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A SOLAR-DRIVEN AMMONIA-BASED THERMOCHEMICAL ENERGY STORAGE SYSTEM

KEITH LOVEGROVE†, ANDREAS LUZZI and HOLGER KREETZ
Centre for Sustainable Energy Systems, Department of Engineering, Australian National University, Canberra, ACT 0200, Australia

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Abstract—During 1998, over 20 years of research at the Australian National University came to fruition with the successful operation of the world-first solar-driven ammonia-based thermochemical energy storage system. This paper presents the latest results obtained with this system which operates at a nominal power level of 1 kW_{chem} and uses a solar reactor design which is an improved version of a prototype first tested in 1994. Progress made in scaling the system up to accept the full 15 kW_{sol} input from the 20-m^2 dish concentrator being used, is also presented. The experimental results indicate that ammonia dissociation receiver/reactors are ideally suited to operation through solar transients and that stable operation of ammonia synthesis heat recovery reactors can be achieved at temperatures well suited to the production of superheated steam for Rankine cycle power systems.

1. INTRODUCTION

Concerns over the negative impacts from an enhanced greenhouse effect and other environmental and resource depletion problems associated with fossil fuels have set the stage for renewable energies to play a major role in the 21st century. Recent years have seen dramatic annual growth of over 30% in the installation of wind and photovoltaic power technologies. To date growth of this magnitude has not been seen with solar thermal electric technologies. 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 14 years on a fully commercial basis in Southern California (Pilkington Solar International, 1996). Various studies of solar electricity generation costs have been made (e.g. Trieb *et al*., 1997). There seems to be general agreement that modern large wind farms can produce electricity with levelised energy costs (LEC) cheaper than modern nuclear plants and coming close or being cheaper than fossil fuel plants in some locations. Solar thermal plants, by whatever route, remain more expensive than wind but are still well ahead of photovoltaic power systems.

Reasons for the apparent inertia in construction of solar thermal systems appear to be not technical, but rather a question of the minimum size needed to achieve economies of scale. Based on this interpretation, the lull in construction should only be temporary since major growth in renewable energy use will inevitably extend demand into system sizes well suited to solar thermal plants.

The theme of the 1999 ISES Solar World Congress was 'Solar is Renewable' which seems to be something of a truism. However, it does point to the issue of energy storage. A technology could not be said to be truly renewable if it still requires fossil fuel backup. Solar thermal technologies via thermochemical conversion paths offer the prospect of systems with inherent energy storage for continuous (24-h) production 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.

2. THE CONCEPT

In closed-loop thermochemical energy storage

†Author to whom correspondence should be addressed. Tel.: +61-2-6249-5433; fax: +61-2-6249-0506; e-mail: stg@faceng.anu.edu.au

systems, a fixed inventory of reactants passes alternately between energy storing and energy releasing reactors with provision for ambient temperature storage of reactants in between. 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.

The group at the Australian National University (ANU) has reported steady progress on the investigation of a closed-loop thermochemical energy storage system using ammonia over a period of more than two decades (Carden, 1977, 1987; Lovegrove and Luzzi, 1996; Luzzi and Lovegrove, 1997). Use of the ammonia reaction:

$$NH_3 + \Delta H \Leftrightarrow 1/2N_2 + 3/2H_2 \quad (1)$$

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 over 100 years of industrial experience with the 'Haber Bosch' process to call upon.

A solar thermal power station based on the concept could appear as shown in Fig. 1.

Multiple-dish solar concentrator units (Kaneff, 1999) are joined to a central plant by an array of high-pressure gas pipelines. This 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 of a design 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.

If the whole system is operated with a fixed volume, then the pressure would vary in proportion to the fraction of the inventory present as a 3:1 H_2:N_2 gas. Alternatively, reversible expander/compressor units may be employed between sections of the storage pipe to ensure that both solar storage and heat recovery reactors operate under conditions of constant pressure. This second scenario is preferred on ideal thermodynamic performance grounds but carries costs in terms of extra components and flow losses. A thermoeconomic optimisation of a complete system would ultimately determine this choice.

The ANU group has investigated the thermodynamic and economic viability of applying the concept to large scale power production. Lovegrove *et al.* (1999) carried out a thorough exergy analysis of a complete system operating at 30 MPa (corresponding to the upper limit of commercial ammonia synthesis practice; Appl, 1993). It was found that a 71% 'exergetic efficiency' for the heat recovery process would result when high, but industrially achievable, system component performances were assumed. When realistic receiver and Rankine cycle ef-

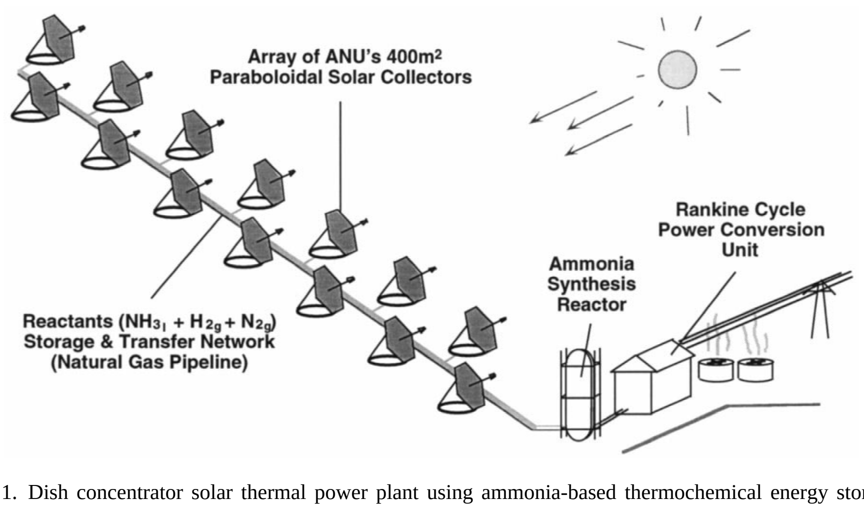

Fig. 1. Dish concentrator solar thermal power plant using ammonia-based thermochemical energy storage.

ficiencies were factored in, an overall solar-to-electric conversion efficiency of around 20% resulted. This is an encouraging result for a complete system offering 24-h baseload output.

Working in the other direction, a system study for a hypothetical 10 MW_e base-load power plant (Luzzi *et al.*, 1999) concluded that a 'pre-commercial' demonstration system of this size could be built using 400 ANU large (400 m^2) dishes and a standard 1500 t/day ammonia synthesis reactor. Using a 7% discount rate, a LEC of AUD 24c/kWh was predicted. In line with cost trends experienced with other emerging renewable energy technologies in general and with solar thermal power plants in particular (Pilkington Solar International, 1996), it is reasonable to predict a rapid fall to LECs of the order of AUD 0.12–0.15 per kWh_e or lower, once the technology is commercially adopted.

3. SOLAR DRIVEN CLOSED LOOP EXPERIMENTS

3.1. Laboratory system

Fig. 2 shows the experimental arrangement used. The heart of the system is the 20-l vessel that stores both undissociated ammonia and the 3:1 hydrogen/nitrogen gas mix that results from dissociation. Liquid ammonia from the bottom can be drawn off and passed via a circulation pump, gas-backed accumulator and flow control valve to either an electrically heated dissociation reactor or a small solar driven receiver/reactor mounted on ANU's 20-m^2 paraboloidal concentrator. After cooling in a counterflow heat exchanger, the reaction products are returned to the top of the 20-l storage vessel.

Independently of the energy storage process, energy recovery is carried out using an ammonia synthesis reactor. Gas is taken from the top of the storage vessel, compressed by a circulation pump and stored in a 10-l buffer pressure vessel. From here it passes through a chilled separator to remove a large fraction of the ammonia vapour that is also present in the gas mix and then to the synthesis reactor. The product gas from the synthesis reactor also flows to the top of the 20-l storage vessel. Liquid ammonia that drains to the bottom of the 10-l buffer from the separator is also periodically bled back to the 20-l vessel.

The whole system operates at constant volume and so the pressure increases as the ammonia in the vessel is dissociated. The massflow through the two reactors is measured with 'Rosemount' corriolis effect massflow transducers. The liquid level in the 20-l vessel is determined with a 'Rosemount' level detector that senses the hydrostatic pressure difference between the top and bottom of the vessel. Pressure transducers and numerous thermocouples make up the balance of the instrumentation. All variables are logged on a PC via a 'Chessel 4500' data acquisition system.

The solar reactor (shown in Fig. 3) is an

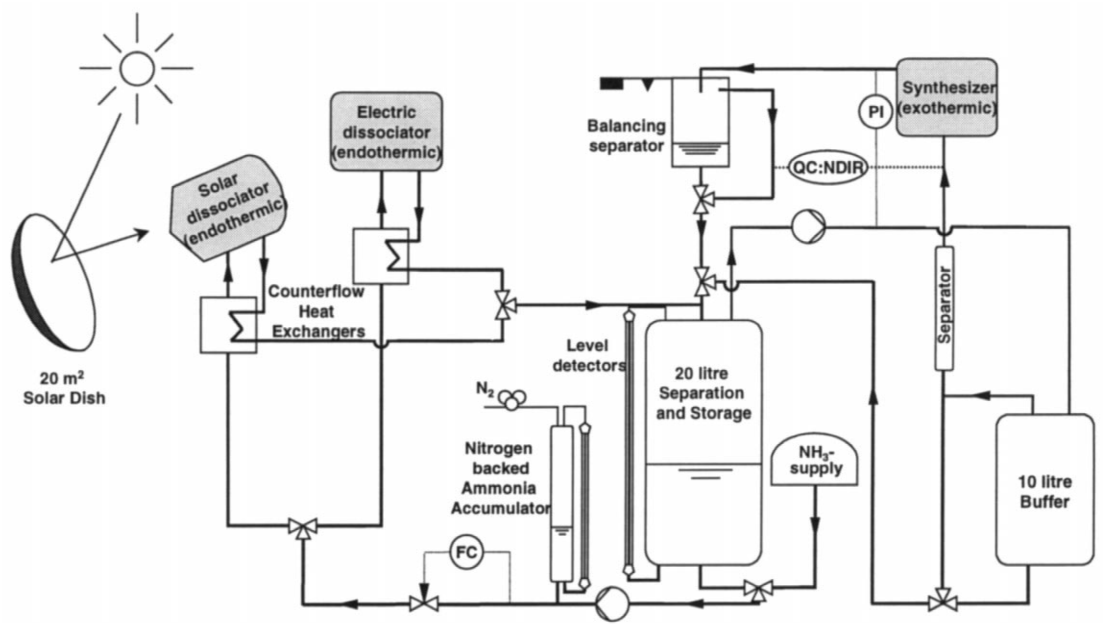

Fig. 2. Experimental arrangement used for laboratory-scale closed-loop experiments.

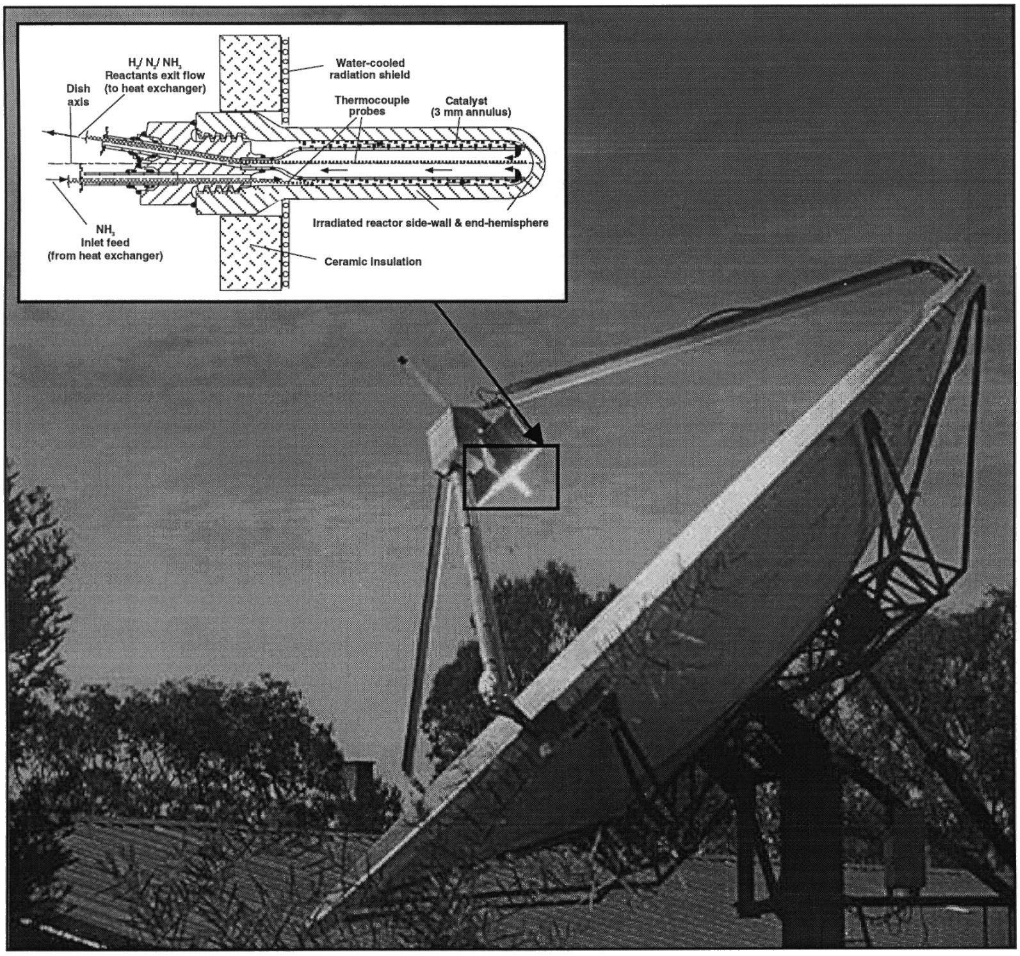

Fig. 3. Ammonia dissociation reactor/receiver in operation on ANU's 20-m^2 solar concentrator.

improved version of a design previously tested (Luzzi and Lovegrove, 1997). It differs from the previous model in that the endcap is sealed against leaks by welding rather than using a copper gasket. It has a reduced thickness of catalyst bed, as modelling indicated that the significantly improved heat transfer associated with higher gas velocities strongly reduced the reactor wall operating temperature and outweighed the loss of catalyst surface area. The reactant flow direction has also been reversed, ammonia now enters from the base and flows through the catalyst bed toward the tip. This reversal of flow direction allows the hot product gases to give up some of their heat to the bed as they pass back down the centre tube. The reactor holds 39 g (compared to 70 g in the previous design) of Haldor-Topsøe's 'DNK–2R' iron–cobalt catalyst.

The ammonia synthesis heat recovery reactor is based on a 1-m-long Incoloy-800 tube filled with Haldor-Topsøe 'KM1' iron catalyst. Its design and operation are described in detail in an associated paper (Kreetz and Lovegrove, 2000).

3.2. Results

The system was operated in closed-loop mode with electric heating for the first time on the 10th of April 1998. Following that successful experiment, a number of changes were made and the new solar reactor was completed. This culminated in the first solar-driven operation on the 26th of September 1998.

Fig. 4 shows data from the operation of the system during a 5-h-long run on the 29th of January 1999.

The experiment was conducted in two parts. From 17 to 87 min, the solar reactor was operated during a period of intermittent cloud cover, while the ammonia massflow was varied between 0 and 4 g/s to keep the reactor at a high operating temperature throughout. The system started at a pressure of 9.5 MPa with a 177.5-mm level of ammonia in the storage vessel. At the end of the

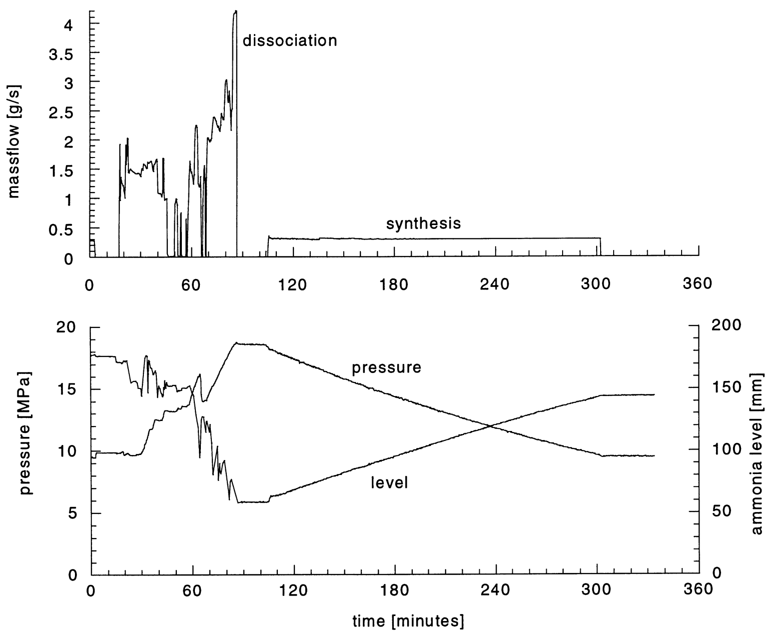

Fig. 4. Evolution of key variables during the solar-driven closed loop experiment on 29th January 1999.

85-min period of solar energy storage, the system pressure had increased to 18.6 MPa and the ammonia liquid level reduced to 59.2 mm. This represents an average rate of energy storage (based on the enthalpy of reaction of 66.9 kJ/mol) of 1.1 kW_{chem}. Fig. 5 shows the behaviour of the insolation levels, the solar reactor bed exit temperature and the massflow during this period. The close correlation between insolation levels and reactor temperature can be seen, together with the variations in massflow that were made to keep the reactor temperature as close as possible to the design operating temperature of 650°C. Reducing massflow to maintain high operating temperatures ensures that the maximum possible reaction rates are maintained at all times. The intermittent nature of the sun provided a demonstration of the ability of solar ammonia dissociation reactors to operate smoothly and effectively through transients.

Referring back to Fig. 4, the solar reactor was shut down at 85 min and the pressure and ammonia level remained constant for a further 19 min. After this the synthesis reactor was operated with a constant massflow of 0.3 g/s of synthesis gas and external temperatures of close to 450°C. Operation of the synthesis reactor continued for 195 min at an average rate of chemical conversion of 346 W_{chem}. This brought the system to 9.54 MPa and the ammonia level to 144 mm, close to the initial conditions.

Fig. 6 shows the experimentally measured and numerically modelled[1] internal and external temperatures within the synthesis reactor, plus the predicted extent of reaction at the 150-min point

[1] Kreetz and Lovegrove (2000), discuss the 2d. packed bed reactor model and the verification of its application to the synthesis reactor in detail.

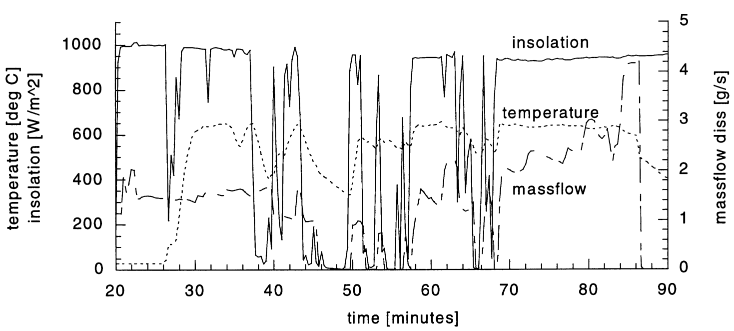

Fig. 5. Operation of the solar reactor during the closed loop experiment on 29th January 1999.

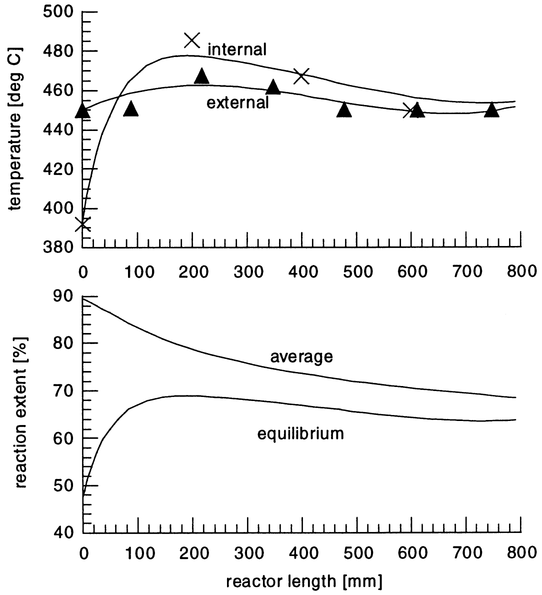

Fig. 6. Measured and predicted temperatures and predicted reaction extents in the synthesis reactor during pseudo steady state operation at the 150-min point on 29th January 1999.

at which the pressure was 15 MPa. At the beginning of the bed, reactants entered at slightly below the wall temperature. Thereafter, the bed centre temperatures were hotter than the walls, confirming that the reaction was producing heat. The wall temperatures up to 475°C also demonstrate that ammonia synthesis reactors can recover heat at temperatures useful for electric power generation.

3.3. Scale up to 15 kW_{sol}

During the second half of 1999, the system was scaled-up to accept the full 15 kW_{sol} input from the 20-m^2 dish. Fig. 7 illustrates the design of the scaled-up solar reactor. Twenty 0.5-m-long Inconel catalyst-filled tubes of similar design to the 1 kW unit are positioned in a conical arrangement around a water-cooled cavity receiver aperture. Reactant inlet and outlet tubes for each reactor tube are joined for parallel flow, to disk-shaped inlet and outlet manifolds, which also form the apex of the conical construction. Water cooling was adopted for the cavity aperture to provide a reliable and fail-safe experimental design. Thermal performance could be improved at a later stage by using cold ammonia feed to provide this cooling function. The assembled system without insulation fitted is shown in Fig. 7.

The scaled-up heat recovery reactor is constructed from a bundle of 19 tubes virtually identical to the 1 kW prototype. The design and the partially completed assembly are shown in Fig. 8. As with the solar reactor, the tubes operated in parallel flow via manifolds. In contrast to the 1 kW heat recovery reactor, the scaled-up unit is thoroughly insulated and will demonstrate high-temperature heat transfer to air blown between the tubes. The unavailability of further supplies of Haldoe-Topsøe's 'KM1' catalyst meant that an alternative iron catalyst with similar performance ('Synetix S6-10') was used instead. Based on the performance of the small unit, heat recovery at a level around 10 kW_{th} is expected.

The majority of the remaining existing system

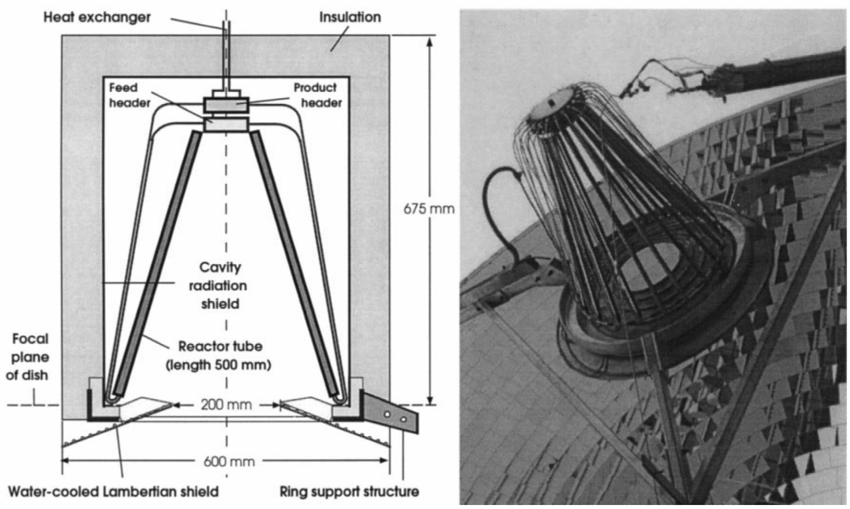

Fig. 7. Design of the cavity receiver with 15 kW_{sol} solar ammonia dissociation reactor and its assembly on ANU's 20-m^2 dish without insulation fitted.

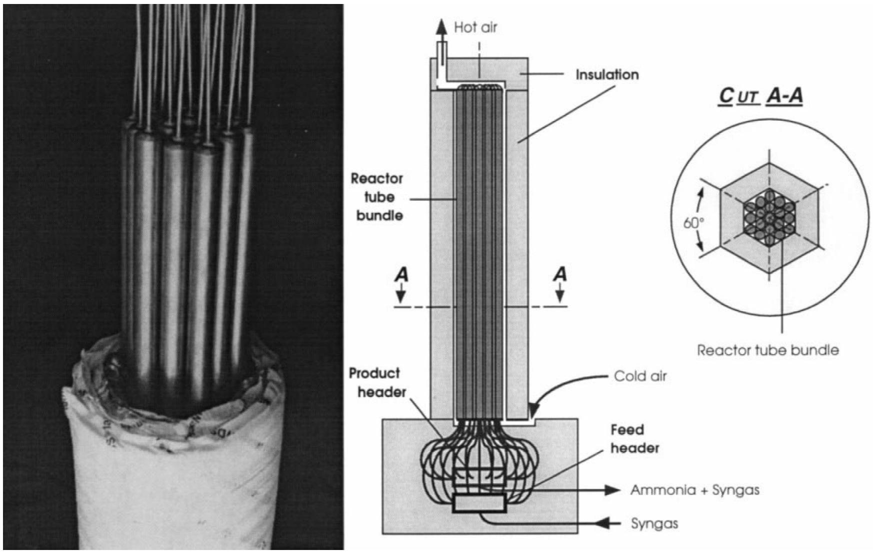

Fig. 8. Design of the 10 kW_{th} ammonia synthesis heat recovery reactor and heat recovery tube assembly partially inserted in insulated containment.

components function directly with the larger reactors. Some massflow control elements required upgrading and a larger-volume reactant storage vessel has been incorporated to complete the scale-up.

4. CONCLUSIONS

After over 20 years of investigation, 1998 has seen the first complete demonstration of closed-loop thermochemical storage of solar energy by ammonia dissociation. This small laboratory-scale system has shown that:

- ammonia dissociation receiver/reactors are ideally suited for operation through solar transients,
- ammonia synthesis heat recovery reactors are capable of stable, predictable operation with heat recovery at temperatures suitable for high-quality superheated steam production and
- reactant storage and handling, for the ammonia system at pressures up to 30 MPa, can be achieved using standard components and manufacturing techniques.

This has led to the design and construction of components to scale the system up to accept the full input from ANU's 20-m^2 dish. This success in the experimental area complements encouraging conclusions from thermodynamic and economic system studies and suggests that this technology could be one of the most cost-effective routes to the provision of continuous 24-h solar electricity.

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