

Hydrogen from Ammonia Plant Purge Gas

Review of recent developments in the field show the economic attractions of cryogenic processing due to dependability and flexibility.

A.A. Haslam and W.H. Isalski
Petrocarbon Developments Ltd.
Manchester, England

In the present energy situation, ammonia purge gas can provide a source of hydrogen that is unlikely to be rivalled in economic terms by any hydrogen manufacturing process. This is because cryogenic hydrogen recovery processes can be basically very simple, and flexible, and because of their simplicity extremely reliable.

It has been recognized for many years that ammonia plant purge gas represents one of the most valuable industrial purge gas sources from which hydrogen may be extracted. Its particular advantages are that it is relatively free from complex impurities which would be potentially troublesome in a cryogenic plant and it has been traditionally available in predictable quantities over long periods. Its value as fuel is somewhat low because of the presence of nitrogen, argon, and the low calorific value hydrogen, though it is available at high pressures, which is always a good starting point for any cryogenic process.

In the recent past, when ammonia plants were by present standards comparatively small, the only justification for hydrogen recovery was a requirement for hydrogen in some industry near the ammonia plant, rather than for recovery of hydrogen for recycle to the ammonia plant itself.

The economic forces of increasing plant size and rocketing raw material costs are rapidly bringing about a change in the traditional situation so that it may soon become standard practice to recycle recovered hydrogen from ammonia purge gas in order to minimize feedstock requirements. It is therefore prudent for ammonia producers and others concerned with this industry to consider the implications of hydrogen recovery.

Traditional recovery technique is cryogenic

In the following, the basis shall be considered to be a fairly typical 1,000 ton/day ammonia plant in which purge gas having the following characteristics is available:

Composition: hydrogen, 60.0 mol.%; nitrogen, 20.0 mol.%; argon, 3.5 mol.%; and methane, 16.5 mol.%. Ammonia content will be 50 ppm. at greater than 1,515 lb./sq.in.abs. The gas will be water-saturated, the assumption being that a water wash will have been carried out at a high pressure to recover the bulk of ammonia present initially. The purge gas will be flowing at 2.8 to 3.6 x 10⁵ stand.cu.ft./hr.

The basic process traditionally used for hydrogen recovery is cryogenic, and because of this the ammonia and water impurities are removed in a pre-treatment system to

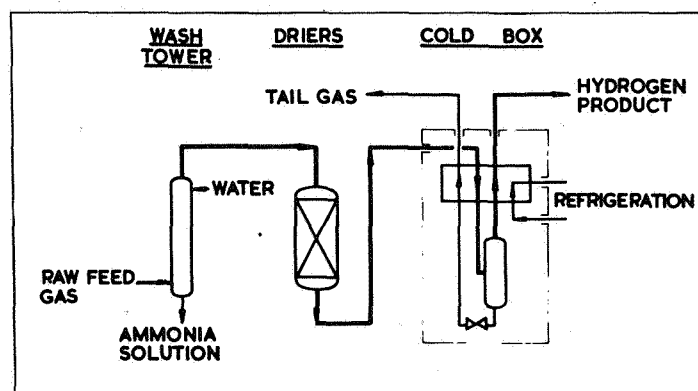


Figure 1. Simplified flow scheme of ammonia purge gas purification plant.

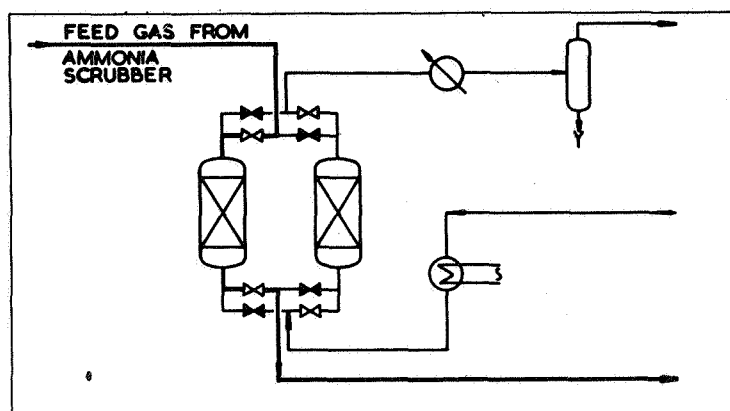


Figure 2. Schematic of adsorber system for water and ammonia removal.

avoid solidification problems within the cryogenic section of the plant. The simplified flow scheme shown in Figure 1, on which all these hydrogen recovery processes are based, consists of a pre-treatment section followed by a cryogenic process in which the purge gas is cooled and partially condensed in counter-current heat exchange with product and tail gas streams. Because of the volatility difference between hydrogen and other components, methane followed by argon and nitrogen are preferentially condensed leaving a vapor phase enriched in hydrogen. After reheating to approximately ambient temperature in heat exchange against cooling feed gas, the hydrogen is available as product suitable for recycle into the synthesis loop, or for other purposes.

A refrigeration input is necessary to achieve the low temperatures needed to condense nitrogen and other components.

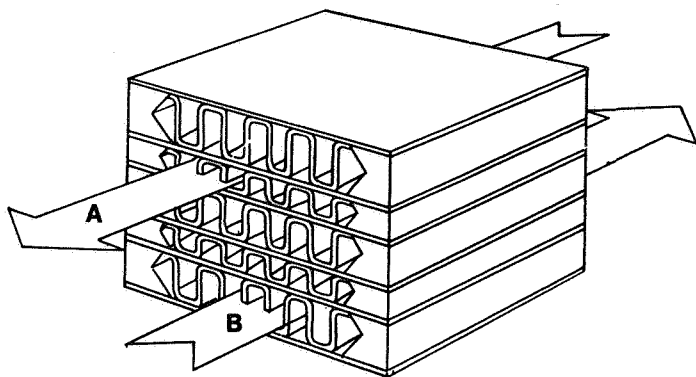


Figure 3. Contra-flow arrangement for multiple stream exchanger.

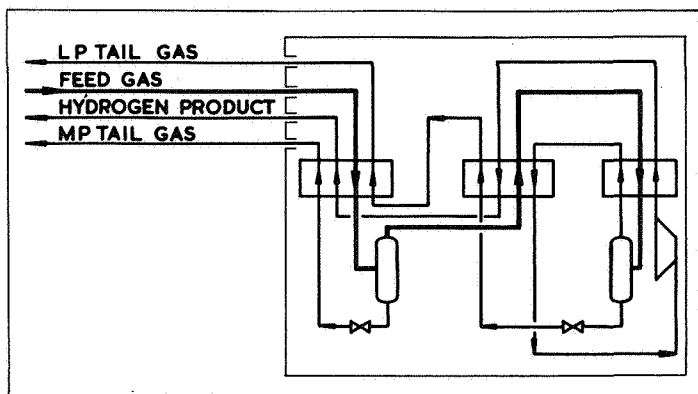


Figure 4. Simplified flow scheme for the hydrogen recovery coldbox at ICI at Billingham.

Pre-treatment is normally carried out in adsorbers, shown in Figure 2, in which ammonia and water are reduced to less than 1 ppm. each. Two adsorbers are typically used, operating automatically on a fixed-time cycle so that one adsorber is being regenerated while the other is in service. At the end of the regeneration period the adsorbers are automatically switched over so that the regenerated bed comes into contact with untreated gas and the spent bed is purged with hot regeneration gas. Regeneration is normally carried out by passing tail gas (from the cold box) first through a heater and then through the bed requiring regeneration.

The cold box consists of a vertical, steel-clad structure in which the cryogenic processing equipment is located. Equipment within the cold box is generally of aluminum and consists of a series of dip-brazed aluminum plate fin heat exchangers, illustrated in Figure 3, a series of vapor/liquid separators, and an expansion turbine. The space surrounding the process equipment within the cold box is filled with a highly efficient powdered insulating material (perlite).

In the early 1960's, a process was developed embodying the above principles. It is briefly described, and shown in Figure 4. Having first scrubbed most of residual ammonia from it, the ammonia purge gas was then passed from the water wash tower through an adsorption unit to remove water and traces of ammonia. Adsorption was carried out at approximately 1,000 lb./sq.in.abs. The pressure was then reduced to about 615 lb./sq.in.abs., and the dry, ammonia-free purge gas passed into a cold box. The gas was cooled in

counter-current heat exchange with revert tail gas and product streams and a phase separation carried out at approximately -30°F . At this point the vapor phase contained about 92% hydrogen, the remainder being nitrogen, argon, and traces of methane. The vapor was then further cooled in two subsequent heat-exchange stages designed to virtually eliminate the argon and methane at the final phase separation temperature of -341°F . Elimination of the higher concentrations of these components at a higher temperature was necessary to avoid potential solidification at the low temperature end of the process.

The resulting vapor phase from the final separation step provided a hydrogen stream of the required product purity, that is to say, in excess of 98 vol.-%. After expansion through a high-speed, refrigeration-producing turbine and various stages of heating within the cold box, the hydrogen product was delivered to battery limits at approximately ambient temperature. Condensed materials separated within the cold box were evaporated and re-heated against the feed stream in order to recover as much refrigeration as possible.

It is interesting to examine some of the more important parameters in this process, bearing in mind the basic objective: to produce a high purity hydrogen stream by a relatively simple cryogenic route.

Three factors involved in the pressure

The pressure of the basic separation process was established by consideration of three primary factors:

1. *Phase equilibria.* If a simple cryogenic process were to be used (that is, not one involving distillation, absorption or adsorption operations) then optimum separation for maximizing hydrogen purity will be governed by the phase equilibrium relationship for hydrogen and nitrogen. It is clear from Figure 5 that for maximum hydrogen enrichment from phase equilibria considerations the optimum pressure for the process is approximately 590 lb./sq.in.abs.

2. *Mechanical limitations.* If high-efficiency, aluminum plate fin heat exchangers are used (this is now virtually standard practice for multi-stream cryogenic process involving two-phase heat transfer), the process must operate at a pressure for which this type of equipment is suitable. At the time this process was developed, the maximum safe operating pressure for standard units was approximately 615 lb./sq.in.abs. (it is currently approximately 800 lb./sq.in.abs.).

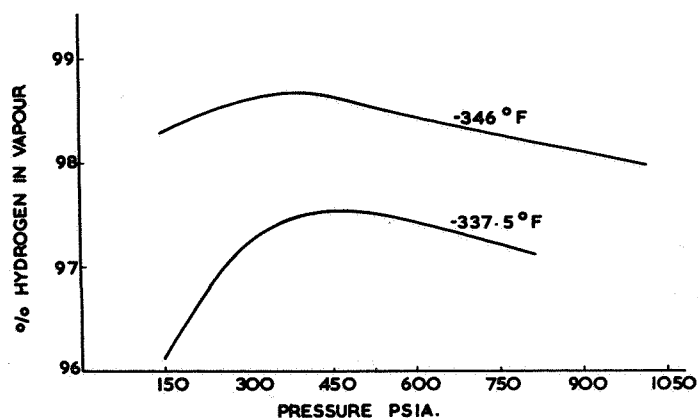


Figure 5. Isotherms graph of percentage hydrogen in nitrogen at various pressures from Redlich-Kwong data.

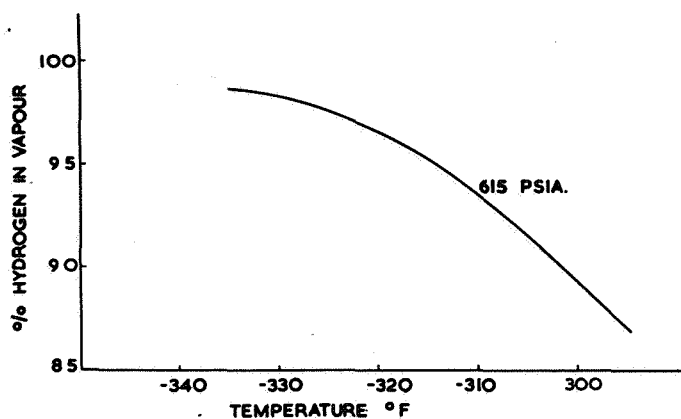


Figure 6. Graph of percentage hydrogen in nitrogen at 615 lb./sq.in.abs. and various temperatures from Redlich-Kwong data.

3. *Feed gas refrigeration potential.* This term refers to the potential refrigeration energy which may be made available by expansion of the gas from high to low pressure. By this definition, it is clear that the feed gas pressure at cold box entry should be as high as possible within the constraints imposed by the other primary parameters. It is thus evident that for the process described above, approximately 615 lb./sq.in.abs. is the optimum operating pressure.

A second important parameter is the final phase separation temperature. The selection of this temperature is made by consideration of hydrogen, nitrogen phase equilibria including careful attention to the proximity of the solid phase.

At the selected pressure of 615 lb./sq.in.abs., it was decided that the final phase separation temperature should be -341°F . This gives the best degree of hydrogen enrichment (product quality) without the danger of solid nitrogen forming in the condensate piping or the turbine exhaust, as seen in Figure 6.

A plant of this type and embodying the above described principles was built, has been in operation for several years at the Imperial Chemical Industries Agricultural Division site at Billingham, England. The design process parameters outlined above were achieved, and as a result the plant continues to run successfully producing hydrogen at a purity in excess of 98%.

Cold box needs safety considerations

Apart from the usual safety considerations associated with a plant processing or producing hydrogen and methane, it is apparent that the cold box requires rather special consideration. It is clearly undesirable in any cold box operation where flammable gases are being processed to allow a situation in which an undetected leak could occur in the insulation-filled interspace thus allowing a hydrogen/hydrocarbon/air explosive mixture to form. Therefore, cold boxes processing flammable materials are normally purged with an inert gas, such as nitrogen.

In this case, however, it is clear that there would be some difficulty in purging with nitrogen at atmospheric pressure, as shown in Figure 7. The vapor pressure of nitrogen is such that condensation occurs at atmospheric pressure at approximately -320°F . Therefore, the nitrogen

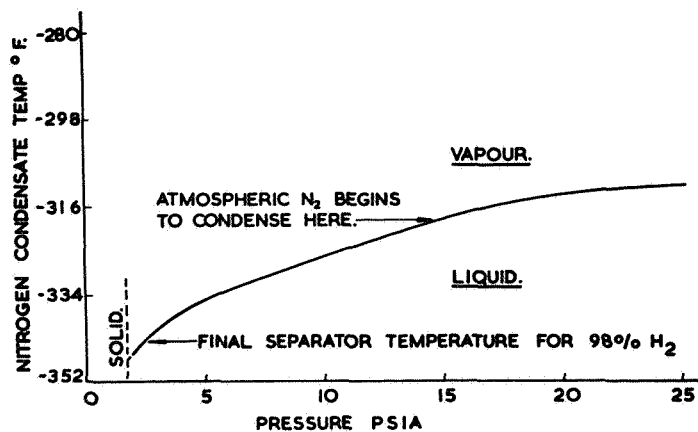


Figure 7. Nitrogen vapor pressure curve.

purge would liquefy on some of the lower temperature equipment within the cold box. This problem can be overcome by operating the purge system at a suitable vacuum and thus condensation may be avoided. However, with a system of this type the cold box structure must be a relatively expensive cylindrical pressure "vessel" suitable for vacuum operation. It should also be noted that the use of vacuum introduces a secondary potential hazard, namely that of drawing air into the cold box. To minimize this secondary risk, the cylindrical cold box structure is required to be all-welded construction, built to the usual stringent codes associated with pressure vessels.

In addition, the vacuum pump suction should be continuously monitored for oxygen, hydrogen, and methane.

An alternative method of preventing oxygen penetration into the cold box without introducing secondary risks is to deliberately purge the cold box with a small bleed from the hydrogen product stream. In this situation, the concept of the pressure vessel for the cold box structure is no longer necessary; therefore, significant economies can be made. The cold box structure is, of course, protected with relief devices which vent into the flare header, and leaks can be detected by monitoring the purge flow at inlet and exit. The very much higher thermal conductivity of hydrogen relative to nitrogen does not in practice significantly increase the heat-in-leak to the cold box, perhaps indicating that the controlling transfer in the interspace is convective rather than conductive.

Both methods of operation have proved satisfactory in service, and several plants are in operation utilizing these purging systems.

An alternative arrangement has also been considered which superficially appears attractive. The basic concept is the increase of external temperatures of those process items where nitrogen condensation could occur. This could be achieved by locally insulating those sections of plant below liquid nitrogen temperatures with vapor-sealed polyurethane foam, the effect being shown in Figure 8. In practice, because of the somewhat complex geometry of the plate fin exchangers, piping, etc., and because of the high coefficient of expansion of aluminum, an effective vapor seal could not be obtained in practice. Consequently it proved impossible to prevent nitrogen condensation on the cold surface.

It has been argued that nitrogen condensation in the

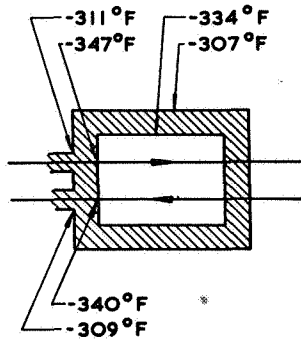


Figure 8. Part of the lowest temperature region, showing the temperature profiles through insulation.

interspace is not in itself detrimental to cold box operation, the argument being that although condensation may occur in small localized areas the liquid formed is re-evaporated as it drains into the warmer sections of the box and consequently the total purge requirements are not increased. While this undoubtedly occurs, the additional refrigeration load imposed on the cold box heat balance is such that the overall process conditions cannot be maintained and indeed plant start-up with this arrangement proves to be impossible.

Production of the low temperature

A consideration of the overall heat balance for cold box operation shows that supplementary refrigeration is always necessary. The refrigeration input is needed to balance the effects of heat-in-leak and also refrigeration losses brought about by the inevitable "warm end" temperature difference between the incoming and outgoing streams.

The optimum temperature level at which refrigeration should be applied depends mainly upon capacity flexibility factors. If, for example, a very high degree of capacity flexibility is required, then a "cold end" refrigerated cycle is usually required. On the other hand, if only moderate flexibility requirements are needed, then supplementary refrigeration may be applied at a relatively high temperature level.

In the "cold end" refrigerated cycle, shown in Figure 9, the only economic means of producing refrigeration is to pass the hydrogen product stream through a turbo-expander. This, of course, involves a fairly significant pressure drop on the hydrogen product stream. Consequently

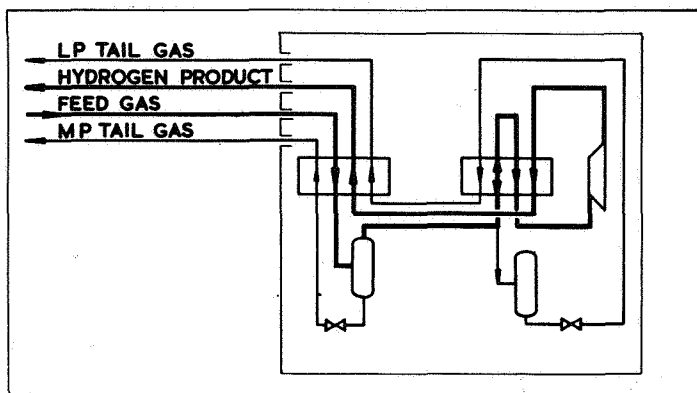


Figure 9. Typical cold box flow scheme for ammonia purge gas purification with a cold-end refrigeration turbine.

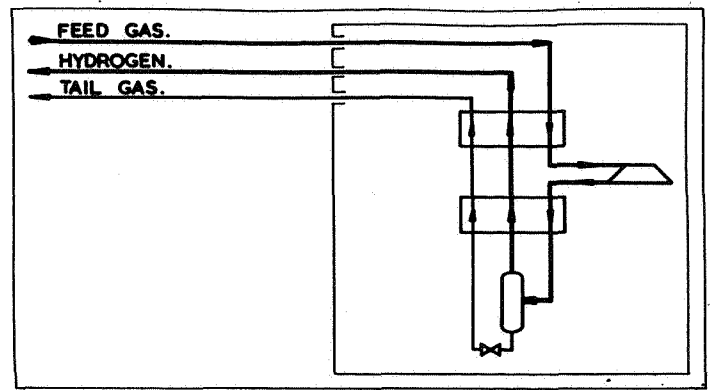


Figure 10. Interstage or intermediate refrigeration supplied by a feed gas expansion turbine.

with this type of cycle it is not normally possible to produce hydrogen product at a pressure of more than 200 lb./sq.in.abs. The turn-down characteristics are, however, extremely good; and on a large plant, operation can be maintained quite effectively at only 25% of design throughput.

The turbo-expander must be selected carefully, not only because it needs to maintain a high efficiency at widely varying loads but also because the gas passing through the machine is always close to its dewpoint; and at the exit close to the solidification of nitrogen the machine must be capable of coping with some liquid and even solid nitrogen formation.

In the interstage refrigeration cycle, refrigeration is applied at some intermediate point in the feed gas cooling process. To achieve a reasonable degree of flexibility, refrigeration at a temperature level of about -226°F is necessary and is normally applied in one of two ways.

Firstly, if a relatively high pressure drop can be tolerated, a feed gas expansion turbine can be employed, as seen in Figure 10. This would normally be a single stage machine similar to the type used in the "cold end" cycle. Alternatively, a separate refrigeration cycle may be employed, as shown in Figure 11, in which nitrogen at low pressure is compressed in a single-stage standard air compressor, cooled in heat exchange with returning low-pressure nitrogen, and expanded in a turbine to produce cold and the necessary temperature level. The cold low-pressure nitrogen is then heated to approximately ambient temperature in the process and in nitrogen/nitrogen heat exchangers and returned to the compressor suction.

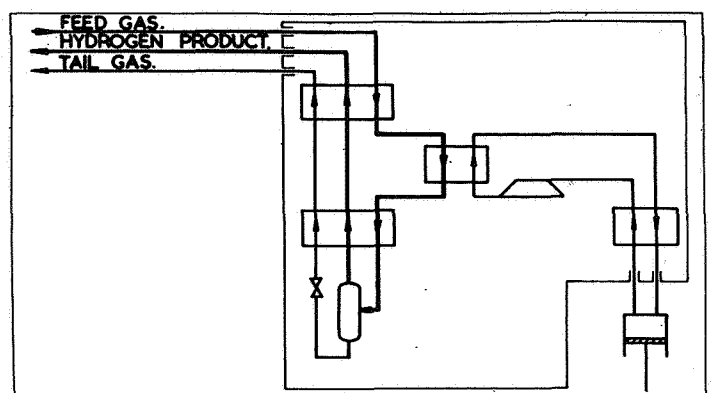


Figure 11. Intermediate refrigeration using a closed nitrogen compression/expansion cycle.

The main advantage of this arrangement is that the pressure drop across the plant is very small and the refrigeration input is relatively independent of process stream conditions. It should be noted, however, at low feed gas throughputs the cycle will become inoperative because of refrigeration inadequacies in the colder sections of the plant.

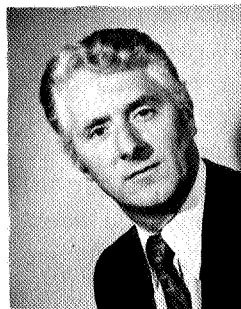
The foregoing discussion has been concerned largely with the recovery of a relatively high-purity hydrogen stream. For ammonia plant recycle purposes, however, providing the argon and methane concentration can be reduced to a reasonable level—say not more than 1% (volume of methane + argon), then a product stream containing significant quantities of nitrogen is not only acceptable but desirable. To maintain the basic concepts of simplicity and economy, it is preferable to maintain the cooling, condensing, and phase separation principles without resorting to relatively costly and complicated low-temperature distillation arrangements.

The required objective can be most effectively achieved with an interstage refrigerated cycle of the type described above, utilizing a feed gas expansion turbine.

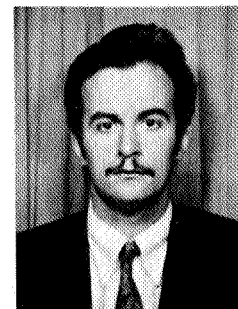
For the specific duty of hydrogen recovery for ammonia plant recycle, a major process simplification can be made, because the degree of hydrogen enrichment required is not so great, hence the very low temperatures needed for pro-

ducing 98% hydrogen are not required. In consequence therefore, further heat transfer and vapor/liquid stages normally needed to avoid solidification of argon and methane are no longer necessary. The cold box process is then reduced to a simple single-stage separation operation, seen in Figures 10 or 11.

In a typical 1,000 ton/day unit, approximately 95% of the hydrogen available in the purge gas would be recovered and returned to the synthesis gas compressor at a convenient pressure, typically about 415 lb./sq.in.abs. The product stream composition would be approximately as follows: hydrogen, 92 vol.-%; nitrogen, 7%; argon plus methane, 1% max. #



HASLAM, A.A.



ISALSKI, W.H.