

MANUFACTURE OF SYNTHETIC NITROGENOUS FERTILIZERS IN INDIA

Part III. Processes for the Synthesis of Ammonia

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It has been mentioned in Part II of this series that the synthetic process for ammonia was first worked out on a commercial scale in 1913 by Haber and Bosch and plants were erected at Oppau and later at Leuna (Merseburg) in Germany to carry on the process on a large scale. These two factories, between them, are now equipped to fix nearly a million tons of nitrogen per year. The working details of the Haber Process were kept a close secret even after the close of the War, but the principles underlying it were successfully developed into commercial practice independently in other countries, e. g. in America, France, Italy and England. The chief of these modified processes are those of Claude (France), Casale (Italy), Fauser (Italy), Mont Cenis (Germany) and F. N. R. L. (U. S. A.). The main differences between these methods lie in :— (a) the source from which hydrogen is obtained ; (b) the method of separating oxygen from the nitrogen of the air ; (c) method of purifying hydrogen and nitrogen ; (d) nature of catalyst used ; (e) temperature of reaction ; (f) pressure employed ; and (g) method of removing ammonia from the system.

Some of the main technical differences between these methods are shown in Table I.¹

TABLE I. Comparison of Synthetic Ammonia Processes.

Method.	Pressure atm.	Reported Tem. °C	Reported conversion maximum %	Recirculation of unchanged gases.	Catalyst.
Mont Cenis	100	400	40	Yes	Iron Cyanide Complex.
Haber-Bosch	200	550	8	Yes	Iron granules "promoted"
Fauser	300	500	12.5	Yes	Do.
F. N. R. L.	300	475	30	Yes	Do.
Casale	750	475	40	Yes	Do.
Claude	900	600	40	No	Do.

The world installed capacity for direct synthetic ammonia production was distributed in 1934 among the several processes as follows:— Haber-Bosch 35.2% (mostly in Germany), Casale 14.9 (in France, Italy, U. S. A. and Japan), Fauser 11.9 (in France, Italy and Netherlands), Claude 9.4 (France and U. S. A.), Imperial Chemical Industries 8.5 (England), Mont Cenis 8.0 (Switzerland), Nitrogen Engineering Corporation 6.5 (Norway and U. S. A.), General Chemical Co. 6.2 (U. S. A.), F. N. R. L. 2.0 (U. S. A.).

The above processes can be grouped broadly into two classes:— (1) those which work at low or moderate pressures, and (2) those which work at high pressures. To the former class belong the Mont Cenis, Haber-Bosch, Fauser and F. N. R. L. systems; and to the latter class belong the Casale and Claude processes.

The advantages of working under high pressures are:— (1) the capacity to handle more material in a given reaction space, compared with processes using low pressures (thus "convertors" of about 25 inches diameter and 12 feet height can synthesise 30 tons of ammonia per day in the high pressure system, as compared with the Haber-Bosch "convertors" of diameter 4 feet, height 20 feet and walls 7 inches thick. (2) Higher percentage conversion. Thus, the Claude and Casale processes achieve 40% conversion into ammonia, against 8% obtained in the Haber system. The Mont Cenis is, however, an exception, since it obtains the same high degree of conversion even though it works at 100 atmospheres pressure only. This is due to the very active Iron-cyanide complex which is used as the catalyst. (3) The ammonia formed by high pressure synthesis can be directly liquefied as anhydrous ammonia, whereas in the low pressure systems, it has to be absorbed in water to form dilute ammonia and later distilled again.

The disadvantage of working under high pressures is the extra chance of accidents and the necessity for using very durable and highly resistant metal for the conversion chambers. To obtain such resistant material which would work satisfactorily at moderately high temperatures below 500°C is easy nowadays. The case is, however, different when high pressures are combined with high temperatures, as in the Claude process, where pressures of 900 to 1000 atmospheres are combined with temperatures above 600°C. Ordinary types of resistant steel break down under these conditions. The practical application of the Claude process was delayed for a number of years, till a satisfactory type of metal could be manufactured, suitable for the purpose. At present a special alloy of nickel, chromium, tungsten and iron is used and has been found to work satisfactorily.

The use of such special alloys, in addition to increasing the cost of the plant, raises certain important issues, e. g. as to whether it will be possible to prepare such resistant alloys in the necessary quantities in this country in times of need, should the foreign supply be cut off. It would, obviously, be wise to adopt a process which would incorporate the advantages of high pressure synthesis without rendering the use of such super-resistant metal quite necessary.

From this point of view, the Casale Process has many points in it that commend themselves to our favourable consideration. It works at about 475°C and does not require the special resistant alloys needed for the Claude plant. Moreover, the "promoted" iron catalyst can be prepared in this country itself. The method incorporates all the advantages of high pressure synthesis and has been adapted to work on electrolytic hydrogen, for which purpose special types of efficient batteries have been devised.

Before going further into the choice of a final technique, we shall consider in more detail the economics of the different methods of obtaining hydrogen and nitrogen. It has been estimated that as much as 70 to 75% of the total cost of production of synthetic ammonia is involved in the preparation and purification of the 3 : 1 mixtures of hydrogen and nitrogen, required for the purpose. It is, therefore, obviously of importance to consider which of the present methods in vogue are the most economical under the conditions existing in this country.

Of the two components, nitrogen and hydrogen, the cost of production of nitrogen is almost inappreciable, compared with the cost of production of hydrogen. Thus, for fixing one ton of nitrogen, the volume of nitrogen gas theoretically required is about 28,750 c. ft. at N. T. P., which can be produced at a cost less than Rs. 5 including depreciation on machinery; but the cost of production of the necessary amount of hydrogen, say about 90,000 c. ft., may easily go up to Rs. 200 or more.

The important sources for commercial hydrogen are:— (1) Water Gas; (2) Coke Oven Gas; (3) Electrolysis of water; (4) Steam-iron reaction; (5) By-product hydrogen from the production of chlorine, fermentation processes etc.; (6) Natural gas. Of these sources, Nos. 5 and 6 are not available at present in large quantities in India; and method 4 is not cheap, since the reaction between steam and iron comes to an early equilibrium and, moreover, the ferric oxide formed has to be reduced again. Methods, 1, 2 and 3 are the ones generally adopted on the large scale, and the extent to which they have contributed to the supply of hydrogen for the production of synthetic ammonia, is shown in Table II.³

TABLE II. Sources of Hydrogen for the production of ammonia.

Source.	1926-27	1933-34
	%	%
1. Water gas	89.0	37.0
2. Coke Oven gas	3.0	25.0
3. Electrolysis of water	6.4	16.0
4. Other sources:— e. g. by-product hydrogen from brine, fermentation etc.	1.6	2.0

Of the sources 1, 2 and 3, source 2 (coke oven gas) is available only in Bihar and Bengal, since there is no coking industry in other provinces of India. Hence, for the other provinces, the alternative is between sources 1 and 3, viz. water-gas or electrolysis of water, as the source of hydrogen.

In the Haber-Bosch process, a mixture of water-gas and producer gas is used. The approximate composition of these gases is shown in Table III.

Water Gas. This is prepared by passing steam into a bed of incandescent coke, the temperature of which is maintained between 1400°C and 1000°C, when the following reaction takes place:— $H_2O + C \rightarrow CO + H_2$. Since the reaction is endothermic and the temperature tends to fall below 1000°C, a blast of air is frequently let in to raise the temperature to 1400°C,

and the carbon dioxide evolved is separately let off. Thus, a portion of the coke is burnt away to carbon-dioxide and only 50 to 60% of it is obtained as carbon monoxide. About 1000 c. ft. of straight water gas are produced for every 40 lbs. of coke (total) consumed.

TABLE III. Composition of Water Gas and Producer Gas.

	Straight Water Gas		Producer Gas	
		%		%
Carbon dioxide	3.7	...	5.2
Ethylene	1.0
Oxygen	0.5	...	0.2
Carbon monoxide	42.3	...	26.3
Hydrogen	47.9	...	14.4
Methane	0.6	...	1.8
Nitrogen	3.4	...	51.1
Others	1.6
		<u>100.0</u>		<u>100.0</u>

Producer Gas. This is obtained by passing a continuous mixture of air (7 volumes) and steam (1 volume) over low grade coal. The amount of steam used per lb. of coal gasified is about 0.4 to 0.5 lb. One pound of bituminous coal yields about 60 c. ft. of gas, semi-bituminous coal about 30 c. ft. and lignite about 28 c. ft.

In the Haber-Bosch method, as already mentioned, a suitable mixture of water-gas ($\text{CO} : \text{H}_2$ about 1 : 1), producer gas ($\text{N}_2 : \text{CO}$ about 2 : 1) and additional steam is sent through a hot catalyst of "promoted" ferric oxide, when the carbon-monoxide is converted into an equivalent amount of hydrogen, according to the reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. The proper (roughly equal) volumes of water gas and producer gas are chosen to give at this stage hydrogen and nitrogen by volume of 3 : 1. The mixture is next passed through an elaborate system of scrubbers and purifiers, which remove most of the other gases and impurities which are likely to poison the catalyst during the synthesis of ammonia.

For the fixation of one ton of nitrogen, roughly 30,000 c. ft. of nitrogen gas and thrice that volume of hydrogen are necessary. These correspond, roughly, to a mixture of 70,000 c. ft. water-gas and 60,000 c. ft. of producer gas; and to obtain this mixture are required about $1\frac{1}{2}$ tons of coke, 1 ton of coal and about 10—11 tons of steam. The cost of these materials could be easily calculated from the local prices for coal at any centre. It would not pay to adopt the above method where the price of coal is above Rs. 10 per ton. An advantage of the Water-gas method is that about 100,000 c. ft. of carbon dioxide are obtained as a by-product per ton of nitrogen fixed, which may find some application in the later stages of manufacture, e. g. in adopting the gypsum process for ammonium sulphate or in preparing urea.

Where a cheap source of electricity is available, say at a price lower than Rs. 50 per k. w. yr., it is possible to use the hydrogen obtained by electrolysis of water in the manufacture of synthetic ammonia. Various

special types of cells suitable for the purpose have been designed, e. g. (1) Knowle's multipolar cell and Knowle's column cell (bell type); (2) Pechkranz cell (filter-press type) and (3) Fauser cell (diaphragm type). The Fauser and Pechkranz cells have found much favour in the synthetic ammonia industry. In all these cells, the consumption of current is about 150 k. w. hrs. per 1000 c. ft. of hydrogen obtained which works out to 13,500 k. w. hrs. or about 1.5 - 1.6 k. w. yrs. per ton of nitrogen fixed. Where D. C. current is not available, a transformer has to be set up and the total consumption of current may go up to 1.75 k. w. yrs. per ton of nitrogen fixed.

The main disadvantage of the electrolytic method is the high capital cost of the electrolytic system as compared with the Water gas method. On the other hand, the hydrogen obtained by the method of electrolysis is very pure and it is unnecessary to incur the further expenses of purification necessary with water gas. Further, oxygen is obtained as a by-product, which may find a sale and serve to lower the cost of hydrogen. In countries such as Italy, which have no coal, the electrolytic method for hydrogen has been successfully adopted in the manufacture of synthetic ammonia (e. g. in Casale and Fauser processes).

The comparative costs of producing ammonia from the different sources of hydrogen have been discussed by Pollitt,⁴ who gives the following data as regards investment and manufacturing charges:—

TABLE IV.

Costs of producing ammonia from different sources of hydrogen (1930-31)

Source of hydrogen.	Investment per metric ton-year of ammonia			Manufacturing cost per metric ton of ammonia as 25% liquor.
	Plant.	Buildings.	Total.	
	\$	\$	\$	\$
Electrolytic ...	198	25	223	34-57*
Water gas ...	148	22	170	35
Coke Oven Gas ...	141	19	160	44
Coke Oven Gas†	94	30

* Depending upon local cost for electrical energy.

† From E. F. Armstrong, Chemical Trade Journal, November 1931.

Nitrogen Gas. As regards nitrogen gas, it has been obtained (1) by passing air over red-hot coal or copper; (2) by liquefying air and then fractionating it, for which purpose the plants of Linde and Claude are best suited; (3) by burning hydrogen in air; this last method is practical only on a small scale or where hydrogen can be obtained very cheap. In the Fauser process, 10% of the ammonia prepared is mixed with air and passed through platinum gauze, when the residual gas consists mostly of nitrogen.

Of the above methods, Claude's plant for liquefaction of air and subsequent fractional evaporation, has given very satisfactory results at a number of synthetic ammonia factories, and can be recommended for adoption in cases where water-gas is not used.

Derivatives of Ammonia. Though ammonia, as such, finds some application in industry, e. g. in refrigeration plants, most of it is converted into derivatives, e. g. ammoniacal fertilizers and urea or oxidized to nitric acid.

Ammonium sulphate is probably the predominant form in which synthetic ammonia appears on the market and almost all of it is used as fertilizer. Where local supplies of sulphur are available, as in Sicily, Japan and U. S. A. or pyrite ores as in Spain and U. S. A., it is convenient to manufacture the necessary sulphuric acid for the preparation of ammonium sulphate. In other countries, e. g. Germany and England, which do not possess sufficient supplies of sulphur or pyrites, but which possess good deposits of gypsum, successful attempts have been made to prepare ammonium sulphate by passing ammonia and carbon dioxide into calcium sulphate, suspended in water. This is a cheap method of preparing ammonium sulphate and the necessary CO_2 is generally obtained as a by-product in the manufacture of water-gas and producer gas used for the synthesis of ammonia.

But the popular preference for ammonium sulphate in fertilizer practice, is only of recent origin, say from the beginning of this century. Before that, the fashion was to use sodium nitrate from Chile. Sodium nitrate suffers from the disadvantage that its continued use renders the soil alkaline and unproductive. On the other hand, ammonium sulphate suffers from the opposite disadvantage, viz. that the continued use of it renders the soil acidic—especially on light soils—due to the accumulation of sulphuric acid.

Serious efforts, through propaganda and demonstrations, are being made by fertilizer companies, both in Europe and in America, to induce the agricultural clientele to use fertilizers other than ammonium sulphate; and it is satisfactory to note that the sale of such fertilizers, e. g. ammonium phosphate, ammonium chloride, urea and various nitrate fertilizers, now exceeds that of ammonium sulphate. Indeed, it is now possible to run a synthetic ammonia plant and to dispose of its products for fertilizer purposes, without being under the necessity to manufacture sulphuric acid or to use gypsum. This is of special significance to India, which does not possess any abundant deposits of sulphur or rich sulphide ores.

Oxidation of Ammonia to Nitric Acid. An important outlet for ammonia lies in its oxidation to nitric acid catalytically, by mixing it with air (11%) and passing it through finely divided platinum gauze; the oxides of nitrogen so formed are further oxidized and absorbed in dilute acid to form 50% Nitric acid.

The dilute acid can be used directly for the manufacture of various fertilizers, e. g. ammonium nitrate, calcium nitrate, sodium nitrate, etc. The disadvantage of some of these nitrates, from the fertilizer point of view, is their deliquescent nature. This has been partially got over by admixing the nitrate with bone-meal, calcium carbonate, gypsum or potassium salts. Thus, we have on the market compound nitrates, such as ammonium sulpho-nitrate, potassium ammonium nitrate, bonemeal ammonium nitrate, calcium ammonium nitrate and trade products such as Nitro-chalk, Calnitro, Leuna saltpeter etc.

Such compound nitrates are now finding increasing sale, since they contain, in addition to nitrogen, other valuable plant nutrients such as potash, calcium, phosphoric acid etc.

For purposes of munitions and for the dye-stuff industry, the dilute nitric acid has to be concentrated to 95—98% by addition of concentrated sulphuric acid and redistillation.

Urea. Another fertilizer that is coming into favour is urea, which can be obtained by passing ammonia and CO_2 into an autoclave held at 130° to 140°C . Urea is rich in nitrogen (contains 46.6% N as compared with about 20% in cyanamide and ammonium sulphate) and is easily assimilated by plants. An interesting fertilizer derivative of urea is calcium urea nitrate, in which urea replaces the four molecules of water in calcium nitrate and renders the product much less hygroscopic.

General Review and Conclusions. It is evident from what has been said in this and the earlier parts of this series, that the manufacture of synthetic ammonia offers the best starting point for covering the whole field of nitrogenous fertilizers, e. g. nitrates, ammonium salts, urea etc.; and it is possible to run the plant and market its products, even independently of imported sulphur or gypsum, should it be so necessary.

Of the different processes for the manufacture of synthetic ammonia, those of Casale and Fauser seem to possess several marked advantages over others.

Of the different methods of obtaining hydrogen and nitrogen the water gas and coke oven gas methods are suited to Bihar and Bengal; but in other provinces, the atmospheric liquefaction method for nitrogen and the electrolytic method for hydrogen can be adopted, provided a cheap source of electricity is available which could supply current at Rs. 40 to Rs. 50 per k. w. yr.

It would be advantageous to attach an ammonia oxidation unit to the synthetic ammonia plant and to manufacture compound fertilizers such as calcium ammonium nitrate, ammonium sulpho-nitrate, bonemeal ammonium nitrate etc., in addition to simple compounds such as ammonium sulphate, ammonium phosphate and ammonium chloride. Urea and its derivatives, such as calcium urea nitrate, may also be included in the programme.

A small plant for the manufacture of sulphuric acid from imported sulphur may be added, for the preparation of super-phosphate, ammonium sulphate etc.

References.

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2. *Chemical Nitrogen*—Report 114, Second Series of U. S. A. Tariff Commission, U. S. A. Govt. Printing Office, Washington, 1937, page 51.
3. *Chemical Nitrogen*, loc. cit., page 41.
4. Report of Col. G. P. Pollitt before the Second World Power Conf., Berlin, 1930; vide *Chemical Nitrogen*, loc. cit., page 42.