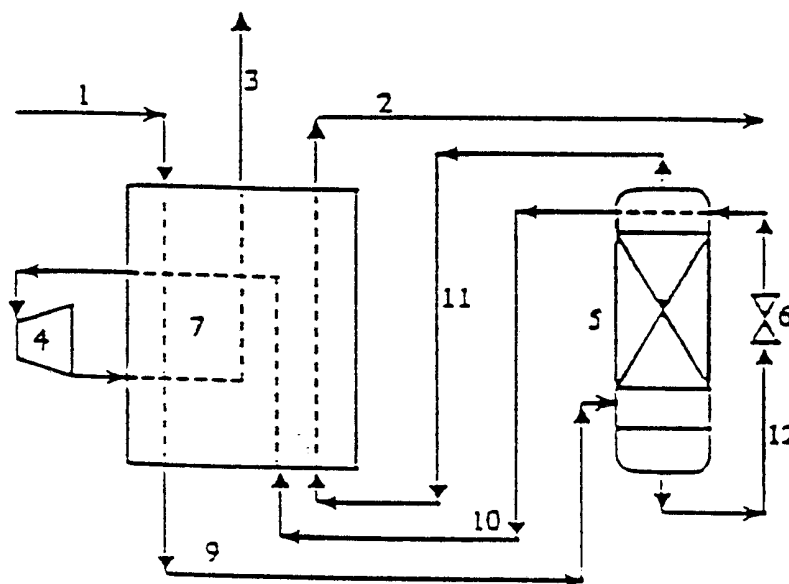




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(21) International Application Number: PCT/NO92/00015 (22) International Filing Date: 22 January 1992 (22.01.92) (30) Priority data: 910272 23 January 1991 (23.01.91) NO (71) Applicant (for all designated States except US): NORSK HYDRO A.S [NO/NO]; N-0240 Oslo 2 (NO). (72) Inventors; and (75) Inventors/Applicants (for US only) : EIMER, Dag, Arne [NO/NO]; Kvartsvn. 21, N-3900 Porsgrunn (NO). ØI, Lars, Erik [NO/NO]; Blåkløkkevn. 4B, N-3900 Porsgrunn (NO). (74) Agent: SUNDNES, Arne; Norsk Hydro a.s, N-0240 Oslo 2 (NO).		(81) Designated States: AT (European patent), AU, BE (European patent), BG, BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), RO, RU, SD, SE (European patent), US. Published <i>With international search report.</i>

(54) Title: METHOD FOR PURIFICATION OF SYNTHESIS GAS**(57) Abstract**

The present invention relates to a method of purification of ammonia synthesis gas subsequent to pre-purification. The pre-purified gas from a preceding unit is cooled from its process temperature to saturation temperature level and fed to a distillation column for separation of the gas into purified synthesis gas and vent gas containing the removed CH_4 , Ar and excess N_2 . The separation is performed at substantially the same pressure as in the preceding unit. The vent gas is heated to the final vent temperature with intermediate pressure release through a pressure relief valve and at least one expansion turbine. The purified synthesis gas is heat exchanged with the pre-purified synthesis gas. Most of the CH_4 content of the vent gas can be removed in a second distillation column prior to final pressure release. H_2 can be removed from the vent gas prior to CH_4 removal.

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Method for purification of synthesis gas

The present invention relates to final purification of ammonia synthesis gas, subsequent to removal of CO, CO₂ and H₂O and prior to the ammonia synthesis by applying a cryogenic unit for removal of CH₄, Ar and excess N₂.

In connection with ammonia production it is important to purify the synthesis gas and adjust the relative amounts of nitrogen and hydrogen before the gas is supplied to the ammonia synthesis. Removal of CO, CO₂ and H₂O can be performed relatively easily. A high degree of removal of CH₄, Ar and simultaneously removal of excess N₂ has been difficult to obtain economically. Especially for low pressure synthesis this latter purification is of great importance.

From US patent No. 3,442,613 it is known a hydrocarbon reforming process for production of synthesis gas, comprising a cryogenic unit for final purification of the synthesis gas. The final purification with regard to removal of undesired components is acceptable, but this is obtained at the cost of a high pressure drop and loss of energy from the gas.

The object of the present invention was to develop a final purification process producing an ammonia synthesis gas substantially free of CO, CH₄ and excess N₂ without significant pressure loss and being more energy efficient than known processes.

A further object was to recover CH_4 from the gas in order to improve the overall economy of the process and avoid discharge of CH_4 to the environment.

Having considered all the available processes and the various process combinations for final purification of the gas mixture in question, the inventors decided to further investigate utilization of cryogenic units. The reason for this was that it had been found that a most pure synthesis gas having the correct H_2/N_2 ratio could be produced by means of such cryogenic units. The question was whether the process itself could be altered and made more energy efficient without losing effect with regard to purification of the final synthesis gas.

As stated above, a major disadvantage of a known final purification process is the pressure drop through the cryogenic unit. The inventors therefore investigated various alternatives of the process streams through the said unit in order to minimize the pressure drop. It was then found that it was not necessary to reduce the pressure of the incoming gas before it was supplied to the separation unit. If the incoming gas containing the undesired gas components was simply cooled from the process temperature of the preceding unit, for instance a methanation unit, ahead of the cryogenic unit to saturation temperature and supplied to a distillation column at about preceding process pressure, required removal of undesired components could still be obtained. It was further found that more of the inherent energy could be recovered by carrying out the decompression of the vent gas to about atmospheric pressure through an expander. Within this concept it was also possible to recover most of the CH_4 from the vent gas by simple distillation without further use of external energy. The cost of such CH_4 recovery could be justified not only from its value, but also from an environmental point of view. Discharge of hydrocarbons into the atmosphere from petrochemical plants is

becoming increasingly undesired. Hydrogen can also be recovered economically within this concept with small investment in an extra unit.

The scope of the invention and its special features are as defined in the attached claims.

The invention and its advantages will be further explained in the following description of the drawings and the examples.

Fig. 1 shows a conventional process utilizing a cryogenic unit for final purification of synthesis gas.

Fig. 2 shows a process according to the invention.

Fig. 3 shows a process according to the invention comprising recovery of CH_4 from the vent gas.

In Fig. 1 pre-purified synthesis gas from the methanation step is fed to a cryogenic unit as process stream 1 to a heat exchanger unit 7 with intermediate decompression in a turbine 4. The cooled gas 9 is fed to a distillation column 5 where CH_4 , Ar and excess N_2 are removed from the synthesis gas which leaves the top of the column 5 through pipe 11. The final purified synthesis gas is then heated in a heat exchanger 7 and fed to an ammonia synthesis unit (not shown) through conduit 2. The removed gas components leave the bottom of the column 5 through pipe 12 and further through a pressure relief valve 6. This vent gas is then heated at the upper part of the column 5 which it leaves through conduit 10. The vent gas is further heated in the heat exchanger 7 and is discharged to the atmosphere through conduit 3.

In Fig. 2 a process according to the invention is shown where the pre-purified gas 1 is fed directly through the heat exchanger 7 and through conduit 9 to the distillation column 5. According to this process the removed components, i.e. the vent gas 10 from the column 5, are heated in heat exchanger 7, but in between two heat exchanging steps its pressure is reduced in a turbine expander 4.

In Fig. 3 a process according to the invention comprising CH_4 recovery is shown. Incoming gas 1, possibly mixed with recovered H_2 , is again simply cooled in a heat exchanger 7 and fed directly to column 5 through conduit 9. In this case the bottom fraction from column 5 is first expanded over valve 6 and then heat exchanged at the top of column 5 and then fed to a second distillation column 8 through conduit 13. Recovered CH_4 leaves the bottom of column 8 through conduit 14 and is passed through heat exchanger 7 before it is returned to the processes ahead of the cryogenic unit for further conversion or combustion.

The hydrogen recovery unit (not shown) can be placed in stream 12 between valve 6 and the heat exchanger on top of column 5.

The top fraction of column 8 leaves through conduit 16 and its pressure is reduced in turbine 4, wherefrom it is fed through conduit 17 back to column 8 for being heat exchanged before the vent gas 18 is finally heated in the heat exchanger 7 and discharged from the cryogenic unit through conduit 3.

Example 1

This example shows final purification of synthesis gas according to a conventional process as shown in Fig. 1 to which reference here is made.

Pre-purified gas 1 is fed to the cryogenic unit from which purified gas 2 leaves. The composition of the various gas streams is stated in Kmol/h.

Comp.	Incoming gas (1)	Vent gas (3)	Purified gas (2)	% Removed
H ₂	5359.1	60.8	5298.3	1.14
N ₂	2725.6	955.2	1770.4	35.05
Ar	39.9	27.0	12.9	67.9
CH ₄	197.7	196.6	1.14	99.49

The H₂/N₂ ratio of purified synthesis gas (2) was 2.9977.

The distillation column 5 was run at 24.8 bar and the incoming gas 1 had a pressure of 27.8 bar being reduced to 24.8 bar over the turbine 4. The vent gas leaving the distillation column 5 was reduced to 3 bar over the reduction valve 6. The total pressure drop through the cryogenic unit was 3.4 bar, and this corresponds to approximately 0.7 MW.

Example 2

This example shows a process according to the invention as shown in Fig. 2. Incoming gas (1), vent gas (3) and purified gas (2) had the following composition in Kmol/h:

Comp.	Incoming gas (1)	Vent gas (3)	Purified gas (2)	% Removed
H ₂	5359.1	70.1	5289.0	1.31
N ₂	2725.6	957.4	1768.2	35.13
Ar	39.9	25.1	14.8	62.8
CH ₄	197.7	196.9	0.80	99.58

The H₂/N₂ ratio of purified synthesis gas (2) was 2.9916.

Incoming gas (1) had a pressure of 27.5 bar, and the distillation column 5 was run at 27 bar. The pressure in the vent gas (3) leaving the distillation column 5 was reduced from 27 bar to 3.6 bar of the reduction valve 6 and further down to 2 bar over the turbine 4.

The pressure drop in the cryogenic unit was 0.5 bar.

Example 3

This example shows a process according to the invention comprising recovery of CH₄ as shown in Fig. 3.

The composition in Kmol/h for the various gas streams was:

Comp.	Incoming gas (1)	Vent gas (3)	Purified gas (2)	% Removed
H ₂	5759	277.0	5482.00	4.81
N ₂	4887	2636.5	1831.15	62.53
Ar	63	30.6	11.50	81.75
CH ₄	192	5.2	1.01	99.48

The H₂/N₂ ratio of purified synthesis gas (2) was 2.9937.

96.76% of the CH₄ was recovered from the vent gas.

As can be seen from the examples, the effect with regard to removal of CH₄, Ar and excess N₂ from the synthesis gas is substantially the same for the conventional process and the process according to the invention. However, the invention also includes recovery of more than 96% of the CH₄ content of the pre-purified gas as shown in Example 3. Also a substantial amount of the hydrogen content in the vent gas can be removed by means of minor investments as indicated for the process according to Fig. 3.

The present invention thus gives a process that maintains the advantages of the known process, and in addition to that a substantial recovery of energy is obtained. By choosing the presently defined process for the cryogenic unit, the pressure drop is reduced substantially, representing savings of at least 0.7 MW having a value of approximately 2 mill. NOK/year. Recovery of for instance 187 Km³ CH₄/h (Example 3), i.e. about 24000 ton/year CH₄, as fuel gas, corresponds to a value of approximately 10 mill. NOK per year. By expanding only a fraction of the gas, and at a lower total pressure in an expansion turbine, reduced turbine costs will be obtained.

The possibility within the same concept to recover CH₄ and H₂ from the vent gas further improves the economics of the process, which can utilize conventional units like heat exchangers, distillation columns and expanders, but combines these units in a special way and runs these at especially chosen operating conditions.

If for any reason it is found advantageous to allow a higher content of CH₄ from the reformer section, the present process is especially advantageous, particularly when practised according to claim 3, i.e. recovery of both CH₄ and H₂ from the vent gas.

The method according to the present invention is especially advantageous in combination with low pressure ammonia processes where the ammonia synthesis can be performed at substantially the same pressure as the methanation, as no recompression of the synthesis gas is necessary after the final purification step.

Claims

1. Method of final purification of ammonia synthesis gas subsequent to pre-purification by removal of CO, CO₂ and H₂O, comprising application of a cryogenic unit for removal of CH₄, Ar and excess N₂, characterized in that the pre-purified gas from a preceding unit is cooled from process temperature in said unit to saturation temperature level and fed directly to a distillation column for separation of the gas into a purified synthesis gas and a vent gas containing the removed CH₄, Ar and excess N₂, and that the separation is performed at substantially the same pressure as in the preceding unit and that the vent gas is heated to final vent temperature with intermediate pressure release through a pressure relief valve and at least one expansion turbine and that the purified synthesis gas is heat exchanged with the pre-purified synthesis gas.
2. Method according to claim 1, characterized in that most of the CH₄ content of the vent gas is removed in a second distillation column prior to final pressure release in the expansion turbine and the reflux for the second distillation column being provided by partial condensation by heat exchange with the turbine outlet followed by heating this heat exchanged turbine outlet, the vent gas, and the finally purified synthesis gas against the pre-purified synthesis gas entering the process.

3. Method according to claim 1,
c h a r a c t e r i z e d i n t h a t
both CH_4 and H_2 are removed from the vent gas and the
hydrogen is removed from the vent gas prior to the
 CH_4 removal and removed as a separate process stream
to be heat exchanged with the pre-purified gas and
then mixed therewith ahead of said heat exchanging
step.

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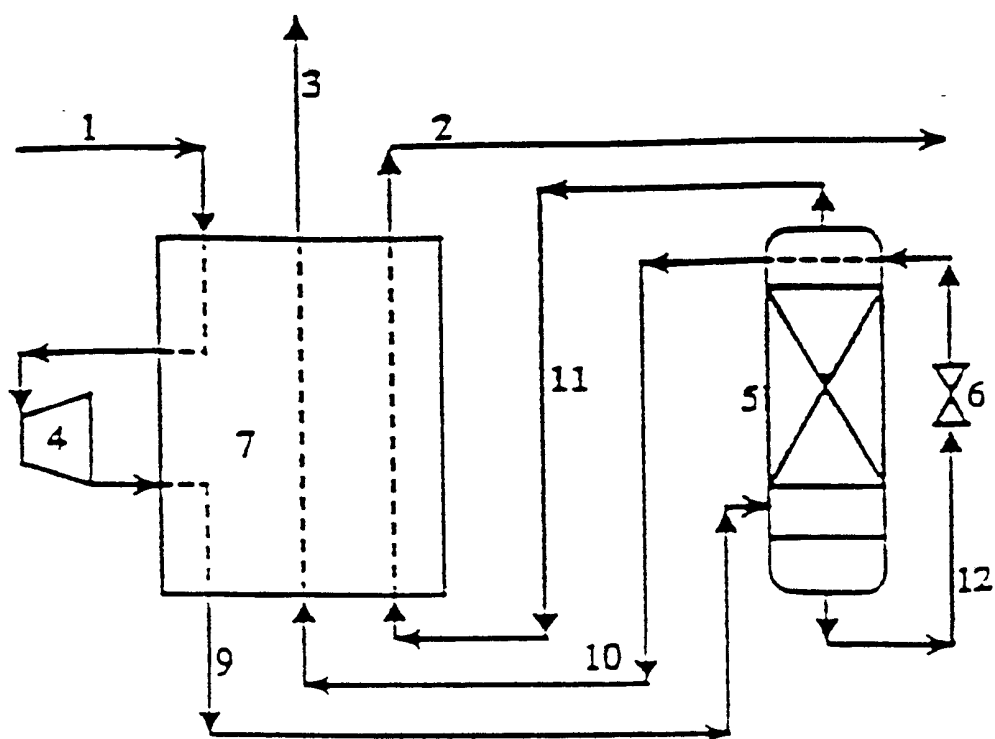


Fig. 1

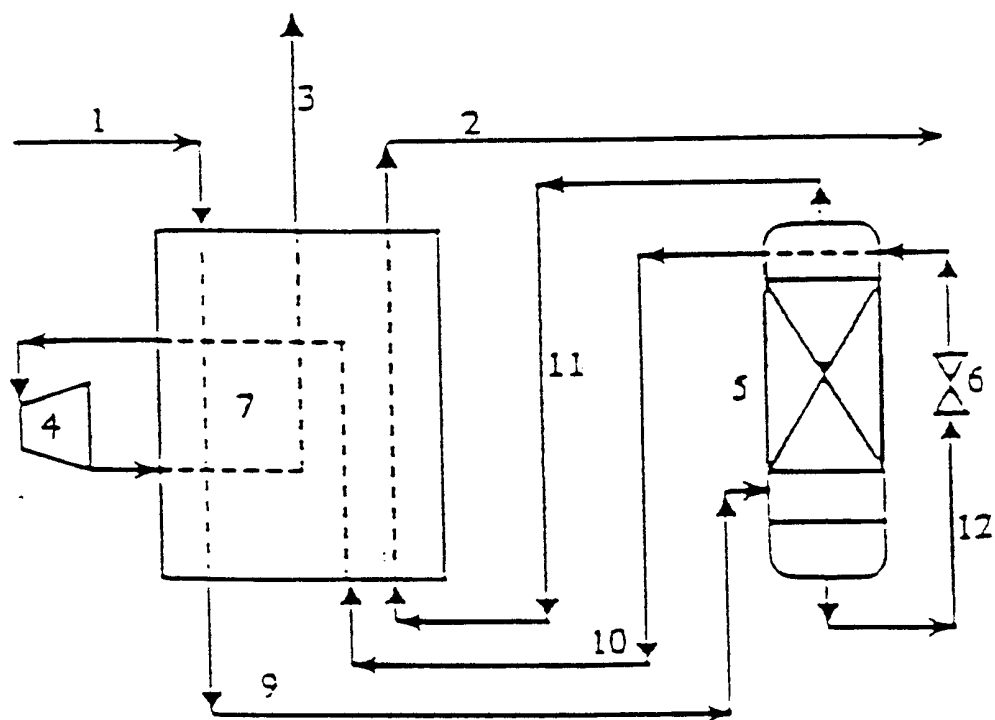


Fig. 2

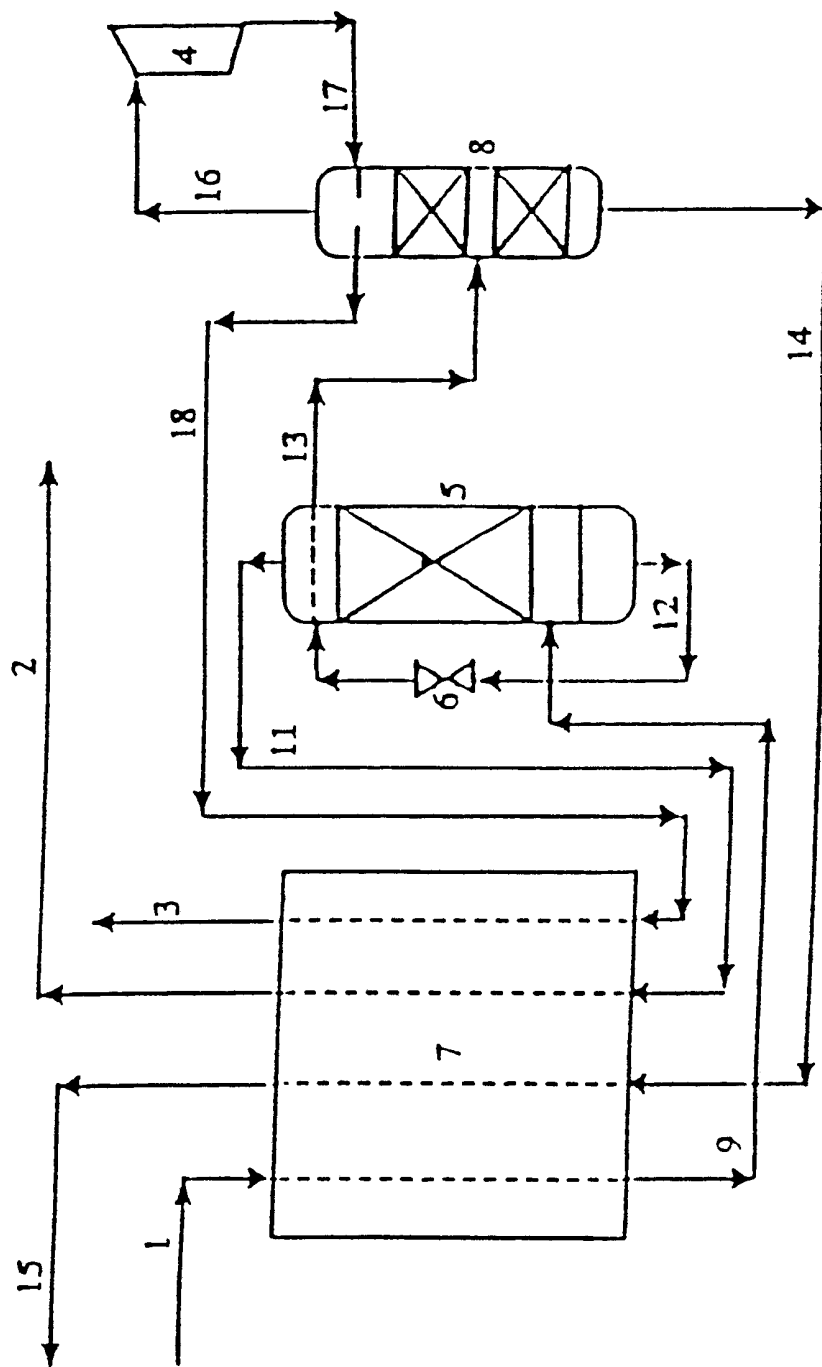
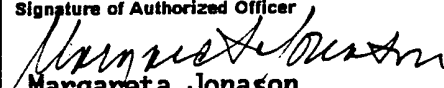


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/NO 92/00015

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: C 01 B 3/50, F 25 J 3/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 01 B; F 25 J	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	SE, B, 449740 (FOSTER WHEELER LTD) 18 May 1987, see page 4, line 1 - line 23; page 5, line 16 - line 24; page 6, line 16 - line 33; page 7, line 5 - line 21 --	1
X	DE, A, 1592352 (LINDE AG) 17 December 1970, see page 4, line 10 - line 17; page 6, line 4 - line 13; page 11, line 15 - page 12, line 16 --	1
X	FR, A1, 2418770 (L'AIR LIQUIDE, SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE) 28 September 1979, see page 1, line 37 - page 3, line 18 --	1,2
<p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
22nd April 1992	1992 -04- 27	
International Searching Authority	Signature of Authorized Officer	
SWEDISH PATENT OFFICE	 Margareta Jonason	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	US, A, 4549890 (BERNARD R. BLIGH) 29 October 1985, see column 3 - column 5 --	1-3
Y	DE, A, 1792285 (LINDE AG) 28 October 1971, see page 3, line 17 - line 21; page 8 --	1
Y	EP, A2, 0119001 (EXXON RESEARCH AND ENGINEERING COMPANY) 19 September 1984, see page 10, line 30 - line 34 & EP, A3, 0119001 -- -----	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/NO 92/00015

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 28/02/92. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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