OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

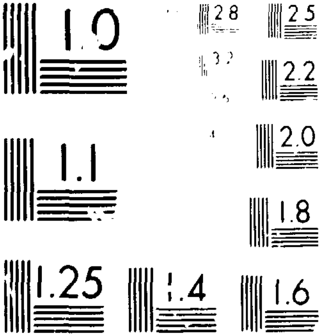
Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org


1.0
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

11043

Distr.
LIMITED

ID/WG.364/2
21 January 1982

ENGLISH

United Nations Industrial Development Organization

Technical Conference on Ammonia Fertilizer
Technology for Promotion of Economic Co-operation
among Developing Countries

Beijing, People's Republic of China, 13 - 28 March 1982

HYDROGEN RECOVERY FROM AMMONIA PURGE GAS
THE PETROCARBON EXPERIENCE *

by

W.H. Isalski**

---

* The views expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

** Section Manager for Hydrogen Recovery Plants, Petrocarbon Developments Limited, Petrocarbon House, Sharston Road, Manchester M22 4TB, United Kingdom.

Paper presented at the meeting by Mr. D. Watson, Director, Sales and Business Development, Petrocarbon Development Limited, Petrocarbon House, Sharston Road, Manchester M22 4TB, United Kingdom.

V.82-20830

Summary

This paper outlines the technology offered by Petrocarbon Developments Limited for hydrogen recovery from ammonia synthesis purge gas. The paper describes the process aspects and considers the economics of installing and operating a typical unit. The effect on the ammonia plant is considered and the extensive operating experience is used to discuss the plant flexibility.

INTRODUCTION

The ever-increasing cost of hydrocarbon feedstock coupled with an increase in demand for ammonia has created a situation where ammonia producers must continue to increase the efficiency of their operation (and where possible, maximise output of ammonia).

The majority of larger capacity single train ammonia producing units adopt the classical hydrocarbon reforming synthesis gas production technique to provide feedstock for the synthesis of ammonia. In such cases it is necessary to purge a significant volume of gas from the ammonia synthesis loop in order to prevent build-up of Argon and Methane.

Petrocarbon has, for many years, been aware of the potential value of this purge gas and has to date designed, constructed and successfully commissioned twelve plants to recover hydrogen from it. Initially six of these plants were specifically designed to recover high purity hydrogen for sale to petrochemical companies on nearby sites. However, current economics, in general, favour recycle of hydrogen to the synthesis loop.

With this in mind, Petrocarbon has designed, constructed and successfully commissioned a further six hydrogen recovery units for the USA and Canada, specifically designed to produce a lower purity hydrogen product for recycle to the ammonia synthesis loop. The product also contains a significant quantity of nitrogen, but at the same time the inerts (Argon and Methane) are kept to a minimum, making the gas suitable for recycle. Petrocarbon has currently been awarded a further three orders for similar units in the USA and Indonesia which are currently in the construction phase.

The current plants are designed to produce a 90% hydrogen rich recycle gas stream which contains less than 1.4% argon + methane. This hydrogen-rich product is delivered to battery limits at 7 .4 kg/cm^{2}g. The Plant also produces a fuel gas product which is delivered to battery limits at a pressure that matches the requirements on the ammonia plant.

Ammonia is recovered from the feed gas and delivered as saturated anhydrous liquid product at about 26 kg/cm^{2}g.

PROCESS DESCRIPTION

The process, shown in figure (1), is very simple and may be conveniently described in two sections:

- Pretreatment Section
  where any ammonia present in the feed gas is removed by water washing and molecular sieve adsorption. The ammonia may be recovered as anhydrous liquid product.

- Low Temperature Section
  where the hydrogen-rich purge gas is separated into a recycle hydrogen stream and a fuel gas product.

Pretreatment Section

Feed gas enters the Plant through a control valve at the desired process pressure, passes through the feed gas preheater and is admitted to the base of an ammonia absorption column. Ammonia is removed from the gas by absorption in a lean aqueous ammonia (or water) solution.

A rich aqueous ammonia solution is withdrawn from the base of the absorber, pre-heated and passed into an ammonia regeneration column. Rich solution can be delivered as product if required. The ammonia product is drawn off to battery limits from the regeneration column overheads via a condenser. Reboil is provided by using medium pressure steam. Hot lean solution is drawn off the base of the regeneration column, cooled, pumped to high pressure and returned to the absorber. Feed gas leaving the absorber, substantially free from ammonia, is then passed into adsorbers, where residual ammonia together with water from the absorption operation are removed on molecular sieves. Two adsorbers are employed operating on a fixed time sequence control such that one unit is on-line whilst the other undergoes regeneration.

Low Temperature Section

The dry, ammonia-free purge gas from the adsorbers enters the cold box where the gas is cooled in a cold box exchanger against revert hydrogen product and fuel gas streams together with a small quantity of supplementary refrigeration. A vapour/liquid phase separation in a feed gas separator is carried out to produce a hydrogen-rich vapour phase and a liquid phase containing some nitrogen, a large proportion of argon and methane, and a small proportion of dissolved hydrogen.

A small quantity of hydrogen product stream is injected into the fuel gas liquid to provide sufficient re-evaporation of liquids to cool the feed gas to the required temperature, while still maintaining the required pressure of the fuel gas. This hydrogen injection scheme is a patented feature of Petrocarbon plants.

The hydrogen product stream is warmed to approximately ambient temperature in heat exchange with the incoming feed gas and delivered to battery limits. The liquid phase from the separator is expanded to fuel gas pressure along with the injected hydrogen and also evaporated and re-heated to approximately ambient temperature.

Fuel gas leaving the cold box heat exchanger is split, a sidestream being used for adsorber regeneration and the remainder by-passed and mixed with the spent regeneration gas. The combined fuel gas product stream is then delivared to battery limits at the required pressure.

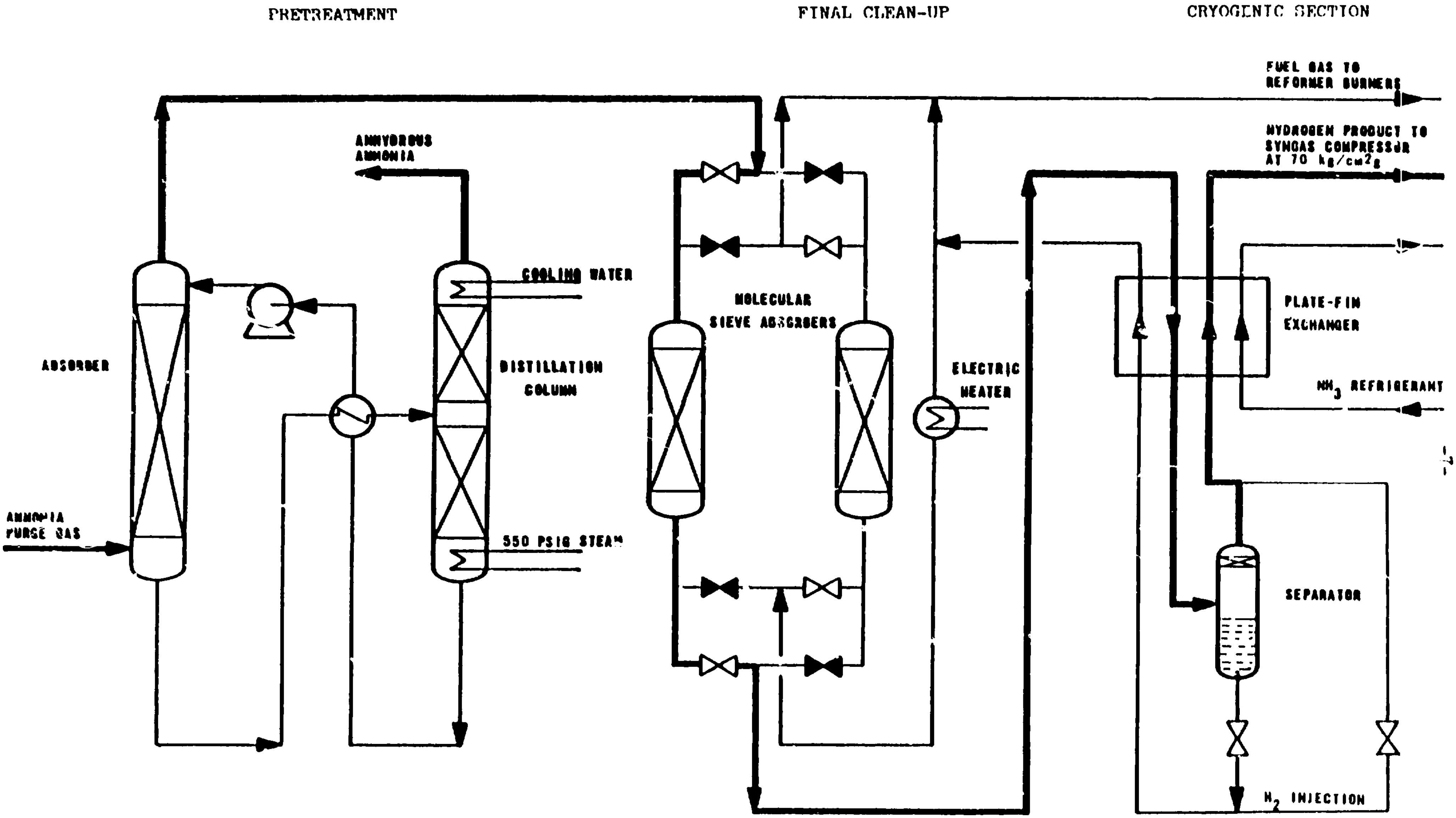


FIG. 1 SIMPLIFIED FLOW DIAGRAM OF PETROCARBON HYDROGEN RECOVERY UNIT.

FEED GAS COMPOSITION AND PLANT FLEXIBILITY

The majority of large capacity single or multiple train ammonia units adopt the classical steam reforming route for converting naphtha or natural gas into synthesis gas. A typical composition of synthesis gas is shown in Table A. It should be noted that thoughout the shift conversion catalyst life, the whole of the argon + methane level range is covered because of the decreasing catalyst activity. The composition of the purge gas from the synthesis loop, also shown in Table A, varies over the range because of operator adjustment of the purge flowrate and the changing catalyst activity in the shift conversion, methanation and synthesis stages. Therefore the hydrogen recovery plant must be capable of operating over the whole range of the given compositions whilst maintaining the overall recovery of hydrogen. One of the primary considerations in the Petrocarbon process design is in fact flexibility.

TABLE A

RAW SYNTHESIS GAS AND LOOP PURGE GAS COMPOSITIONS

Component	Feed Gas to Synthesis Loop	Loop Purge Gas	
	Range Mole %	Normal Mole %	Range Mole %
Hydrogen	73-76	63	60-65
Nitrogen	23-25	21	19-22
Argon)	0.8-1.5	4.5	3-5
Methane)		8.5	7-10
Ammonia	NIL	3.0	1.5-3.0
Temperature	38°C	-23°C to 15°C	
Pressure	Approx. 28 kg/cm^{2}g	approx. 140 kg/cm^{2}g	

PERFORMANCE OF THE PETROCARBON PROCESS

The basic process, Figure 1, is designed to produce a 90% hydrogen-rich recycle gas stream which contains less than 1.4% argon + methane. This hydrogen-rich product is delivered to battery limits at 70 kg/cm^{2}g for recycle into the synthesis loop. The Plant also produces a fuel gas product which is delivered to battery limits at the required pressure. (Ammonia may be recovered from the feed gas and delivered as saturated anhydrous liquid product at about 26 kg/cm^{2}g). Table B shows the composition of the hydrogen-rich product and the fuel gas produced from this plant. While the product hydrogen composition remains the same, the fuel gas composition varies according to the pressure at which the fuel gas can be returned to the battery limits. However, the fuel gas composition usually falls in the range given in Table B.

TABLE B
HYDROGEN RECOVERY PLANT PRODUCTS

	Composition Mole %	
Component	Hydrogen Rich Product	Fuel Gas
Hydrogen	90	10-15
Nitrogen	8.5-9.0	40-50
Argon	0.7-0.9	9-14
Methane	0.3-0.6	25-33
Temperature	approx. 15°C	approx. 15°C
Pressure	70 kg/cm^{2}g	See Table(C)

The amount of hydrogen recovered depends on the pressure at which the fuel gas must be returned to battery limits because of the varying amounts of hydrogen product injection requirements. As a guide, Table C shows the recoveries that can be expected for various fuel gas pressures. The recoveries are based on the normal composition of the feed gas and hence if the fuel gas pressure is known, the approximate fuel gas composition can be calculated.

TABLE C

DEPENDENCE OF HYDROGEN RECOVERY ON FUEL GAS PRESSURE

Overall Cold Box Hydrogen Recovery, %	Fuel Gas Pressure, kg/cm^2g
95	1.5
93	3
91	4

In addition to hydrogen, 97.5% of the ammonia present in the feed gas can be recovered as 99.5% pure product by stripping the rich solution from the wash operation. This section requires additional cooling water and 40 kg/cm^2g. steam.

PLANT CAPACITIES AND UTILITIES

Petrocarbon currently offers a range of cryogenic hydrogen recovery plants suitable for most of the existing ammonia plant facilities in the world.

These hydrogen recovery plants are suitable for purge gases on single and multiple train ammonia facilities, where a single train capacity is currently 1000 MTPD. Table D gives the capacity and utility data for two plant sizes assuming a normal feed gas composition. These data assume that recovery of anhydrous ammonia has been incorporated in the process.

TABLE D

Plant Designation	HP1000	HP2000
Ammonia Plant Capacity	1000	2x1000
Ammonia Purge Gas Flowrate (NCMH) (i.e. capacity of Hydrogen Recovery Plant)	9500	19000
Utilities		
Power Consumption (kWh/h - average)	55	95
Cooling Water (M^3/h @ 10°C rise)	38	75
Steam (kg/h @ 40 kg/cm^2g for NH_3 recovery)	630	1250
Molecular Sieve (kgs of 5A every 4 years)	1700	3300
Nitrogen, Dry, Oil-free (NCMH)	3-5	3-5
Instrument Air (NCMH)	50	50
Refrigerant (Kcals/h @ -33°C)	6300	8800
Capital Cost		
Budget price for complete unit delivered site		
(Price basis - US Dollars - Jan 1982)	$900,000	$1,200,000
Estimated erected cost of unit inclusive of connection of off-sites	$1,300,000	$1,700,000

ECONOMIC EVALUATION OF HYDROGEN RECOVERY UNIT

The potential returns on investment in a Petrocarbon hydrogen recovery plant vary to a large extent, depending on the mode of operation the ammonia plant operator has selected or is compelled to select because of physical constraints or bottlenecks. The investigations and decisions involved in selecting the mode of operation are beyond the scope of this paper. However, the varying modes of operation fall into three distinct options as outlined below. The figures given are based on a HP 1000 unit and should be used on a pro-rata basis to calculate data for the HP 2000 unit.

Case 1 - Fuel Saving

Maintaining the same ammonia production and recycling the hydrogen product to the synthesis loop saves feedstock plus fuel gas. Typical savings expected are as follows:

Plant Designation	HP 1000
Savings in natural gas feedstock and fuel (NCMH), after making allowances for the fuel value lost in the recycled H_2 product.	800
Extra ammonia (MTPD) from ammonia wash and stripping only.	4.5

In this case the reformer output of hydrogen is reduced by about 4-4.5%.

Case 2 - Increased Production Efficiency

Maintaining the same natural gas feedstock plus fuel to the reformers and recyling hydrogen to the synthesis loop can increase ammonia production as follows:

Plant Designation	HP 1000
Increase in synthesis loop ammonia production (MTPD)	14.5
Extra ammonia recovered from wash and stripping operation (MTPD)	4.5

The extra compression and refrigeration energy is required to make the extra 14.5 MTPD of ammonia in the synthesis loop. This energy is equivalent to about 0.6 MM Kcal/metric ton of ammonia.

In this case the reformer output of hydrogen is reduced by about 1.6-2%.

Case 3 - Maximisation of Production

Maintaining the same reformer output of hydrogen, provided that there are no limitations in equipment, the ammonia production can be increased to the following:

Plant Designation	HP 1000
Increase in synthesis loop ammonia production (MTPD)	54
Extra ammonia recovered from wash and stripping operation (MTPD)	4.5
Supplement of natural gas for fuel (NCMH)	1740

Extra compression and refrigeration energy is required to make the extra 54 MTPD of ammonia in the synthesis loop. This energy is equivalent to about 0.8 MM Kcal/metric ton of extra ammonia.

It is clear from the above cases that there are many profitable options for operating the hydrogen recovery unit. However, with the potential for increasing the ammonia production by up to 6% the profitability of a hydrogen recovery unit is very high indeed.

PLANT OPERATION EXPERIENCE

Although all of these plants are designed to produce hydrogen product of 90% purity with varying recovery, depending on fuel gas pressure as shown in Table C, the operators in general wish to maximise the hydrogen recovery. Therefore the hydrogen injection is usually turned to zero and the recovery increases to around 95%. If the fuel gas pressure is moderately high at about 4 kg/cm^2g, the hydrogen purity falls off to about 88% with a consequent rise in nitrogen content and a small rise in inerts level. The effect of the increased inerts is very minimal on the synthesis loop and is usually overcome by increasing the purge rate by about 6-10% over the normal purge rate. The hydrogen recovery units HP 1000 and HP 2000 both easily cope with this extra purge rate with no deterioration in purity or recovery. The big advantages of this mode of operation are:

1) highest hydrogen recovery
2) increased nitrogen recovery
3) No operator intervention required to maintain purity by varying injection rate.

When the plants operate in this mode they maintain very stable operation throughout the normal variations in purge gas composition and flowrate expected during day to day operation of the ammonia plant.

Table E below, shows the various operating modes that can be adopted with the same unit. These values are based on tests done on some of the hydrogen plants already in operation.

TABLE E

PLANT. OPERATIONAL FLEXIBILITY (Values are given in mole %)

Case	1	2	3	4	5
H_2 purity	90	89.2	87.5	86.9	83.6
H_2 recovery	92	94.4	94.6	94.7	95.2
Inerts Rejection	94	33.2	91.3	90.5	85.7
Increase in* Purge Rate	6	8	9	10	16.5
N_2 Recovery	25	29.7	34.7	36.5	46.2

* It is assumed here that the operator maintains the same inerts in the synthesis loop throughout. The percentages given are approximate.

The unit has the extra capability to handle the extra purge rates quoted above.

From some test data gathered from our operating plants the operators found some benefits in purging harder than normal to reduce the inerts in the synthesis loop. Typically 10-15% more purge was processed and this resulted in a fall of inerts by the same amount i.e. from say 13 down to 11.1% Argon + Methane. This saved power in the synthesis loop even though the hydrogen product was produced at only 70 kg/cm^2g.

Because the plants only have one machine, i.e. reflux pump with its automatic standby, there is virtually no maintenance work required. The plant on-stream times are in excess of 8000 hours between shut-downs. The shut-downs are usually scheduled for the overall ammonia plant shut-down. In fact, some of the cryogenic units have worked for 12 000 hours or more before shut-down. There has been no evidence of any deterioration in performance whatsoever in the hydrogen recovery units. Molecular sieve requires replacement every 4 - 5 years.

The gas savings and increases in production claimed in the above economic evaluation are borne out by data from four of the plants in operation today. No reliable data could be obtained from the others because of lack of good metering facilities on the ammonia plant.

nclusion

The installation of Petrocarbon hydrogen recovery units treating ammonia purge gas is an attractive proposition whether the ammonia plant operator is considering gas savings or boosted production. Petrocarbon HP 1000 and HP 2000 units have been shown to be economic and reliable in the field. The wide operating experience has shown the units to be more flexible than originally envisaged when yielding moderate recoveries of nitrogen with the hydrogen being recycled.

REFERENCES

HYDROGEN RECOVERY PLANTS - AMMONIA PLANT PURGE GAS DESIGNED AND INSTALLED BY PETROCARBON DEVELOPMENTS LIMITED

Client	Location	Plant Throughput MMSCFD	Plant Throughput Nm^3/h	Hydrogen Purity %
I.C.I. Agricultural	U.K.	33.6	37,500	98
Sumitomo Chemical	Japan	8.8	9,800	98
Lummus/Pemex	Mexico	8.3	9,200	99
Montecatini Edison	Sicily	9.7	10,900	99
Polimex	Poland	9.5	10,600	98
Polimex	Poland	18.5	26,000	98
Vistron	U.S.A.	11.3	12,600	91
American Cyanamid	U.S.A.	12.5	14,000	90
Agrico Chemical	U.S.A.	8.4	9,400	90
Agrico Chemical	U.S.A.	8.4	9,400	90
Agrico Chemical	U.S.A.	17.4	19,400	90
C.I.L.	Canada	14.2	15,900	90
P.T. Pusri	Indonesia	24.0	26,900	90
C.F. Industries	U.S.A.	18.2	20,400	87
C.F. Industries	U.S.A.	18.2	20,400	87