

PROPOSAL FOR THERMOCHEMICAL DEMONSTRATION PLANT

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Identification of project

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The project is to build an experimental plant that demonstrates thermochemical energy transfer based on the dissociation and synthesis of ammonia. The ammonia system is unique in that it is free from side reactions and is not hampered by undue corrosion problems or the need for excessive temperatures. It is based on well established industrial practice (both for synthesis and dissociation) from which considerable knowledge and technology can be drawn. It is a high pressure system, a characteristic that is often seen as a disadvantage but in fact considerable advantages lie in the resulting small component sizes, exceptionally high energy density and improved heat transfer coefficients. Optimum pressure for systems containing gas, such as the ammonia system, has been shown to be about 150 atm on the basis of minimising pipeline transmission costs. The system operating pressure for ammonia is close to this optimum, more so than for other currently proposed systems. Because it is a two-phase system a high degree of flexibility is inherent i.e. neither dissociation or synthesis needs to proceed to completion since separation of the unreacted components is simple.

Each reversible chemical reaction possesses a characteristic effective Carnot source temperature which dictates the minimum efficient operating temperature. The ammonia system possesses one of the lowest effective temperatures (330C) which allows relatively low practical values of dissociation temperature (700C with current catalysts). On the other hand it possesses the unique characteristic of spontaneously rejecting a fraction of its exothermic output as near-ambient heat and this enables the thermodynamic transformation of the remaining heat to well above the effective source temperature (again 700C is a typical achievable value). This has an important bearing on the production of mechanical work which for the ammonia system may be achieved by passing the synthesis gas directly through a gas turbine. Apart from the simplicity and efficiency of this scheme it naturally gives rise to two levels of pressure: 300atm and 120 atm, a situation which may be exploited to enable the dissociators and pipeline to operate at the more suitable lower pressure whilst still allowing the synthesiser to operate at the higher pressure. The prospects for producing a simple yet economically viable system have therefore been considerably enhanced by the introduction of this concept.

The ammonia system is therefore well worth attention in its own right and is particularly well suited for research into thermochemical energy transfer.

Previous work at A.N.U.

The key staff members have been working on aspects of the ammonia thermochemical system intermittently since 1974. This effort has been performed against a sound background of original theoretical work especially in thermodynamics and full scale (order of 10MW) system analysis. Many major difficulties have been overcome including the explosion of an ammonia shipping container connected to the plant. Experimental work aimed at verifying the theoretical basis of thermochemical energy transfer began with high pressure dissociation and has extended to building many of the major components required for an energy transport loop. Having done this foundation work we are now poised ready to go on to the next logical step:

construction of a synthesiser and the completion of a loop having two pressure regimes (in keeping with the current concept of a large scale plant). Over several years there has evolved a well equipped laboratory containing amongst other things components for producing high pressure nitrogen in quantity, evacuation and flushing systems, a facility for storing liquid ammonia and for pumping it to 300 atm, a disposal facility in which ammonia is removed by washing the waste gas, an all-purpose reticulation system comprising high quality valves, filters, pressure reliefs and 6mm steel tubing, pressure vessels for the storage and separation of reactants, nitrogen backed accumulators, flow meters, pressure transducers, thermocouples, a computer-based data gathering and processing facility and a weighable pressure vessel for the absolute determination of synthesis, dissociation, flow rates and nitrogen/hydrogen ratio. Many of the components and instruments have been designed and built in-house because commercial suppliers were unobtainable. A recent procurement has been a 300atm pressure vessel (internal dimensions approximately 300mm diameter, 1m long) capable of housing the synthesiser, synthesis heat exchanger, heat extraction tubes, thermal insulation and tubes for cooling the vessel walls (also used for calorimetry).

Known Problems

These relate to the unique requirements of a small scale demonstration plant and do not in any way reflect on the practicability of a full scale system for which appropriately sized components developed for the ammonia industry are available.

Procurement or development of a reliable source of pressurized, stoichiometrically proportioned, nitrogen/hydrogen (independent of the experimental dissociator). This may consist of a standard low pressure dissociator and gas compressor or a high pressure dissociator employing an incandescent dissociating element.

Development of low flow (order of 1 gm per sec) circulating pumps suitable for liquid ammonia and nitrogen/hydrogen gas mixtures at the system pressures, with a compression ratio of the order of five and with tolerable seal leakage.

Procurement or development of pressure regulators (including back pressure regulators) and flow regulators suitable for low flows of liquid ammonia and synthesis gas.

Development or procurement of technology for making high temperature (600C), hydrogen-tight joints with small bore tubing (3mm), preferably demountable.

Procurement and training of suitable staff.

Definition of Tasks.

1. Produce an operational basic system comprising dual pressure loops and pressurized sources of liquid ammonia, nitrogen and nitrogen/hydrogen (the latter gases mixed in stoichiometric proportions). The loops comprise

reservoirs, a weighable vessel, liquid and gas circulating pumps with flow regulators, pressure regulating systems, liquid and gas flow monitors as well as all appropriate connecting tubing and valves. The source of high pressure ammonia comprises a low pressure (10 atm) storage tank and a pump. The source of nitrogen comprises a liquid nitrogen pump and heater together with pressure measuring and regulating equipment. The nitrogen/hydrogen source is to be procured by outside contract if possible (otherwise built in-house) and is to be independent of the experimental dissociator (also a source of nitrogen/hydrogen) so as to enable parallel development of both loops.

The basic system is to contain a means of continuously determining the nitrogen/hydrogen ratio by weighing a containment vessel at known pressure. This is essential for monitoring any preferential leakage of hydrogen and for enabling leakage make-up.

Each loop may be operated partly full of liquid so that gas flow can be measured by displacement. This task will be complete when (1) steady circulations of liquid and gas are demonstrated whose absolute values may be determined by weighing, (2) when the establishment of two steady pressure regimes is demonstrated, and (3) when a gas analysis capability is demonstrated.

2. Produce an operational electrically heated dissociator system coupled to the basic system described in (1) above. The dissociator system is to comprise a catalyst tube, heater, counterflow heat exchanger and appropriate temperature instrumentation. The task will be complete when acceptable levels of dissociation have been demonstrated and good data obtained on the working characteristics of the dissociator.

3. Design a synthesiser system comprising the pressure vessel subsystem, heat dump subsystem and instrumentation. The pressure vessel subsystem comprises a catalyst container, heat exchanging tubing, counterflow heat exchanger, thermal insulation and instrumentation all housed in a cold wall pressure vessel. The heat dump subsystem comprises a water circulating pump and cooler. The task includes the development of a model for determining the optimum layout and estimated performance of the pressure vessel subsystem. It also includes the procurement of firm quotations for the major components.

4. Produce an operational synthesiser system which converts to ammonia a proportion of the feedstock provided by the nitrogen/hydrogen source or generated by the dissociator system. This task will be complete when the synthesiser system is operating at an acceptable level and when consistent measurements have been obtained on its working characteristics.

5. Produce an operational energy transfer loop by coupling the dissociator and synthesiser systems together and by integrating their control and instrumentation. The task will be complete when automatic energy transfer is demonstrated for steady and varying heat inputs, and when reliable data has been obtained on the performance of the loop over a range of conditions.

6. Produce a design for a solar heated dissociator system based on data obtained to this point. This task will include a model study and the procurement of firm quotations for major components.

7. Produce an operational dissociator using solar energy. The task will be complete when the dissociator is operating satisfactorily and good performance data has been obtained.

Present status.

As explained above the extensive and essential groundwork for this proposal has already been accomplished. The existing facilities put us in the position where Task (1) is partially complete. The completion of Task (2) depends on refurbishing an existing dissociator and its temperature instrumentation. For Tasks (3) and (4) a containment vessel has been designed and built and is on site. With regard to the remaining tasks we have considerable experience in relevant design and technology gained in the course of performing design studies, and in building and testing a range of components including a low pressure (120 atm) synthesiser rated at about 0.5 KW.

Resources required

P.O. Carden will be project leader and R.E. Whelan full-time manager. The fast track approach to the management of this project is favoured. This could be implemented by commencing task (3) and the remainder of (1) immediately. Since the performance of the dissociator is presently unknown this method requires a particularly flexible approach to the design of the synthesiser. Two streams would progress in parallel one stream comprising tasks (1) and (2) and the other tasks (3) and (4). Task (5) would require the confluence of the two streams. Similarly task (6) could commence after the completion of (2) and in parallel with (5). Thus to implement this approach design and experimental assistance is required: for design, a mature design draftsman and for experimentation and building, two technical officers together with appropriate support from the Research School of Physical Sciences' workshop.

It would be of considerable advantage to employ a post doctoral fellow on the project and in the latter stages one or two students.

Special assistance is also required with regard to the known problems listed and others as they might arise. It is envisaged that this assistance will be obtained from specialist manufacturers on a contractual basis where ever possible.

The times for each task, estimated on a "no major problems" basis and assuming the above human resources, are

task 1	14 months (includes 1 month for staff training and "clean up"
2	6
3	4
4	15
5	12
6	5
7	12

Total project time is estimated as follows:

task 1	14 months	task 3	4 months
2	6	4	15

critical path time 20 months			
contingency @ 30% 6			
task 5	12	task 6	5
		7	12

critical path time 17 months			
contingency @ 30% 5			

Total project time 48 months			

Salaries and overheads:

Procurement of full time management:	\$1000 per month	\$48,000
Design draftsman	\$32,000 p.a. for 36 months:	\$96,000
2 Technical officers	\$21,000 p.a. each for 48 months:	\$168,000
Allowance for PDF and students for 24 months ea		120,000

		\$432,000

Materials and equipment.

Current estimate:	\$120,000
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External contracts:

Current estimate:	\$150,000
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Total estimated project cost in current \$Australian	-----	\$702,000
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Procedure:

- (1) This proposal needs to be firmed up in accordance with the requirements of both parties.
- (2) The foregoing assumes that both parties will enter into a contractual commitment covering the entire project with provision for review at key

points. Reporting is to be on a task or time basis. Adoption of fast track implies that the project will be managed on the assumption that it will be successful i.e. tasks need not be carried out in strict sequence if the efficient use of resources dictates otherwise. On the other hand frequent reviews will be implemented to ensure that the work plan remains viable.

(3) The work will be carried out with an emphasis on understanding the underlying mechanisms, obtaining reliable measurements and correlation with known or developed theory.

Description of demonstration plant.

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The power level is set at approximately 1kw this being at about the optimum level determined by trade-offs between scale proportional costs and the costs associated with small flows e.g. provision of accurate measuring instruments and the reduction of leakage. The synthesiser proves to be the most difficult component to design and the most costly. In practice it is necessary to bring the catalyst up to operating temperature before synthesis can commence. Thus an electrical heater located in the synthesiser system is almost mandatory and this is also required for initially reducing the oxide catalyst with hydrogen. Given that there has to be an electrical heater, its presence is exploited in the following way.

One of the important problems is the disposal of the high grade heat (500C) in the absence of an engine or other appropriate load and in a manner that will allow both a high degree of variability in synthesiser output as well as independent control of the synthesiser temperature. One method is to thoroughly insulate the synthesiser and take off the exothermic heat via a secondary fluid to an external heat dump. We have tried this approach. It led to a disproportionately large amount of thermal insulation; hence the choice of a hot wall pressure vessel; hence mechanical and thermal stress problems, difficulties with hot lead-throughs and with the selection of a suitable high temperature secondary fluid.

The alternative approach is to deliberately reduce the amount of insulation so turning it into the escape path for the exothermic heat and at the same time degrading it to a manageable temperature. In this scheme the electrical heater is turned into a heat shield by which the synthesiser temperature may be controlled. Thus the sum of the exothermic heat and the electrical heat tend to remain constant and demonstration of energy transfer amounts to showing that the sum of the two electrical power inputs (p_1 and p_2 in the diagram) is constant though each may vary widely.

We emphasise that the seemingly contrived nature of the scheme is only a consequence of the small scale of the demonstration and the unavailability of a suitable load. In no way does it reflect upon the practicability of a large scale system. The cold wall pressure enclosure simulates what is practical on a large scale and the apparent disproportionate amount of thermal insulation required to prevent undue loss is only a consequence of the volume-to-surface ratio which strongly disfavors miniturization.

Although the scheme lacks a certain realism it is on the other hand quite practical from the experimental and cost point of view. It allows the use of a reasonably sized cold wall pressure vessel enclosing all the associated high pressure components so converting them effectively into low pressure components with considerable benefits in cost reduction and in design flexibility.

It is intended that the exothermic output will be controlled primarily by means of the flow of feed stock (nitrogen and hydrogen). Increasing the flow should increase the heat output though not proportionately. Similarly the rate of heat absorption is to be controlled by the flow of ammonia to the dissociator. This in turn will be automatically varied so as to maintain a constant dissociator temperature through variations in heat input to the dissociator. The two processes of dissociation and synthesis will be kept in

step by linking them to a common vessel kept partly full of liquid ammonia at a constant level. The level will be maintained by varying the flow of feedstock in response to changes in level thereby causing the manufacture of ammonia to match the rate at which it is dissociated.

Level changes in the common separator will be detected by weighing. The apparatus for doing this exists and was developed mainly for enabling the absolute determination of rates of dissociation and synthesis, calibration of flow meters and measurement of nitrogen hydrogen ratio (by weighing a pressurised gas sample).

POTENTIAL FOR MARKETABLE SYSTEM

Applications

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The ammonia thermochemical system is particularly applicable to distributed point focusing solar energy systems of minimum size about 10MWe. There is no known inherent upper limit to system size. The concept relates essentially to heat transport from many receivers to a single heat recovery centre. The single striking feature that has caught the attention of engineers and entrepreneurs is that high temperature heat is effectively transported at ambient temperature and in fluids of high energy density. Consequently the cost of transporting heat has been dramatically reduced, thermal losses have been eliminated and the prospect of lossless thermal storage has been introduced. The ammonia system is particularly well suited to power generation by gas turbine operating directly in the reactant gas stream. The output may also be configured for process heat up to 800C or cogeneration of heat and power.

Alternative systems

The two most prominent competitors of the ammonia reversible reaction are the $\text{SO}_2\text{-SO}_3$ reaction and the family of hydrocarbon reactions typical of which is the steam-methane system. Of these ammonia has the lowest heat of formation but as compensation it has the highest energy density. It has the lowest effective Carnot temperature but the least problem with high temperature materials and the least stringent requirements for mirror precision. The ammonia system is one of the least prone to corrosion. The hydrocarbon reactions invariably have difficulties with side reactions i.e. complete reversibility does not occur. The ammonia reaction has no such problem.

The steam-methane reaction which has been developed in West Germany for the extraction of heat from a nuclear power plant for distribution to numerous surrounding factories requiring process heat is not particularly suited to solar energy where the reverse configuration is required: numerous heat sources and a single load. This is because for most reactions one end of the transport loop is more complex than the other and for practical reasons the complex end ought to be the one with the single connection.

The distribution pipes for the $\text{SO}_2\text{-SO}_3$ system must be operated at and insulated for 100C otherwise they will become blocked with a thick viscous sludge of SO_3 . Moreover the pipes must be fitted with trace heaters to enable start-up.

No such problem exists with the ammonia system. In fact the two phase nature of this system is exploited to great advantage giving it certain unique features which greatly add to its practicability. At ambient temperature the two sides of the reaction are represented by a liquid: ammonia, and a gas: a mixture of nitrogen and hydrogen, which spontaneously separate from one another. This means that neither the endothermic or exothermic reaction need proceed to completion or to any predetermined extent. This unique feature provides a useful degree of flexibility: the control of reactant flow to each receiver may be decoupled from the reaction extent or quality of the exiting fluid; when each receiver is deliberately oversupplied automatic temperature regulation occurs by virtue of the fact that the temperature

will always assume that value which endows the catalyst with a reactivity commensurate with absorbing the heat input. The high density of liquid ammonia allows the economical provision of a buffer storage facility that permits decoupling of the exothermic end from the endothermic ends for short periods.

The ammonia system is also unique in that it is a high pressure system: high pressure is required to favourably influence the equilibrium constant for synthesis, to increase the concentrations at the catalyst surfaces and to effect separation of liquid ammonia without refrigeration. The pressure required for synthesis is up to 300ats. This pressure is however within the "thin wall" range for pressure vessels and the few required are of straightforward design having ambient temperature walls. Vessels suitable for 10MWe synthesisers have been developed for the ammonia synthesis industry.

The need for a high pressure is compensated for in a number of ways. High pressure leads to small components and high heat transfer coefficients. It enables the use of a gas turbine for extraction of work directly from the synthesis gas stream. This has significant beneficial consequences in improved efficiency and reduced cost resulting from the elimination of a steam loop and greater operational simplicity. A further benefit is that the energy transport pipelines may be operated at very close to the economically optimum level about 110ats: any higher and the walls become predominantly thick and expensive and also pumping losses tend to become significant; any lower and costs associated with the large diameter dominate.

Finally, looking well ahead there is the real prospect of incorporating economical seasonal storage into a network of ammonia based solar power plants. This would be achieved by using aquifers, underground storage reservoirs enclosed above by a water saturated dense cap rock and below by mobile ground water contained in porous rock or sand. These often contain natural gas which demonstrates their capability of being absolutely leak tight. This is true even with hydrogen. The mixture to be stored viz nitrogen and hydrogen is environmentally compatible with such storage. (Ammonia is easily stored in large refrigerated tanks at ambient pressure). The pressure of these reservoirs is determined by depth typically 1.1Km for the required 110atm. Costs are related to the power rating of the encased drill hole typically 10MWe. Thus seasonal storage might be provided for about \$1 per electrical watt.

Configurations of the ammonia system

For systems generating power by means of a directly coupled gas turbine two configurations have been considered. They are the isobaric system operating at the single nominal pressure of 300 atm and the dual pressure system operating at 300atm for the synthesiser and 110atm for the dissociators. The latter has the advantages that the lower pressure is more favourable for economic transport of the reactants and for the process of dissociation. Against this a feed stock compressor is required to overcome the pressure step. In practice this is not a separate item but manifests itself as a roughly 15% increase in the size of the compressor that is normally part of a closed loop gas turbine system. Ammonia liquid is released between the stages of compression and is available at a range of intermediate pressures.

Work may be recovered from this in the run down to the 110atm level but it is not sufficient to compensate for the compression of feed stock. The thermodynamic source of compensation for the net energy deficit is a decrease in the heat of reaction for dissociation at the lower pressure and, taking into account the mechanical efficiencies involved, this might be expected to be about 95% effective. Thus there are trade-offs to be assessed before the dual pressure system can be finally adopted. Nevertheless it is currently favoured.

Energy balance

Using available data (a large part of which was provided by this research group) it is possible to draw up an energy balance and reactant flow diagram for the full scale module envisaged of about 10MWe capacity. Fig 3 is an example that indicates a work recovery efficiency with respect to received thermal energy of about 32%.

Costs

In 1979 Davy Pacific, a Davy International company, was commissioned to report on the feasibility of the solar ammonia process. They reported that it was possible to design a workable system for 10MWe. The cost would be \$29.2 million including auxiliary oil fired boilers and gas turbines for overnight power generation. The operating cost would be 15 cents per Kw. (These figures were in \$Australian). At that time the direct coupled gas turbine concept had not been developed so their study was based on the employment of a steam loop. The costs included \$12.5M for the collectors and site preparation as well as a 20% contingency allowance. Using this report as a basis, and omitting the overnight facility, we estimate the cost of the gas turbine concept as 88% of the above and the net power output 63% greater.

In the long term one would expect further improvements as research data and operating experience are gained. For example it would pay if the cost of the turbine were increased by 50% in order to gain an additional 5% of thermal efficiency. Turbine designers used to conventional power generation have yet to be confronted with this option. Again the sizes of reaction vessels are directly related to catalyst reactivity which in turn is very sensitive to temperature. Trade-offs between catalyst type and cost, catalyst life, temperature and reactivity need careful consideration once the relevant data becomes available most probably from research.

Answers to criticisms

Ammonia has poor heat of reaction.

Compared with other candidate reactions this is true on a molar basis. But what counts is energy density and this quantity is dependent on system pressure as well as heat of reaction. The pressure for the ammonia reaction adequately compensates for the low heat of reaction without being excessively high.

Ammonia synthesis is a high pressure reaction and is therefore "difficult".

To an industrial chemist interested in the easiest method for making a particular chemical the pressure necessary for the synthesis of ammonia must understandably appear to be a nuisance. But to an energy engineer interested in the cost-effective transportation of reactants over a pipeline, the optimum sizing of components, improved heat transfer and the matching of the reaction to a prime mover, the system pressure for ammonia should be seen as a desirable attribute. Operation of the pipeline at near optimum pressure is possible and the gas turbine will have an unusually high power/weight ratio.

Leakage is serious.

Leakage at the rate of 3% of the loop flow would render the system unworkable because the energy needed to manufacture the leaked reactants would about equal the energy output of the system. However the tolerance limit of 0.1% is readily obtainable according to the Davy report and is achieved regularly in current ammonia synthesis plant.

Experience of the ammonia synthesis industry is that there is a net energy input. Hence the exothermic end of the loop can't work in practice.

This observation comes from taking a very superficial view of the synthesis process. Energy goes into the commercial synthesis process in three main forms: the hydrogen for the feed stock comes from natural gas or naphtha; the feedstock needs to be compressed from its formation pressure to the synthesis pressure; often refrigeration is employed to extract ammonia. The combined effect of these energies greatly exceeds the exothermic heat. However for thermochemical energy transport none of these three processes occur apart from what is needed to prime the system initially. Therefore the above criticism is without rational foundation.

There will be an environmental problem if ammonia leaks out.

For the very good reason stated above the system would have to close down if leakage were above 0.1%. But if massive leakage did occur the danger to humanity and the environment would be no greater than currently exists in the vicinity of ammonia manufacturing, storage and shipping facilities. This is minimised by the fact that ammonia vapour is lighter than air and quickly ascends out of harms way. In high concentrations ammonia is dangerous to humans because of its caustic nature but at low concentrations it is thought sometimes to be beneficial (e.g. smelling salts). Ammonia leakage does no permanent damage to the environment because that part which reaches the upper atmosphere is dissociated by ultra violet radiation and the remainder returns to earth as a trace component of rain water. Plants use both naturally occurring and man-made ammonia as a vehicle for nitrogen fixation and consequently ammonia can be said to be the source of all protein both in plants and animals. It can therefore hardly be called a hazard to the environment.

Catalysts are unavailable for the duty required.

The most commonly used synthesis catalyst, and the cheapest, is iron (with certain important additives). The recommended maximum operating temperature for this is 810K. Hence a suitable synthesis catalyst for the gas turbine concept exists. There is no known reason why this should not be adaptable to dissociation but data on space velocity in this application is unavailable. An estimate of the amount of catalyst required for dissociation can be made using the reaction rate equations developed to explain catalytic synthesis. Using this approach it appears that 10 to 20 cc/KWth is possible at 810K. These quantities are compatible with the large point-focusing collectors currently being contemplated. Other catalysts such as nickel may permit higher operating temperatures and may therefore be more effective. One of the important outcomes of operating the demonstration plant would be the acquisition of performance data for a range of catalyst candidates.

Corrosion is a problem

Corrosion is only a problem where ammonia mixes with water as might occur around a leak. Even then there is no serious problem except with alloys containing copper. These must be avoided in the construction of the plant. Otherwise steel is the most satisfactory material the type being chosen to suit the temperature and strength required.

Additional heat is required to boil the ammonia before dissociation occurs and latent heat is lost during synthesis.

It is true that there is a low grade heat component that "goes along for the ride" in the ammonia process. But in the gas turbine version this component contributes to the total work output and is neither an embarrassment or a waste. One needs to be reminded that solar power systems have been built that rely wholly on such low grade heat. As compensation the cost of the collectors may be reduced by lowering their precision: the distribution of angular error may be such that only 70% of the surface reflects to a cavity focus the remainder reflecting to an area surrounding the cavity entrance that operates at around 100C.