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DEMONSTRATION OF AN AMMONIA-BASED
CHEMICAL HEAT PIPE: A RESEARCH PROPOSAL

Energy Conversion Technical Report No 19

O M Williams

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Department of Engineering Physics

INSTITUTE OF ADVANCED STUDIES

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1. INTRODUCTION

One of the major research efforts of the Energy Conversion Group has been directed over the past four years towards understanding the operation of thermochemical energy transfer systems or Chemical Heat Pipes as they are becoming more popularly termed. Over this period, the ammonia/hydrogen-nitrogen system proposed by Carden [1] has been studied in some detail through high pressure dissociation experiments [2], development of thermodynamic data [3-5], and a general thermodynamic analysis [5-9] defining the desired operating characteristics and maximum efficiencies for work production. In overseas work, Chubb [10,11] of the USA has been developing the sulphur dioxide/sulphur trioxide system, in West Germany the water/methane (Eva/Adam) system is being investigated for the purpose of distributing heat from nuclear power plants during periods of low demand [12], and recently Lenz [13] of the USA has become interested in the ammonia system. There have also been a number of paper studies [14-16] on candidate chemical systems but few reports of active experimental work.

The ANU Energy Conversion Group has been deeply involved in the pioneering stages of this new field of energy research and the work has now reached the point where it is desirable that a laboratory demonstration of an ammonia-based chemical heat pipe be mounted. The basic reasons for embarking on such a demonstration programme are as follows:

- To test the technical feasibility of ammonia-based chemical heat pipes in transferring virtual high grade heat between a thermal source and an output steam generator.
- To demonstrate the inherent energy storage property of chemical heat pipes by continuous operation of the steam generator in combination with an intermittent thermal source.
- To assess the efficiency of thermochemical energy transfer and to gauge the quality of the output steam for the purposes of work production.
- To optimise the system operation for maximum energy transfer and work production and compare the observed performance with the limiting thermodynamic performance [6].
- To gain operational and design experience prior to a detailed design and economic assessment of the utilisation of ammonia-based chemical heat pipes for 1-10 MWe solar power generation in remote areas.
- To assess and select catalysts for operation in ammonia-based chemical heat pipes.
- To operate the chemical heat pipe in combination with paraboloidal solar collectors and solar thermochemical absorbers (Stage II).

In order to complete the case for support of development of a laboratory scale ammonia-based chemical heat pipe, it remains to list the areas in which chemical heat pipes relate to the overall development of a future energy strategy:

- Energy transfer from a distributed solar collector array to a central plant where high grade heat is regenerated [1].
- Energy transfer between the central absorber and base power plant in the central tower/heliostat solar power system [14].
- Long term energy storage (through storage of the products of the endothermic reaction) [17].
- Solar electricity generation for remote users at the 1-10 MWe level [18].
- Distribution of high grade process heat from a nuclear power plant during periods of low demand [12].
- Distribution of high grade process heat from a remote thermal plant to industrial consumers [19].
- Synthetic liquid fuel production [19] (long term).

None of these potential applications can be assessed on any proper basis until the technical feasibility of chemical heat pipes has been established by demonstration. While there are no major problems envisaged at present which would prevent the ammonia-based system from satisfactory operation, there is as yet insufficient evidence to warrant complete confidence. The only

way in which such confidence can be established is by demonstration on a laboratory scale and in this proposal the research and development programme required to mount such a demonstration is outlined.

2. SCALING THE EXPERIMENT

It is important that the proposed demonstration plant should match the requirements for a full-scale plant, a criterion which has some bearings on the selection of the optimum scale for a laboratory experiment. For the present purposes it is convenient to match the scale to the requirements for 1-10 MWe solar power generation for remote areas (Figure 1). In such a system, high pressure ammonia is dissociated at the focus of each paraboloidal dish in a solar collector array and virtual heat in the form of the chemical energy bound in the hydrogen-nitrogen mixture is transported to a central plant. Electricity is generated at the central plant by operation of an ammonia synthesiser supplying high grade heat in the form of superheated steam to a conventional steam turbine and alternator. The output heat from a laboratory ammonia synthesiser should therefore be supplied in such a way as to match the inlet steam requirements of a conventional steam turbine operating with several stages of reheat and regenerative mixins. That is, the synthesiser should be expected to supply high grade heat but not necessarily low and medium grade preheating obtainable by regenerative mixing in the steam turbine cycle.

Although long term energy storage is available from the ammonia-based chemical heat pipe in the form of underground storage of the high pressure hydrogen-nitrogen mixture [17], it is expected that the first generation of solar power plants at the 1-10 MWe level would operate initially in a hybrid mode with several hours of above-ground hydrogen-nitrogen storage in high pressure tanks and fossil fuel backup for night operation and for operation during long periods of inclement weather. The economics of such a system would need to be justified in terms of annual fuel savings. For the laboratory experiment, however, the storage aspect can be demonstrated by suitable tank storage of the hydrogen-nitrogen mixture without recourse to the ultimate economics of such a system.

The minimum scale of the experiment is determined essentially by the need at the second stage to couple the chemical heat pipe to a solar input, the obvious choice being the paraboloidal mirror system being developed concurrently by the ANU Energy Conversion Group. Two 10 m^2 paraboloidal solar collectors operating at an efficiency of 75% for 6 hours each day would give a thermal input of 90 kWh/day, which equates to a continuous thermal output (neglecting synthesiser losses) of 3.75 kWt. That is, the laboratory ammonia dissociators would need to be rated at typically 7.5 kWt (2 off) and the synthesiser rated at typically 4 kWt. It is shown below in Section 3.2 that gas storage of typically 1.5 m^3 at 300 atmospheres pressure is required to support continuous operation of such a system. While it is not intended to run a steam turbine from the system, it is of interest to note that achievable electrical output would be

somewhat in excess of 1 kWe. Operation below this level would not be regarded as a practical demonstration for the purposes of transferring the results of the experiment to the desired operation at the 1-10 MWe level. Operation of the laboratory experiment at a level much in excess of 4 kWt continuous is on the other hand precluded on the grounds of increased cost for little discernable benefit over the lower scale.

We are thus in a position to summarise the basic requirements for the proposed laboratory demonstration of the ammonia-based chemical heat pipe. Maximum system pressure is chosen as 300 atmospheres which is compatible with standard high pressure design techniques and is typical of the operating pressures of current ammonia synthesis plants. The critical elements of the system would be:

- 10 kWt laboratory high pressure ammonia and dissociator operated at typically 750°C and 300 atmospheres.
- 1.5 m^3 5000 psig hydrogen-nitrogen storage vessel designed also as the system liquid/gas separator.
- 4 kWt continuous ammonia synthesiser with heat extraction in the range $350-550^{\circ}\text{C}$.
- 7.5 kWt solar thermochemical absorber based on ammonia dissociation for operation at the focus of a 10 m^2 paraboloidal solar collector (Stage II).

3. BASIC OUTLINE OF THE DEMONSTRATION PLANT

The outline of the proposed demonstration plant is shown in Figure 2. Basically, high pressure liquid ammonia is pumped to the dissociator where high grade heat at 700-750°C is absorbed in promoting the dissociation of the ammonia into its complementary hydrogen-nitrogen mixture. A counterflow heat exchanger is provided in order to preheat the incoming ammonia and cool the outgoing gas mixture toward ambient temperature, thus minimizing thermal losses in the connecting pipework. The product mixture is separated into gas and liquid phases in a gravitational settling tank which doubles as the high pressure ammonia and hydrogen-nitrogen storage vessel. In order to recover the high grade heat, the hydrogen-nitrogen mixture is pumped to the system synthesiser where the heat is released in the range 400-600°C as the heat of the exothermic synthesis reaction. The product mixture is returned to the separator and again, a counterflow heat exchanger is used to provide preheating and to minimise thermal losses.

The heat released during the synthesis reaction is extracted from the system by means of steam tubes positioned appropriately in the synthesiser catalyst bed. The steam is heated in the range 350-550°C, simulating the principal heat and reheat requirements of a modern steam turbine. As discussed above, regenerative mixers would normally be used to provide the water preheating. In the proposed demonstration plant, preheating is provided by an electric heater with full account of the difference in operation included when assessing the overall

energy transfer performance of the system. The preheating could alternatively be provided by desuperheating a portion of the output steam, although such a procedure does deviate from the required simulation of standard steam turbine operation.

More detailed system design is shown in Figures 3 to 5 and the important system components are described below in Section 4. The system is designed to operate in three different modes depending on the energy storage requirement. During the development programme each mode would be assessed to determine operational viability in relation to the potential applications listed in Section 1. The three modes of operation are described in the following paragraphs.

3.1 Continuous Isobaric Operation Without Significant Storage

This mode of operation is the most simple but at the same time does not simulate the intermittent energy source characteristic of a solar power plant. The system operation may be gauged by reference to Figure 2. The laboratory dissociator would be operated continuously (electrically heated) at a level of typically 4-5 kWt, producing sufficient hydrogen-nitrogen mixture to supply the feed requirements of the synthesiser. Significant volumes of gas storage would not be essential although storage would be desirable for the purpose of decoupling the respective operations of dissociator and synthesiser. System performance would be measured in terms of the thermal energy transfer between the electrical input at the dissociator and the output steam, taking suitable account of the water preheater used to simulate the effect of a regenerative heating cycle.

The thermal quality of the output steam would be measured and used to assess the thermodynamic performance in terms of anticipated work production. The system parameters such as synthesiser temperature profile would be varied and a suitable comparison made between the observed and thermodynamic limiting performances.

3.2 Isochoric (Constant Volume) Operation with Storage

The most simple way in which the system can operate continuously from an intermittent heat source is in a constant volume mode where the system pressure is permitted to fall as the hydrogen-nitrogen mixture is consumed during the source-off period, and is restored to its maximum value during the source-on period. It is envisaged that the system pressure would vary between a maximum of 300 atmospheres under full storage conditions and a minimum of 100 atmospheres. Given the specified operation at 90 kWh/day thermal input to the system, with 22.5 kWh transferred directly to the output during the source-on period, sufficient storage volume must be available to accommodate the hydrogen-nitrogen mixture equivalent to the remaining 67.5 kWh. An estimate of the storage requirement V can be obtained from the ideal gas law

$$V \Delta P = \frac{\Delta m}{M'} RT$$

where M' is the molecular weight of the hydrogen-nitrogen mixture and where Δm is the mass change from synthesis gas to ammonia

corresponding to the system pressure change ΔP . An allowance of 20% of the storage volume to accommodate the liquid ammonia is added to the gas storage estimate, giving an overall storage volume of 1.3 m^3 . A design volume of 1.5 m^3 is adopted to allow a suitable margin for inaccuracy in the estimates.

The particular advantage of the isochoric mode of operation is that, apart from the storage volume, no additional equipment is required for operating the system compared to the isobaric operation outlined in Section 3.1. The response of the synthesiser to the slow changes in system pressure will need to be monitored carefully, the change in limiting work recovery efficiency falling from 54% to 46% as the system pressure falls from 300 to 100 atmospheres [4].

3.3 Isobaric Operation with Storage

Continuous isobaric operation using an intermittent source can be implemented by alternate compression and decompression of ammonia to and from the high pressure storage vessel. In this case, the level of liquid ammonia in the high pressure vessel would vary between 10% and 90% during the source-off period, maintaining a constant system pressure of 300 atmospheres. A reversible compressor/expansion engine would need to be employed between the high and low pressure storage reservoirs (Figure 2), allowing work to be recovered during the ammonia decompression.

The major problems anticipated with operation in this third mode are associated with the dissolved hydrogen and nitrogen within the high pressure ammonia (1.2% at 300 atmospheres [4]). On decompression in the expansion engine, the gases would be released from the solution and would then reside as a permanent gas phase above the liquid ammonia in the low pressure tank. In order to prevent the pressure in this tank from rising too high, either the gases should be vented or alternatively the gas phase should be compressed and delivered back to the high pressure storage vessel. The problem of dissolved gases represents somewhat of a complication which, although not being intractable, would best be avoided in the first instance. Operation in this mode is therefore relegated until such time that the alternative modes outlined in Sections 3.1 and 3.2 have been investigated.

4. COMMISSIONING THE SYSTEM

The basic elements of the chemical heat pipe are shown in Figure 3, with details of the synthesiser system and the gas quality control shown in Figures 4 and 5 respectively. The following procedure would be adopted for commissioning the system:

- Pressure test all parts of the system and flush with dry nitrogen to remove dirt and grit.
- Evacuate the low pressure ammonia tank and fill with high purity ammonia and sufficient nitrogen to give an overall pressure of typically 300 psig, thus allowing cavitation problems to be avoided.

- Evacuate the main system and prefill the high pressure storage vessel with ammonia to the 20% level.
- Calibrate the dissociation circulation pump by pumping ammonia to the accumulator and sensing the change in ammonia level.
- Reduce the dissociator catalyst while pumping ammonia through the system compressor from the low pressure storage tank. The water-contaminated ammonia may be rejected from the system if necessary.
- Operate the dissociator (with ammonia pumped from the low pressure tank) to produce 3:1 hydrogen-nitrogen mixture for filling the high pressure storage tank to the desired system operating pressure.
- Pump the hydrogen-nitrogen mixture through the synthesiser and preheat for catalyst reduction, following the procedure outlined in Vancini [20]. Monitor the water content of the outlet gas mixture using the gas quality control system.
- After catalyst reduction, reject the water-contaminated ammonia and refill the system with fresh ammonia and hydrogen-nitrogen mixture. The system is now ready for operation.

Once the system has been commissioned, operation would follow one of the modes outlined in Sections 3.1 to 3.3. Details of the system operation are discussed below in relation to the

system component description outlined in the following sections and will be developed further as the system design becomes better defined.

5. SYSTEM COMPONENTS

5.1 Ammonia Dissociator

The ammonia dissociator will be designed at either the 5 kWt or 10 kWt level, with no pretensions towards solar thermochemical absorber operation. The dissociator would employ essentially the same counterflow heat exchanger as used successfully in the Mark IV dissociator [2], suitably scaled to the increased level of operation. Alternatively, several heat exchangers in parallel at the same scale of the Mark IV design would be used. The catalyst chamber design is envisaged in the form of several parallel thick-walled tubes (Incoloy 800) packed with catalyst and heated electrically using Pyrotex heating wire. The end of each catalyst tube would be accessible through a blanked Ermeto-type coupling maintained at essentially ambient temperature, not being in the main gas flow path. This feature would enable ease of access for catalyst replacement and assessment of different catalysts. The dissociator would be designed to operate at a working pressure of 300 atmospheres and at 750°C maximum temperature.

Operation of the dissociator would be dependent on the available catalysts for ammonia dissociation. Thus far, only the ICI 47-1 catalyst has been tested, being characterised by a packed volume of 15 cm³/kWt for operation under conditions of

uniform power density and maximum temperature 750°C at 300 atmospheres (Figure 6 of ref [2]). Under such conditions, an energy storage efficiency of 80% is obtained. Improved operation would be possible under essentially isothermal conditions obtained by non-uniform windings of the Pyrotex heating wire [2].

It would be desirable to reduce the catalyst volume requirement by use of more active catalysts. Enquiries are at present being made to identify a more suitable catalyst and a number of catalysts will be tried when the prototype laboratory dissociator is constructed. Ammonia synthesis catalysts will also be tested for roles in ammonia dissociators. The location of a more active dissociation catalyst is a very important aspect defining the future designs of solar thermochemical absorbers and represents a search that should be performed with some vigour.

The basic characteristics of the proposed dissociator are summarised as follows:

- Isothermal operation at 750°C and 300 atmospheres.
- Tubular heat exchanger following Mark IV design.
- Parallel tubular catalyst chamber with accessible end ports for catalyst replacement.
- Non-uniform heating by Pyrotex heating wire.
- Energy storage efficiency in excess of 80%.
- High catalyst activity to better than $15\text{ cm}^3/\text{kWh}$.
- Operation at 5 kWh or 10 kWh.
- Ammonia flow rate typically $0.33\text{ g s}^{-1}/\text{kWh}$.

5.2 High Pressure Storage Vessel

It has been shown above in Section 3.2 that the high pressure gas storage vessel requires an internal capacity of 1.5 m^3 for isochoric operation of the system between 100 and 300 atmospheres. Test pressure would be set at 8000 psia and the vessel manufactured from alloy steel (3% Cr, 1% Mo, 45000 psi yield stress) with small bore top closure (Dave Pacific Pty Ltd, private communication). In order to minimise manufacturing costs, access to the vessel would be through a single top port with tubular inserts to access the liquid phase at the bottom of the tank. The vessel would be fitted with a liquid level sensor accurate to within typically 1% of full scale. Optimum shape of the vessel would be determined from the manufacturing options and installation requirements at the laboratory site. Overall manufacturing cost may limit the initial installation to a lower capacity.

5.3 Low Pressure Ammonia Tank

The ammonia storage tank would be manufactured from carbon steel with capacity of typically 1 m^3 to accommodate the requirements of isobaric operation with storage (Section 3.3). Design pressure would be selected at 500 psia in order that permanent gases could be inserted into the vapour phase in order to avoid cavitation problems. The tank would be equipped with liquid level sensor, gauge glass, and thermocouple well. Optimum shape would again be determined from the manufacturing options.

5.4 Ammonia Synthesiser

5.4.1 Internal Volume Requirements

The ammonia synthesiser represents the most critical component of the chemical heat pipe. It is essential that the design for the demonstration plant be chosen to match the operation of a full-scale synthesiser at the 1-10 MWe level, as typified by the ICI quench converters described in Attachment I. Given the enthalpy change of 3.3 kJ/s for ammonia synthesis, a 1000 tonne/day plant corresponds to a thermal output of 38.2 MWt. We obtain for the 1000 tonne/day plant (1100 short tons) listed in Table 1 of Attachment I, a catalyst volume rating equal to $0.8 \text{ m}^3/\text{MWt}$ and total internal volume rating equal to $1.5 \text{ m}^3/\text{MWt}$. The corresponding catalyst volume rating quoted by Carden [1] is $2.4 \text{ m}^3/\text{MWt}$, assuming a mean catalyst bed density of $1.7 \text{ tonne}/\text{m}^3$. For the present demonstration plant where it will be desirable to tailor the synthesiser temperature profile to follow closely the equilibrium line [6], a procedure that corresponds essentially to operating at lower catalyst activity, it would seem sensible to derate the ICI figures by a factor of about 3 to ensure an adequate design margin. This would result in an overall synthesiser internal volume rating of typically $5 \text{ m}^3/\text{MWt}$, including catalyst volume and steam pipes. The design margin adopted here would need to be lowered if costs of the proposed synthesiser pressure vessel became too high.

5.4.2 Synthesiser Pressure Vessel

There are two options for the synthesiser pressure vessel, as shown in Figure 6:

- (a) A hot wall pressure vessel of a high strength alloy such as incoloy 800, operating at temperatures up to 600°C. The vessel would be fully lassed by Kaowool insulation.
- (b) A cold wall pressure vessel with the catalyst chamber accommodated in an inner vessel surrounded by insulation at the high pressure.

For continuous operation at 4 kWt, the inner volume containing the catalyst and heat extraction tubes would need to occupy about 20 litres, given the above ratings of 5 m³/MWt. By adopting a length to diameter ratio of 4 for the cylindrical catalyst chamber, we obtain a characteristic length of 75 cm and diameter of 19 cm. Sufficient extra length would be required at each end to provide room for internal pipe manifolds and thermal expansion bellows.

The major problem with the hot vessel option is associated with suitable design of the full dimension end closures, consistent with operation at the high temperature. Overall conduction losses could be reduced to low levels by packing sufficient thermal insulation around the high pressure jacket.

The major problem with the cold vessel option is associated with the increased scale required for the internal thermal insulation inside the pressure jacket. It is shown in Appendix I that the overall internal volume per unit length for a given fractional conduction loss α through the cylindrical wall is given in terms of the thermal capacity \dot{Q}/L per unit length as

$$\frac{V}{L} = \beta \frac{\dot{Q}}{L} \exp \left[\frac{4\pi K \Delta T}{\alpha \dot{Q}/L} \right]$$

where β is the active volume ratio in m^3/Mwt and K is the thermal conductivity of the internal insulation. The internal volume is plotted as a function of the thermal capacity in Figure 7 for the case $\beta = 5 m^3/Mwt$. It is assumed here that the insulation is filled with high pressure nitrogen in pressure balance with the gas mixture in the catalyst chamber. It is not possible to allow the hydrogen-nitrogen mixture into the insulation region because of the deleterious effect on the thermal conductivity of the insulating jacket. This restriction means that the cold vessel option must have a suitable pressure balance mechanism between the inner catalyst chamber and the nitrogen-filled insulating jacket and that further, the shell confining the catalyst chamber and steam tubes must be sufficiently thick to withstand pressure differences of up to 500 psi caused by frictional pressure drop along the catalyst bed.

The thickness of internal insulation required for the cold vessel option may be assessed by reference to Figure 7. Allowing a 5% conduction loss and a 4:1 length to diameter ratio for the

catalyst chamber, we obtain for 4 kWt operation a pressure vessel inner diameter equal to 42 cm and catalyst chamber inner diameter equal to 19 cm. That is, in order to reduce losses to a tolerable level so that full-scale operation may be satisfactorily simulated, the larger fraction of the internal volume must be occupied by insulation. It is interesting to note that this same feature is unimportant for full-scale ammonia synthesis which at the 1000 tonne/day level is characterised typically by \dot{Q}/L equal to 3.2 MWt/m (Attachment I). It is clear by extrapolation of Figure 7 to high values of \dot{Q}/L that such a reactor requires only a thin skin of insulation in order to reduce conduction losses to a low fraction of the energy throughput.

In summary, it would appear that there are two options available for synthesiser pressure vessel - either hot wall or cold wall - and that neither lies outside the scope of a laboratory demonstration. The choice will ultimately depend on cost and on ease of operation. The first step in any thorough design assessment will be to identify the optimum choice for the required demonstration.

5.4.3 Catalyst Chamber Design

At the present time, the catalyst chamber design and synthesiser temperature control system design are somewhat fluid but the basic outline can be gauged by reference to the quench gas option drawn in Figure 3. The basic design criterion is again that the demonstration plant should match the operation of

a full-scale plant and in particular, be required to provide high grade heat in the temperature range 350°C to 550°C as outlined above in Section 2. The catalyst chamber would most probably be of multistage design for adequate temperature profile control, with the main proportion of reaction heat removed by means of longitudinal steam pipes. The incoming synthesis gas is preheated in the synthesis heat exchanger external to the main pressure vessel and constructed by following the same design principles as for the dissociator heat exchanger.

Temperature control is established either by the quench gas option shown in Figure 4, or by using lateral pancake-shaped steam coils in place of the gas mixing chambers. In the first instance, the choice would be governed as much by simplicity of operation as by the need to maximise potential work output by minimising all sources of irreversibility. This latter design criterion would need to be examined carefully in any later optimisation procedure.

It has been shown in our theoretical studies [6] that in order to maximise work production from the synthesiser it is desirable to tailor the temperature profile across the reactor to follow a line of essentially constant work recovery efficiency. The type of reaction profile expected from the reactor outlined here for either quench gas or lateral steam coil control is shown on the T-H diagram of Figure 8. With good design of longitudinal steam tube geometry (for example, the steam tubes can be coiled with decreased spacings in the initial part of the catalyst bed where more heat is released), there need be little, if any, rise in temperature across the catalyst bed, and thus the role of the

quench gas or lateral steam coil is relegated to that of fine temperature control. In the quench gas case, an additional heat transfer path would need to be provided to remove heat from the heat exchanger due to the mass flow imbalance between the input and output gas streams, as shown in Figure 4.

There are many details of synthesiser design that need assessment but at this stage there is little to be gained until the design has been firmed. Suffice to say that the overall design does not appear to be outside the expertise of the Energy Conversion Group, given that some thought is applied to retaining simplicity, perhaps even at the expense of fully optimum operation in the first instance. Details of the reaction kinetics will be considered before the design is finalised, and indeed the computer code developed to simulate the dissociator operation can be modified simply to simulate the synthesiser operation under given design conditions.

5.5 Circulation Pumps

Both the dissociator and synthesiser circulation pumps are double-acting intensifiers that have been developed in this laboratory following pressure sealing difficulties due to the poor quality of the Sprague intensifiers used in the past. The Sprague air motors which provide 3000 lbf from a 100 psig air supply are suitable for driving the circulation pumps.

The pumps have been designed so that the air drive acts only against the pressure differential between the inlet and outlet ports and not against the full system pressure. The pumps are characterised by the following specifications:

Stroke: 2.5 cm

Maximum cyclins rate: 3 Hz

Dissociator PUMP bore: 2 cm

Synthesiser PUMP bore: 5 cm

Maximum ammonia throughpout: 22 g/s ($\Delta P = 0$)

Maximum synthesis gas throughpout: 22 g/s at 300 atm ($\Delta P = 0$)

8 g/s at 100 atm ($\Delta P = 0$)

Pressure drop at stall: 6800 psis (dissociator)

1000 psis (synthesiser)

The pressure drop limitation on the dissociator circulation pump due to the tensile stress in the main connecting rod between the high pressure cylinder and the air motor is 1300 psi, a limitation that could be improved by better design of the connecting mechanism.

Since the pumps are both positive displacement units, they provide a good basis for development of a simple flow control system based on automatic adjustment of the air flow to the air motor. The dissociator pump speed can be servoed to the dissociator temperature or alternatively set at a constant level. The synthesiser pump speed determines the level of output heat from the synthesiser and will need to be set consistent with the amounts of synthesis gas mixture held in storage. The water pump controlling the flow through the steam pipes is critical in the sense that it defines the coarse control of the synthesiser temperature profile. A fail-safe procedure will need to be developed in the event of this pump ceasing operation during an experiment.

5.6 Gas Quality Control System

In closed loop operation, it is important that the quality of the 3:1 hydrogen-nitrogen mixture be continually monitored, particularly since the system will inevitably be more prone to hydrogen loss than to nitrogen loss. The gas monitoring system based on a mass spectrometer and turbo-molecular pumping unit is shown in Figure 5. This system enables high pressure samples of the output from the synthesiser to be analysed after decompression initially to 1 psia and then to the 10^{-4} - 10^{-5} torr level required at the mass spectrometer inlet. In the event of a significant deviation from the ideal 3:1 hydrogen-nitrogen mixture, the system can be used to adjust the mixture by addition of either pure hydrogen or pure nitrogen, or any specified mixture, into the sampling volume. The gas quality monitoring system would be utilised also during the synthesiser catalyst reduction procedure to ensure that the water content did not rise above typically 10000 ppm (see Attachment I).

6. SUMMARY

In this report, a proposal has been outlined for development of an ammonia-based chemical heat pipe on a laboratory scale. The development is motivated by the need to assess the technical feasibility of the chemical heat pipe, to compare the observed operation with the known thermodynamic operating limits and to gain operating experience sufficient to specify a design for a chemical heat pipe at the 1-10 MWe level. We have endeavoured to

show that the scale of the proposed development, while not trivial, is not outside the range of competence of the ANU Energy Conversion Group. It is believed that the scale chosen for the demonstration plant is consistent with the need to maintain an essentially linear scaling of the observations to full-scale operation at a 1-10 MWe level.

While the basic system components required to mount the demonstration have been specified where possible, the present assessment has not been advanced to the stage where detailed operational procedures are fully defined. Such an advancement has an important bearing on the design details of the system and would be performed before the first stage of development of the chemical heat pipe demonstration. Safety aspects of the experiment and, in particular, the selection of a suitable location for the high pressure vessels and synthesiser would also be an important consideration before the first stage of development.

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APPENDIX I

Internal Volume Requirements for Ammonia Synthesiser
with Internal Thermal Insulation

We consider a cylindrical ammonia synthesiser of radius R and length L . The synthesiser is fitted with an axial cylindrical reactor of radius r containing catalyst beds and steam tubes. The remaining annular space is filled with thermal insulation. We wish to calculate the overall internal volume V of the synthesiser in terms of the thermal capacity \dot{Q} under conditions where there is a constant fractional conduction loss α given by

$$\alpha = \dot{Q}_{\text{loss}} / \dot{Q} \quad (\text{I.1})$$

The conduction loss is defined by the standard formula

$$\dot{Q}_{\text{loss}} = \frac{2\pi K L \Delta T}{\ln(R/r)} \quad (\text{I.2})$$

where K is the thermal conductivity of the insulating layer and where ΔT is the temperature difference across the insulation.

The catalyst activity is rated according to the factor β which defines the active volume including catalyst beds and steam tubes per unit thermal capacity

$$\beta = \pi r^2 L / \dot{Q} \quad (\text{I.3})$$

and by combining (I.1), (I.2) and (I.3), we obtain for the overall internal volume

$$\frac{V}{L} = \beta \frac{\dot{Q}}{L} \exp \left[\frac{4\pi K \Delta T}{\alpha \dot{Q}/L} \right] \quad (I.4)$$

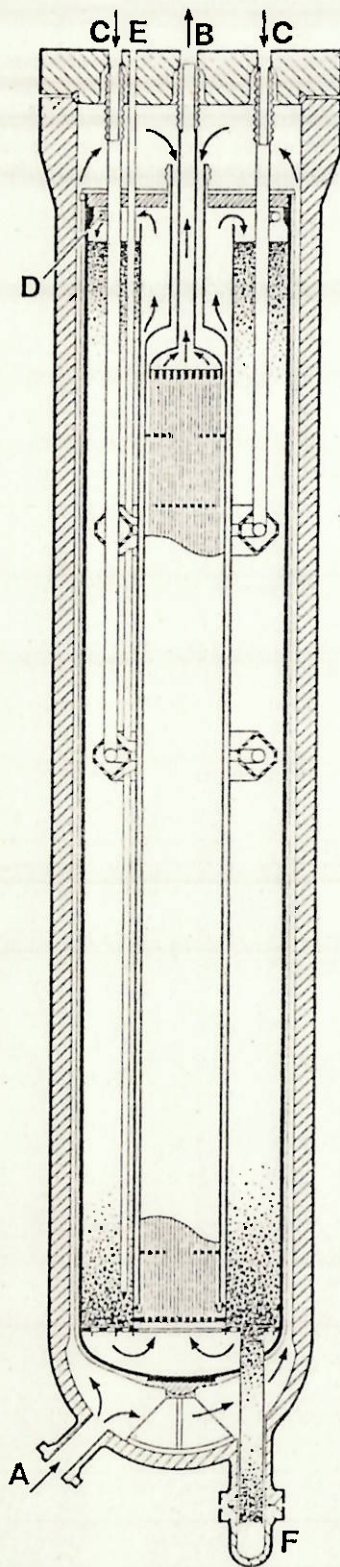
where, also

$$\frac{V}{L} = \pi R^2 \quad (I.5)$$

It is seen from (I.4) that at the large values of \dot{Q}/L typical of large ammonia converters, the internal volume tends towards the active volume and R tends towards r . That is, for large reactors, only a thin skin of insulation is required to reduce the conduction loss to a small fraction of the overall thermal capacity of the reactor. On the other hand, the exponential term in (I.4) becomes progressively more important as \dot{Q}/L is lowered, particularly for high values of thermal conductivity and low conduction losses. Given a chosen value of the loss factor α , the optimum choice for small reactor size would lie in the vicinity of the minimum on the characteristic curve defined by α , as seen in Figure 7. The exact choice would normally be constrained by the practical limits on the length to diameter ratio for the cylindrical active volume.

ICI Quench Converter for Large Ammonia Plants

Figure 1



- A Gas Inlet
- B Gas Outlet
- C Quench Gas Inlet
- D Direct by-pass gas distributor and/or start up heater gas inlet
- E Pyrometer
- F Catalyst discharge nozzle

INTRODUCTION

Since 1963 ICI has installed several new ammonia plants of increasing capacity on various sites in the United Kingdom and the world. As the size of ammonia plants increased it has been recognised that there is a need for a simple converter for use in large single-stream plants.

The key points in evolving a converter design are:—

- Economy in size
- Simplicity and efficiency of operation
- Easy loading and unloading of catalyst
- Simple and quick erection
- Easy internal inspection and maintenance
- Safe entrance for inspection and repair

The ICI Quench Converter was designed to fulfil the above conditions, and is suitable for a range of outputs from 600–1650 tons/day. The first converter of this design, with a capacity of 956 tons/day, has recently been successfully commissioned on one of ICI's existing ammonia plants at Billingham and has proved to be extremely successful in operation.

FEATURES OF THE CONVERTER

The converter is shown diagrammatically in *Figure 1*. The catalyst is contained in a single annular bed surrounding the central heat exchanger. Quench gas is introduced at intermediate points down the catalyst bed by means of the specially designed gas distributors. A detailed description of this and other features of the converter is given below.

QUENCH GAS DISTRIBUTION

The outstanding feature of the converter is the continuous bed of catalyst which allows simple charging and discharging of the catalyst and also permits efficient use of converter volume by eliminating the usual space-wasting voids which are otherwise necessary to achieve quench gas introduction and mixing.

These advantages are made possible by the use of the gas distributor—often referred to as a lozenge—which is carefully designed to introduce quench gas with maximum efficiency of mixing whilst at the same time occupying the minimum volume within the cartridge space. The converter, of which the distributor is a feature, is the subject of U.K. Patent 1105614 and U.S. Patent Application 448191. It is also patented in a number of other countries.

The elimination of inter-bed support grids and voids has meant that capital cost savings can be quoted over most conventional converters in the range of 650–1650 tons/day.

The lozenge distributor shown diagrammatically in *Figure 2* consists of a central perforated pipe through which the quench gas is introduced. This is surrounded by a diamond-shaped frame covered with wire mesh or perforated plate fine enough to prevent catalyst particles passing through into the interior. The shape of the lozenge is such that the catalyst

completely surrounds its outer surface without leaving any voids. The gap between each side of the lozenge and the catalyst bed retaining walls is sufficient to allow free flow of the catalyst during charging and discharging.

As the resistance to flow of the path through the lozenge is considerably smaller than the alternative path through the surrounding catalyst, most of the gas (about 95%) passes into the distributor and mixes with the quench gas. The mixed gas then passes into catalyst below the lozenge where an even temperature front is re-established.

CARTRIDGE SHELL

The cartridge shell is insulated on its outer surface. It is located in the pressure vessel by means of a spherical seat, thus simplifying the problems of centralising the cartridge during construction.

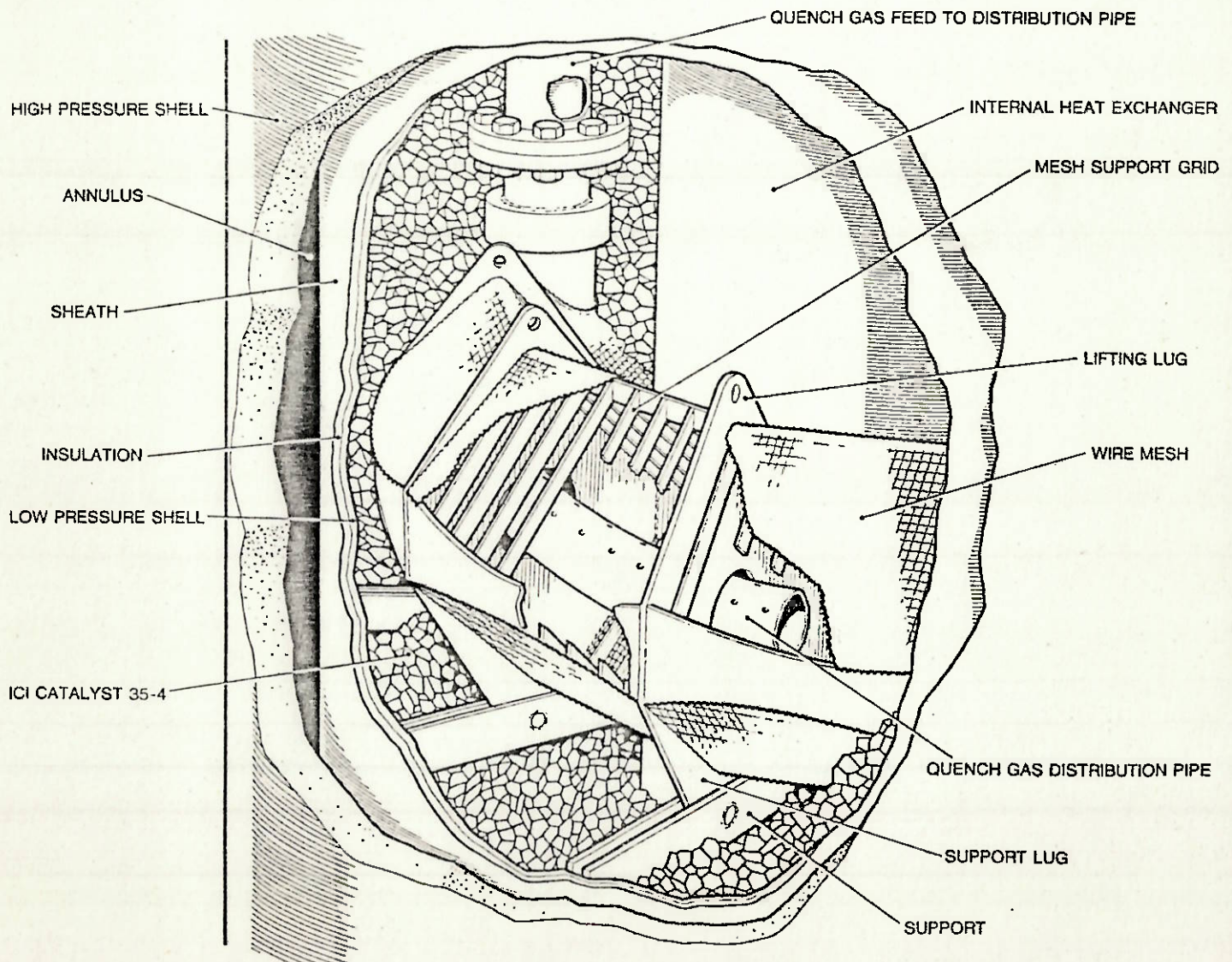
HEAT EXCHANGER

As the heat exchanger is a completely separate unit from the cartridge shell, the two parts are transported separately and the exchanger is simply lowered into the converter after installation of the cartridge. No joint or seal is required between the exchanger and cartridge shell. The exchanger can therefore be easily removed for maintenance.

CATALYST DISCHARGE NOZZLES

The catalyst is discharged from the converter through the nozzles at the base of the vessel, the catalyst in the upper beds flowing round the lozenge distributors. Only a small quantity of catalyst is left in the bottom of the converter, and as this is unlikely to be poisoned it need not be removed unless entry to the vessel is required for other reasons.

Figure 2



PRESSURE VESSEL

The pressure vessel and its closure are not designed by ICI, but may be obtained from any experienced fabricator, in this field. ICI can, however, offer a suitable high pressure joint design.

The cartridge is designed for use in a pressure vessel with a full bore closure. Whilst not an essential feature of a quench converter design it has been used by ICI for a number of important reasons:—

- (1) The cartridge may be withdrawn easily to allow inspection of the complete inner surface of the pressure vessel. At the same time any necessary maintenance to the cartridge insulation may be carried out.
- (2) All parts of the cartridge are easily removable for maintenance. It is well known that the stainless steels used in the construction of all ammonia converter cartridges are subject to nitriding attack and parts must therefore be replaced periodically. The use of a full bore closure means that the work can be carried out quickly with the minimum loss of production time.
- (3) Any work involving entry to the converter can be carried out with greater safety. A man inside the converter has better ventilation, better light and a better escape route than in vessels which have to be entered via a manhole or series of manways.

The design is limited to the maximum diameter for which it is believed a successful full bore pressure vessel closure can be made. This varies with pressure and at the moment is limited to an internal diameter of 100 inches for vessels operating at about 4,500 psig. The recently commissioned ICI Quench Converter at Billingham operates at less than 2,100 psig and internal diameter of the pressure vessel is 131 inches. This large closure has not given rise to any difficulties. The limiting diameter for operation at 3,000–3,500 psig is about 110–115 inches.

HIGH GRADE HEAT RECOVERY

Heat may, of course, be recovered from the converter effluent gas, the temperature of which is about 500°F. Should recovery of higher grade heat be required, an alternative converter design is available, in which part of the effluent gas is taken from the converter immediately after leaving the catalyst bed. Heat recovery can be of the order of 1.5×10^6 Btu per ton of ammonia. The remaining gas passes through the internal heat exchanger as usual. A converter of this type is necessarily larger and more expensive, mainly because the mean temperature difference in the internal heat exchanger is reduced.

The high temperature gas taken from the bottom of the converter is usually used to preheat boiler feed water. The effluent is then further used to preheat the converter feed and quench gas.

CONVERTER SIZE

The size of an ammonia converter depends on the process conditions as well as on the size of the plant. There is not therefore a simple relationship between the size of the converter and the output of the plant it can serve. Typical figures from recent designs are however, given in *Table 1*. *Table 2* gives details of typical 1300 short tons/day ICI Quench Converters and illustrates variation in size with pressure.

SERVICE TO CUSTOMERS

If required ICI will provide the contractor with assistance in the erection of the cartridge and in the reduction of the catalyst within it. If the customers wish, ICI can provide advice, free of charge, on the optimum temperature profile and quench gas rates at any time during the life of an ICI catalyst charge, using the customer's own data.

TABLE 1
Typical figures from
recent ICI Quench Converter designs

Output	(short tons/day)	660	990	1100	1650
Pressure	(psig)	4700	3200	4250	3220
Inlet gas:	Ammonia %	4.0	3.0	3.2	1.4
	Inerts (CH ₄ +A) %	15.0	12.0	15.0	12.0
Converter inlet rate	(mm scfh)	10.6	18.0	18.5	24.5
Catalyst volume	(ft ³)	740	1170	1100	2400
Pressure vessel					
Internal diameter	(inches)	80	96	95	109
Length	(inches)	437	493	472	700
Weights (short tons):					
Cartridge shell		14.2	34.2	22.8	56.4
Heat exchanger		15.5	30.0	25.4	23.8
Pressure vessel		130	128	182	240
	(excluding cover)				

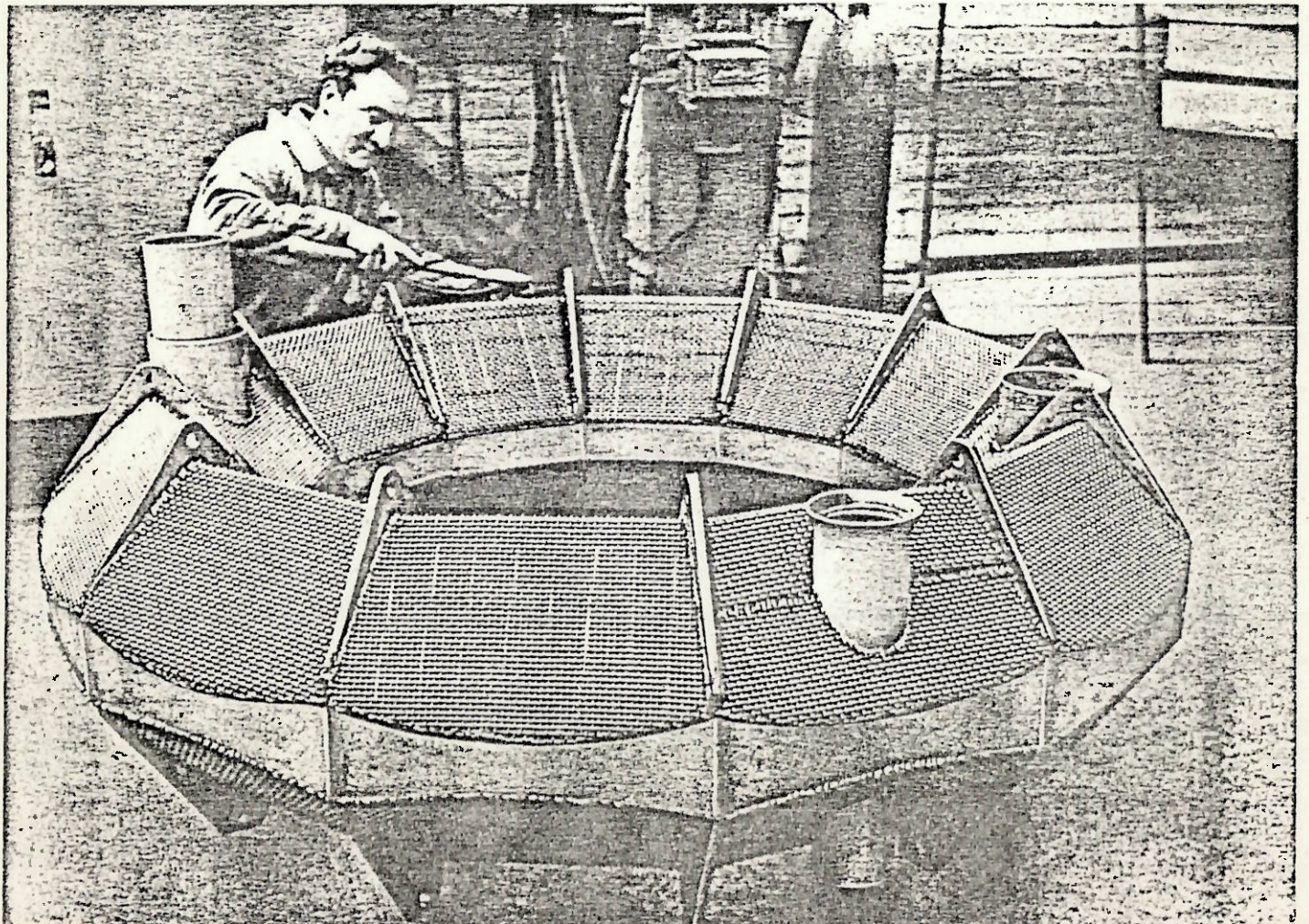
TABLE 2
Typical figures for ICI Quench
Converters of 1300 short tons per day capacity

Pressure	(psig)	2200	3200	4000	4700
Inlet gas:	Ammonia %	2	2	2	2
	Inerts (CH ₄ +A) %	12	12	12	12
Converter inlet rate	(mm scfh)	25.8	21.2	19.8	19.0
Catalyst volume	(ft ³)	2600	1730	1320	1030
Pressure vessel					
Internal diameter	(inches)	120	102	96	89
Length	(inches)	663	606	528	488
Weights (short tons):					
Cartridge shell		68.5	40.8	29.2	23.6
Heat exchanger		37.1	25.4	20.7	17.9
Pressure vessel		186	184	187	189
	(excluding cover)				
Converter pressure drop	(psi)	140	104	87	91

Advantages of ICI Quench Converter

- Efficient mixing of quench gas gives an even temperature profile across the catalyst bed
- Elimination of voids between catalyst beds gives maximum utilisation of converter volume
- Economically competitive converter designs based on advanced computer program and up-to-date research on reaction kinetics
- Lozenge distributors permit rapid loading and unloading of the continuous bed of catalyst
- Full bore closure gives good access for inspection and maintenance
- Separate cartridge components reduce weights to be lifted and simplify installation and maintenance
- Recovery of high grade heat possible
- Design backed by ICI's forty years' experience in ammonia manufacture and converter design and fabrication

Lozenge distributor under construction in ICI Agricultural Division's workshops



MECHANICAL CONSIDERATIONS

An ammonia converter cartridge is complex and operating conditions are severe. Design temperatures of different parts range from 120°F to 950°F and it is subject to heavy loads from the deep bed of abrasive catalyst.

To achieve reliable operation under these circumstances, it is desirable that a converter design should be as simple as possible, incorporating well tried and proven features. The ICI Quench Converter satisfies this requirement.

Various factors must be considered in the design, including thermal expansion. Overall expansion is allowed for by installing expansion bellows on the connections to the cartridge. Uneven gas distribution, particularly at start-up and shut-down, can bring about different mean wall temperatures on two opposite sides of the cartridge. In severe cases this may cause bending of the cartridge. The gas distribution in the ICI Quench Converter has been demonstrated to be very good and the design also allows for changing or emergency conditions in which bending of the cartridge might occur.

Uneven gas distribution can also mean that optimum use of the catalyst cannot be achieved, and therefore particular care has been taken to ensure that the distribution of cold gas in the lozenge distributor is good. Aspects that have been considered include the proportion of gas actually passing through the lozenge, the effect of heat transfer to the cold gas pipe, and the position and size of the holes in the pipe. Experimental work and computer calculations on the behaviour and performance of the distributor have been carried out as required to produce the present efficient design.

Experimental work has also been carried out to assist in the prediction of the heavy loads exerted by the catalyst on the various retaining walls of the cartridge.

Bellows are used for all gas connections to the cartridge. These are more effective in preventing leakage of cold gas into the cartridge than the alternative method involving the use of packed glands. Leakage results in a reduction in catalyst temperature and in extreme cases causes loss of converter autothermicity. If cold gas enters one side preferentially, cartridge bending as described above could result. It is therefore important that reliable gas connections are used.

ASSEMBLY CONSIDERATIONS

As the cartridge, heat exchanger, and pressure vessel cover are all about the same weight, and the cartridge need never be lifted whilst full of catalyst, the lifting gear required during construction is minimal. With an efficient construction team, and all necessary equipment available, it has been shown to be possible to install the cartridge and heat exchanger in the vessel, load the catalyst and complete the closure of the vessel in under 200 hours.

OPERATING EXPERIENCE

An ICI Quench Converter has been installed to replace a converter on an existing ammonia plant at Billingham, and was successfully commissioned in February 1969. The principal features of this converter are as follows:—

Pressure vessel internal diameter	131 inches
Cartridge length	480 inches
Design output	956 tons/day
Operating pressure	2080 psig

The converter cartridge was fabricated in ICI Agricultural Division's workshops at Billingham, where over sixty ammonia converter cartridges have been manufactured in the past forty years.

Following the start up, which took only four days, the converter produced ammonia consistently at 106% of flowsheet rate at 1950 psig, the limitation being the availability of synthesis gas. Shortly after start up, the converter was capable of an output of at least 1050 tons/day.

Distribution of gas within the converter has proved to be very efficient. Thermocouples placed at opposite points on a diameter within the converter have shown that the horizontal variation in temperature is only 2–4°C.

The converter contains approximately 190 tons of ICI Catalyst 35-4 which was not pre-reduced. Experience with this catalyst has shown that its activity is not impaired by rapid reduction, and it was accordingly reduced rapidly with a fixed limit to the water content in the gas leaving the converter of 10,000 ppm. The water concentration in the effluent gas actually reached a peak of 9000 ppm and subsequent determinations of catalyst performance showed that the activity was normal for newly reduced catalyst.

Two further ICI Quench Converters have been constructed. One, with a capacity of 825 tons/day is awaiting commissioning, and the second, of 695 tons/day capacity, will be commissioned during 1970.

*Further information may
be obtained from*



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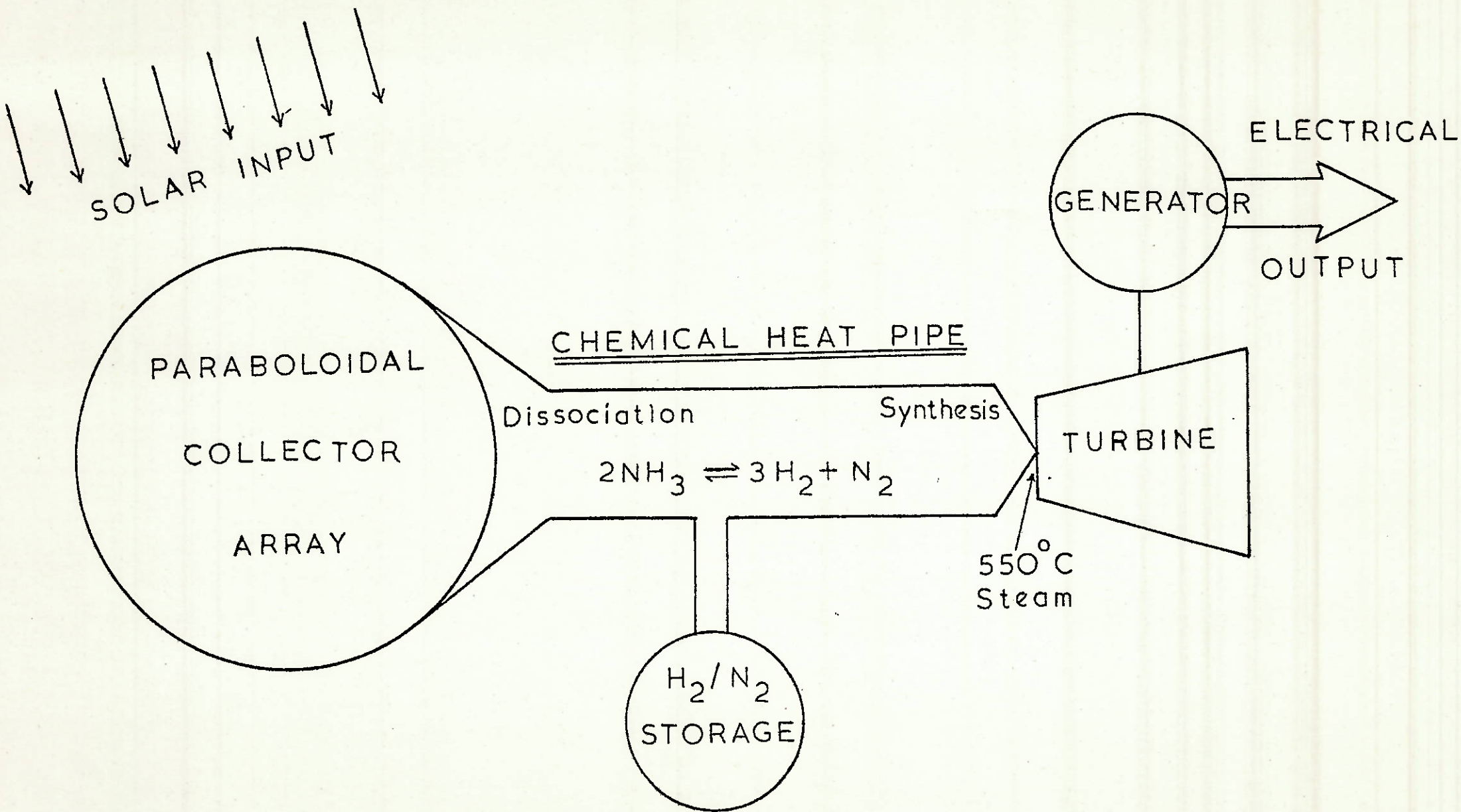


FIGURE 1: Chemical heat pipe application for 1-10 MWe electricity generation

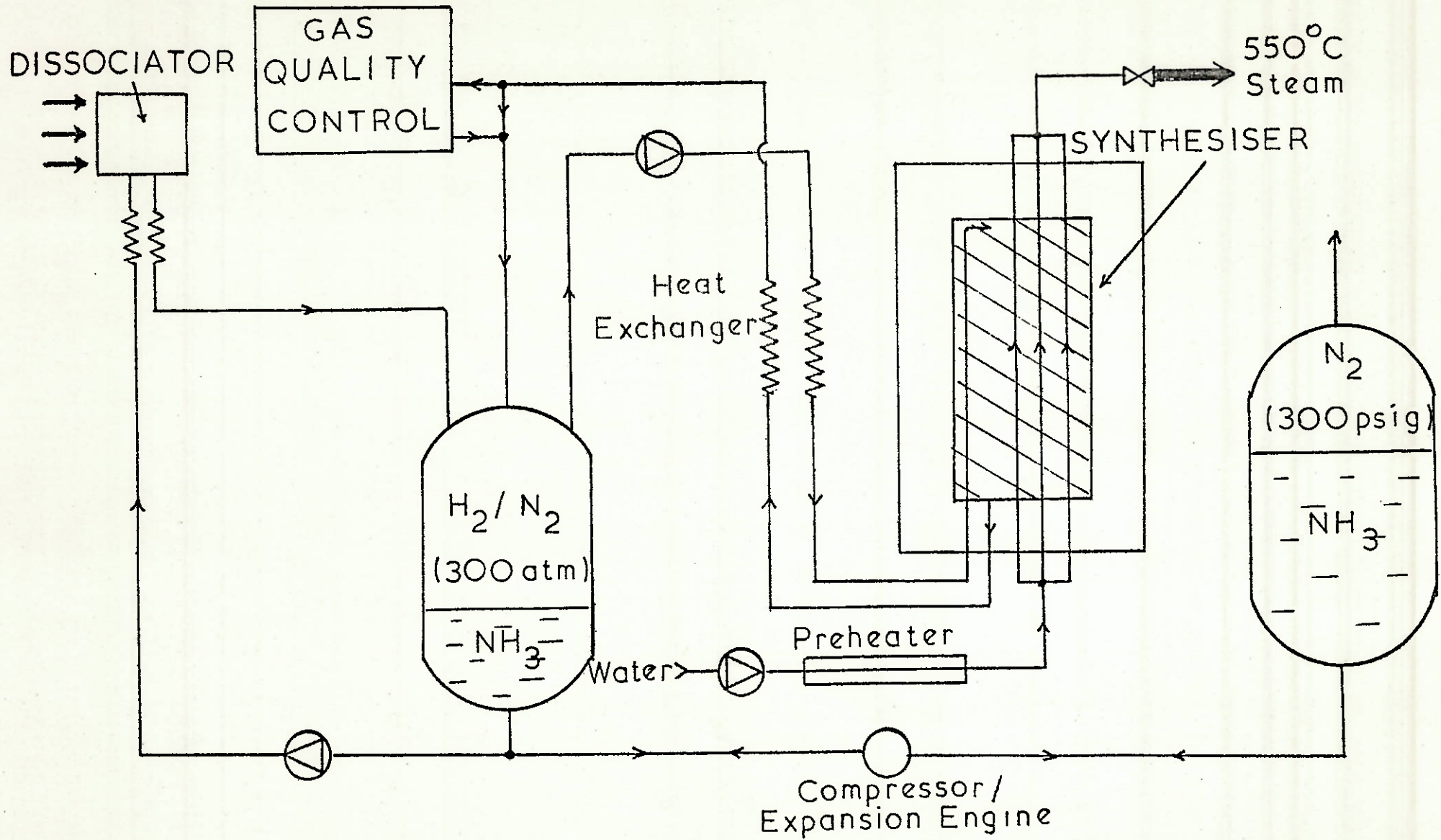


FIGURE 2: Schematic diagram of the proposed demonstration plant for the ammonia-based chemical heat pipe

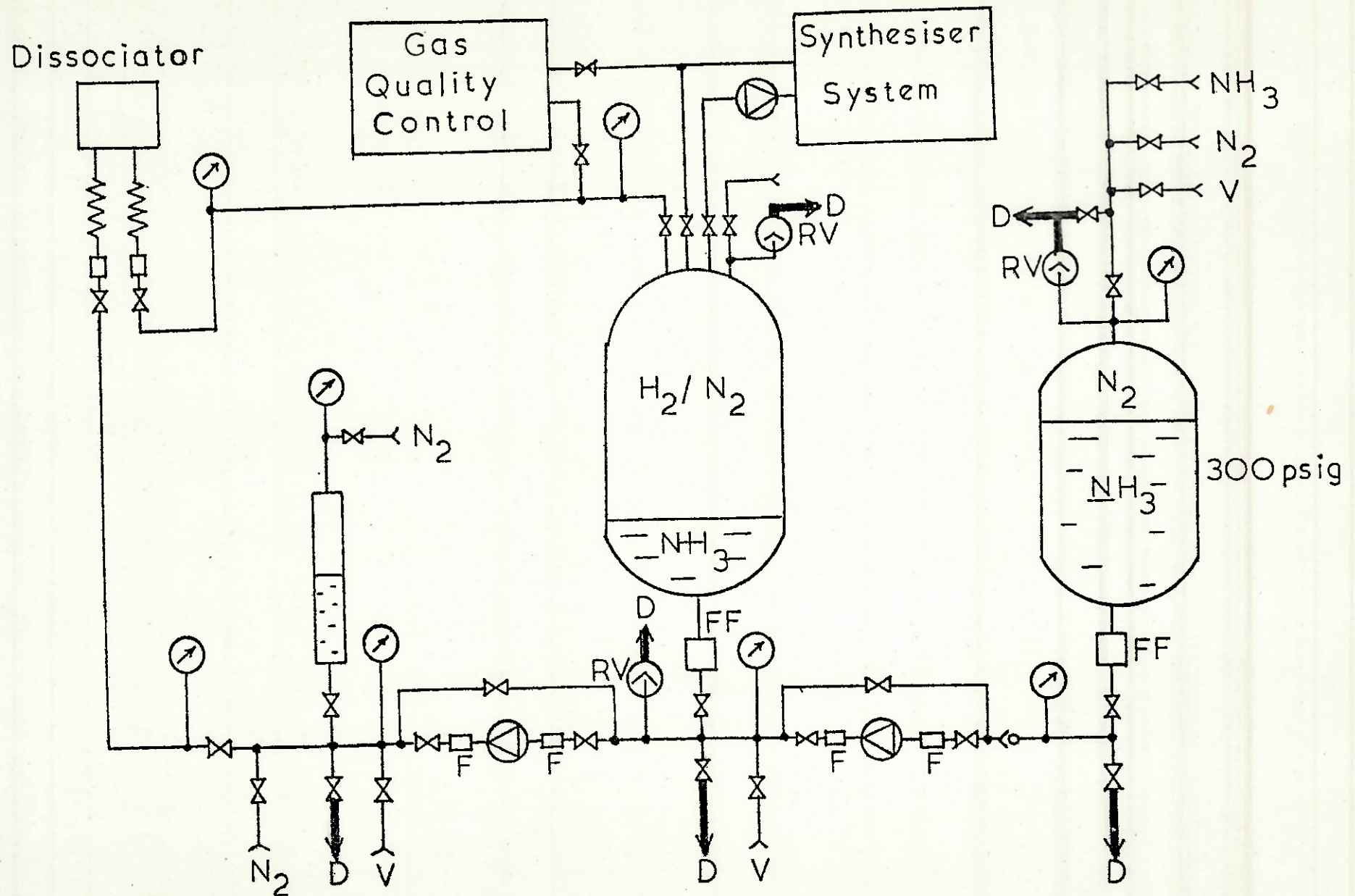


FIGURE 3: System design for the chemical heat pipe
 D = Drain, V = Vacuum, RV = Relief Valve, F = Filter, FF = Fast Flow Valve

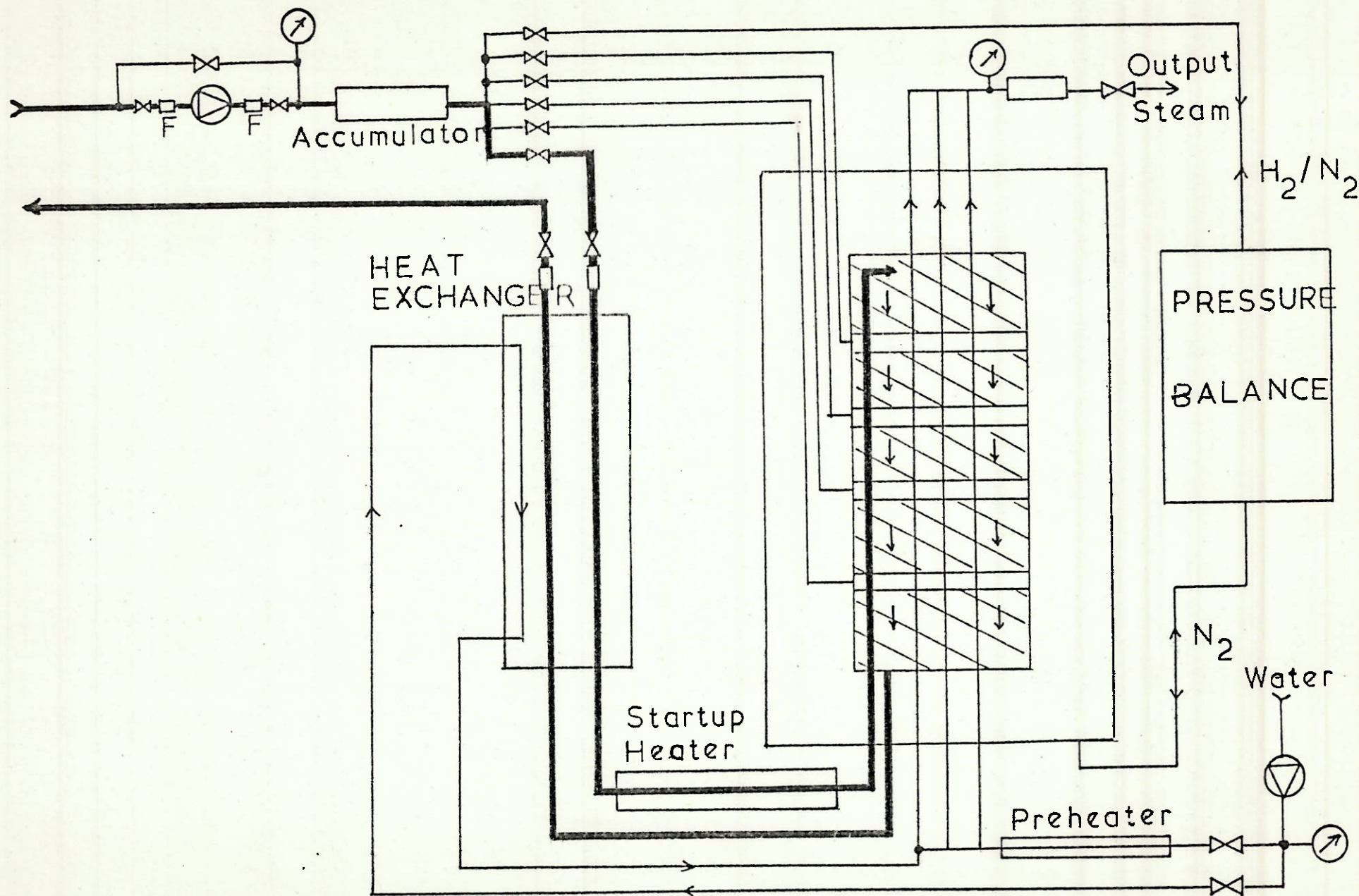


FIGURE 4: Synthesiser system design with quench gas option

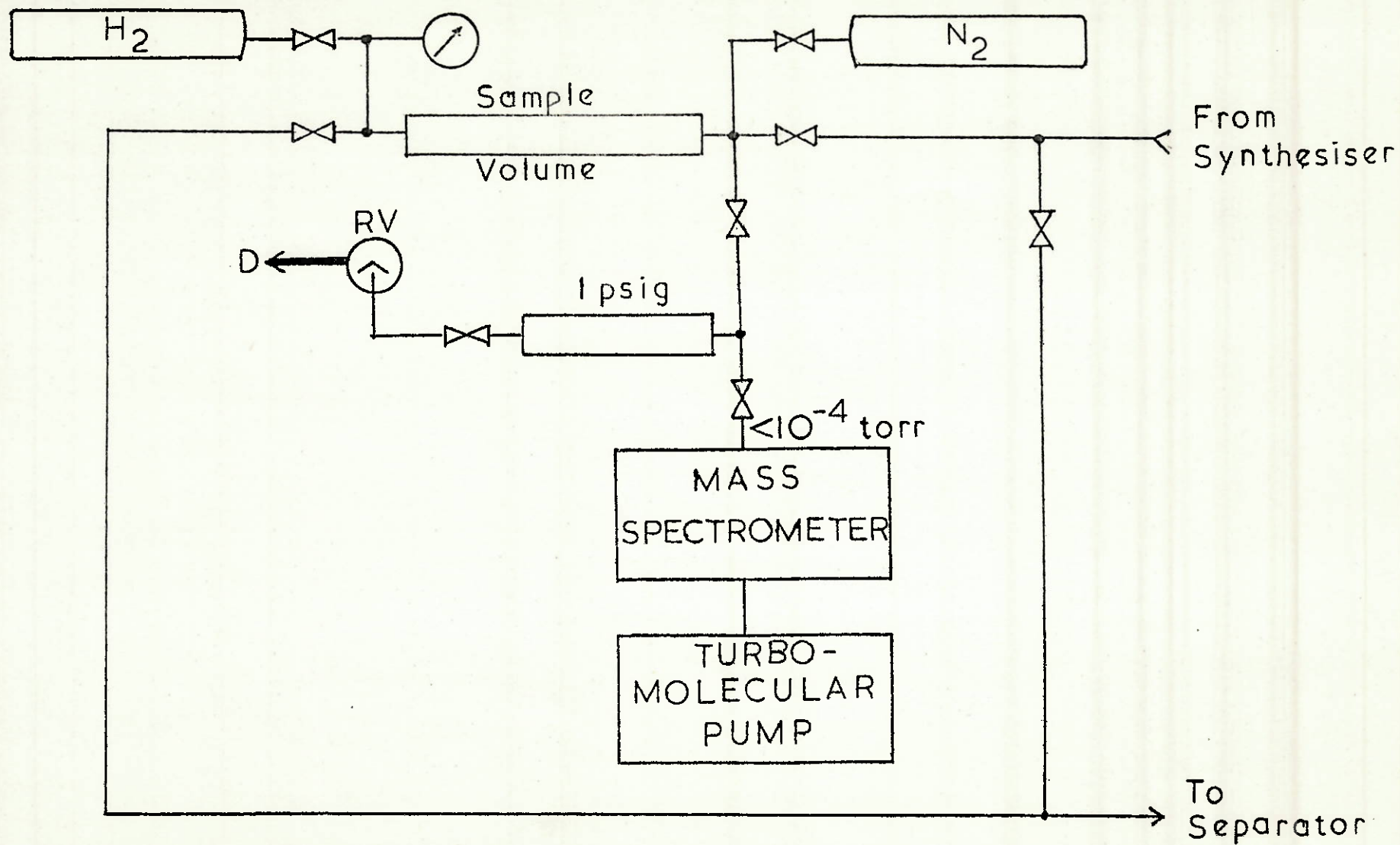
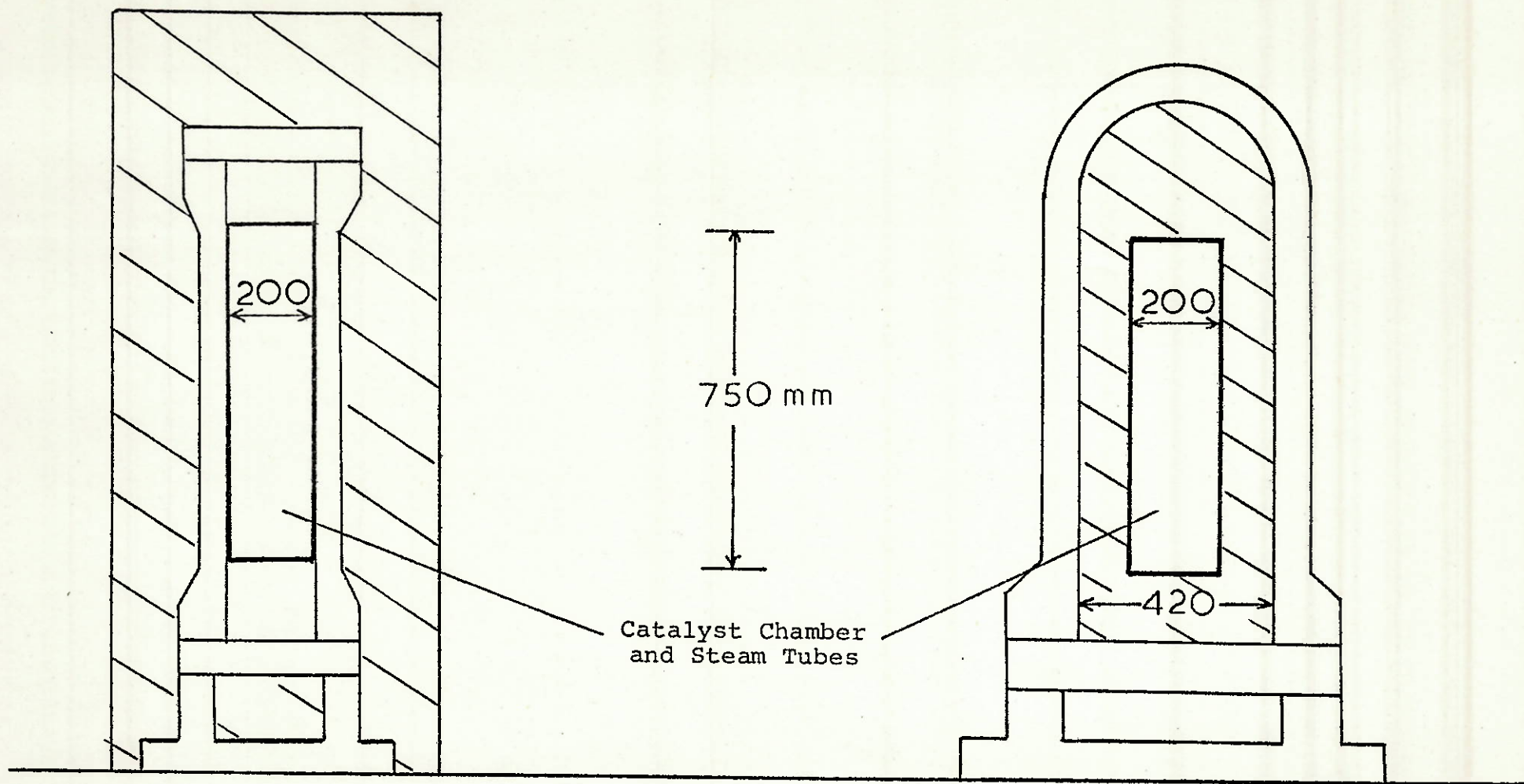


FIGURE 5: Gas quality control system



(a) Hot-wall option
Incoloy 800 or equivalent

(b) Cold-wall option
Low alloy steel

FIGURE 6: Synthesiser pressure vessel options

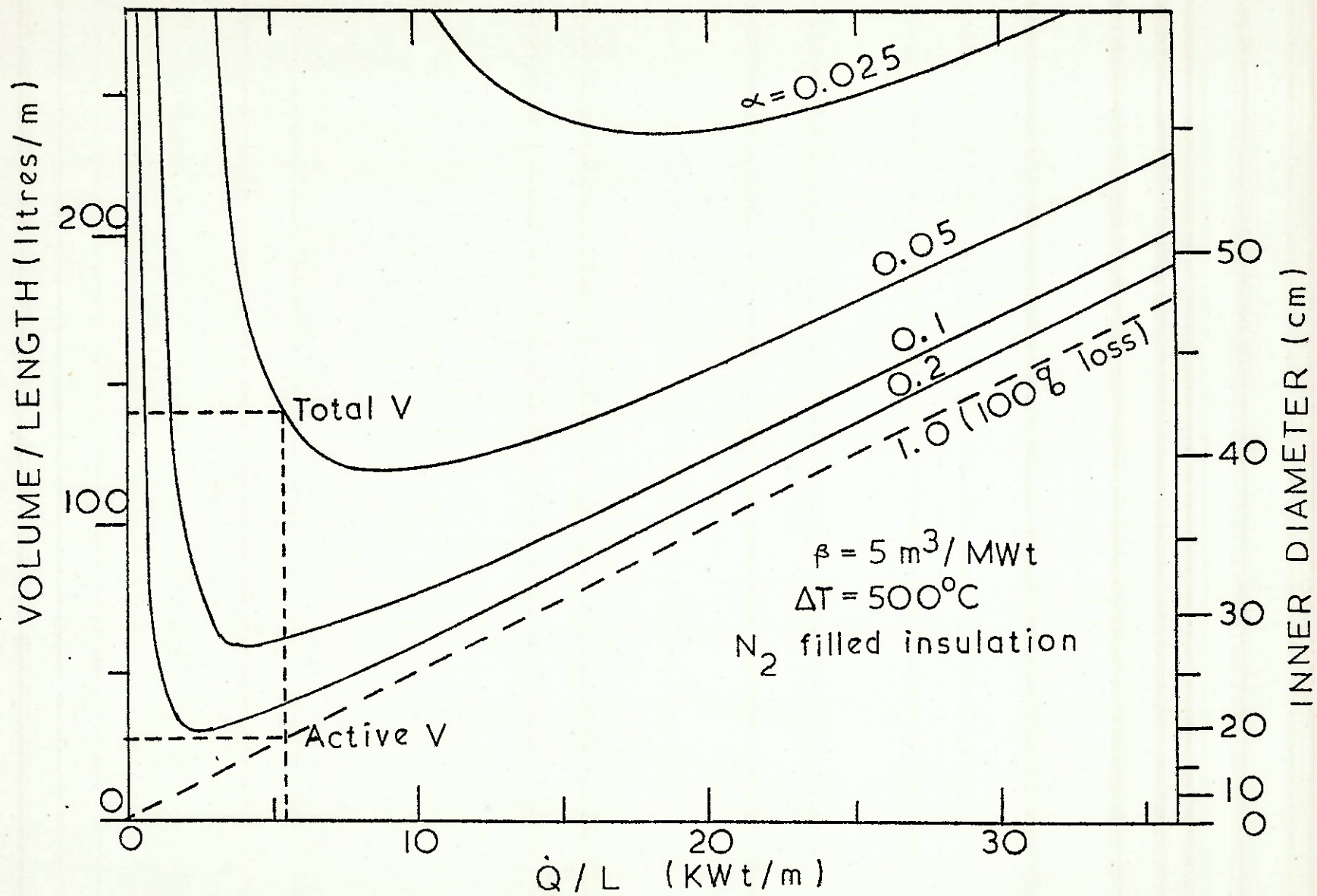


FIGURE 7: Relationship between synthesiser internal volume and thermal capacity for given conduction loss

