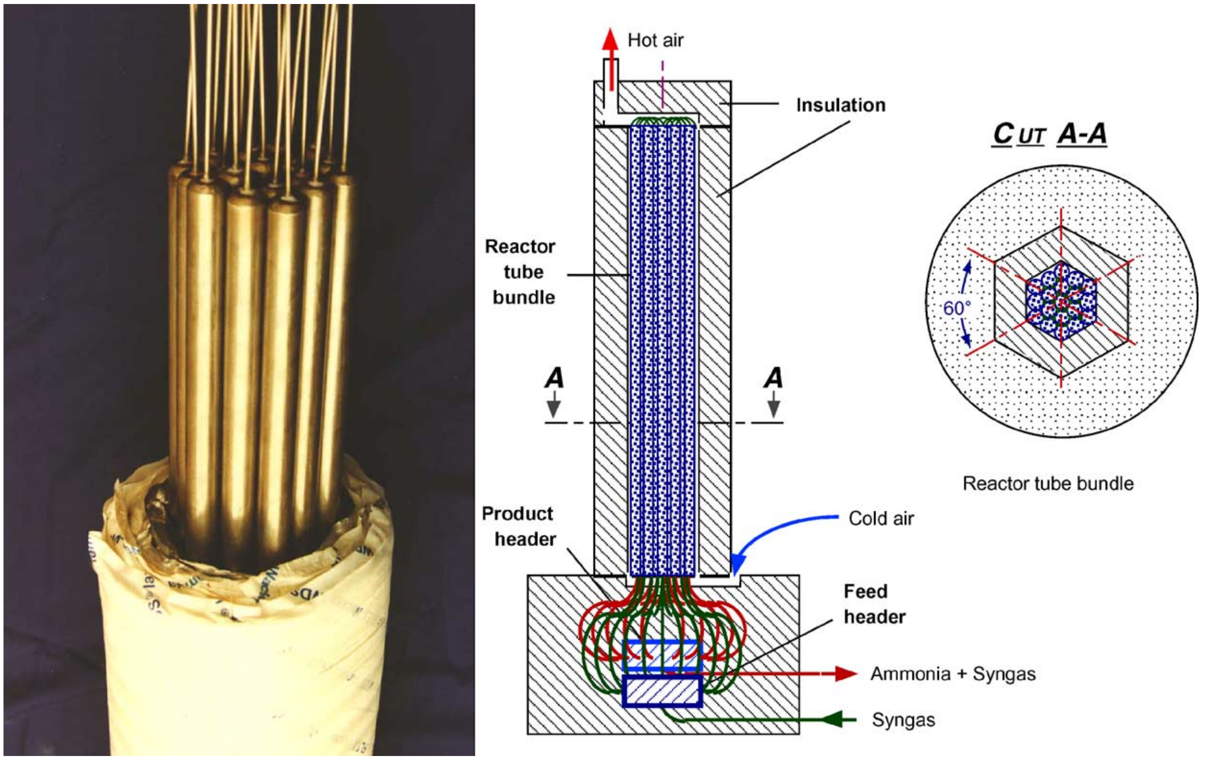


Fig. 8. Design of the 10 kW_{th} ammonia synthesis heat recovery reactor and heat recovery tube assembly partially inserted in insulated containment.

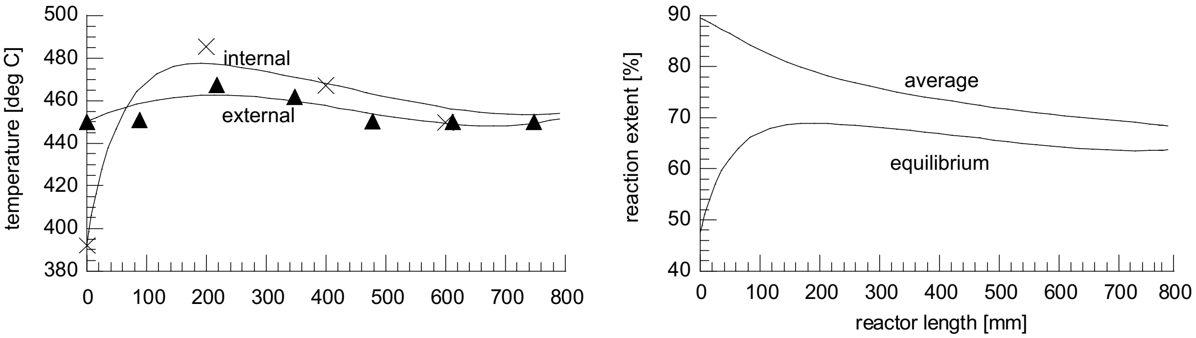


Fig. 9. Measured and predicted temperatures and predicted reaction extents in a single tube 1 kW_{chem} synthesis reactor.

power and maximum net exergy output for the case of 20 MPa and 0.9 $g\,s^{-1}$ operation.

Each curve represents a different slope of wall temperature profile, with the average temperature adjusted by variation of the temperature at $z = 0$. The gas inlet temperature was assumed to be 50 °C lower than the $z = 0$ wall temperature in each case. In case of thermal output profiles, a clear maximum thermal output level of 993.5 W is evident at an average reactor wall temperature of 475 °C, produced with a $z = 0$ temperature of 500 °C and a slope of -0.5 °C cm^{-1}. It is apparent that the most important variable is the average wall temperature and that close to maximum power output can be obtained with a range of wall temperature profile slopes.

In case of net exergy rate, maximum output is apparent at 431.82 W, with an average temperature of 494 °C produced with $z = 0$ temperature of 475 °C and a slope of 0.5 °C cm^{-1}. This corresponds to 861.58 W effective power, and it is seen that a sacrifice of approximately 13% in thermal output results in maximised net

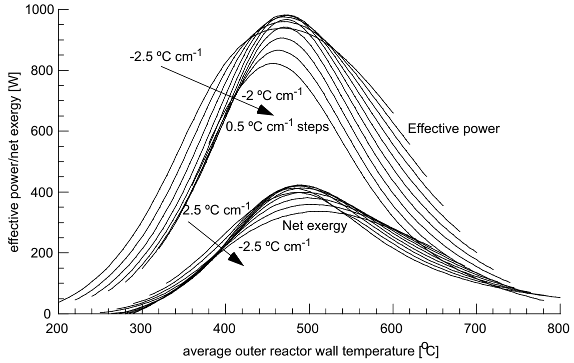


Fig. 10. The effect of varying the outer reactor wall temperature profile on effective power level (top array of curves) and net exergy output (bottom array of curves. Pressure: 20 Pa; mass-flow: 0.9 $\mathrm{g\,s^{-1}}$; reaction extent inlet: 0.98.

exergy rate of the reactor. In the context of an 'exergo-economic optimisation' (Bejan et al., 1996), this would be re-interpreted as the need to provide for an approximately 15% larger reactor in order to achieve the increase in exergy rate output (corresponding to the temperature increase whilst maintaining the same thermal output). This is low enough to suggest that such trade-offs are likely to be worth considering.

It is apparent from the array of net exergy rate curves that the most important variable is the average outer reactor wall temperature and that, similar to the 'effective power' array of curves, maximum exergy rate output can be obtained with a range of wall temperature profile slopes. Highest performances can be achieved with slightly higher average temperatures than for maximum thermal power output, as was expected.

4.2. Operation with trough concentrators

Whilst the ANU group is primarily interested in the development of dish concentrators, trough concentrators have the benefit of many years of large scale proven operation in the Californian SEGS plants, plus are the subject of continued investigation by many groups around the world. This has motivated an initial investigation of the possibility of operating an ammonia based system using trough concentrators. The receivers of the LS3 Luz collectors used in the SEGS plants operate at around 400 °C, the ammonia cycle is possibly the only practical thermochemical cycle that can operate with energy input at this temperature. As well as the advantages of energy storage and transport free from thermal loss, the ammonia cycle offers other potential advantages to a trough based system. A major advantage is that heat recovery can be achieved at a consistent high temperature in the region of 450 °C irrespective of the operating temperature of the receiver. This arises from the natural separation of ammonia from the hydrogen/nitrogen gas within the storage volume. As a result the heat recovery system is always fed with the same composition of feed gas, irrespective of the extent of dissociation achieved in the receiver reactors. The result is a "chemical heat pump", if heat input is at less than the output temperature, the penalty is a reduced level of dissociation and an associated loss in heat exchanger efficiency, so the second law is not violated. Continuous heat output at 450 °C would remove the need for gas fired superheating that is employed with the SEGS plants.

Various configurations of receiver reactor design have been modeled for an LS3 trough assuming the use of the same Haldoe Topsoe catalyst used with the dish receiver/reactor. It has been established that simply filling a single reactor tube with catalyst within the existing LS3 evacuated tube receiver design, would not provide sufficient energy conversion due to low reaction rates. However construction of a cavity receiver based on six 2 in. 'Schedule 40' pipes operated as 2 parallel sets of 3 in series looks feasible. Modeling indicates that such an arrangement would operate at an average temperature of 391 °C. It would have a thermal efficiency of 70%, dissociate 36.8% of the ammonia flow (by mass) and the resulting heat exchanger efficiency would be approximately 74%, leading to an overall energy storage efficiency of 52%. This preliminary result is encouraging and suggests further investigation is warranted.

5. Conclusion

A complete solar driven closed-loop thermochemical energy storage system using ammonia has been demonstrated. This pilot-scale system has shown that ammonia dissociation receiver/reactors are well suited for operation through solar transients and ammonia synthesis heat recovery reactors are capable of stable, predictable operation with heat recovery at temperatures suitable for high-quality superheated steam production. In addition, reactant storage and handling, for the ammonia system at pressures up to 30 MPa, can be achieved using standard components and manufacturing techniques.

Exergetic optimisation of heat recover reactors offers the potential for small but worthwhile efficiency improvements. The most important parameter is the average temperature, suggesting that close to optimum performance should also be achieved with minor changes in operating conditions in conventional industrial reactors.

In addition to the proven operation using dish concentrators, there is also considerable potential for the application of the ammonia based system to the widely used "Luz" trough concentrator technology.

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