

STATUS OF AMMONIA-BASED THERMOCHEMICAL ENERGY TRANSFER

P.O. Carden

Department of Engineering Physics
Research School of Physical Sciences
Institute of Advanced Studies
Australian National University
Canberra, Australia

ABSTRACT

Of the many thermochemical energy transfer systems proposed, the ANU's ammonia based concept is now amongst the foremost. This paper reviews the development of the concept and describes its present status.

Early in the development, attention was focussed on deriving an output of electrical power rather than heat. The primary application was the gathering of heat energy from an array of solar collectors and applying it to a single thermal power station of fairly conventional design.

Although this early version was technically feasible and economically encouraging it clearly needed further considerable development before it could be said to be viable.

A major advance in development was the reconfiguration of the exothermic terminal so as to produce work directly from the thermochemical fluid stream. This same reconfiguration also enabled a much more favourable operating pressure for the endothermic terminal viz 90 atmospheres. The new arrangement was simpler, less expensive, more efficient and made the catalytic absorbers more practical.

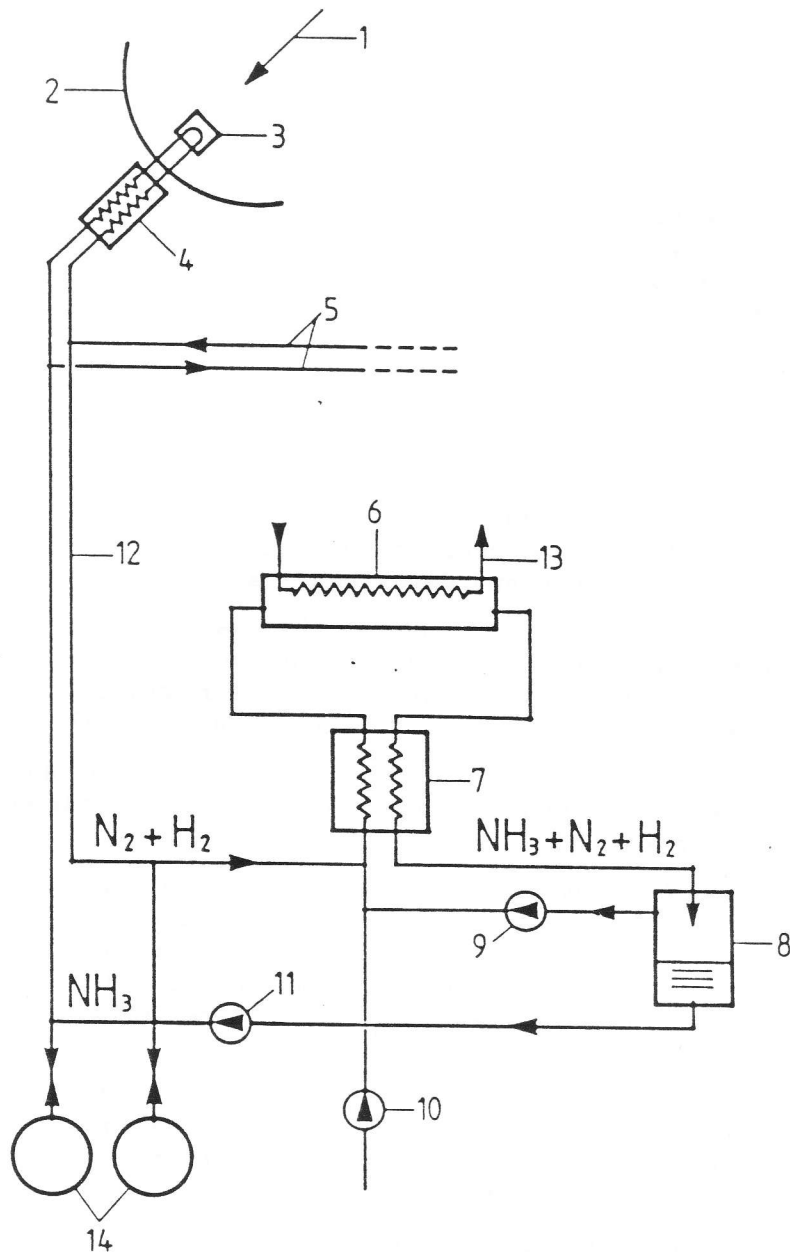
Other improvements have been due to the escalation in the economic size of solar collectors to presently 300m² and the lowering of the exothermic pressure from 300 atmospheres to 200 atmospheres made possible by improvements in ammonia converters.

A further substantial advance is anticipated with the advent of ceramic based reciprocating expanders which will have adiabatic efficiencies exceeding 90%.

ORIGINAL CONCEPT

The original concept of ammonia based thermochemical energy transport was published in Solar Energy (Carden (1977)). As shown in Fig. 1 it is a means of transferring heat from a field of solar collectors to a central power plant, based on the reaction $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. The main attractions of such a scheme are that the energy transfer occurs in ambient temperature pipes and there is the prospect of energy storage. In fact the underground storage of inert gas mixtures such as nitrogen-hydrogen offers the only known prospect of virtually limit-less seasonal energy storage (Carden and Paterson (1979)).

Figure 1: Schematic diagram of original concept.



1. Solar heat input; 2. one of many collectors; 3. focal catalytic dissociator; 4. Counter-flow heat exchanger; 5. Pipe lines from other collectors; 6. Central plant catalytic synthesiser; 7. Counter-flow heat exchanger; 8. Phase separating vessel; 9. Gas circulating pump; 10. System compressor; 11. Liquid circulating pump; 12. Pipe lines at ambient temperature; 13. Heat output to power plant; 14. Storage vessels.

The ammonia system has some other attractive features. It employs readily available substances which are environmentally compatible. Ammonia is relatively harmless, is mostly non-corrosive and is even beneficial in small doses, being the basic substance involved in the intake of nitrogen and the generation of protein in plants. The ammonia reaction is also completely reversible: there are no side reactions (which often plague other thermochemical systems).

But the original concept had some embarrassing features. Dissociation at high pressure was an unknown area so one calculated, as best one could, the amount of catalyst needed. Fortunately the original estimates suggested the amounts would be of a practical size. The system operated isobarically at the high pressure of 300 ats. This was dictated by the available synthesis catalysts, the reaction equilibrium and the need to extract the synthesised liquid ammonia without refrigeration (which would have been energetically unfavourable).

It seemed that the high pressure feature was inescapable so it behaved one to make the best of it. There were in fact some redeeming features: high pressure meant high density and this in turn meant pleasingly compact components and good heat transfer. It was suggested that some of the small pipe lines could be produced and laid continuously - more like a cable than a pipe line - with corresponding significant savings. It was subsequently shown however (Williams (1978)) that the optimum pipe line pressure was near 100 ats rather than 300.

In the original publication (Carden (1977)) the economic aspects of the concept were considered in depth, leading to the conclusion that, all things considered, it was a promising concept.

CRITICISMS

However it was not long before the voices of criticism were evident. A panel of advisers acting for the Department of Science recommended that substantial funds be allocated towards furthering the ammonia based concept. At that time (1978) there was considerable competition for funds so it is probably not surprising that the work was controversial and that there were critics. Coming under fire were the system energy balance and underlying thermodynamic development. It was pointed out that the commercial production of ammonia, far from giving an output of energy, required a nett input. The latent heat of vapourisation and the phase separation work needed to be rigourously accounted for.

There were internal criticisms too. Workers in the research team were aware that not all the output heat was of sufficiently high grade to be useful for power generation. A component appeared at 100-150°C with significant work potential, but there was no practical way of recovering this work. It seemed that the ammonia system was mainly applicable to special situations where use could be made of this low grade heat.

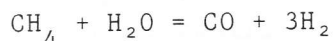
A second internal criticism arose from our experiments and related model studies. It was shown that available catalysts were not sufficiently reactive to enable a satisfactory dissociator design and in fact a ten-fold improvement was called for (Williams (1980)).

Most of the above criticisms were answered through major published studies. Those that remained, principally the two internal criticisms, persisted until the arrival and fruition of some completely new ideas affecting the original concept.

In the meantime a firm theoretical basis was established which spawned several new analytical tools applicable to thermochemical systems in general. The T-H diagram was introduced as the principal diagrammatic medium (Fig. 2). The concept of work recovery efficiency was introduced, defined in terms of reaction path (Fig. 3) and related to an effective Carnot temperature for the reaction (Carden and Williams (1978)). Expressions for phase separation work were derived and used to model states near the phase boundary (Williams and Carden (1979)). This work was adapted to a corresponding states model for the generation of a comprehensive set of thermodynamic data for stoichiometric mixtures of N, H, and NH₃ (Williams (1978)).

CREDIBILITY

The credibility of the work was further enhanced by a parallel study by the chemical engineers Davy Pacific P/L who issued an encouraging report in 1979 and are currently working on a new report. However on the world scene the ammonia system was considerably less prestigious than the SO₃ based system being researched in U.S.A. (Chubb (1975)) and the CH₄ + H₂O system being developed in West Germany (Hilberath and Teggers (1968)).



Summarising, at this point in time (1980), the economics were promising and so was the practicability, except that the high pressure was still an embarrassment, there was an unwanted output of low grade heat and dissociation at 300 ats was a problem.

NEW THOUGHT

The new ideas alluded to above have been called "direct generation of work" (Carden (1985,1987)). They affect the exothermic terminal to the extent that work is now the direct output of the terminal rather than heat. As shown in Fig. 4, expanders and compressors are placed strategically in the thermochemical fluid streams in much the same way as in a gas turbine system. Fine tuning of this arrangement requires just two stages of expander and many stages for each compressor (a large number is energetically favourable; a small number costs less - 3 or 4 stages per compressor is a suitable compromise).

The consequences of this new thought are the following.

- a) The high pressure feature is turned into a unique advantage.
- b) Work recovery efficiency is improved due to the more favourable reaction path (Fig. 5).
- c) Two pressure levels are available. The lower pressure at about 90 ats makes dissociation with available catalysts a practical proposition.
- d) The lower pressure 90 ats corresponds to the economic optimum for the pipe system.
- e) The system is simpler and cheaper because the steam circuit has been eliminated.
- f) Condensation of ammonia at the exothermal terminal is now performed isothermally at the sink temperature (near ambient). The low grade heat unavoidably generated in the original concept has been put to work. The near-ambient temperature waste heat is now simply that which must flow to the sink of any heat engine. Isothermal condensation

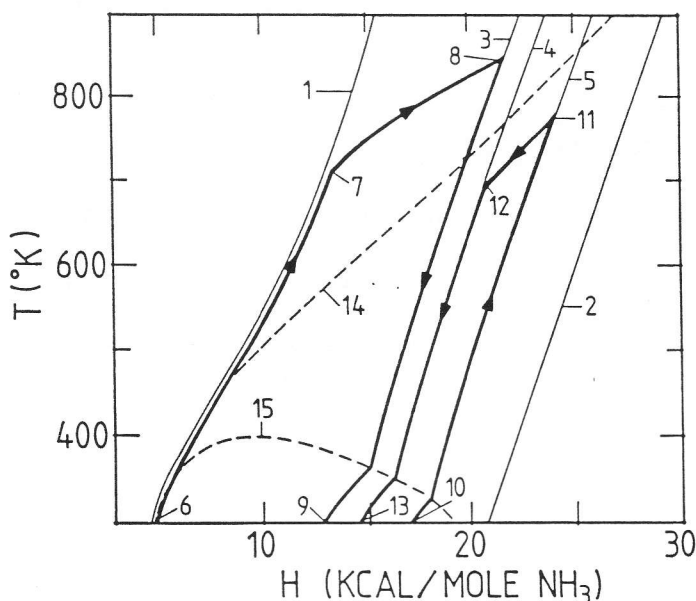


Figure 2: T-H diagram for stoichiometric mixtures of NH_3 , N_2 and H_2 at 300 atms.

1. Contour for pure NH_3 ;
2. Contour for $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2$ mixture;
- 3, 4, 5. Contours for mixtures of NH_3 , N_2 and H_2 at increasing reaction extents δ defined by the molar proportions

$$(1-\delta)\text{NH}_3 + \frac{\delta}{2}\text{N}_2 + \frac{3\delta}{2}\text{H}_2$$

- 6, 7, 8, 9. Path for dissociation (7-8) and associated counter-flow heat exchanger;
- 10, 11, 12, 13. Path for synthesis (11-12) and associated heat exchanger;
14. Reaction equilibrium line;
15. Dew line (two phases below dew line).

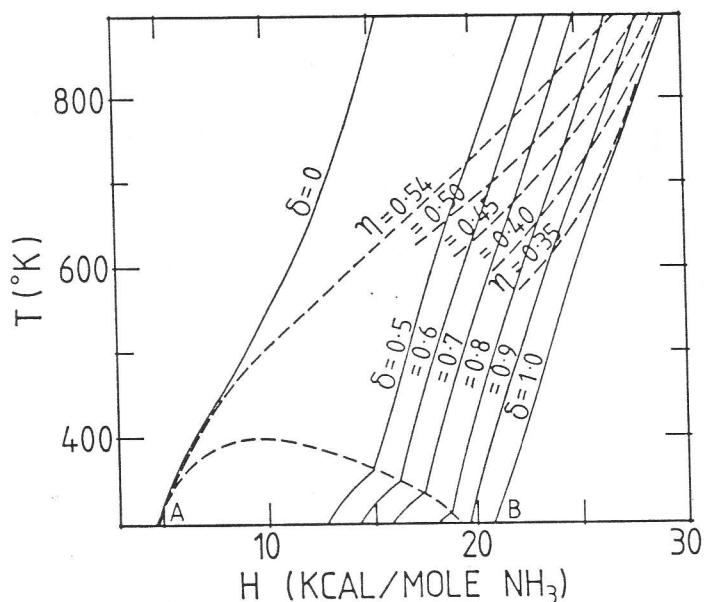


Figure 3: T-H diagram showing contours of work recovery efficiency applicable to synthesis reaction paths at 300 atms and an engine sink temperature of 300°K.

A reaction path along the equilibrium line gives the maximum possible η equal to 0.54. This is equivalent to $\Delta G/\Delta H$ where the differences refer to the input and output of the exothermal terminal-points A and B on the diagram. Other, more practical paths, are less efficient.

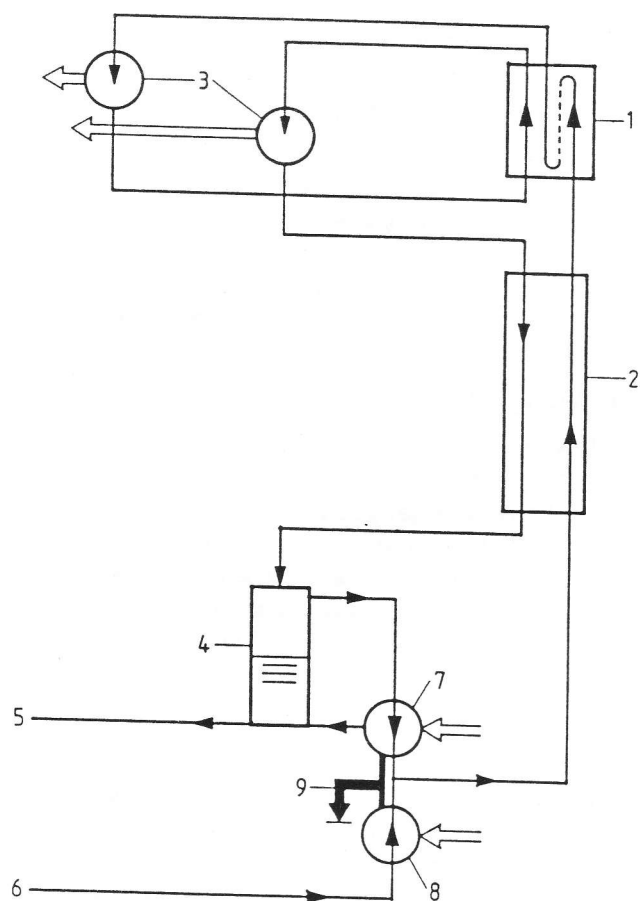


Figure 4: Diagram of exothermal terminal arranged for direct generation of work.

1. Reaction chamber containing reheat tubes at 200ats; 2. Counter flow heat exchanger; 3. Work producing expanders; 4. Phase separator; 5. Ammonia line at 80ats to array of collectors; 6. Return line for products of dissociation; 7. Multistage compressor which squeezes out NH_3 ; 8. Multistage compressor; 9. Heat output at sink temperature.

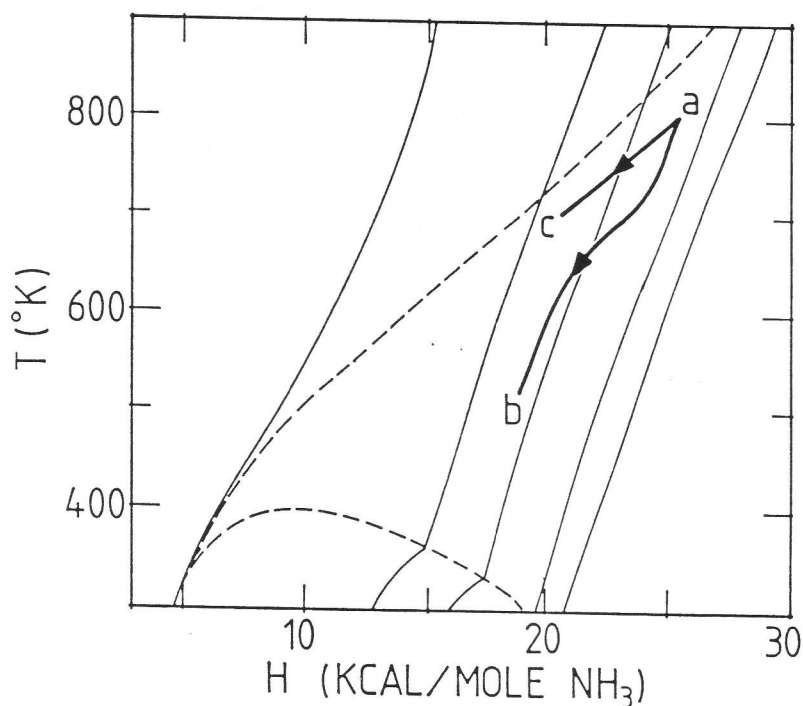


Figure 5: T-H diagram showing reaction paths a-b for generation of superheated steam. a-c for direct work generation.

Read in conjunction with Fig. 3, these curves show that direct work generation is inherently more efficient.

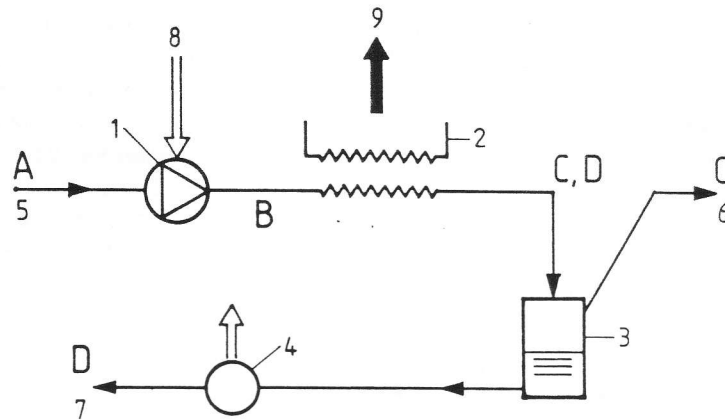


Figure 6(a): One stage of the compressor 7 of Fig. 4 showing:

1. Stage of compressor; 2. Cooler; 3. Separator; 4. Liquid engine;
5. Gaseous input to stage; 6. Gaseous output from stage at higher δ ;
7. Liquid output; 8. Work input; 9. Heat output of stage.

Points A ... D relate to Fig. 6(b)

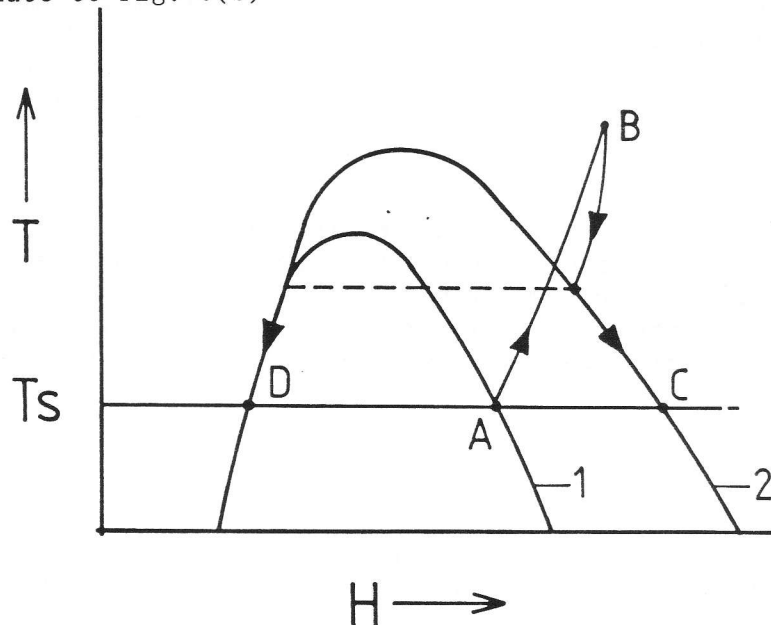


Figure 6(b): T-H diagram corresponding to Fig. 6(a)

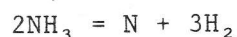
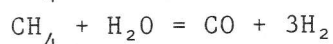
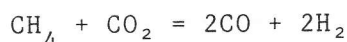
Dewline 2 is for a slightly higher pressure than dewline 1. Adiabatic compression occurs from A to B. Isobaric cooling occurs from B. When dewline 2 is reached condensate begins to form until at the sink temperature T_s there are the two phases C and D.

arises ideally from a large number of successive stages of compression in which a small cooler and phase separating vessel are placed between each pair of stages (Fig. 6). Each stage of compression takes in a saturated gaseous mixture and compresses it by a small percentage (in terms of pressure). The corresponding temperature rise is several degrees. The new state is still gaseous but, as it is cooled back to ambient, condensation of liquid ammonia occurs because of the new position of the dew line at the new slightly elevated pressure. Effectively the ammonia is being "squeezed out" of the gaseous mixture as the pressure rises through the stages.

Several developments in technology have also helped make direct work generation a success. First there is the trend towards much larger collectors (300m^2) than was previously contemplated (10m^2). Besides being themselves more economical these collectors provide advantages in scaling up the dissociators and connecting pipes. Davy Pacific (now Davy McKee Pacific) have alerted us to improvements in catalysts, which should enable the synthesis pressure to be reduced to 200ats, and to the applicability of multistage reciprocating compressors having efficiencies over 90%. By inserting these new figures into our concept model one deduces a thermochemical system efficiency of over 26% (efficiency defined as the ratio of net work out to net heat into dissociators). The corresponding pressure for dissociation and pipe lines is 94 ats. Capital costs, assessed in normal commercial engineering terms, are currently estimated at approximately \$4500/kWe (excluding storage). We may also look forward to non-lubricated ceramic reciprocating expanders of over 90% efficiency to replace the present turbo expanders of 87%.

NEW STATUS - CONCLUSION

The solid work of previous years has finally given new status to the ammonia system. In a 1985 publication of the U.S. Department of Energy (Fish (1985)) it is shown that most of the latest reaction screenings list the ammonia reaction among the three most promising. It has since become evident that the following three reactions will generally be considered the most important.



It is apparent that the ammonia system, invented and researched in Australia, is now regarded internationally as among the leading candidates for thermochemical energy transport, and this has occurred before the full impact of the new thought has had time to be felt.

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