



**TOGETHER**  
*for a sustainable future*

## OCCASION

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



**TOGETHER**  
*for a sustainable future*

## 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.

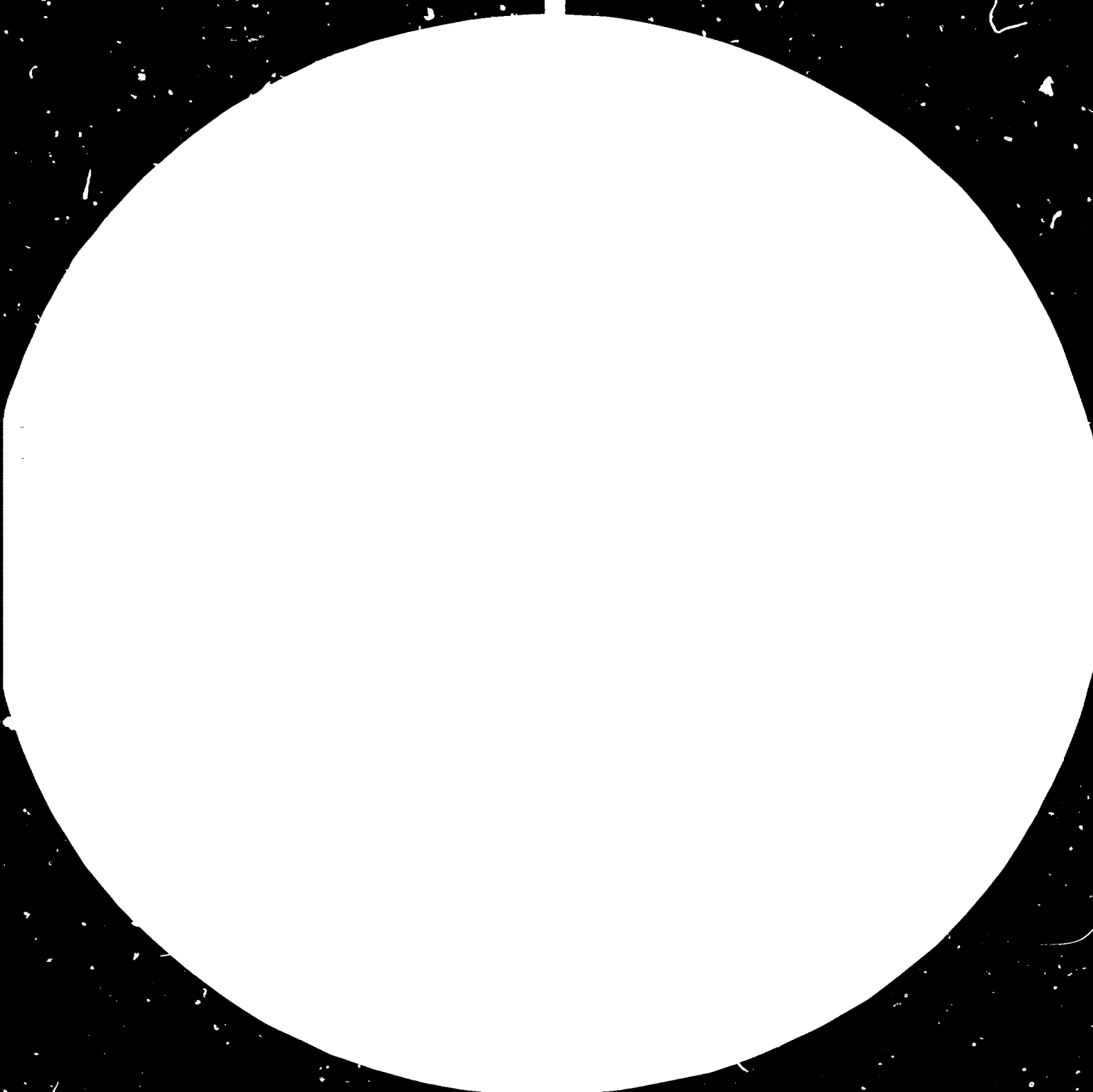
## FAIR USE POLICY

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.

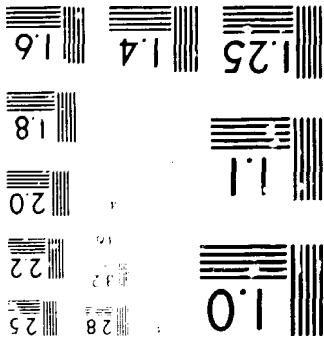
## CONTACT

Please contact [publications@unido.org](mailto:publications@unido.org) for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at [www.unido.org](http://www.unido.org)



MEASURING RESOLUTION IN THE HUMAN VISUAL SYSTEM





11097



Distr.  
LIMITED  
ID/WG.364/7  
12 February 1982

United Nations Industrial Development Organization

ENGLISH

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

FUTURE TRENDS IN AMMONIA TECHNOLOGY\*

by

Ahmad Shah Nawaz\*\*

\* 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.

\*\* Chemical Consultants (Pakistan) Ltd., 6-B, Gulberg 11, Lahore, Pakistan



Primary Reforming: Reforming processes are currently available for 40 - 45 atmospheres. With current energy costs, these are now fully justified.

Currently Steam/gas ratios are between 3 and 4.5, with the newer plants having the lower steam/gas ratios.

Secondary Reforming: The gas leaving the primary reformer at a temperature of  $760^{\circ}$  -  $820^{\circ}$ C is mixed with air and further reformed, leaving at a temperature of  $950^{\circ}$ C -  $1020^{\circ}$ C. All the Nitrogen required is introduced at this point.

Shift Conversion: The gas is then cooled and the heat recovered, and the Carbon Monoxide is thereafter catalytically shift converted to Carbon Dioxide (with reduction of Steam to hydrogen) in two stages: a High Temperature and a Lower Temperature stage.

Carbon Dioxide Removal: After further cooling, the Carbon Dioxide is removed by chemical absorption, with the regeneration of the Carbon Dioxide both by pressure reduction of the solution and with recovered heat.

Methanation. The remainder of the Carbon Dioxide and Carbon Monoxide is then catalytically methanated, which gives a gas containing 1 to 1.5% inerts. However when the LT catalyst gets old, this can rise to 2% inerts.

Compression: The Synthesis gas is then compressed to the required pressure (today 150 to 280 atmospheres) and passed over an appropriate catalyst, with temperatures of  $450$  -  $480^{\circ}$ C, to produce Ammonia.

Ammonia Loop. The synthesis gas is cooled and the Ammonia liquified (under usual pressure conditions as a liquid at  $-33^{\circ}$ C), and the unreacted gas is recycled (generally through the final stage of the Compressor), mixed with fresh synthesis gas and passed to the reactor.

An Ammonia Plant of the type described above has a general heat requirement of around 8.5 million Kcals/ton Ammonia.

### 3. Improvements currently being installed.

In many of the plants which are being currently designed, changes are being made to improve overall efficiency. Of these the most important are:-

#### Primary and Secondary Reforming.

Combustion air preheat is already common and Process air preheat is being installed in all new plants. The feed is also being preheated to higher temperatures.

The net overall saving by these changes is estimated at 0.6 million Kcals/ton Ammonia.

#### Shift Conversion.

No basic changes are being currently made but catalysts are improving and it is possible to keep CO down to a point where inerts after methanation are 1 - 1.2 per cent only.

Systems are available for the selective oxidation of the CO left after LT conversion, to CO<sub>2</sub>, thus reducing hydrogen loss in the methanation section, and reducing inerts.

Carbon Dioxide Removal: Systems are now available where the heat requirements for Carbon Dioxide regeneration are eliminated. Among important ones are the physical type absorption Systems but these give less carbon Dioxide recovery. The savings in use of such systems can be substantial over systems installed 7-8 years ago.

Removal of Inerts: The removal of inerts is of extreme value, both in lowering the energy requirements for re-circulation and in the purge gas loss. For instance with 1% inerts and an admissible purge equal to 5% of the incoming gas, the inert content in the circulating gas can rise to 20%. With no inerts the mole percent of Ammonia at equilibrium (starting from 3:1 Hydrogen: Nitrogen mixture) is 27.44% at 200 atmospheres and 450°C but with 20% inerts this drops down to only 17.87% under the same conditions.

Physical absorption systems are now available for removal of H<sub>2</sub>O, CO and even N<sub>2</sub>. However the most important of the removal systems is Cryogenic purification.

It should be pointed out that if the Cryogenic purification system is adopted, the air to the Secondary reformer can be increased, and the H<sub>2</sub> : N<sub>2</sub> ratio adjusted through the Cryogenic system. Alternatively if pure Oxygen is available, this can also be accomplished by use of Oxygen rather than air.

Compression: In recent years, the use of Centrifugals has been axiomatic. Centrifugals are available for lower capacities now, but for small plants their value is doubtful. It should be pointed out that savings in the use of Centrifugals is only around 0.4 million Kcals/ton Ammonia.

Synthesis Converter and Ammonia Loop. Newer baskets as well as some changes in catalytic temperatures give a closer approach to equilibrium. For instance in one Pakistani plant, the change has resulted in Ammonia conversion (at 225 atmospheres) from 16% to near 22%.

Several systems are available for lower pressure drops in the Converter and Ammonia Loop thus reducing recycling energy. Among these are the use of spherical catalysts, and mixed flow systems in the reactor, as well as the reduction in the inerts mentioned above.



All these improvements have resulted in energy requirements of around 7.3 million Kcals/ton Ammonia, or with Cryogenic purification, around 7.0 million Kcals/ton Ammonia.

#### 4. Future Improvements in Classical Ammonia Technology.

These improvements can be divided into 2 types:-

- (a) Improvements in the near future.
- (b) Improvements in the more distant future.

#### 5. Immediate Improvements in Classical Technology.

All the improvements currently being considered, or where new processes are being offered deal with energy efficiencies of the Ammonia System.

Among individual improvements which are likely to be available in the near future are:-

(a) Increases in reformer pressure. This has been a steady process and is likely to continue as energy costs rise.

(b) Possibilities exist in the reformer combustion taking place under pressure. This would make tube wall thicknesses less, allow easier heat transfer, and make the recovery of heat from the combustion gases easier. However the Reformer walls would have to be pressurised and this can be costly.

(c) The recovery of additional heat from the combustion gases is perhaps the most important potential saving. As much as 1 million Kcals/ton Ammonia is lost in older systems, although the loss in modern systems is less. However heat recovery systems from the combustion gases are still untried, except for such uses as steam superheating.

(d) Waste Heat Boilers are now available for the Ammonia loop. However the long-term life of these (due to the presence of Ammonia) needs further examination.

(e) The use of absorption - desorption refrigeration systems in the Ammonia loop, with the heat required for such systems coming from various sources within the Ammonia cycle itself is now coming into use. This is reported to reduce consumption to around 7 million Kcals/ton Ammonia, and when coupled with inert removal down to as little as 6.5 million Kcals/ton Ammonia (3).

(f) The greater superheating of the steam in the steam system of the plant could give almost a direct saving. However, this would have to be carefully studied on an overall energy basis.

(g) The Ammonia Reactor currently operates at around 80% of equilibrium. Changes in the Reactor design, possibly coupled with temperature changes would bring conversion much closer to equilibrium. The removal of traces of Ammonia in the loop (by absorption) would also help.

(h) The use of a steam turbine for the syngas compressor is only useful if the rest of the steam heat can be utilised, possibly in the fertilizer section of a Ammonia - Fertilizer Complex.

The processes where these, and other modifications have been proposed and which are available and would become commercial in the near future have been summarised in a recent paper (3) and need not be discussed here.

Some of the offered processes include low-pressure loops, but a true low pressure loop would require a low pressure synthesis reactor, and this cannot be considered to be an immediate possibility.

6. Future Improvements in Classical Technology.

The major future breakthrough in the classical Ammonia technology must come from the development of a Low Temperature Ammonia synthesis catalyst.

Ammonia equilibrium conversion data from a 3:1 Hydrogen: Nitrogen mixture is given in Table I below:

Table - I

Mole Percentage of Ammonia at Equilibrium.

Temperature °C	Pressure, atm			
	30	50	100	300
300	30.25	39.41	52.04	70.96
350	17.78	25.23	37.35	59.12
400	10.15	15.27	25.12	47.00
450	5.86	9.15	16.43	35.82
500	3.49	5.56	10.61	26.44

It will be seen that at 50 atmospheres and 300°C, the conversion to Ammonia is better than at the current 300 atmospheres and 450°C.

Several attempts have been made to find low temperature Synthesis catalysts, but no commercial catalyst with a fast enough rate of reaction at 300°C - 350°C is yet available commercially.

However there are several patent applications. ICI has a Cobalt - Iron catalyst and the activity at 350°C is reported to be 60% higher than a cobalt - free catalyst (4). Lummus (5) has Cerium activated catalysts effective at 400°C, and Casale(6) has patented a spherical catalyst which they claim is effective at 350°C - 400°C.

The LT catalyst would revolutionize the Ammonia technology and would permit a common operating pressure (after accounting for pressure drops) from reforming to Synthesis. This would eliminate Syngas compression, and allow small plants to be economical with large plants.

Several low pressure processes have been announced (40 to 60 atmospheres and in any case, below 100 atmospheres) with synthesis and reforming pressures being similar. Of these Kellogg and ICI processes may be mentioned. Per pass Ammonia concentrations are 12 - 15%. However the processes still need to be commercially proven.

At the same time a breakthrough in this field is now due and should not be more than 5 years away.

#### 7. Improvements in Non-Classical Technology.

The availability of non-conventional sources of energy, of which solar energy is the most important, would not have any direct impact on Ammonia technology because the available temperatures are too low.

However if Solar electrical power could be developed cheaply, this could allow the resurgence of the electrochemical and allied processes (hydrogen from water, nitrogen from air).

At present only a few water electrolysis plants exist of which 3 (2 in Norway, 1 in Egypt.) are large installations, and act as a base for Ammonia.

Current consumption figures are reported (7) at 34 MM BTU/ton Ammonia or about 8.7 million Kcals/ton Ammonia.

This is higher than other energy sources and since much more electricity is required, it is less balanced also.

It should also be pointed out that solar radiation, even in the tropics seldom exceeds 300 BTU/ft<sup>2</sup> and even if we assume 20% energy conversion to electricity about 500,000 ft<sup>2</sup> of solar panel surface (50,000 Sq.metres) would be required per ton of Ammonia.

This would not be possible as an economic proposition even if solar energy develops rapidly.

## 8. New Technologies.

### 8.1. Nitrogen Fixing Crops.

There are a number of new technologies which must be mentioned in a paper of this type.

Before considering these technologies, the possibility of an Agricultural breakthrough must also be considered. The use of Leguminous crops as a source of Nitrogen and the appropriate rotations using these crops have been known for 400 years. As late as 1950, about 75 million acres (about 30 million hectares) of leguminous crops were adding 2 million tons Nitrogen to soils in the U.S. With the availability of cheap Nitrogen as a fertilizer the use of leguminous crops has reduced.

The efficiency of atmospheric nitrogen fixation by leguminous crops can, probably, be increased. In addition a number of non-leguminous families, which fix Nitrogen, have also been identified and need to be further developed.

In most cases, the Nitrogen fixation of such Agricultural crops, tends to reverse when Nitrogen concentrations in the soil increase and this could put a limit upon their usefulness.

However, since many of these crops tend to flourish in the tropics they should be given more agronomic significance, and research on these crops may pay dividends.

### 8.2. Production of Ammonia from Enzymes

The biochemical crop mechanism appears to be an oxidation - reduction of the Nitrogen under  $2H^+$  and  $O^-$  ions in the soils. Ammonia is undoubtedly formed in the reduction reaction and this could possibly yield to the production of Ammonia by biochemical action.

The recent isolation of "Nitrogenase", the Enzyme which catalyses the combination of the Nitrogen from the air and hydrogen from water is undoubtedly a breakthrough in this direction. This enzyme's protein structure is now being established and soon new genetically prepared enzymes may be built-up to do the work more efficiently.

In actual practice, it is possible to transfer the characteristic of fixing nitrogen from known species by genetic engineering, to completely unrelated species and this can also be a breakthrough.

The genetic capability does not stop there. It may be possible one day to have a wheat or maize in which genetic transfer has resulted in the direct fixation of Nitrogen, thus doing away with most of the markets for fertilizer Nitrogen!

However all this is in the future and chemical engineering still remains in the forefront for Ammonia technology.

### 8.3. New Chemical Approaches

The obvious new chemical approach is to first produce a chemical complex which can take up Nitrogen ( $N_2$ ) from the air and thereafter react it with another product which could reduce the Nitrogen to Ammonia. The first was solved in 1965, and the second in 1970.

It has been found that a molybdenum complex which binds dinitrogen can be made to react with an iron-sulphur complex, which reduces the Nitrogen to Ammonia. Yields are only 2% - 4%.

It should be remembered, however, that the yields obtained by Haber in 1904 on the Classical Ammonia process were only 0.5%. Even with the introduction of higher pressures, Nerst only obtained 0.9% conversion in 1906 but the first commercial plant started in 1913 !

### 8.4. The Ultimate Biochemical Process.

Finally a word about the ultimate biochemical process. It would be nice to have a process where Air is bubbled through biomass containing the right type of bacteria (many free Nitrogen fixing bacteria are known) and to obtain Ammonia in commercial quantities. Then all of us Chemical Engineers could retire gracefully. However that is not going to happen in a hurry. The bacteria to be developed would have to be a special one which can quickly fix Nitrogen and react with hydrogen from cellulose etc. giving a reasonable Ammonia yield. The Ammonia in such cases is more than likely to be converted rapidly to Amino Acids, and this would also have to be guarded against.

The great advantage of such processes is the potential that they could be at farm level or multi-farm level, not requiring the large investment which are today a necessary expenditure of a developing country's finances.

However there is a time scale involved - say, at least, 20 years, but this remains in the realm of conjecture.

References

- (1) For instance, Sauchelli: "Fertilizer Nitrogen" ACS Monograph No.161, New York (1964).
- (2) Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edn. Vol.2. p.268.
- (3) U.Zardi, A.Antonini, Nitrogen, Nov./Dec. 1979.
- (4) ICI Patent Application. British. 044,995/77 (October 1977).
- (5) Sze Wang, U.S. Patent No. 3,992,328
- (6) Ammonia Casale, Italian Patent application No.47920A/79 (1979).
- (7) Data from Norsk - Hydro.



