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# UNIDO FERTILIZER MANUAL

## SECTION VI-AMMONIA

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# II PRODUCTION OF AMMONIA

## History of Ammonia Synthesis:

As mentioned in chapter I, synthetic ammonia ($NH_3$) has become the principal source of all nitrogen fertilizers, particularly since 1945. At present, over 95% of all commercial fertilizer nitrogen is supplied by or derived from synthetic $NH_3$: only minor percentages are supplied by natural sodium nitrate, byproduct $NH_3$ from coke-oven gas (usually recovered as ammonium sulfate), calcium cynamide, and other minor sources. The rest of the ammonia produced finds its use in the production of resins and animal feed polyamides, polyacrylonitrile, industrial explosives and dye stuffs. The ammonia synthesis process was developed mainly by Fritz Haber starting in 1904, and by 1909 he demonstrated the process on a laboratory scale of 80 g of $NH_3$ per hour(1). Carrying out the high-temperature, high pressure process on a commercial scale presented formidable problems with the technology and materials of construction then available. Carl Bosh, working with Haber, is generally credited with developing the process-first in a pilot plant and then on a commercial scale of 30 tpd. Production started in 1913 at Oppau, Germany.

The chemistry of the process is simple; the reaction is:

$$3H_2 + N_2 \longrightarrow 2NH_3$$
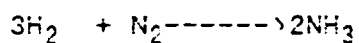
The reaction is exothermic; the net heat of reaction is about 11,000 cal/g-mole at 18 °C (647 Kcal/kg of $NH_3$), assuming $NH_3$ is in the gaseous state. The net heat released by the reaction increases with increasing temperature and may be 15%-20% higher at the usual operating conditions of 400 - 500 °C.

TABLE 1.  PERCENTAGE OF AMMONIA AT EQUILIBRIUM FROM A 3:1 MOLAR MIXTURE OF HYDROGEN AND NITROGEN

| Temperature, °C | Pressure, atm | | | | | | |
|---|---|---|---|---|---|---|---|
| | 10 | 30 | 50 | 100 | 300 | 600 | 1,000 |
| 200 | 50.66 | 67.56 | 74.38 | 81.54 | 89.94 | 95.37 | 98.29 |
| 250 | 28.34 | 47.22 | 56.33 | 67.24 | 81.38 | 90.66 | 96.17 |
| 300 | 14.73 | 30.25 | 39.41 | 52.04 | 70.96 | 84.21 | 92.55 |
| 350 | 7.61 | 17.78 | 25.23 | 37.35 | 59.12 | 75.62 | 87.46 |
| 400 | 3.85 | 10.15 | 15.27 | 25.12 | 47.00 | 65.20 | 79.82 |
| 450 | 2.11 | 5.86 | 9.15 | 16.43 | 35.82 | 53.71 | 69.69 |
| 500 | 1.21 | 3.49 | 5.56 | 10.61 | 26.44 | 42.15 | 57.47 |
| 550 | 0.76 | 2.18 | 3.45 | 6.82 | 19.13 | 31.63 | 41.16 |
| 600 | 0.49 | 1.39 | 2.26 | 4.52 | 13.77 | 23.10 | 31.43 |
| 650 | 0.33 | 0.96 | 1.53 | 3.11 | 9.92 | 16.02 | 20.70 |
| 700 | 0.23 | 0.68 | 1.05 | 2.18 | 7.28 | 12.60 | 12.87 |

Source: From A. T. Larson and R. L. Dodge (1923). Journal of the American Chemical Society, 45:2918; and A. T. Larson, Ibid. (1924), 46:367-72.

The reaction does not go to completion; equilibrium conditions are such that increase in pressure favors high conversion to ammonia, while increased temperature decreases conversion as shown in table 1(2). Thus it is possible to obtain about 90% conversion at 300 atm and 200° C. However, at the same pressure but at 700 °C, equilibrium conversion is only 7.3%. At a constant temperature of 450°C, conversion increases from 2.1% at 10 atm to 35.8% at 300 atm and 69.7% at 1,000 atm. However, the rate of reaction is very slow at 200 °C and increases with temperature, thus, a compromise must be selected between reaction rate and equilibrium values. The search for a catalyst to increase the reaction rate has received much attention both by Haber and subsequent investigators. Haber's first studies were made with an iron catalyst, which was not very active. Later, he found that osmium or uranium was much more effective, but these elements were scarce and expensive. Still later (about 1911) it was found that certain impurities increased the activity of an iron catalyst. After several thousand formulas had been tested, a doubly promoted iron catalyst was selected that was produced from magnetite ($Fe_3O_4$) with additions of potassium, alumina, and calcium. (The magnetite is reduced to metallic iron by the hydrogen during the operation.) This type of catalyst is still the standard material in present use with some refinements with promoters. A fundamentally different low temperature synthesis catalyst which consist of ruthenium deposited on an active carbon support, promoted by barium, and alkali metal preferably Cesium has been developed. This catalyst is claimed to be 10 to 25 times more active than the conventional ammonia synthesis catalyst. This catalyst allows a successful operation in the range of 320-470 C and at a pressure of 70-100 atmosphere. This type of catalyst is now being used by Kellogg and ICI.(37)

Even with the best catalysts available, the reaction rate is a limiting factor, and compromise must be reached between long retention time which would require a large, expensive converter and conversion efficiency. the usual compromise results in a conversion equivalent to 70%-80% of equilibrium. Since equilibrium under usual operating conditions may correspond to 25%-35% conversion, the actual may be 17%-28%, for example.

In order to improve conversion, Haber originated the concept of the ammonia synthesis loop, in which the gas leaving the converter is cooled to condense most of the ammonia as a liquid which is removed from the gas. Then the remaining gas (unreacted $N_2$ and $H_2$) is reheated and returned to the synthesis converter with fresh synthesis gas. He also recognized that much of the cooling could be done by heat exchange between the cool gas entering the converter and the hot gas leaving it.

Thus, the basic principles of the ammonia synthesis process were well known to Haber and his co-workers and serve as the basis of the modern ammonia production industry.

Data from the Haber Bosch work did not become available outside Germany or outside their company (BASF) for many years because of company secrecy and the 1914-18 war. A Haber process plant built during the war at Sheffield, Alabama, U.S.A., by U.S. Army Ordnance was based on information obtained by U.S. Intelligence. However , the information on the ammonia synthesis catalyst was not complete, and the plant did not operate (3). After the war, the U.S. Government established the Fixed Nitrogen Research Laboratory to develop the necessary technology, and in 1921 the first synthetic ammonia plant was built in the United States by the Atmospheric Nitrogen Corp., Now Allied Chemical Co. By 1932 there were 10 ammonia plants in the United States with a total design capacity of 287,000 tons of N per year.

During the early years of World War II, the U.S. Government realized that, if the United States became involved in the war, its fixed nitrogen supply would be inadequate to meet the demand for munitions. As a result, 10 more plants were built with a total N capacity of 595,000 tpy. During the late years of the war and the years following, the output of these plants was diverted to fertilizer, primarily ammonium nitrate. The demand for fertilizer increased rapidly, and by 1965 there were 53 plants in the United States with an estimated annual capacity of 3.8 million tons of N. Major improvements in ammonia production technolog, were (1) the use of natural gas or naphtha as feedstock in the late 1940s and 1950s and (2) the development of centrifugal compressors in the 1960s. These developments, in combination with increased scale, progressively lowered the cost of ammonia and of nitrogen fertilizer. In 1974 world production capacity was estimated at 62.5 million tons, in 1991, the world capacity had increased to 112.3 million metric ton and forecast capacity after 1996 is 137.308 million metric tons of N.(38)

Most of the plants built before 1945 were based on coke. In the original Haber process coke was used in a water-gas generator which operated in a cycle of "blow" and "make". In the blow cycle the coke was burned with air until the temperature of the coke was increased to a suitable level (above 1000 °C). Then the air was turned off and steam was blown through the hot coke bed forming CO and $H_2$ by the water-gas reaction:

$$C + H_2O \cdots\cdots \quad H_2 + CO$$
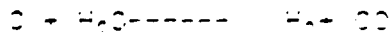
The reaction is endothermic and quickly cools the coke bed to the point that it must be reheated by another blow cycle.The "make" gas typically contained 50% $H_2$, 40% CO, 5% $N_2$, and 5% $CO_2$. To provide the necessary nitrogen separate gas producers which also used coke were blown continuously with air to obtain producer gas containing 62% $N_2$, 32% CO, 4% $H_2$, and 2% $CO_2$. The two gases were collected separately in gas holders and mixed in the proper proportions to give an $N_2$: $H_2$ ratio of 1:3 in the final synthesis gas. As an alternative, the gas producer could be blown continuously with a mixture of oxygen-enriched air and steam to produce gas of the desired composition. In some later plants, such as the TVA plant built in 1942, a semi water gas process was used in which the "make" gas was partially oxidized with secondary air thus obviating the need for separate air-blown gas producers. In this case the "make" gas contained 36.3% $H_2$, 21.8% $N_2$, 36.2% CO, and 5.5% $CO_2$. The nitrogen content could be adjusted to that stoichiometrically required by adding some of the blow gas. Extensive cleaning of the gas was required to remove dust, sulfur, and other impurities. The gas was compressed in several stages with purification steps in between. The first step was the "shift reaction" of conversion of CO and steam to $H_2$ and $CO_2$.

$$CO + H_2O ----> H_2 + CO_2$$
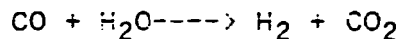
The next step was $CO_2$ removal at about 25 atm by water scrubbing. A third step was removal of residual CO by scrubbing with "copper liquor" (copper acetate and formate solution) typically at about 200 atm. The final stage was the ammonia synthesis step described previously, which was carried out at various pressures from 200 to 1,000 atm, depending on the process.

The total energy consumed by the coke-based process for fuel, feedstock, and mechanical energy was 88 Gj per ton of $NH_3$ as compared with about 27-30 GJ/ton for modern natural gas plant. The labour requirement was about 1800 men versus 60 for the modern plant.a.

Direct use of coal or lignite as feedstock was begun as early as 1926 using the Winkler gasifier. Partial oxidation of heavy fuel oil was developed, and steam reforming of natural gas and light hydrocarbons was used commercially in 1940 but did not become popular until the 1950s. At present, steam reforming of natural gas and naphtha is estimated to account for over 80% of all ammonia production. Some other feedstocks such as liquefied petroleum gas (LPG) and refinery tail gas are treated by steam reforming; therefore, the total ammonia production by this method may be as much as 85%. The great majority of new ammonia plants that are planned or are under construction will use natural gas; therefore , the short-term trend will be toward greater

use of this feedstock.Natural Gas supplies are higher now than ever before. China and to some extent India are the only countries using other than natural gas for ammonia

The technological improvements mentioned above and other improvements too numerous to mention, coupled with increase in scale, have resulted in a steady decline in ammonia production cost from over $200 ton in 1940 to about $30/ton in 1972. After 1972 the trend was reversed and costs have risen, mainly because of increased cost of feedstocks and a sharp increase in plant construction cost. The increased construction cost was caused primarily by increased material and labor costs and partly by more complicated heat and energy recovery equipment which became necessary to conserve expensive fuel. More stringent pollution control regulations also were a factor.

Before the change in the energy prices in 1973, the energy efficiency of ammonia plant was not considered very important after the energy crises, the fuel prices have increased to a much higher level. For example in the united states in 1960s 80% of ammonia production cost were capital related now 70% is the gas cost alone, the proportion is even greater is Europe. Thus the technological improvement which occurred from early 1970 until today emphasized greatly on improving the existing conventional processes to obtain a better efficiency. Today's ammonia plants claim to consume energy between the range of 27-30 GJ/ton . Minor economics which were possible by increase in the scale above 1000-1200 tpd were also tried. In Canada, Germany, Russia and USA, plants with rated capacity above 1600 tpd are in operation. Designs are available for 2000 tpd plants but their economics at present are doubtful.

Further technological improvements are expected, but none are foreseen of such a magnitude as to reverse the present upward cost trend due to rising fuel, feedstock, and construction costs.may be in future one 2000 tpd zoo mid $NH_3$ plant becomes more economical than two 1000 mtd plants.

## Steam Reforming Processes

### Thermochemical Data

Since steam reforming processes account for over 90% of the world's ammonia production, this type of process will be described in more detail than the others. Figure 1 is a block flow chart of the steam-reforming process using natural gas as feed stock It shows the principal chemical reactions and typical pressure levels. The overall approximate chemical reaction may be written.

$$7CH_4 + 10H_2O + 8N_2 - 20_2----- 16NH_3 + 7CO_2$$
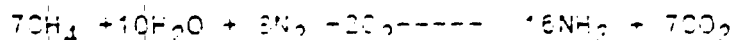
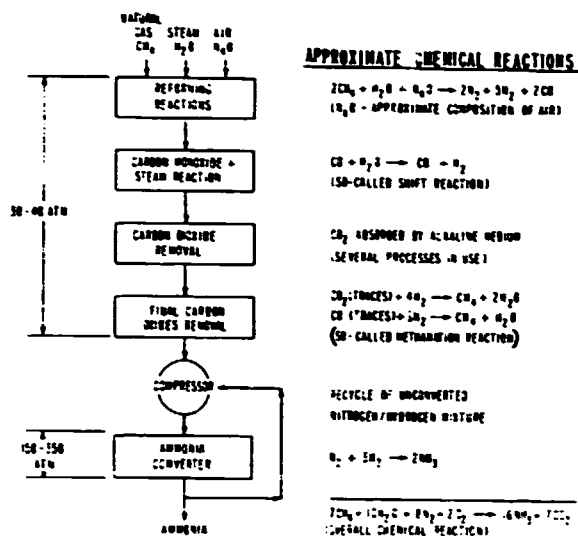## FLOW CHART OF AMMONIA SYNTHESIS
### (STEAM REFORMING OF NATURAL GAS)



Figure-1:Flow chart of ammnia synthesis(Steam reforming of natural gas.)

Using the standard heats of formation, the heat of the overall reaction may be calculated as follows:

| Reactants | kcal/g mole | | kcal, Total for Above Equation |
|---|---|---|---|
| $CH_4(g)$ | -17.89 x 7 | = | -125.23 |
| $H_2O(1)$ | -68.32 x 10 | = | -683.20 |
| $N_2(g)$ | 0 | | 0 |
| $O_2(g)$ | 0 | | 0 |
| Total reactants | | | -808.43 |
| **Products** | | | |
| $NH_3(1)$ | -16.06 x 16 | | -259.96 |
| $CO_2(g)$ | -94.05 x 7 | | -658.35 |
| Total products | | | -918.31 |
| Net heat of reaction | | | -109.88 |

Thus, the overall reaction is exothermic to the extent of about 110 kcal for the equation shown above, assuming $NH_3$ in the liquid state or about 30 kcal for $NH_3$ in the gaseous state. Since the reaction, as written, produces 17 x 16=272 g of ammonia, the net heat released by the reaction amounts to about 404,000 kcal/ton of liquid ammonia or 110,000 kcal/ton of gaseous ammonia. At first thought, this may seem contrary to the general conception that ammonia production consumes a tremendous amount of heat. However, if the large amount ( 7 g-moles) of $CH_4$ were burned to $CO_2$ and $H_2O$, about 1,543 kcal (LHV) would be released which is equivalent to about 5 million kcal/ton of $NH_3$ (about 21 GJ/t). Therefore, production of ammonia consumes energy in the sense that t

uses as feedstock a material that could other-wise be used as fuel.

The various steps of ammonia production are carried out at different temperature levels ranging from 0 to 1200 $^{\circ}C$; thus, fuel must be used to heat the reactants. While much of the heat is recovered, substantial portion is lost. As a result, natural gas based conventional ammonia plants with the most efficient heat recovery systems require about 8.6 million kcal (36 GJ) for fuel and feedstock (6). This requirement is based on the low heating value (LHV) of methane, which does not include the heat of condensation of water vapor that is formed in the combustion of methane. In addition, a substantial amount of electrical energy is required (20-50 kWH/ton) even though most of the mechanical energy is supplied by turbines driven by steam that is generated by the heat recovery in the process. Today's ammonia plant is said to be a state of art optimized plant which includes a number of energy optimization steps. The total energy consumption of a today's ammonia plant is around 6.92-7.2mkcal Or 29-30 GJ/ton of ammonia which includes the mechanical power also. Table 2 shown typical temperature levels in the steps of $NH_3$ production by steam reforming of natural gas, the main reaction occurring in each step. and the standard heats of the reactions. It will be noted that all the reactions are exothermic except the steam reforming of methane.

Table-2, Chemical Reactions, Temperatures, and Heat of Reaction in Production of Ammonia from Methane.

| Step | Reaction | Typical Temp., °C | $\Delta H^{\circ}$, kJ/g-mole [a] |
|---|---|---|---|
| Steam reforming [b] | $CH_4 + H_2O = CO + 3H_2$ | 790-820 | +206.2 |
| Secondary reforming [b,c] | $CH_4 + 1/2O_2 + (2N_2) = CO + 2H_2 + (2N_2)$ | 900-1200 | -35.6 |
| Shift reaction | $CO + H_2O = CO_2 + H_2$ | 200-450 | -91.8 |
| Carbon dioxide removal | (Physical separation) | 70-105 | - |
| Methanation | $CO + 3H_2 = CH_4 + H_2O$<br>$CO_2 + 4H_2 = CH_4 + 2H_2O$ | 250-450 | -206.2<br>-165.0 |
| Ammonia synthesis | $3H_2 + N_2 = 2NH_3$ | 300-500 | -91.8 |
| Ammonia condensation | $NH_{3(gas)} = NH_{3(liquid)}$ | 30 to -30 | -21.0 |

a. Heat of reaction taken from reference (1); + sign indicates heat absorbed; - sign indicates heat released. To convert to kcal, multiply by 0.239.
b. For simplicity, a single reaction is shown for the reformer step which represents the predominant net reaction. However, the chemistry is much more complex. In particular, a significant amount of $CO_2$ is formed in these steps.
c. Completion of reaction 1 also takes place in secondary reforming.

Thus, there is a wide difference in temperature level for the various steps. Therefore, heat-exchange equipment

comprises a large proportion of the ammonia plant cost.

## Feedstocks for Steam-Reforming Process

Natural Gas:  As mentioned previously, natural gas is the principal feedstock for ammonia production; it currently accounts for over 75% of the world's ammonia production (6). Natural gas is classified as "associated" or non-associated".  Associated gas occurs with crude oil, it is liberated from the oil when the pressure is released in the oil-gas separator plant.  Its composition varies with the pressure at which the separator is operated.  Since methane is the most volatile, it can be released at a relatively high pressure, a separation can be made in which methane is released first and the less volatile gases, ethane, butane, and propane, are collected separately.

The higher hydrocarbons usually have a higher value for petrochemical production or for sale as liquified petroleum gas (LPG) than methane.  Therefore, in most cases, these products are sold separately, and the term "natural gas" usually refers to the fraction that contains mostly methane with only small percentages of ethane and higher hydrocarbons.  For use as ammonia feedstock, methane is preferable to the higher hydrocarbons since all carbon in the feedstock is converted to carbon dioxide or monoxide which must be removed from the ammonia synthesis gas. Therefore, the lower the carbon:hydrogen ratio in the feedstock, the smaller and less expensive the purification units in the synthesis gas preparation will be.

In ammonia-urea complexes, where all of the ammonia is used to make urea, the amount of $CO_2$ derived from methane feedstocks may not be sufficient for the urea plant needs. Urea requires a $CO_2$:$NH_3$ ratio of 1:2 whereas, the production of ammonia by reforming pure methane produces a $CO_2$:$NH_3$ ratio of 7:16 according to the approximate equation given earlier.  In this case it would be advantageous if the natural gas contained enough higher hydrocarbons to supply enough $CO_2$ for urea production. This is often the case as shown by the example of natural gas composition given in table-3.

TABLE 3.  COMPOSITION OF TYPICAL NATURAL GAS

| Constituent | % by Volume | |
| --- | --- | --- |
| | At Well-Head | As Delivered by Pipeline |
| $CH_4$ | 75.9 | 93.3 |
| $N_2$ | | 2.0 |
| Argon | | 0.4 |
| $CO_2$ | 7.3 | 0.01 |
| $H_2S$ | 8.9 | <5 ppm |
| Hydrocarbons | | |
| $C_2H_6$ | 3.3 | 3.3 |
| $C_3H_8$ | 1.2 | 0.9 |
| $C_4H_{10}$ | 0.8 | 0.2 |
| $C_5H_{12}$ | 0.5 | 0.01 |
| $C_6H_{14}+$ | 2.3 | |

As an alternative, extra $CO_2$ can be obtained from stack gas
during the combustion of fuel in the reformer furnace, but
this alternative is relatively expensive.Another way to
balance $CO_2$ is to burn about 5% of the gas after the $CO_2$
absorber.(i.e to reformer fuel) Result is a small loss in
efficiency but a balanced plant.

In the past, associated natural gas has often been regarded
as an unwelcome byproduct of petroleum production, and this
is still the case in some countries where there is no means
for economical recovery or use. In such cases the gas may be
pumped back into the oil-bearing formation to "pressurize"
it an, thus, augment the flow of oil, or it may be "flared",
i.e. wasted by burning in open air.The amount of natural gas
that is flared is substantial.  Efforts are being made to
utilize it by establishing ammonia, methanol, or other
petrochemical plants or energy-intensive industries such as
aluminium production  or by liquefying the gas for shipment.
However, these efforts involve much time and capital and
often entail enormous difficulties because of the remote
locations and hostile environments ranging from deserts
and tropical jungles to arctic regions.

Both associated and non-associated natural gases vary widely
in composition; the example in table 3 is only an
illustration. Gas from some non-associated deposits may be
nearly pure methane.  In other deposits gas may contain
higher percentages of $H_2S$, $CO_2$ or both.  Other usually
minor, constituents are $N_2$ and sometimes He (helium).  The
$CO_2$ and $H_2S$ usually are removed by scrubbing before delivery
by pipeline to the point of combustion or its use, the $H_2S$
made to by its elemental sulfur which may be a byproduct
typically of some acid.

## Methane from Sources Other than Natural Gas

Obviously methane from any source could be used as feedstock
for ammonia production; some of these sources have been
mentioned in chapter V.  One promising source is anaerobic
decomposition of waste organic material or of "biogas"
(vegetable cellulosic materials) such as forest waste or
vegetative crops. Anaerobic fermentation produces a gas
containing about 55% CH4; the remainder is mainly $CO_2$ which
can be readily removed by scrubbing with monoethanolamine
(MEA) or other solvents.  In several cases, methane from
these sources is sold to natural gas pipeline distributors
for mixing with natural gas at prices ranging from $3.00-
$5.00/1,000 std (300-667/1,000m3). It has been estimated
that methane from such sources could supply a significant
percentage of present and probable future ammonia needs. In most of the
projects the cost presumably is partially borne by waste

disposal, but by some estimates biogas produced from vegetative crops would be competitive or cheaper than alternate ammonia feedstocks such as coal or naphtha. Methane is produced in many small bio-gas pits in India; in China it is reported that over 400,000 marsh gas pits produce methane from night soil, grass, stalks, waste water, garbage, etc(9). The methane is used for rural cooking and for some industrial uses such as fuel for small cement plants, fuel to drive water pumps, etc. While it is not known to be used for ammonia production, obviously the gas could be used for this purpose if enough gas could be collected at one location for an economical scale of operation. In this connection, it has been estimated that 5 million ft3/day (142,000 m3/day) of crude gas containing about 60% methane can be collected from a sanitary landfill at Mountain view, California, for 6-10 years (7). No doubt, urban waste from larger cities could be used to generate enough methane for even a 1,000 tpd ammonia plant.

Processes are now available for partial oxidation of solid waste under pressure with oxygen. Result is more efficient in time and space than other routes to syngas. However, much development work is needed to establish the technical and economic feasibility of large-scale production of methane from urban waste and to dispose of the residual which can be useful for fertilizer.

Liquefied Petroleum Gas-LPG which contains mainly butane and propane has been used as ammonia feedstock in Japan. Liquefied natural gas (LNG) also is used in Japan. These materials are relatively expensive and are not much better than naphtha.

Synthetic natural gas (SNG) is practically pure methane produced from coal. It was tried in U S A but proved to be a disaster. It is much economical to use coal direct. even a coke oven gas generation plant is more economical

Naphtha: In those areas of the world where natural gas is unavailable, naphtha became a favored feedstock for ammonia production by steam reforming, particularly in the period of 1960-74 when naphtha was relatively cheap. In many countries the amount of naphtha produced in oil refining exceeded the demand. Naphtha is the lighter fraction of hydrocarbons, boiling from about 40 deg.C to 130 deg.C with an average molecular weight of about 88 and an H:C atomic ratio of about 2.20. Straight-run naphtha is preferred to naphtha produced from higher hydrocarbons by cracking or hydrocracking because the latter usually contains sulfur compounds that are difficult to remove. The composition and properties of a typical naphtha are given in Table-4

Table-4. Composition and Properties of typical Naphtha.

| Constituent or Property | Average Value |
|---|---|
| Specific gravity at 15.5°C | 0.686 |
| Initial boiling point, °C | 41 |
| Final boiling point, °C | 131 |
| Unsaturates, % (volume) | 1 |
| Aromatics, % (volume) | 4 |
| Saturates, % (volume) | 95 |
| Total sulfur as (ppm by wt) | 368 |
| $H_2S$ | 2 |
| RSH | 146 |
| $R_2S_2$ | 119 |
| $R_2S$ | 80 |
| S | 1 |
| Unreactive S | 20 |
| C, % | 84.4 |
| H, % | 15.7 |
| Mol wt | 88 |
| Heating value, kcal kg | 10,500 |

Since 1974 the price of naphtha on the world market has risen more rapidly than that of other feedstocks because of the demand for naphtha for use in the manufacture of motor fuel and petrochemicals (ethylene, propylene, etc.) Therefore, several plants original designed to use naphtha have switched to other feedstocks such as natural gas, LNG, or LPG. Where other feedstocks are not available, these plants are being shutdown In the word 59% of the total world's ammonia production is based on naphtha and condensate.

The process for steam reforming of naphtha was developed mainly by Imperial Chemical Industries (ICI) in England and has been widely used in Europe, Japan, and many developing countries. The main technical problem was to avoid carbon formation on the reforming catalyst without excessive steam consumption. This problem has been solved by modifications of the catalyst composition.

**Refinery Gases:** Petroleum refineries and petrochemical operations produce a variety of byproduct gases that can be used as fuel or feedstock or both. The composition of refinery tail gas varied widely, it usually contains $H_2$ $CH_4$, and higher hydrocarbons and can be used as ammonia feedstock by steam reforming. The amount of tail gas available is likely to be insufficient for an economical scale of ammonia production unless the refinery is a very large one. Another drawback is that the volume and composition of the tail gas may very according to the demand for the various refinery products, and these variations can cause difficulties in the ammonia plant operation. Also, refineries often have a use for the components of the tail gas. For instance, the hydrogen can be separated and used in hydrogenating and cracking heavier fractions.

In the production of ethylene (by cracking naphtha), a byproduct gas stream containing mainly methane and hydrogen is produced. Several other petrochemical processes produce byproduct gases that are usable as ammonia feedstock either by steam reforming or cryogenic separation of hydrogen.

Only a few ammonia plants in Europe and Japan use refinery tail gas.

Coke-Oven Gas--Coke--oven gas contains about 55% $H_2$, 25% $CH_4$, 8% CO, 6% $N_2$, plus minor amounts of higher hydrocarbons, $CO_2$, and various impurities. Presumably, it could be used for ammonia production by steam reforming after purification, but the usual practice is to separate the hydrogen by a cryogenic process involving a liquid nitrogen wash. Many steel producing plants have an air separation unit to supply oxygen for use in steel production, thus the liquid nitrogen is available from this source. The cryogenic process produces a nitrogen-hydrogen gas mixture suitable for ammonia synthesis, and the remaining gas mixture of CO, $CH_4$, and heavier hydrocarbons is used as fuel. The main drawback is similar to that of refinery tail gas, the amount of coke-oven gas depends on coke production which, in turn, depends on steel production. Only a few plants use coke-oven gas for feedstock.

China still produces much ammonia from coke oven gas. Steam reforming (Primary plus secondary) or oxygen enriched air secondary reforming are both reasonable alternates to the cryogenic system.

Heavy Oil--Liquid hydrocarbons heavier than naphtha are used for ammonia feedstock by partial oxidation processes which will be discussed in a later section of this chapter. However, there has been some interest in applying the steam-reforming process, and Toyo Engineering Corp. has reported successful development on a pilot plant scale (10) the successful operation of the Pilot plant was reported when using crude oil from several sources or heavy residual oil by Toyo Engineering Corporation. Little detail is available about the process, but it involves use of two newly developed catalysts in the primary and secondary reformer. Both catalysts are unaffected by sulfur. The primary reformer catalyst is effective in reforming the methane remaining in the gas from the first reformer. The gas from the reformers still contains all of the sulfur (as $H_2S$) that was present in the feedstock, which would have to be removed in a subsequent purification step as in partial oxidation processes. Potential advantages of the process compared with partial oxidation processes are lower investment cost (an air separation plant is not required) and lower energy consumption.

**Other Feedstocks**--Methanol or ethanol can be used as feedstock in steam reforming processes, but no commercial use has been reported. Other feedstocks such as electrolytic hydrogen, coal, and fuel oil will be discussed separately under applicable process headings. Total ammonia production through other sources are around 2.4%.

**Feedstock prices**-- Prices of feedstocks are often controlled by governments. The price of crude oil on the world market is controlled by the Organization of Petroleum Exporting Countries (OPEC). and the world market price of crude oil derivatives such as naphtha is indirectly controlled by the prices of crude oil. The domestic prices of crude oil and naphtha in oil-producing countries are often controlled by the governments at a lower level than world market prices. Even in oil-importing countries, governments may exercise control of feedstocks such as naphtha by subsidizing refinery operations.

Natural gas prices vary largely depending upon the quality, transport distance amount and pattern of use. Generally plants are located in the gas-producing areas as the gas transportation costs are generally much higher comparing to the finished fertilizer transportation cost. Natural gas prices in the United States as of July, 1978 were controlled at a maximum of $1.43/ 1,000 ft3 ($50.53/1,000 m3). This was the price for gas from new sources delivered to an interstate pipeline. The price of gas delivered to customers via interstate pipeline was also controlled and varied depending on the mix of "old" and "new" gas, transport distance, amount and pattern of use, and whether the contract was for "firm" or "interruptible" gas. Even "firm" gas was subject to curtailment when the supply was not adequate. The interstate price control was lifted before 1980. The result was rise in price to as much as $5.00/MMBTU and then exploration through deeper wells produced much more gas which lowered the price . The price is now approaching $1,00/MMBTU.

Natural gas prices in some European gas producing countries may be $0.80/1,000 ft₃ ($23/ 1,000 m₃). Prices in some developing countries that have ample supplies of natural gas reportedly range from $0.20 to $0.60/1,000 ft₃ ($5.66-$16.98/1,000 m₃) depending on cost of collection and purification, length of pipeline transport, and government policy.

Heavy fuel oil in oil-importing countries may be priced somewhat below crude oil at the refinery, particularly in the case of high-sulfur oil that cannot be used for fuel without expensive pollution control.
European gas prices require investigation. Russain supplies have been unreliable causing prices to rise recently.

The price of coal varies widely depending on its quality, cost of mining, and transport cost.

**Feedstock Requirements:** In nearly all ammonia plants the same material is used as both feedstock and fuel. The fuel requirements may be 40% of the total or more, depending on the extent to which heat recovery equipment is utilized. In previous years when fuel was inexpensive, many ammonia plants were built with minimum heat recovery facilities. Buivadas, et al., give an example of how the fuel requirement (natural gas) was decreased by 34% through more efficient energy use, mainly high-pressure steam generation and preheating combustion air to the reformers (13). The decrease in total fuel plus feedstock requirement was about 15%. The increase in fuel efficiency was obtained at the expense of about 6% increase in plant investment cost.

Thermal efficiency has become a key parameter in comparing (and marketing) processes, possibly achieving exaggerated importance in some instances. However, thermal efficiency is an important concept, despite its publicity emphasis. Unfortunately, its definition is not standardized between various operators, designers, and process licensors. What appears to be the most common definitions for the purposes of this study, has been set out in the following table.

DEFINITION OF THERMAL INPUT AND CREDITS FOR AMMONIA PLANTS

Heat value of input and output per metric ton of ammonia

| Input or out put | Definition of thermal value |
|---|---|
| Feed and fuel | Lower (net) calorific (heating) values (LHV) based on combustion starting and ending at 20 DEG.C with product water as vapor. |
| Electric power required- assuming | Thermal value (LHV basis) of fuel required at modern power station, 34% overall efficiency (i.e. 10,586 KJ/ kWh, 10,040 Btu/kWh |
| Steam | table values (i.e. enthalpy excess over liquid water at 0 deg.C) |

The above table is based on published estimates of thermal efficiencies ( i.e net energy consumptions as defined above and allowing for power import and steam export) for the major feedstocks. Also included are indicative estimates of battery limits capital costs U.S. Gulf Coast, prepared sites with good access and load bearing characteristics, 1990 basis) for 1,000 metric ton per day ammonia production

capacity plants, except anthracite-based plants. It is assumed in all cases that the ammonia is produced as liquid at 33 deg.C and atmospheric pressure.

COST AND THERMAL EFFICIENCIES OF AMMONIA PLANTS
    Based on various feedstocks
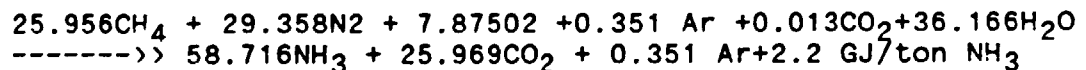
| Feedstock and process route (modern design) | BLCC[1] Mill $ | Overall Thermal Efficiency | |
|---|---|---|---|
| | | Gcal/t $NH_3$ | GJ/T $NH_3$ |
| Anthracite or coke[2], cyclic gasifier | | 13.32 | 55.7 |
| Coal, partial oxidation | 200 | 10.33 | 43.2 |
| Fuel oil, partial oxidation | 150 | 9.70 | 40.6 |
| Naphtha steam reforming[3] | 115 | 7.65 | 32.0 |
| Natural gas, steam reforming | - | 8.70 | 36.4 |

(1) Battery limits capital costs
(2) These cyclic processes are obsolete, except in China
(3) This performance refers to 1970s technology.


A theoretical minimum possible feed energy consumption for the entire process is not easily defined. One simple approach is to imagine an ideal (exothermic) overall reaction , with no recovery losses or purge losses, which reacts methane, air, and steam to give ammonia, carbon dioxide , and argon as products at for instance, 400 deg.C. This could be written in kg mol.

$$25.956CH_4 + 29.358N2 + 7.87502 +0.351 Ar +0.013CO_2+36.166H_2O$$
$$------>> 58.716NH_3 + 25.969CO_2 + 0.351 Ar+2.2 GJ/ton NH_3$$

The corresponding thermal value (LHV) of natural gas feed is 20.8 GJ/ton ammonia, 4.97 Gcal/ton ammonia. If the exothermic overall heat of reaction can be credited, this leaves 18.6 GJ/Ton ammonia. 4.45 Gcal/ton ammonia, as the theoretical absolute minimum. The literature reports various values, without always detailing the calculation basis. Lavers(6) gives 17.4 GJ/ton theoretical minimum, 22.8 GJ/ton as a practical minimum Dybkjaer(7) suggests minimum process feedstock energy of 20.9 GJ/Ton ammonia, with a practical minimum feedstock energy of approximately 22 GJ/ton ammonia. To this must be added the fuel required for primary reforming and feedstock heating ( and or additional feedstock for "internal combustion," if fuel firing of the primary reformer is reduced or abandoned). There are also

significant energy demands for compression, refrigeration, fans, cooling water, and the recovery of carbon dioxide.

The conclusions are:

o    Processes using steam reforming of hydrocarbons plus Haber-Bosch ammonia synthesis are now approaching the practical limits of energy conservation at approximately 27 GJ/ton ammonia.

o    The total energy used for partial oxidation routes, based on heavy fuel oil or coal, will always require at least a 40 percent increase in total energy consumption when compared to the best steam reformer designs.

o    Lower energy efficiency and the increase in fixed investment of at least 50 percent make a large cost advantage necessary for heavy fuel oil or coal in order to justify its use compared to natural gas. A rough calculation indicates that vacuum residual oil would need to be available at 9.24 cents/gallon ($25/metric ton or 61.4 cents/MMBtu HHV) to compete with natural gas at $2.50 MMBtu (HHV) for the production of 1,000 metric tons per day of ammonia in a new plant. In the United States, vacuum residue is sold at approximately three times this price!.

In a natural gas based plant 34% of the gas is used for fuel and 66% for feedstock; in a naphtha-based plant about 38% of the naphtha is used for fuel and 62% for feedstock (13). These values are for plants equipped with good energy recovery systems. Fuel requirements do not include electric power generation or steam generation other than that connected with heat recovery. Modern ammonia plants are self-sufficient in steam supply, and much of the mechanical power is supplied by steam rather than electricity. However, in developing countries, a captive electric generating plant usually is considered essential for a dependable supply of electricity. A good indicator of increased efficiency in ammonia production is the reformer stack temperature previously about 260 $^{\circ}$C it now approaches 100 $^{\circ}$C as more heat is recovered from less stack gas.
Also, if a urea plant is associated with the ammonia plant, additional fuel will be required to supply the steam needed for urea production. Therefore, total fuel requirements may be larger than those mentioned above.

When a high-cost feedstock is used for ammonia production, it may be advantageous to use a lower-cost fuel for heating and for producing steam and electricity. Likewise, when the supply of feedstock (such as natural gas ) is inadequate for both fuel and feedstock, a different material may be used as fuel. Several plants in the United States that use natural gas feedstock are equipped to use a light fuel oil for

heating the reformer. In cases where fuel oil is more expensive than natural gas, the fuel oil system may be used only when the natural gas supply is limited.

Use of heavy oil or coal for fuel could be considered for plants using expensive or scarce feedstocks. However, these fuels cannot be used to heat reformer furnaces unless some extensive modifications are made. Impurities in heavy oil or coal would adversely affect the reformer tubes by causing corrosion or erosion unless design modifications were made. Deane and Browne have described a naphtha based flowsheet in which a non premium fuel is used for preheating the feedstock and the air to the secondary reformer (14). Obviously, there would be no technical problem in using coal for steam and electric power in units designed for that purpose. Direct use of coal for heating the reformer furnace would present serious difficulties, but indirect use such as byproduct gas derived from coal may be technically and economically feasible in some cases.

### Technology of Steam-Reforming Process

A simplified flow diagram for production of ammonia by steam reforming natural gas or naphtha is shown in figure 2. In the following discussion, each of the steps will be discussed in the sequence in which they occur.
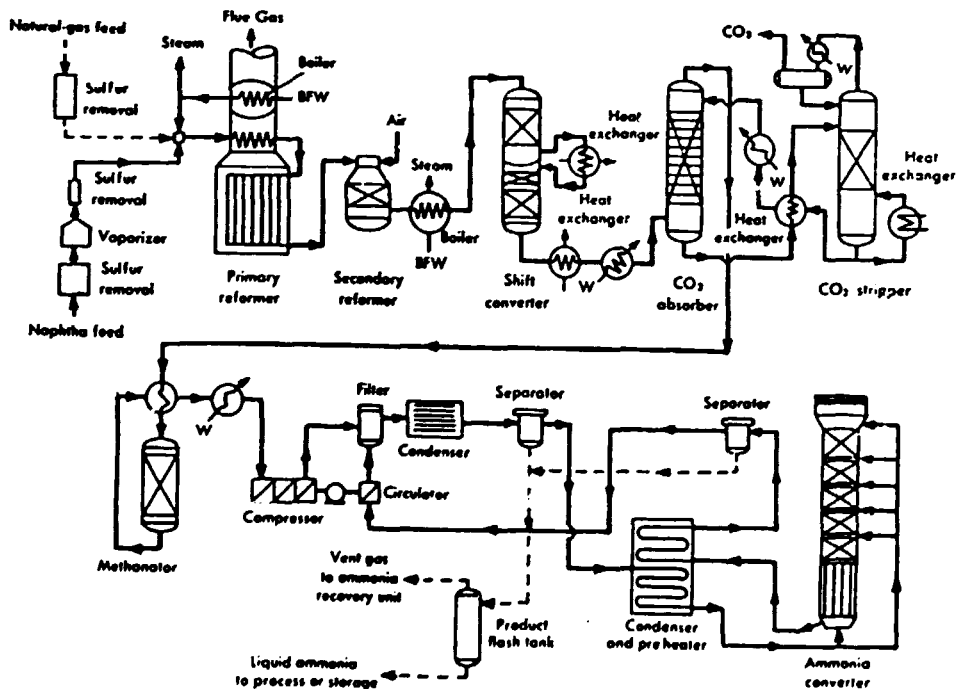


Figure-2 Flow Diagram for Production of Ammonia by Steam Reforming Process

**Feedstock Preparation:** As mentioned previously, most natural gas requires some purification, particularly the removal of $CO_2$ and $H_2S$, which may be done by the natural gas producer if the gas is transmitted by pipeline. If the gas is taken directly from wellheads, the user (ammonia producer) may have to purify the gas. Depending on the source, natural gas may contain entrained dust or droplets of liquid (oil or water) which should be removed by separators, filters, etc.

After the initial purification, natural gas is compressed to reformer pressure, if not already at that pressure, and preheated. Then, any remaining sulfur is removed to avoid poisoning of catalysts. The sulfur may be removed by adsorption on activated carbon at ambient temperature or by absorption by hot zinc oxide (290-400 $^O$C) after the gas has been preheated.

$$ZnO + H_2O ---- Zns + H_2O$$
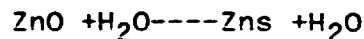
The spent adsorbent is regenerated by stripping with steam or hot gases. In some cases both treatments may be used. Some natural gas particularly associated with offshore reserves may contain significant amounts of chlorides which can poison catalysts particularly the low-temperature shift catalyst. Catalysts or absorbents are available for removal of chlorides. Quartulli describes a pretreatment system for removal of both chloride and sulfur from natural gas or naphtha (figure 3) (15).
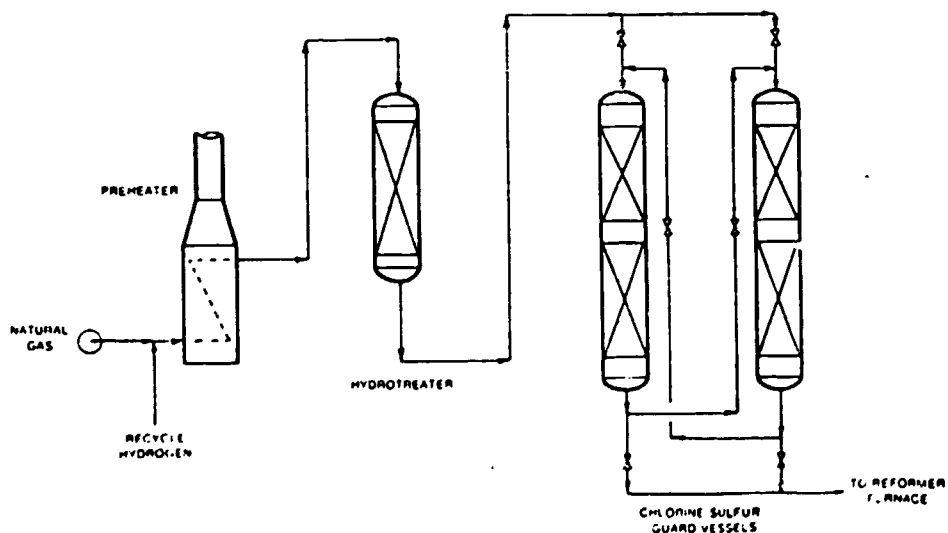


Figure 3. Natural Gas Treating System for Chlorine and Sulfur Removal.

Figure-3. Natural Gas treating System for Chlorine and sulfur removal

The preheated gas or vaporized naphtha is mixed with a small amount of hydrogen (recycled synthesis gas) and passed through a "hydrotreater" containing a catalyst which converts sulfur compounds to $H_2S$ and chlorides to HCl. The catalyst has a nickel molybdenum or cobalt-molybdenum composition. The hydrotreated feedstock is then passed through one or more guard vessels containing layers of chloride removal catalyst (a copper-based material)and sulfur removal catalyst (zinc oxide) This system will effectively remove sulfur in "nonreactive" forms (such as thiophenes) which cannot be removed by zinc oxide without hydro-treating. Molybdenum based catalysts can also be used to hydrogenate olifines that may be present in some natural gases whereas olifines are not catalyst poisons in the strictest define that may can crack or polymerize at high reforming temperature, blocking the active catalysts sites. The ollifines also get removed through hydrotreating.

Since naphtha usually contains unreactive sulfur, hydrotreating or hydrodesulfurization is commonly used in naphtha-based plants. The catalysts (absorbents) used in the guard beds are expensive and cannot be regenerated. Therefore. if the feedstock contains much sulfur or chloride, some means for removing most of these impurities as a pretreatment should be considered. In the case of natural gas, absorption in an alkaline solvent such as monoethanolamine or potassium carbonate, which can be regenerated. is commonly used for removing most of the sulfur.

Sulfur and chlorides (and other catalyst poisons) can enter the ammonia plant in the steam or in the air to the secondary reformer; thus precautions should be taken to eliminate such impurities insofar as is practical. In addition, a layer of guard absorbent may be placed on top of the catalyst, particularly in the case of the low-temperature shift catalyst.

Some natural gases have also been found to contain mercury which is a reformer catalyst poison when present ir large amounts. Activated carbon beds impregnated with sulphur have been found to be effective in removing this metal.

**Primary Reforming:** The purpose of the primary reforming step is to convert the bulk of the hydrocarbon feed to $H_2$ and CO by reaction with steam so that the remainder of the reaction can be carried out in the secondary reformer . This conversion is represented by the following reactions

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$
$$CO + H_2O \longrightarrow CO_2 + H_2$$
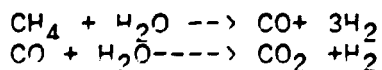
The overall reaction of the system is endothermic and the conversion is favoured by high temperature, low pressure and

high steam to carbon ratio. In the secondary reformer, with the introduction of air the remainder of methane is burn and this supplies the required amount of nitrogen for ammonia synthesis.

The preheated feedstock and high-pressure steam at or above reformer pressure (30-40 atm) are mixed and passed through a large number of tubes (50-400) which are externally heated in a reformer furnace by a fuel which is usually but not always the same as the feedstock (natural gas or naphtha).Traditionally stream:carbon ratios of 3.5-4.0 have been used, but the excess steam adds to the gas volume that must be accommodated in the reformer and subsequent stages and much of its substantial heat content can only be recovered at a relatively low level.

Modern low-energy process deisgns have tended to employ milder conditions during reforming and this has enabled steam:carbon ratios to be lowered with consequent savings in fuel consumptior. Although the theoretical minimum steam:carbon ratio is about 2, for practical reasons ratios of around 3 are used in low-energy plants.

Side reactions in the primary reformer are those which form carbon an undesirable by-product.

$$C_n H_{2n+2} \longrightarrow nC + (n+1)H_2$$
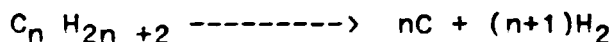
Thermal cracking tends to deposit carbon on the catalyst surface which can reduce the activity of the catalyst near the entrance of the catalyst tubes before sufficient hydrogen has been produced by the reforming reactions to suppress the right hand side of the reaction. Promoters. such as potash, are used to help suppress cracking in natural gas feedstocks containing heavier hydrocarbons. Carbon may also be formed by both the disproportionation and the reduction of carbon monoxide

$$2CO \longrightarrow C + CO_2$$
$$CO + H_2 \longrightarrow C + H_2O$$
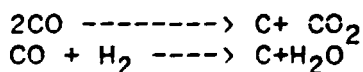
Carbon produced by these latter reactions is formed in the catalyst pores, making it much more difficult to remove. and potentially causing physical breakage. Operating steam to carbon ratios are chosen above the minimum required in order to make carbon formation by these reactions thermodynamically impossible (3). Steam is another potential source of contaminants. Chemicals from the boiler feed-water or the cooling system are poisons to the reformer catalyst. so steam quality must be carefully monitored.

THe reformer tubes are usually centrifugally cast The generally accepted catalyst tube material for catalytic

reformer designs is centrifugally cast 25% chromium-20% nickel (HK-40) alloy having a specified carbon content of 0.35% to 0.45% and providing the optimum combination of strength and weldability. In the 1980s, other materials, most prominently 25 Cr-35Ni-Nb (HP modified) alloy, gained acceptance, allowing operation at higher pressures and temperatures while reducing tube wall thicknesses. Thinner walled-tubes result in less stressful operation because of a flatter temperature profile, as well as allowing more volume for catalyst loading. Tubes are generally designed for a minimum theoretical life of 100,000 h, in accordance with API standard 530. Tube failure mode is normally through creep and/or stress-rupture (45). Higher reforming pressures are favored, because of the lower energy of compression required for the synthesis loop, smaller vessel sizes, easier $CO_2$ removal at higher partial pressures, and more efficient process heat recovery.

Available primary reformer designs differ in the arrangement of tubes and burners, tube material, feed gas distribution, and reformer gas collector systems. A primary reformer furnace is a distinguishing feature of an ammonia plant. The radiant section of a typical Kellogg box type steam reforming furnace is shown in Figure-4
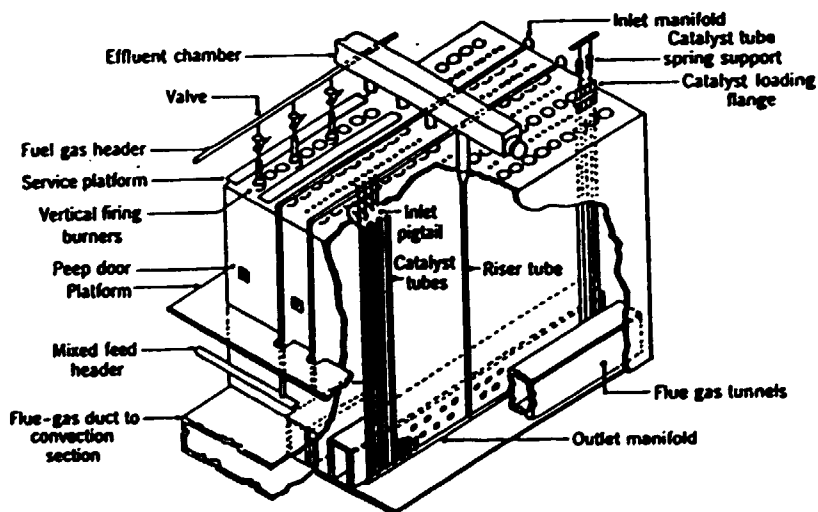


Figure-4 Kellogg Reformer

In the box reformer the catalyst tubes are arranged in parallel single width rows heated from both sides by either gas or liquid fired burners, or both, located in the furnace arch. ICI and Uhde also utilize a top fired configuration for their primary reformer designs(29-30).

In the Haldor-Topsoe primary reformer furnace, the radiant section consists of one or more elongated rectangular furnace cells having vertical catalyst tubes mounted along the center line of the cell in either a staggered double or single straight row. This is a side-fired furnace with flames deflected parallel to the walls which act as radiators. The burners operate satisfactorily on gaseous fuels ranging from hydrogen-rich off-gas to mixtures of vaporized naphtha and steam (46).

In the Foster-wheeler reforming furnace (3), the inclined terrace walls are vertically and uniformly heated by rising flow of hot gases. The catalyst tubes are heated from both sides and the tube support arrangement uses a carefully designed multiple counterweight system. The lineal burners can operate on both gas and light distillate fuel oil. The radiant box is only about 50% efficient, but the heat liberated and not absorbed by the reforming reaction is recovered in the convection section, allowing overall furnace efficiencies of up to 94%, based on a furnace stack gas temperature of about $150_o$C for a desulfurized feed.

The practical limit on the primary reformer exit temperature is determined by tube metallurgy considerations.

The reformer tubes range from 7.5 to 20 cm in diameter with a wall thickness of 0.6-2.5 cm and a length ranging from 3 to 14 m (16). The tubes are packed with catalyst containing nickel on a calcium aluminate base. usually in the shape of a ring about 16 mm in diameter by 16mm long. The nickel content typically is 14%-16%. Promoters such as potassium may be added.to decrease carbon forming tendencies due to heavy hydro carbon or to allow operation at reduced steam/gas ratios.The compositin of the base may be varied to increase its strength, durability, and porosity. The temperature and the high pressure constitute severe conditions that require careful design and operation. The heat in the combustion gas leaving the reformer is used successively to produce steam, to preheat the incoming feedstock-steam mixture, and where fuel economy is important, to preheat combustion air.

The gas leaving the primary reformer usually contains 5%-15% methane (dry basis). The gas temperature usually is in the range of 800-900$^o$C.

Secondary Reforming: The object of the secondary reforming step is to complete the conversion of methane to $H_2$. CO. and $CO_2$ and to supply the required proportion of $N_2$ for $NH_3$ synthesis. This is done by adding air to the amount required to give an N:H atom ratio of 1:3 in the synthesis gas after the shift conversion step. This means that the mole ratio of

$N_2$ ($H_2$ +CO) should be 1:3 in the gas leaving the reformer unless more $N_2$ or $H_2$ can be added in some subsequent step of the process. The part of the combustibles ($H_2$, CO and $CH_4$) in the partially reformed gas, thereby raising the temperature high enough for rapid completion of the reforming.

Although most processes involve the use of air alone, in some cases oxygen enriched air is used to supply more heat and, thereby, take some of the load from the primary reforming step. In fact, it is possible to add enough oxygen so that the reforming process becomes "autothermal" and the primary reforming step can be omitted entirely. On the other hand, less air can be used than required for nitrogen supply, and part of the nitrogen can be added separately, preferably at a later step in the process. This arrangement places more load on the primary reformer but decreases the amount of feedstock required. This can be an advantage when the feedstock is expensive (or in short supply ) and a less expensive fuel is used in the primary reformer.

In the usual case when air to the secondary reformer is the sole source of nitrogen, the heat input is limited to that generated by combustion reactions plus the sensible heat in the preheated air and in the gas from the primary reformer.

A typical secondary reformer is a cylindrical, refractory-lined, insulated vessel. The upper part is empty and serves as a combustion chamber in which the gas from the primary reformer is partially oxidized by preheated air. The lower part is filled with a catalyst similar to that in the primary reformer. The air should be free from dust that might clog the catalyst bed and from catalyst poisons (S, Cl. and As). The air is filtered, compressed to reformer pressure, and mixed with the gas in a burner at the top of the vessel. The combustion causes the temperature to rise to about $1200^{\circ}$C in the combustion chamber. As the hot gas descends through the catalyst bed, it is cooled by the endothermic reforming reactions and leaves the reformer at a temperature of about $950-1000^{\circ}$C. The gas at this point contains, on a dry basis, about 56% $H_2$, 12% CO, 8% $CO_2$, 23% $N_2$, plus argon, and usually less than 0.5% $CH_4$. It also contains excess steam ranging from one-third to one-half of the total gas volume.

Substantial energy savings can be made by leaving more of the reforming duty to the secondary reformer.and this practice is embodied in one way or the other in many recent processes.Various design options that can be incorporated into a new grass root plant or can be used as revamp options are:

o    Increasing the temperature of air to secondary reformer;this improves safety, reduces stack noise and

allows batter control of excess air. This design concept approximately saves energy to the tune of 250-270,000 Kcal/Ton of ammonia.

o    Steam superheating: improves efficiency of the steam turbines and reduce firing at the reformer. It saves approximately 100,000 Kcal/Ton.

o    Saturation of Natural gas feed : saves 30-50% of the process steam, and at the same time reduces the process condensate treatment.

o    The gas stream after hydrodesulpherizer is fed to the natural gas saturator where the natural gas is saturated with process condensate recovered upstream of the carbon dioxide removal system.

o    Lowing steam to carbon ratio to about 3.0 with a standard catalyst and to 2.5 with the new catalyst for reforming and HTS/LTS greatly benefit both utilities and natural gas costs,   but its limitation being the guide reaction leading to carbon formation in the reforming process and it results overheating in HTS converter.

o    Primary reforming by-pass as conceived by HERA process results in energy saving due to low average steam to carbon ratio. but  requires excess air to secondary reformer.

o    Gas heated reformer GHR instead of fred reformer is claimed to be successfully employed by ICI in their LCA (leading Concept Ammonia process) can be used in plants where no steam export is required.

**Carbon Monoxide Conversion:** Gas from the secondary reformer is cooled (generating steam) to about 375oC which is the usual temperature for the shift conversion reaction:

$CO + H_2O --H_2 + CO_2$          Delta H= -9.8 Kcal/mole

The reaction is exothermic; therefore, it is usually carried out in two steps with heat removal between steps.  The rate of reaction is more rapid at high temperatures,  but equilibrium is more favorable at low temperatures.  Thus, it is common practice to operate the first step at a higher temperature than the second so that most of the CO is converted in the first step, and in the second step the CO is reduced to less than 1% (often as low as 0.2%).

Prior to 1960, the same type of catalyst was used in both steps. This catalyst is mainly iron and chromium oxides. about 55% Fe and 6% Cr. It is active only at relatively high temperatures (350-430°C) and is known as a high temperature

shift (HTS) catalyst. The overall activity of HTS catalyst is low, therefore, the gas stream leaving the high temperature shift converter contains a substantial amount of unreacted carbon mono-oxide(usually around 3%). Most LTS catalysts contain zinc and alumina in addition to copper.

The LTS catalyst is much more expensive than the HTS catalyst and is more susceptible to poisoning; thus, it has a shorter useful life. Its advantages are that (1) it is active at a lower temperature range, where equilibrium is more favorable, thus more CO reacts with the steam to form $H_2$ and (2) less excess steam is required.

It is generally agreed that the advantages of the LTS catalyst outweigh its disadvantages, thus it is commonly used in the second step of CO conversion. Some precautions that may be taken to extend the life of the LTS catalyst are (1) scrubbing the air to the secondary reformer with water or dilute alkali solution to remove catalyst poisons, (2) more rigorous purification of feedstock and boiler feedwater, and (3) insertion of guard beds between the high and low temperature shift converters to remove S and CL from the gas. Figure 4 shows a typical arrangement of a sequence of HTS converter cooler, ZnO guard, LTS converter, cooler, and $CO_2$ removal. An alternative, but more expensive, arrangement is to use HTS catalyst in both converters with $CO_2$ removal after each converter. Removal of $CO_2$ after the first conversion step provides more favorable equilibrium conditions so that the CO content can be decreased to a low level in the second step even with the less active HTS catalyst. With either arrangement the CO content can be lowered to about 0.2% or less.

**Carbon Dioxide Removal:** After leaving the shift conversion step, the gas may contain 18% $CO_2$, or more depending on the feedstock composition. It is then cooled if necessary, to a temperature range which depends on the requirements of the absorbent used in the $CO_2$ removal step. Absorption in water was commonly used in pre-1940 plants. Its disadvantages were high energy consumption and loss of $H_2$ and $N_2$ which are appreciably soluble in water at the high pressure used. Recovery of $CO_2$ having adequate purity for urea production was difficult. Between 1940 and 1960, a 20% solution of monoethanolamine (MEA) was favored. Its drawbacks were low absorption temperature, high desorption temperature, corrosion and high utility and investment costs. After 1960, the majority of new plants used potassium carbonate solution with various additives to promote absorption and inhibit corrosion. Its main advantage is lower heat requirements for stripping the $CO_2$ from the solvent. In potassium carbonate processes two important processes are Benfield and G. vetrocoke processes which incorporate venadium oxide and arsenic dioxide respectively as activators. However, there are several other solvents in use, mainly organic liquids,

some of which have a proprietary composition.

The potassium carbonate system operates mainly on pressure differential-$CO_2$ absorption at high pressure and $CO_2$ release at low pressure. In the absorption step the pressure is typically about 30 atm (reformer pressure minus pressure losses), and the temperature may be $100^{O}C$ . The $CO_2$ is absorbed chemically by the conversion of potassium carbonate to bicarbonate. When the solution is regenerated by releasing the pressure to about atmospheric pressure. $CO_2$ and water vapor escape. In some cases, $CO_2$ release may be assisted by stripping with low pressure steam or air. The regenerated solution is returned to the absorber at a temperature of 85-90 $^{O}C$ and is heated by the gas from the LTS shift converter. In this way some or most of the heat required by the $CO_2$ removal process is derived from the heat in the incoming gas.

The original hot carbonate process developed by the U.S. Bureau of Mines was found to be corrosive to carbon steel (55). Various additives have been used in order to improve the mass transfer rate as well as to inhibit corrosion. Vetrocoke, Carsol, Catacarb, Benfield, and Lurgi processes are all activated carbonate processes. Improvements in additives and optimization of operation have made activated carbonate processes competitive with activated MDEA and nonaqueous solvent based systems. Typical energy requirements are given in Table-5.

Table 5 Energy Requirements for $CO_2$ Removal Systems

| Removal System | GJ/mol $CO_2$ |
|---|---|
| MEA | 210 |
| MEA with inhibitors | 140-93 |
| potassium carbonate | 197 |
| potassium carbonate with regenerator(s) | 88-62 |
| activated MDEA with generator(s) | 60-42 |

In contrast MEA absorption regeneration operates on a temperature on a temperature differential with absorption at a relatively low temperature, 27-60$^{O}C$, and regeneration at 100-140 $^{O}C$. Thus, it is necessary to cool the incoming gas to the absorber and to heat the MEA solution in the regenerator with steam and process gas. The MEA process has been improved by the addition of promoters and corrosion inhibitors, thereby lowering heat requirements.

Activated tertiary amines such as triethanolamine (TEA) and methyl diethanolamine (MDEA) have gained wide acceptance for

$CO_2$ removal. These materials require very low regeneration energy because of weak $CO_2$ amine aducct formation, and do not form carbamates or other corrosive compounds (53) Hybrid $CO_2$ removal systems, such as MDEA-sulfolane-water and DIPA sulfolane-water, are aqueous alkaline solutions in a nonaqueous solvent, and are normally used in tandem with other systems for residual clean-up.

Much attention has been given in recent years to methods for removal of acid gases (mainly $CO_2$ and $H_2S$, not only from ammonia synthesis gas, but also from natural gas, synthesis gas for products other than ammonia, and fuel gas produced by coal gasification carbonization. Numerous processes have been developed, and the choice of process for the ammonia plant may depend on a balance between energy cost, capital cost and other factors. The choice of specific $CO_2$ removal system depends on the overall ammonia plant design and process integration, Important considerations include: $CO_2$ slip required, $CO_2$ partial pressure in the synthesis gas, presence or lack of sulfur, process energy demands, investment cost, availability of solvent, and $CO_2$ recovery requirements. Carbon dioxide is normally recovered for use in the manufacture of urea. in the carbonated beverage industry, or for enhanced oil recovery by miscible flooding.

Absorption Systems. Solvents generally perform better at higher partial pressures of carbon dioxide. Because the solubility of acid gases increases as temperature decreases, most absorption systems use supplemental refrigeration to achieve low temperature absorption. Because of the low heat of absorption. the stripping gas is usually air and hence the heat requirement for these processes is negligible. Normally about 70% of the carbon dioxide is recovered by pressure reduction. Higher $CO_2$ recoveries can be achieved by flashing at high vacuum or by reintroducing the stripper overheads in the secondary reformer(58).

The Rectisol process is more readily applicable for acid gas removal from synthesis gas made by partial oxidation of heavy feedstocks. The solvents used in Purisol, Fluor Solvent, and Selexol processes have low vapor pressures and hence solution losses are minimal. Absorption systems are generally corrosion free.

Pressure Swing Absorption. Carbon dioxide can be removed by pressure absorption on molecular sieves. However. the molecular sieves are not selective to $CO_2$ and the gases must be further processed to achieve the high purity required for "over the fence" use as in the urea process. Use of pressure swing absorption for $CO_2$ removal appears most applicable to small. stand alone plants. Since partial oxidation of heavy oil or coal yields gases containing $H_2S$ as well as $CO_2$. the acid gas removal process for this use must be capable of

removing and separating these impurities and converting the $H_2S$ to S or other nontoxic compounds. Some partial oxidation processes produce gas containing small percentages of HCN which must be removed and converted to nontoxic compounds.

A complete discussion of $CO_2$ removal processes is beyond the scope of this manual.However, table-5 taken from Quartulli gives the basic characteristics of 18 major processes (15).

Table-5:PROCESSES FOR REMOVAL OF ACID GASES($CO_2$ AND $H_2S$)

| Process | Solvent | Solution circulation | Acid gas content in treated gas. ppm |
|---|---|---|---|
| | *Reaction systems* | | |
| MEA[b] | 20% monoethanolamine | medium | <50 |
| promoted MEA | 25–35% monoethanolamine plus Amine Guard | medium | <50 |
| DGA[c] | 60% diglycol amine | medium | <100 |
| MDEA[d] | 40% methyl diethanolamine plus additives | medium | <50 |
| Vetrocoke | $K_2CO_3$ plus $As_2O_3$–glycine | high | 500–1000 |
| Carsol | $K_2CO_3$ plus additives | high | 500–1000 |
| Catacarb | 25–30% $K_2CO_3$ plus additives | high | 500–1000 |
| Benfield | 25–30% $K_2CO_3$ plus diethanolamine and additives | high | 500–1000 |
| Flexsorb HP | $K_2CO_3$ amine promoted | high | 500–1000 |
| Lurgi | 25–30% $K_2CO_3$ plus additives | high | 500–1000 |
| Alkazid | potassium salt of 2-(or 3-) methylamino propionic acid | [e] | [e] |
| | *Combination reaction-physical systems* | | |
| Sulfinol | sulfone and 1,1'-imminobis-2-propanol | medium | <100 |
| TEA-MEA[f] | triethanolamine and monoethanolamine | high (TEA) low (MEA) | <50 |
| MDEA–sulfinol–$H_2O$ | | medium | <50 |
| | *Physical absorption systems* | | |
| purisol (NMP) | *N*-methyl-2-pyrrolidinone | medium | <50 |
| rectisol | methanol | medium | <10 |
| fluor solvent | propylene carbonate | [g] | [g] |
| selexol | dimethyl ether of polyethylene glycol | [g] | [g] |

[a]Ref. 54.
[b]MEA is monoethanolamine.
[c]DGA is diglycol amine.
[d]MDEA is methyl diethanolamine.
[e]Dependent on service.
[f]TEA-MEA is triethanolamine-monoethanolamine.
[g]Dependent on pressure.

**Methanation**: The gas leaving the $CO_2$ absorption step still contains about 0.3% CO and 0.2% or less $CO_2$. These oxides must be removed before the ammonia synthesis step because

they would decrease the activity of the ammonia synthesis catalyst and cause deposition of ammonium carbamate ($NH_4COONH_2$) which can cause fouling and stress corrosion cracking in the compressor and in the synthesis loop.. The methanation reactions are;

$$CO + 3H_2 ----> CH_4 + H_2O$$
$$CO_2 + 4H_2 ----> CH_4 + 2H_2O$$
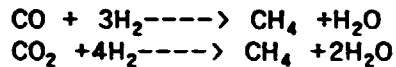
These reactions are the reverse of the reformer reactions, and a similar nickel-based catalyst is used. Most commercial methanator catalysts contain nickel, supported on alumina, kaolin, or calcium aluminate cement. Sulfur and arsenic are poisons to the catalyst, which can also be fouled by carry-over of solvent from the $CO_2$ removal system. It will be noted that each molecule of CO and $CO_2$ consumes three and four molecules of $H_2$, respectively. Therefore, it is necessary to efficiently remove CO and $CO_2$ to the minimum practical level.

**Dehydration:** Use of molecular sieve driers for final clean-up of the carbon oxides and water in the synthesis gas to less than 1ppm levels has gained prominence in low energy ammonia plant designs. The sieves are usually located at the interstage of the synthesis gas compressor to reduce volume requirements. The purified make-up gas can then be combined with the recycle and routed directly to the converter.

**Excess Nitrogen Removal:** A number of low energy processes use excess air in the secondary reformer in order to reduce the primary reformer duty. The surplus nitrogen so introduced has to be removed later in the process. The purifier process shown in Figure 5 incorporates a cryogenic purification step prior to make-up gas compression (59)
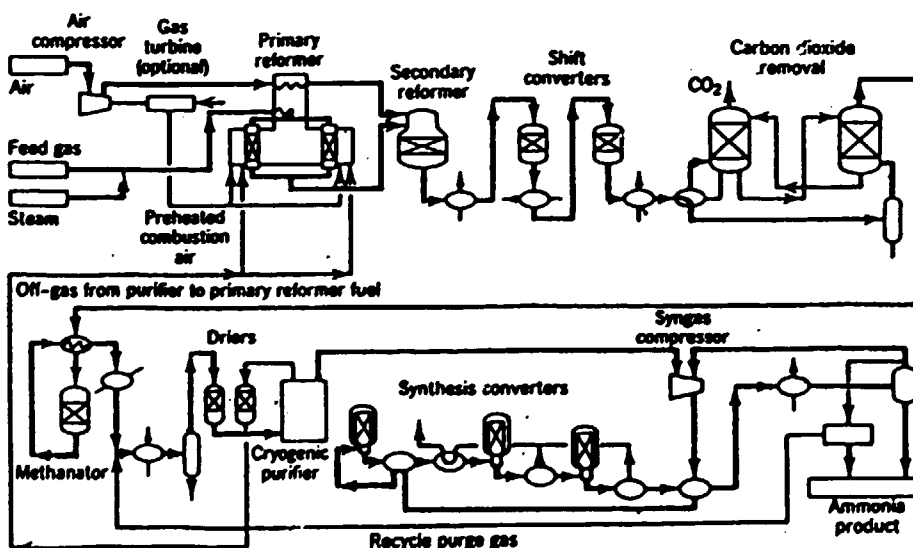


Figure 5. The Purifier System

Methanator effluent is first dried to a very low dew point, then cooled, and expanded in a turbine to liquefied stress is a scrubbed in a rectifying column to remove all but about 0.2% argon and almost all the methane. About half of the carbon monoxide in the feed after methanation is also removed.ICI and Uhde process designs utilize a cryogenic separator to remove surplus nitrogen at synthesis loop pressures (29-30). Pressure swing separation is used in various processes to remove excess $N_2$,$CO_2$ and part of the methane and argon (47).

The methanation step is usually carried out with a gas inlet temperature of 300oC -350oC; therefore, the gas must be preheated to that temperature. Since the reactions are exothermic, the temperature may rise to 320o-400oC at the gas outlet, depending on the CO + $CO_2$ content of the gas. A heat exchanger is commonly used to preheat the incoming gas and cool the exit gas.

Compression: The synthesis gas leaving the methanation step typically contains about 74% $H_2$, 24% $N_2$, 0.8% $CH_4$, and 0.3% Ar, dry basis. The gas must be compressed to the pressure required by the synthesis step. Before centrifugal compressors came into general use, reciprocal compressors were used. these reciprocal compressors often involved as many as five stages of compression with the various gas purification steps at intermediate pressures. Synthesis pressures varied widely from 100 to 800 atm depending on the process. Reciprocal compressors are still used for small plants (less than 500 tpd), but centrifugal compressors are now used in the great majority of new plants having capacities of 600-1500 tpd. Synthesis pressures in these new plants usually are in the range of 150-250 atm, although some of the larger plants may operate at 300-350 atm. It was previously considered that the use of centrifugal compressors was applicable only to plants of 550-tpd capacity or more, but process designs using centrifugal compressors are now offered for plants having capacities as low as 300 tpd. (15).

Centrifugal compressors are drive by steam turbines using high pressure steam generated mainly from hot process gas leaving the secondary, reformer, The steam is exhausted at a lower pressure and used in the reforming process and other process steps.

Reciprocating compressors are driven by electric motors. They are more efficient than centrifugal compressors, typical efficiencies are reported to be 87% for reciprocating compressors as compared with 70% for the centrifugal type. However, reciprocating compressors are more expensive, especially for large plants. The power consumption in plants using reciprocating compressors may range from 600 to 900 kWh/ton of ammonia as compared with

20-35 kWh in plants using steam driven centrifugals. However, this high electric power requirement is offset by lower fuel requirement. Where electricity is cheap or can be generated on site with low cost fuel such as coal and when the ammonia feedstock is expensive, there may be some saving in operating cost from using reciprocating compressors, especially in small plants. The largest plant with reciprocating compressors is reported to produce 670 tpd of ammonia.

Centrifugal compressors usually are built with two or three casings, often with interstage cooling. Compressor design is highly specialized, and the details of design, arrangement, and operation are complex. A typical simplified diagram of a synthesis gas loop is shown in figure 6
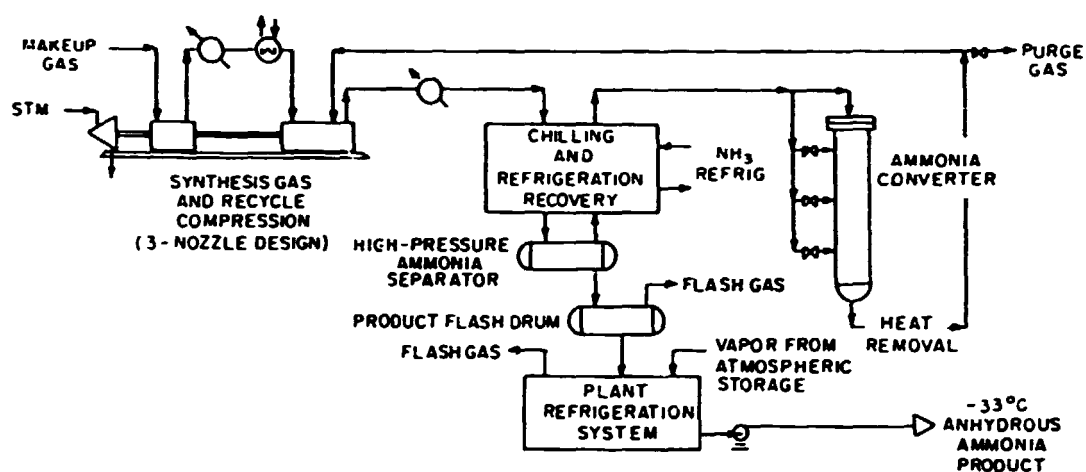
Figure-6 TYPICAL AMMONIA SYNTHESIS LOOP

Cooling and compressing the gas condenses nearly all of the water vapor remaining in it. The compressed gas enters the synthesis loop at various points depending on process design.

The major difference between large plants (centrifugal compressors and small plants (reciprocating compressors )is that large plants use steam drive for compressors. The same system can be used in small by driving reciprocating compressors with a turbine and a gear. This has been done successfully in small plants. and the same or better efficiency achieved as for large plants.

**Ammonia synthesis:** As mentioned previously, ammonia synthesis is commonly carried out at 400-450°C, using an iron catalyst promoted with potassium and alumina. The gas entering the converter consists mainly of gas circulated in the loop with a relatively small amount of fresh synthesis gas called "make-up gas. The gas entering the converter contains $N_2$ and $H_2$ in a 1:3 ratio plus 10-14 "inerts" and about 2% $NH_3$ The "inerts" consist mainly of methane, argon, and sometimes helium if the natural gas feedstock contains that element. (Methane is not, strictly speaking, an inert gas, but the term is used in ammonia synthesis context since it does not participate in the reaction). Since the inert gas concentration tends to increase as the $N_2$ and $H_2$ are removed, it is necessary to vent a side stream of "purge gas" to keep the inert gas concentration at a tolerable level.

The synthesis converter is the heart of the ammonia plant. Early designs were based on tube cooling as exemplified by the TVA converter (61). Although these converters offer good thermodynamic operating characteristics, mechanical complexity limits them to small capacity designs. Large capacity ammonia plants in the 1990s exclusively employ multiple bed converters. The range of these converters differ in type of flow (axial, radial, or cross flow), temperature control methodology quench or indirect cooling), and reaction heat recovery.

In most reactor designs, the cool inlet synthesis gas flows through an annular space between the converter shell and the catalyst cartridge. This flow maintains the shell at low temperatures and eliminates the possibility of hydrogen embrittlement that can occur at normal synthesis pressures. After the gas exits the annular space, it flows to an internally located heat exchanger that preheats the inlet gas to synthesis temperature. Inlet bed temperatures are controlled by quenching the bid effluents with cold synthesis gas. The Kellogg quench converter shown in Figure7 is a classic example of this reactor configuration.

Most modern ammonia converters are designed for radial or cross-flow, and indirect temperature control is provided by a heat exchanger. In the horizontal ammonia converter designed by M.W. Kellogg (see Fig.8) gas flows through shallow longitudinal catalyst beds called slabs contained in an easily removable cartridge. Most of the conversion occurs in the first bed which has the highest driving force to equilibrium. Because of the large cross sectional flow area, the pressure drop is extremely low even with small catalyst particle sizes. A bypass is provided around the intercooler for temperature control. This converter has been successful for numerous large capacity designs. Radial flow converters, such as those designed by Uhde and Topsoe, offer good gas distribution without the penalty of higher pressure

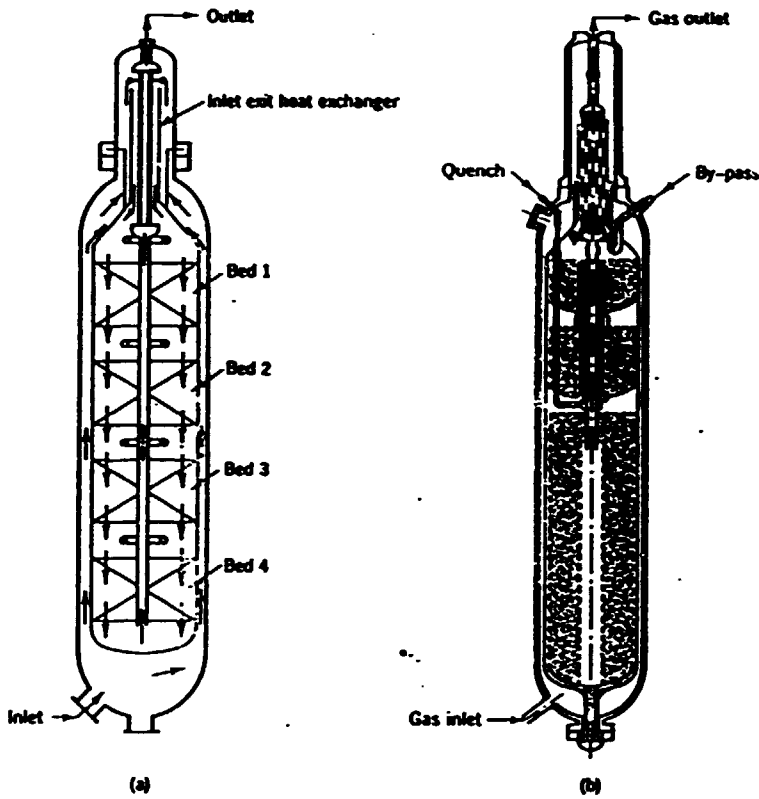drop. Topsoe's series 200 radial) flow converter is shown in Fig. 9.



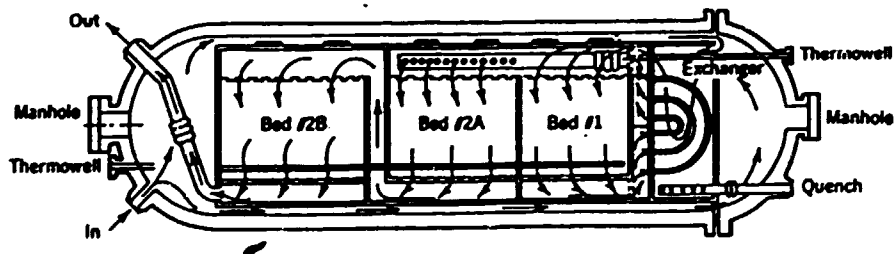Figure-7 Kellogg Quench Converter.



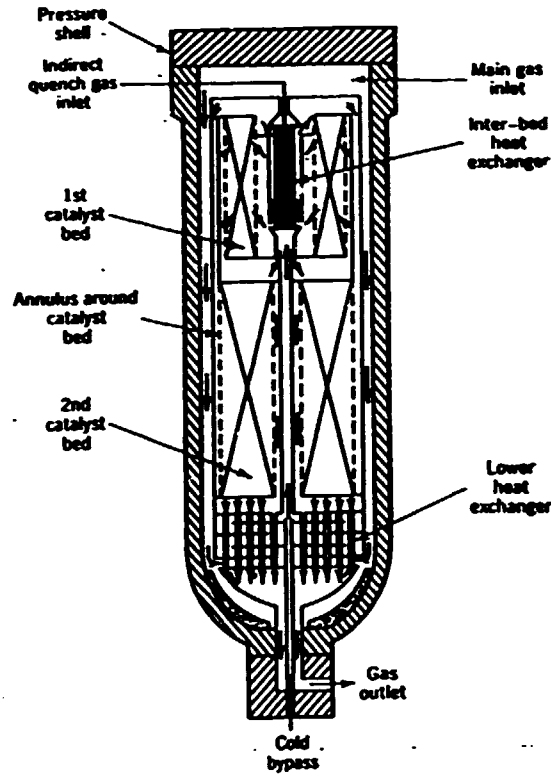Figure-8 Kellogg Horizontal converter.
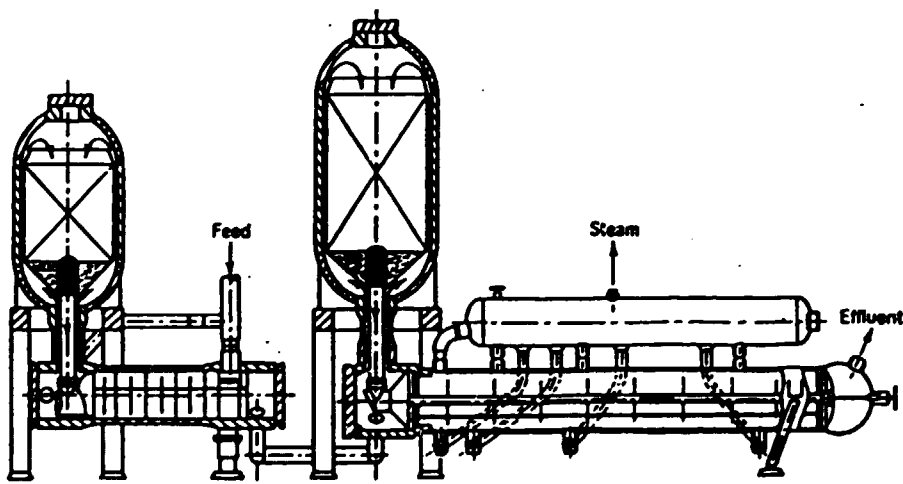
Figure 9 Topsoe's Series S 200 Converter.



Figure 10   C F Braun's Axial Flow Converter.

Ammonia Casale's mixed (axial-radial)converter offers similar advantages. The C.F. Braun axial flow reactor provides interbed cooling outside the pressure shell as shown in Figure 10. Large capacity ammonia plants employ 3-bed intercooled converters to achieve high ammonia per pass conversions at economical space time yields.

The gas leaving the converter will contain 12%-18% NH£, depending mainly on the pressure, conversion per pass increases with pressure. The gas is cooled first by heat exchange with the incoming gas, then by air or water. and finally by refrigeration to condense most of the ammonia as a liquid. The degree of cooling required depends on the pressure. At high pressures much of the ammonia as a liquid. The degree of cooling required depends on the pressure. At high pressures much of the ammonia can be condensed at temperatures obtainable by water cooling. At lower pressures (150-200 atm) increased reliance must be placed on refrigeration. If the ammonia is to be delivered to atmospheric pressure storage, it must be further cooled to -33°C (chapter VII). The gas remaining after ammonia condensation is recycled to the converter by means of a compressor.

The purge gas may be used as supplemental fuel in the primary reformer with or without prior recovery of its ammonia content by water scrubbing.

In some cases it may be worthwhile to separate the purge gas components cryogenically (after $NH_3$ recovery). The $CH_4$ and $H_2$ can be returned to the process, and the argon can be sold where there is a market for it.

In at typical ammonia plant, the purge gas represents 4-6% of the total synthesis gas. A typical purge gas composition for loss t/d plant is should in Table.( ) All modern plants, incorporate systems that could extract the hydrogen from the purge stream. This hydrogen is recycled to the compressor.

Table-I
Purge Gas Input

| Component | Range, mol% | Normal, mol% |
|---|---|---|
| Hydrogen | 60-65 | 64.5 |
| Nitrogen | 19-22 | 21.5 |
| Argon | 3-5 | 4.1 |
| Methane | 6-14 | 7.9 |
| Ammonia | 1.5-3.5 | 2.0 |
| Pressure, bar | 130-250 | 140 |

Hydrogen recovery systems. ryogenic systems combination of cryogenic and member systems are available in the market. Another recovery of utilizing purge gas is the purge gas conversion unit (PGRU) made by Kellogg.

f

## CRYOGENIC SYSTEMS

The technology of cryogenic hydrogen recovery is offered by vendors such as Costain Engineering Ltd., Air Liquide and Linde AG. The cryogenic process works as follows: ammonia is removed from the purge gas by washing with water, followed by molecular sieve drying to provide a clean, dry gas. The solution is passed to an ammonia stripper to recover anhydrous ammonia. The gas is then cooled in a plate-fin heat exchanger, mounted within a cold box, at the maximum allowable pressure (70-80 bars), to give a hydrogen-rich vapor phase and a liquid phase. After separation the hydrogen rich fraction is fed to the intermediate stage of the synthesis gas compressor. The liquid from the separator is expanded and used as fuel gas. Typical recovery rates are 94% of hydrogen and 30% of nitrogen with 90% rejection of inerts.

## MEMBRANE SYSTEMS

The first membrane system was introduced by Du Pont in the early 1970s, but the first system to be commercially marketed was Prism from Monsanto. The company is currently leading the market in membrane gas separation systems through its subsidiary Permea. with nearly two hundred units installed since 1979.

Separation of gases by a membrane occurs due to the differences in diffusivity and solubility within the membrane matrix. The transport rate across a membrane is determined by the size of the gaseous molecule and the type of chemical interactions it has with the matrix. The membrane matrix is much more permeable to molecules such as water vapor, hydrogen and helium, which are "fast" molecules, than molecules such as nitrogen, methane, argon and oxygen, which are "slow" molecules.

The Prism system uses a Polysulphone hollow-fibre membrane with a silicon rubber coat. The coat is used as a top layer to cover any defects in the pore system, so culminating the influence of any imperfections. Thousands of hollow fibres are bundled together in a pressure vessel, to give a large surface area for a small installation. as shown in Fig. 1. The pressurized purge gas enters the shell side and passes along the fibre surface. Due to the difference in partial pressure between the inner and outer surfaces, the hydrogen in the purge gas permeates through the walls to the bore of the fibre, which is sealed at top and opens through a tube sheet at the bottom. The hydrogen-rich permeate gas is delivered at the bottom of the separator at essentially the same pressure as the inlet purge gas.

High ammonia concentrations diminish the performance of the fibre, so a water scrubber is employed upstream of the

separators. The ammonia is then recovered in an ammonia stripper, Fig-11 shows the complete recovery scheme. The scrubbed purge gas is then heated to 32oC and passed into the Prism separators. Depending on the degree of separation required, one or two banks of separators may be used. If a second bank is used the pressure of the permeate gas will be low, and so this is fed to the low-pressure compressor suction.



HYDROGEN RECOVERY FROM AMMONIA PLANT PURGE
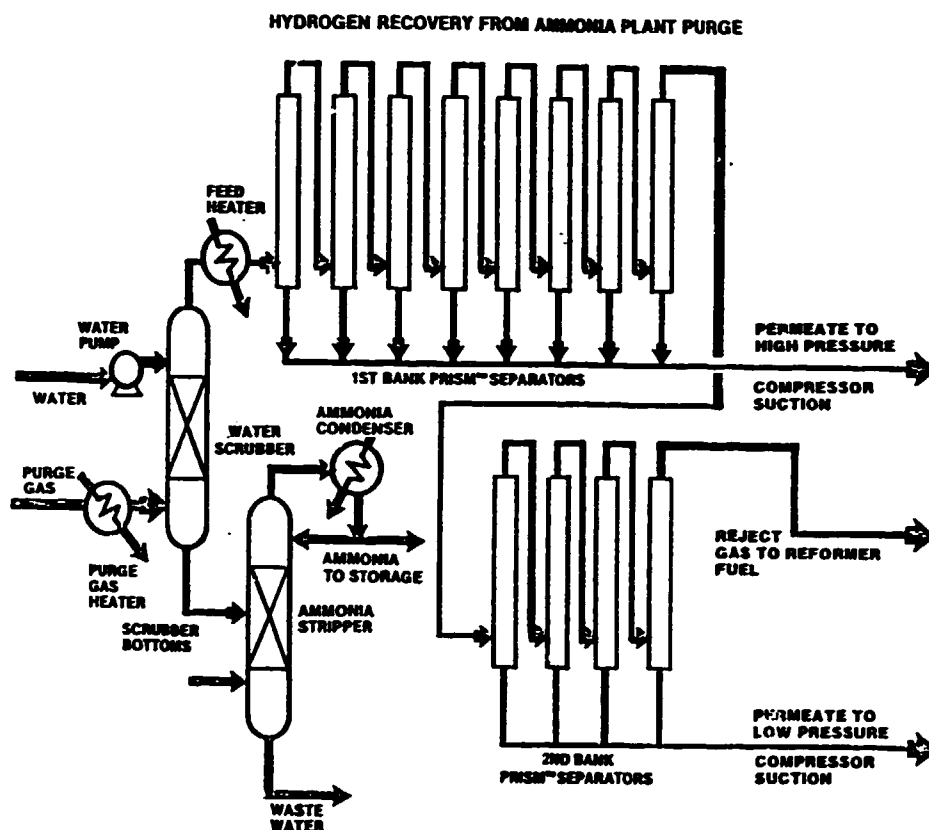
Figure 11 Ammonia Recovery System.

## MODERN LOW ENERGY STEAM REFORMING AMMONIA PROCESSES

Considerable research has been done in steam reforming process in recent years. Many engineering companies have developed their proprietary processes important among these are: M.W. Kellogg process, Haldor Topsoe process, ICI,s AMV process, KTI's PARC process, Braun purifier process. The engineering companies have developed new flow sheets after modification of particular sections of the process in order to improve energy efficiency. Salient features of these processes are given hereunder:

## M.W. KELLOGG PROCESS

The catalytic steam hydrocarbon reforming process produces raw synthesis gas by steam reforming under pressure,

followed by CO. shift purification of raw synthesis gas and ammonia synthesis. The process features efficient integrated generation system, a high level of process heat recovery and use of centrifugal compressors. Exit pressure from the primary reformer is normally 400-500 psig. Exit temperatures from the primary and secondary reformers are approx.1500-1800$^O$F, while shift reaction temperatures are about 800 $^O$F and 500$^O$F for high and low temperature shifts respectively. Synthesis pressure depends on plant capacity and compressor selection. High capacity units involving the use of centrifugal compressors have synthesis pressures in the range of 2000-4500 psig.

## HALDOR TOPSOE PROCESS

It is a low energy process for the manufacture of ammonia from gaseous, liquid or solid hydrocarbon feed stock. Main features of the process are desulfurization of the hydrocarbon feedstock by means of hot zinc oxide at about 400$^O$C, in case of refractory sulphur compounds a hydrogenation step is installed upstream of zinc oxide vessel. Reforming is done in two steps, primary reforming and secondary auto-thermal reforming. Topsoe designed furnace is of side wall fired type. High temperature shift is operated at about 392$^O$F and low temperature conversion is done at 356$^O$F. $CO_2$ removal is based on absorption of $CO_2$ by means of physical absorption for which no heat of regeneration is required. Ammonia synthesis is based on Topsoe S-200 radial flow ammonia convertor. The loop pressure is in the range of 2000-3125 psig depending on local condition.

## AMV PROCESS

In the AMV process greater than stoichiometric amount of air is fed to the secondary reformer. This subsequently reduces natural gas feed and fuel requirements of the primary reformer. Other main difference is ammonia synthesis loop which operates at 60 to 100 bar. A new synthesis catalyst has also been developed. This results in lower operating temperature and increased conversion efficiency.

## ICI's LCA PROCESS

ICI's LCA (Leading Concept Ammonia) process.is distinguished by the fact that energy efficiency at small scale (i.e. around 400-500 t/d) is virtually the same as for large plant low energy processes. Economy of scale is being challenged by small is beautiful in these times of slower capacity growth and rationalization!

By stark contrast, the LCA process uses the heat generated in the (exothermic) secondary reformer to heat directly the catalyst tubes in the primary reformer.

The arrangement to achieve this is also simple enough, the primary reformer sits above the secondary reformer. As with other processes so far described, excess air is fed to the secondary reformer, but then all the heat required in the primary reformer is taken from the hot process gas leaving the secondary reformer, rather than radiant heat from fuel fired burners. Thus the cathedral like structure of a conventional primary reforming furnace is substituted by the proprietary Gas heated reformer, GHR, in which the catalyst tubes are effectively arranged in a compact refractory lined heat exchanger. Since the requirement to raise steam from the reaction heat of the secondary reformer is much reduced, a totally integrated team system is no longer necessary.

Carbon dioxide, inerts and excess nitrogen are then removed from the raw synthesis gas plant. Ammonia synthesis itself takes place at low pressure, below 100 bar, using highly active catalyst.

Electric drives are used for most rotary equipment, and because there are no turbine drives there is no need to raise 100 bar steam. Steam production is limited to 60 bar . ICI has stated that the net energy consumption of the process, as demonstrated at its two 450 t/d units at Severnside, UK, is 29.4 GJ/tonne ammonia.

## KTI's PARC PROCESS
This process is said to be particularly suitable for smaller plants, yet claims energy efficiency comparable with much larger plants. PARC process was developed by combining a number of proven techniques. An air separation unit is used to provide pure nitrogen for ammonia synthesis, the oxygen enriched toil gas from this unit is combined with the combustion air fed to reformer. Before ammonia synthesis the raw synthesis gas is purified by a pressure swing adsorption system. In the synthesis loop an axial radial type converter is used which is vertical design containing stacked modular catalyst beds in which the gas flows in a predominantly axial manner in the first zone of catalyst bed and in a radial flow in the second zone. Advantages claimed for it include high conversion yields, low pressure drops and low investment costs.

## BRAUN PURIFIER PROCESS

Main features of the process include mild primary reforming, secondary reforming with excess air, cryogenic purification of synthesis gas and ammonia synthesis in adiabatic converters. Primary reformer temperature is generally less than $700^{\circ}C$ instead of over $815^{\circ}C$ as in conventional reforming. Fuel requirements in thus reduced. In the cryogenic purifier step excess nitrogen is removed, methane and argon too are removed from synthesis gas. This results in saving in compression power. In addition higher

concentration of methane can be tolerated at secondary reformer outlet. Mixture of methane, excess nitrogen and argon removed provides the gas needed to regenerate the drier and fuel for the primary reformer. Further complete removal of water and traces of carbon oxides lengthens the life of the synthesis catalyst. Synthesis converter contains a single adiabatic catalyst bed, ammonia synthesis is carried out in two or three converters. All heat exchange is external and quench cooling is not required. Excessive catalyst temperatures cannot occur under normal conditions.

Another means for utilizing purge gas is a purge gas conversion unit (PGCU) made by Kellogg. The unit consists essentially of a second ammonia, synthesis loop in which the purge gas is compressed, passed through a converter containing ammonia synthesis catalyst, and then cooled to recover additional ammonia . After ammonia recovery, a relatively small purge stream is drawn off for use as fuel and the remainder is recycled to the converter. The unit can be added to an existing ammonia plant. Since it converts 75% of the hydrogen in the purge gas to ammonia, ammonia production is increased by about 5% without increasing feedstock requirements. The ratio of additional investment and operating cost to incremental ammonia recovery is said to be quire favorable.
Figures 12, 13, 14, 15, 16, and 17 are the flow diagrams of the above processes respectively.
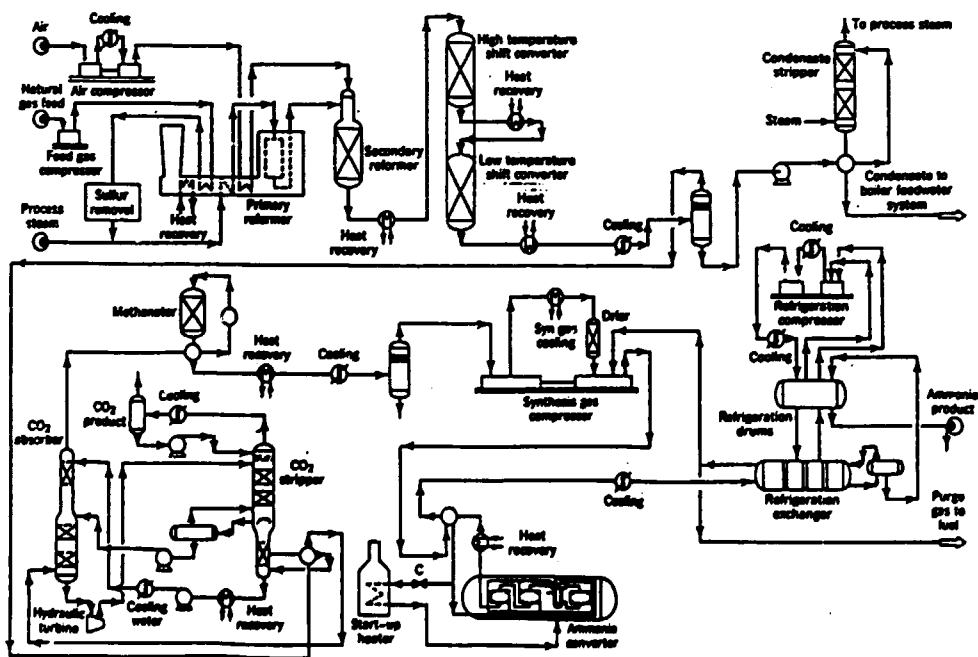


Figure 12.Flow Diagram of Kellogg Process.
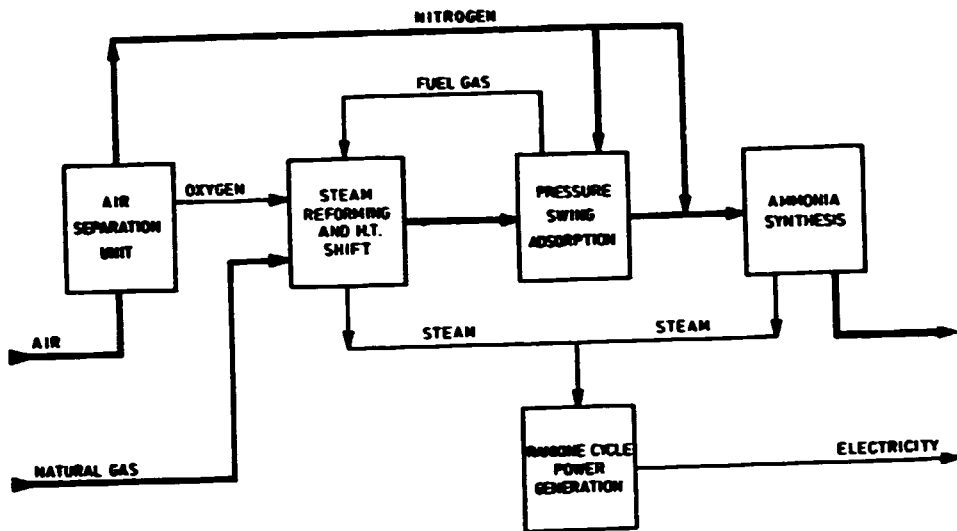
Figure 13.Flow Diagram of Haldor Topsoe Process.
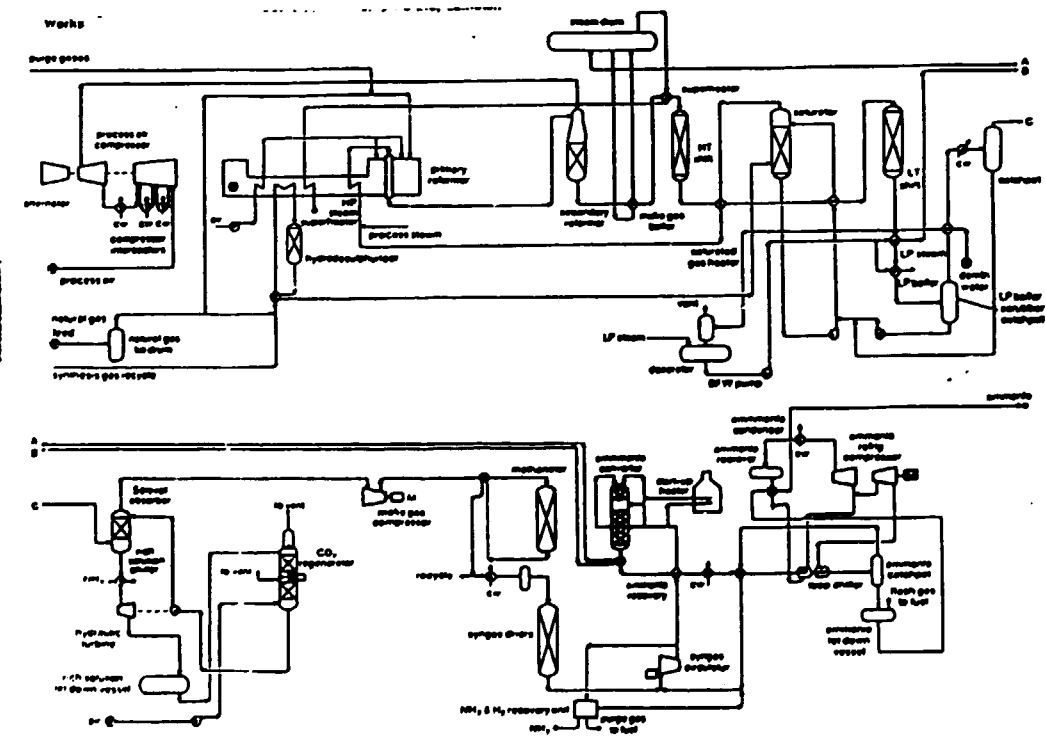


Figure 14 Flow diagram of AMV Process.
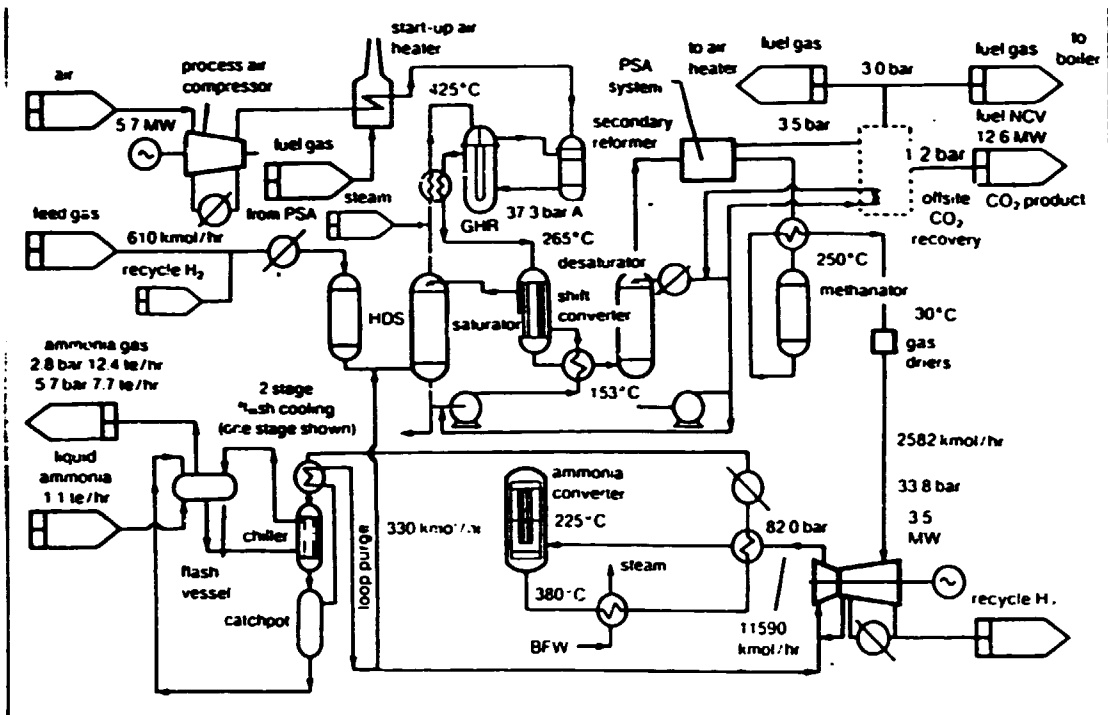
Figure 15 Flow Diagram of ICI's LCA Process.
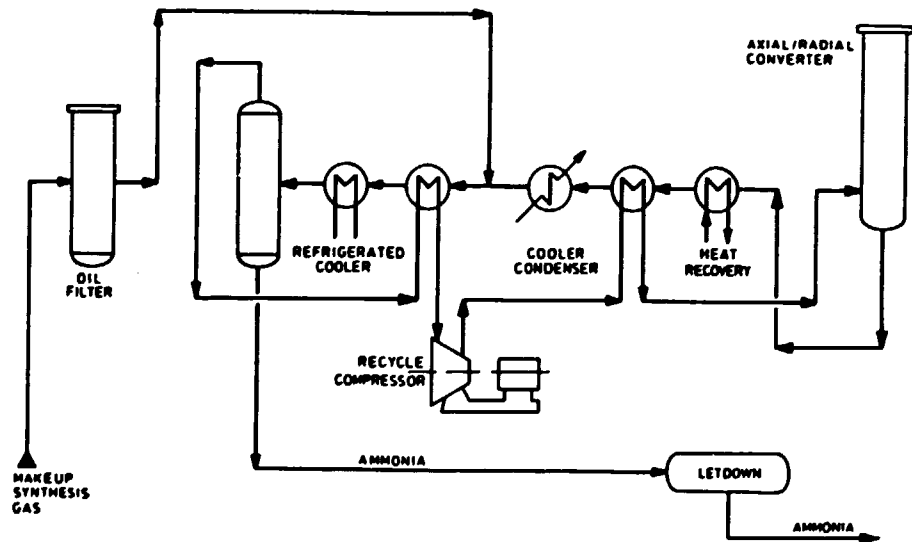


Figure 16. Flow Diagram of KTI PARC Process.
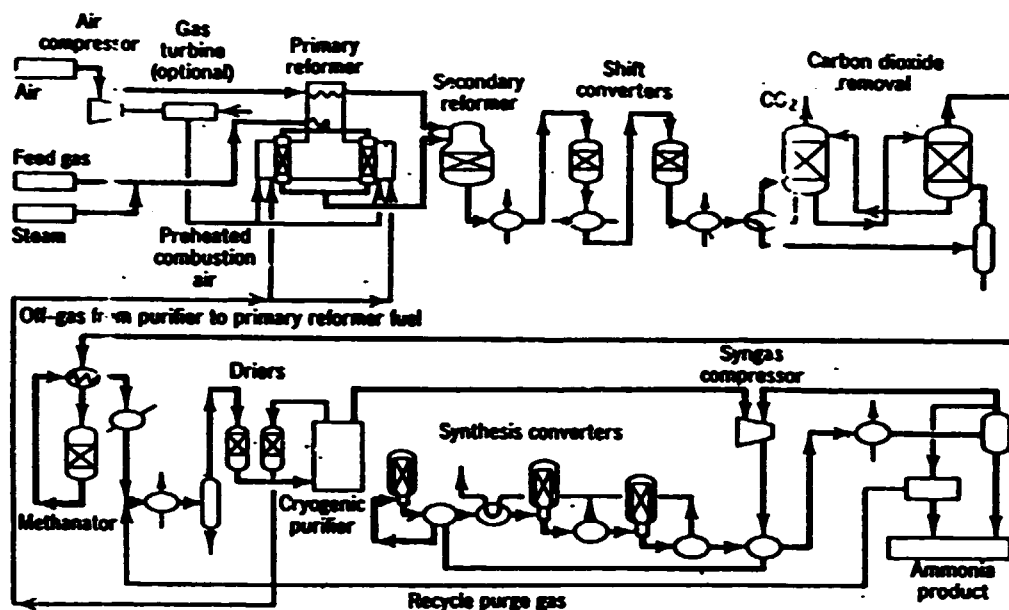
Figure 17. Flow Diagram of BRAUN Purifier Process.

## PARTIAL OXIDATION PROCESSES USING HYDROCARBON FEEDSTOCK

Hydrocarbons heavier than naphtha can be used as feedstocks for ammonia production by partial oxidation processes. Natural gas and naphtha also can be used, but since the plant cost for the partial oxidation process is considerably higher than that for steam reforming, the lighter feedstocks seldom are used. However, the partial oxidation process does offer the advantage of wider choice of feedstock with greater tolerance for impurities. The main disadvantage is the higher capital cost since an air separation plant is required to supply oxygen to the gasification step and nitrogen in a later step.

Crude petroleum can be used as feedstock, but the most common feedstock is heavy residual oil from petroleum refining processes which has had the more valuable lighter fractions removed. Such oil may contain 3.5% S, depending on the sulfur content of the crude oil and the refining process. using such oil for fuel or power generation would involve expensive equipment for pollution abatement in most countries; therefore, it is often available at a relatively low cost. The capital cost difference has been reduced recently as pressure in the gas generation step have approached 100 atm, thus reducing expensive syn gas compression.

The feedstock requirement typically is about 0.74 tons of heavy oil per ton of ammonia (17). In addition, about 0.23 tons of oil or the equivalent in other fuel is required for generation of steam and electricity. In contrast with the steam-reforming process where most of the fuel is used in the reforming furnace, which requires a premium grade of fuel, the auxiliary fuel for a partial oxidation process is used in a separate unit which can use coal, for example.

The principal partial oxidation processes are known as the Texaco, Shell, and Koppers-Totzek processes. The koppers-Totzek process is also used for coal and will be described under that heading. The Shell and Texaco processes are generally similar. Figure 18 is a simplified flow diagram of the partial oxidation process.

Figure 19.Simplified Flow Diagram of the Partial Oxidation Process

The gasification pressure in partial oxidation processes has been gradually increased to a range of 60-90 atm which helps save energy for compression. Lembeck describes a flowsheet using Texaco's partial oxidation technology in which gasification and purification are carried out at 72-90 atm(17). Heavy fuel oil is preheated and pumped into the gasifier together with high pressure steam and preheated oxygen from an air separation unit. The reaction takes place at a high temperature (1200o-1500oC), and no catalyst is required. The chemical reactions involved are complex and not completely understood. However, it is generally believed that the oil is cracked to form carbon and methane and other hydrocarbon gases; these products are partially oxidized to CO, $CO_2$ and $H_2O$, and partially converted by steam to CO and $H_2$. A typical composition of the resulting gas is 46% $H_2$, 47% CO, and 4% $CO_2$ dry basis with small percentages of $H_2S$ and $N_2$. A considerable amount of soot (carbon) remains suspended in the gas.

The hot gas is quenched with process water to the inlet temperature of the shift conversion step ( about 300 $^{o}C$), and most of the soot is removed in water which goes to a soot recovery unit. The soot is eventually recycled in the oil feedstock or used as fuel for steam generation. and the water from which the soot was recovered is recycled to the quench step. The quenching step also vaporizes some of the water into the gas stream, which supplies water vapor needed for the shift reaction.

The shift reaction is carried out with a recently developed cobalt-molybdenum catalyst; thus, the CO content of the gas is reduced to about 1%. The next step is removal of $CO_2$ and $H_2S$ by a Rectisol scrubbing process using methanol as the solvent. The $H_2S$ is recovered separately and sent to a Claus process unit for conversion to elemental sulfur. Since the $CO_2$ is of adequate purity for urea production and is available at 2.5 atm and 40oC, compression costs are lowered.

The final purification step is a liquid nitrogen wash process which uses liquid nitrogen from the air separation plant. This process removes CO and also lowers the $CH_4$ and argon content to a very low level. These impurities leave the process in a gas stream which is useful as fuel in steam generation.

Prior to the nitrogen wash, residual $CO_2$ must be removed by caustic scrubbing and water is removed by silica gel or other desiccant to prevent freezing of these gases in the nitrogen wash column.

After purification, nitrogen is added to adjust the $N_2:H_2$ ratio to the stoichiometric 1:3 ratio, and the gas is compressed to 230 atm for ammonia synthesis. This step is

similar to that described under steam reforming processes. However, it is claimed that, because of the efficiency of the nitrogen was step in removing impurities and inerts, the synthesis step can be operated without gas purge and, consequently, with higher efficiency. Also the gas purity contributes to long life of the synthesis catalyst.

It should be noted that the total fuel and feedstock requirement is 0.97 tons of heavy oil per ton of ammonia. This amount represents enough fuel to generate all of the steam and electric power required by the process including the air separation plant.

Supp describes an ammonia plant built in and operated by VEBA Chemie (Germany in 1972. This plant uses heavy residual oil (2.5% S) which is gasified by the Shell partial oxidation process (18). The plant is capable of producing simultaneously 1,215 tpd of ammonia and 450 tpd of methanol but has sufficient flexibility to produce variable proportions of the two products up to a maximum of 1,400 tpd of ammonia or 600 tpd of methanol. Either unit can be operated independently. A second ammonia plant with a capacity of 1600 tpd came into production 1978 and was revamped in 1989 to expand its capacity to 1950 tpd.

The process is generally similar to that described above with some exceptions that relate to the coproduction of methanol. However, one basic difference is that $H_2S$ and $CO_2$ are removed before the shift conversion step by a Rectisol scrubbing step, and $CO_2$ formed in the shift conversion is also removed after shift conversion by Rectisol scrubbing. Final purification is performed by liquid nitrogen wash as in the previous example. The low impurity content of the ammonia synthesis gas is illustrated by the analysis that shows less than 10 ppm of $CH_4$, less than 30 ppm of Ar, and less than 1 ppm of CO and all other impurities.

The Shell gasification process differs from the Texaco process mainly in that a waste heat boiler follows the gasifier and a different method is used for collecting and recycling the soot.

Capital cost of an Ammonia plant with partial oxidation process are 1.5 to 2.00 times the cost of an Ammonia plant for natural gas reforming.

A naphtha plant costs 15-20% more than the natural gas plant.

## Process for Production of Ammonia From Coal

About 10% of the world's ammonia production is based on coal, coke, or lignite. About half of the coal-based capacity is in the People's Republic of China where there

are over 1,000 small plants with production ranging from 23,000-10,000 TPY (9).Capacity of most of these plants have been increased up to 15,000 to 25,000 tons/yr by modifications and technology improvements (35).

At present their are 18 coal based plant operating in Greece , Yugoslavia, South Africa, Zambia, Turkey, India Japan, Oman and North Korea. The capacity rise is 50 to 1000 tpd. Apart for these plant there are a number of small capacity plants operating in China.

A plant based on coal gasification was started in United States in 1985 but it operated for few years only.

The technology of one of these plants has been described (21).The feedstock was lump anthracite or semianthracite although it was reported that briquetted coal or lower grade coal was used in some plants. In general, the process is similar to the original Haber process which was described previously. The coal was gasified in a semi water gas producer blown alternately with air and steam. Gas purification sequence was water scrub, $H_2S$ removal, shift conversion, $CO_2$ removal by water scrubbing, and copper liquor scrubbing fro CO removal. The gas was compressed in six stages by reciprocating compressors with the purification steps between various stages. The product from the small plants is oft4n used to make dilute ammonia solution (16%-25%) or ammonium bicarbonate for local use, although some of the larger plants make ammonium nitrate.

Several large modern ammonia plants have been constructed recently in China which are based on natural gas, and more are under construction. However, it is planned to continue operation of the small plants and to build more small and medium-size plants (50,000-100,000 tpy). These smaller plants will supply local fertilizer needs in areas where transportation facilities are not adequate.

Texaco coal gasification technology was demonstrated on a small industrial scale in 1982 at TVA. In 1984 Ube industries in Japan commissioned a new front end based on this technology which an existing kellogg 1500 tpd ammonia plant synthesis loop. This Ube's facility in now flexible enough to produce ammonia from coal, petroleum coke, naphtha or LPG as required.

Coal gasification process for ammonia production can be classified according to the method of gasification as fixed-bed (lurgi), fluidized bed (winkler), or entrained bed (Koppers-Totzek and Texaco). The so-called fixed bed gasification is more accurately called a moving bed. Lump coal (5-30mm) is charged at the top and descends countercurrently to the gas stream. As it descends, it is first dried and preheated, then carbonized, and finally

gasified by the oxygen and steam entering the bottom. The coal ash is discharged from the bottom through a grate, or in one modification, as a slag. Because the countercurrent method of operation results in good heat exchange, this method requires lees heat and, hence, less oxygen than the other methods. Also, the expense of drying and fine grinding of the coal is avoided.

The Lurgi moving bed gasifier usually is operated at 30 atm. It requires the least amount of oxygen--one-half to one-third as much as entrained coal gasifiers. It is not necessary that the oxygen be of high purity; 90% is satisfactory. The gas leaves the top of the gasifier at about 450oC and is cooled and washed to remove tar, liquid hydrocarbons, dust, etc. The washed gas contains CO, $H_2$, $CO_2$ $CH_4$, and other hydrocarbons. It is treated by a series of steps including steam reforming, CO shift conversion, $CO_2$ and $H_2S$ removal, liquid nitrogen wash, steam reforming of the methane that is separated by the nitrogen wash, nitrogen addition, and compression to produce ammonia synthesis gas (25).Methods of underground gasification of coal have been developed in Russia and the U.S which are aimed at elimination of mining and reasonable recovery.A system developed by Energy International in the U.S for "sloping bed" cool seam claims 60% coal recovery and provides 8 atm gas thru injection of $O_2$ and steam into the bed.

Some limitations of the fixed or moving bed gasification process are that the coal must be in the form of lumps (5-30 mm), the coal must be of the noncaking variety or pretreated to prevent caking, and various by products are formed (tar, phenolic compounds, light oils, etc.) that must be collected and utilized or disposed of. In preparing the sized coal feed, fines are formed that can be burned in an auxiliary plant to generate the steam and electricity requirements of the process. Tar can also be burned or injected into the gasifier at a point where the temperature is high enough to gasify it.

In the fluidized bed gasification process, of which the Winkler process is the main example, foal or lignite is ground to less that 15-mm practical size and introduced into the fluidized bed through feed screws near the bottom. Steam and oxygen are injected near the bottom of the fluidized bed. In contrast to the gradual increase in temperature of the coal in the moving bed process, the fluidized bed is essentially isothermal (about 1000 $^{o}$C). Consequently, there is neither tar nor other liquid byproducts, and the gas contains mainly $H_2$ and CO with less than 1% $CH_4$. A substantial amount of ash is entrained in the gas stream. The hot gas is cooled by waste-heat boilers and scrubbed to remove ash and then purified in a sequence of steps similar to other processes. The process produces a char containing 6%-12% of the carbon in the feed. About 90% of this char is

removed from the bottom of the gasifier in a dry state; the remainder is recovered by wet scrubbing of the gas. This char can be burned in an auxiliary boiler to supply steam and electricity.

The Winkler gasifier is widely used to make producer gas for industrial and domestic use, but few have been used for ammonia production. Its advantages are that it will work with almost any grade of coal or lignite and that it is adaptable to high-capacity units. Disadvantages for ammonia production are low pressure (1-3 atm), which increases compression costs, and the ash content of the gas, which requires an electrostatic precipitator for final cleanup.

Entrained coal gasifiers are typified by the Koopers-Totzek(KT) and Texaco processes. Most of the present coal-based ammonia plants (except in China) use the KT process. The process is essentially a partial oxidation process as are most coal gasification processes. One K.T. ammonia plant based on coal gases is in operation since 1988 in Finland.

In the KT process coal is dried and finely ground to about 75% through 200-mesh (Tyler).The powdered coal is picked up by streams of oxygen and blown into the gasification chamber through two burners facing each other. More recently, four-burner units have been used. Steam enters through annular openings around the burners. The gasification is complete in about one-tenth of a second at temperatures in the range of $1000o-1200^{O}C$. Part of the ash is fused and removed from the bottom of the gasifier, and part is entrained in the gas. The gas typically contains 56% CO, 31% $H_2$, 11% $CO_2$, and less than 0.1% $CH_4$. After being cooled in waste heat boilers, the ash is removed by wet scrubbing and electrostatic precipitation. The remainder of the ammonia synthesis gas preparation is similar to that described under partial oxidation of fuel oil.

Disadvantages of the process are the need for fine grinding of coal, operation at low pressures (1-3 atm), and higher oxygen consumption than other coal gasification processes.

Texaco partial oxidation of coal has been proven at TVA in the U.S .The plant was built , started and shutdown on the 1970.

The Texaco coal gasification process is the newest one and has not yet been applied to ammonia plants although extensive development work has been done on the gasification process, and it will be used in the TVA demonstration plant.(23)

The Texaco process differs from the KT process in that the finely ground coal is mixed with water to form a thick slurry containing about 45% water oxygen, into a gasifier

which can operate at pressures as high as 180 atm.   The process as applied to ammonia production has been described by Mitzer  and Moe (24). In this case the gasifier is operated at 58 atm and about 1300oC. Fused ash is quenched to 1000oC by a combination of water and cool gas recycle. It then passes through a waste-heat boiler and is cleaned to remove soot and fly ash in a venturi scrubber. The sequence of the remaining steps of synthesis gas preparation is CO shift conversion, removal of $H_2S$ and $CO_2$ by Rectisol wash (cold methanol), and liquid nitrogen wash. As in other partial oxidation processes, the $H_2S$ is converted to elemental sulfur.

## Ammonia from Electrolytic Hydrogen

Several ammonia plants have been built to produce ammonia from hydrogen that is produced by the electrolysis of water. These plants have been located where low-cost hydroelectric power is available in Norway, India (Nangal), Egypt(Aswan), Peru (Cuzco), Iceland, and Canada (Trail, British Columbia). The technology of the electrolytic process  has been described by Mrochek and Grundt (27, 28) Purified water is the feedstock; potassium hydroxide is added to increase the conductivity, but it does not participate in the reaction. Commercial cells vary somewhat in efficiency, but a typical power consumption is 4.3 kWh/ton of ammonia (28). Additional energy is required for an air separation plant to produce the nitrogen required for ammonia production. Energy also is required for compression of the hydrogen and nitrogen and recirculation of the gas mixture through the synthesis loop. the total energy requirement is about 10,200 kWh/ton of ammonia. This energy is equivalent to about 8.8 million kcal/ton of ammonia, which is about the same as for natural gas-based ammonia plants.   However, if fuel were used to generate electricity, nearly three times as much thermal energy would be required since the efficiency of conversion of thermal energy to electrical energy is seldom more than 38%.

Denora claimed to have a cell operation at about 20 atm.This would make ammonia electrolytic ammonia more competitive

The process generates one volume of oxygen per two volumes of hydrogen or about 0.7 ton of $O_2$/ton of $NH_3$; thus, a credit for byproduct oxygen can be taken if there is a use for it. For example, the oxygen can be used in an iron and steel industry. A small additional amount of oxygen would be available from the air separation unit. Another potential byproduct is heavy water (deuterium oxide, $D_2O$. The hydrogen is electrolyzed more rapidly than its isotope, deuterium, thus, the concentration of $D_2O$ in the electrolyte builds up and can be recovered at a rate of 70 g/ton of $NH_3$ (28).

Heavy water is used in some types of nuclear reactors.

The bulk of the investment cost for an ammonia plant based on electrolytic hydrogen is for the electrolyzers. One Norsk Hydro electrolyzer with 235 cells with have a capacity equivalent to about 3.75 tpd of ammonia although smaller or larger ones can be built. Larger plants normally use a number of identical electrolyzers; for instance, a 200-tpd plant would require about 53 electrolyzers in operation. Extra units usually are supplied so that some of the units can be shut down and cleaned without interrupting or decreasing ammonia production. Since the electrolytic process does not produce $CO_2$ ammonia cannot be used to make urea unless $CO_2$ is available from another source. It can be used to make ammonium salts (sulfates, phosphates, or nitrates), or ammonia can be applied to the soil directly either in the anhydrous form or in aqueous solution chapter X).

Since the desired capacity of the electrolysis plant is obtained by installing the required number of units, there is little economy of scale.

The cost of production of ammonia by the electrolytic process is not greatly dependent on plant size but, of course, it is strongly dependent on the cost of electricity,. Thus, if low-cost electricity is available, the electrolytic plant would be competitive with plants using other processes, particularly for small plants.

A particular advantage in developing countries would be the fact that ammonia production from electrolytic hydrogen is a much simpler process than those using other feedstocks.

Hydrogen is also produced as a byproduct of electrolytic production of chlorine and caustic soda, and several small ammonia plants have used this byproduct for ammonia production either as the only feedstock or as a supplementary source. The amount of hydrogen available from chlorine-caustic plants is too small to supply a significant portion of the ammonia needs in most situations.

<u>ECONOMICS OF AMMONIA PRODUCTION</u>

<u>Capital Requirements</u>

Since ammonia production is highly capital intensive, it is especially important that the estimated or assumed capital cost be as accurate and realistic as possible. When the process, feedstock, and location have been selected, an accurate estimate of the capital requirements can be made although even then the actual cost often exceeds the estimate by a substantial amount or, less frequently, is less than the estimate.

For the purposes of this manual, no specific locations will be assumed and, therefore, investment cost estimates illustrate only an order of magnitude. It is hoped that the estimates will be useful as a guide, particularly for comparative purposes, to indicate the effect of such factors as location, choice and price of feedstock, scale of operation, and percentage of capacity utilization on production costs.

Ammonia plant construction costs increased sharply in the period of 1967-74; the 1967 UN manual shows a battery-limits cost of about $11 million for a 900 tpd natural gas-based plant at a U.S. location (29). A similar plant was estimated to cost about $50 million in 1974 (13). Since 1974 cost increases have been minor; a 1978 estimate was about the same ($50 million), implying that cost-saving techniques in the ammonia plant engineering and construction industry have offset rising labor and material costs (30).Today's estimate are around $150 million and the plants are claimed to be much more efficient. However, it is unlikely that greater efficiency will continue to offset rising construction costs in the future.

Types of Estimates: There are three common types of estimates which differ in what they include. The most common type is for a "battery-limits" plant, which consists of the process equipment erected and ready to operate when supplied with specified feedstock and utilities. There is some variation in what facilities are included in the battery limits; for instance, cooling towers for recirculating cooking water and facilities for boiler feedwater treatment may or may not be included. In partial oxidation processes a separate boiler for generating steam and (often) electricity is included; whereas, in steam-reforming processes, sufficient steam is generated in the process to supply process needs for steam and most of the mechanical energy but not electricity. Thus, a battery-limits estimate should have a definition of what is or is not included.

A "turnkey" plant estimate includes not only the battery-limits unit or units but also all supporting and auxiliary facilities necessary for plant operation. It may include roads and railroads within the plant; distribution systems for electricity, water, compressed air, and fuel; offices laboratories; site preparation, storage for raw materials and products; maintenance shops, etc. Usually it does not include roads or railroads leading to the plant. here again, there maybe considerable variation in what is included depending on the plant site. A"green field" or "grass roots" location is one whereas, an addition to an existing production facilities. "Site preparation" requirements are likely to vary widely depending on location. For instance, a marshy location may require landfill and piling, whereas, a mountainous location may require extensive earth and rock

moving to create a reasonably level plant site.

A "project cost" estimate includes the "turnkey" plant plus additional expenses such as a feasibility study; training of operating, maintenance, and supervisory personnel, startup expense, interest on money spent during construction, and working capital. In developing countries the project cost may include training of marketing personnel and many items of infrastructure such as roads, railroads, harbors, piers, and waterways; housing, recreation, cultural, and religious facilities for employees, guest house, commissary, etc. There is some question as to whether all of these improvements in infrastructure should be charged to the plant operation since the generally contribute to the development of the country and the welfare of its people. Housing, for example, usually is at least partially self-supporting from rental to employees. Transportation infrastructure often is utilized for many purposes not directly connected with fertilizer production.

In the present discussion, investment costs will be based on the battery limits cost for an industrial location in a developed country. To arrive at the total cost, 50% of the battery-limits cost will be added except when otherwise stated.

In the last 15 years process designs have been developed and gradually improved for ammonia production by steam reforming of natural gas, naphtha, and other light hydrocarbons in plants using centrifugal compressors. Standard designs have evolved for three capacities--550, 900-1040, and 1360 mt/day (600, 1000-1150 and 1500 short tons/day).

The great majority of new plants built in the last decade have been designed for one of these three capacities even though the capability exists for design of plants using a centrifugal compressor over a range of 270 to 2,700 tpd. The majority of new plants built or ordered in the last decade have been in the 900-1040 tpd capacity range. Since development costs have been spread over a larger number of plants, the investment cost is lower per annual ton of capacity, and this capacity range is generally regarded as the economic optimum scale in most cases. A capacity of 550 tpd usually is regarded as the economic minimum scale for plants using centrifugal compressors, and plants of this size are selected when the market is limited or when the amount of available feedstock is limited. The 1,360 tpd size is sometimes used in locations where site development costs are high, the total project cost may be lower per annual ton of capacity. However, in some cases where site development costs are high, it may be preferable to locate two or more smaller plants at the same site as has been done in Indonesia and South Korea, for example.

Relatively few plants have been built to produce ammonia by partial oxidation of heavy oil or coal, thus, process and equipment design has not been standardized to the same extent as for steam reforming processes. Therefore, there is no reason to suppose that 1,000 tpd is an economic optimum for these processes. In fact, there is some reason to believe that the economic optimum scale may be higher for oil-and coal based processes. For example, Supp implies that 1,600 tpd may be near optimum for ammonia production by partial oxidation of heavy fuel oil when the market is not a limiting factor (18).

For the purpose of further discussion, an investment cost of $110 million will be assumed for 1,000 tpd battery-limits natural gas based ammonia plant located in an industrial site such as the U.S. Gulf Coast, and a total turnkey plant cost of $165 million will be assumed for the base case. This is line with recent estimates obtained from a renowned engineering /construction company the total plant cost includes land, product storage, site preparation and auxiliary and support facilities(31).

The usual assumption that total plant cost is 1.5 times battery-limits cost does not seem appropriate in the case of plants larger or smaller than 900-1,040 tpd because of the unusual relationship between battery-limits plant costs and capacity. For the purposes of the present estimate, the 50% allowance for additional plant costs will be applied only to the base case (1,000 tpd) for other plant sizes the additional plant costs will be assumed to vary as the 0.6 power of the capacity. This assumption leads to the following total plant costs;

## ESTIMATED TOTAL PLANT COSTS

| Feed | Battery (\$million) | Total (\$million) |
| --- | --- | --- |

Working capital will not be included, but an allowance of 5% will be made in the operating cost estimate for "administrative and miscellaneous" cost which includes interest on working capital.

The factor for naphtha-based plants presumably can be applied with some degree of confidence to standardized plant sizes (550 and 1,360 tpd) that are lower and higher than the base case.

It should be emphasized that the investment estimates are not total project costs. Some items that the estimates do not include are:

1.   Escalation of costs beyond 1992.
2.   Interest on capital during construction.

3. Feasibility studies.
4. Training programs and other startup expenses.
5. Contingencies.
6. Electron power generation except in the case of plants
7. Emergency electric-generating facilities to serve as backup for regular power supplies.
8. Import taxes or custom duties.
9. Any unusual expense to ensure water supplies such as dams, reservoirs, long pipelines, or desalination of backup for regular power supplies.
8. Import taxes or custom duties.
9. Any unusual expense to ensure water supplies such as dams, reservoirs, long pipelines, or desalination of seawater.
10. Infrastructure such as housing, roads, or railroads outside the plant, harbor improvement; piers, jetties, airport facilities, etc.
11. Unusual site preparation expenses.

## Production cost and Gate Sale Price Estimates

The following simplifying assumptions are made to arrive at comparative estimates for production costs and gate sale prices.

1. Labor costs--$23.98/man-hour for operating labor only.

Fringe benefits 100% c. of labor, includes administration,

3. Chemical control --20% of labor, includes laboratory personnel and supplies.

4. Miscellaneous supplies--$1.50/ton.

5. Electricity--$0.036/kWh.

6. Cooling water --$0.0164/m3 on a once-through basis (actual requirement may be about 5% of once through requirement when recirculation through cooling towers is used.

7. Boiler feedwater --$0.60/m3.

8. Depreciation --6.67% of plant cost (15-year straight line).

9. Maintenance--3% of plant cost, including labor and materials.

10. Taxes and insurance--2% of plant cost per year.

11. Interest--4% of plant cost per year which may be viewed as 8% interest on one-half of plant cost.

12. Return on investment (ROI)--10% of plant cost/year with

no provision for income taxes.

13.  Administrative and miscellaneous costs--5% of the total
of other production costs, which include allowance for
interest on working capital, startup expense etc.

The base case for 1,000 tpd ammonia plants will assume the
following conditions;

| Fuel and Feedstock | Heating Value (LHV)[a] | Cost, $/Unit (Base Case) |
|---|---|---|
| Natural gas | 10471 kcal/m3 | 0.078/m3 |
| Naphtha | 10,290 kcal/kg | 185/t |
| Fuel oil | 9,722 kcal/kg | 86/t |
| Coal | 6,100 kcal/kg | 38 /t |

-----------------------------------------------------------

(a). Low heating value (LHV)

| Fuel and Feedstock | Requirements per Ton of $NH_3$ Quantity--Million-kcal---cost,$---- | | |
|---|---|---|---|
| Natural gas | 1,421 m3 | 7.37 | 54.90 |
| Naphtha | 7.45 t | 8.56 | 133.09 |
| Fuel oil | 8.56 t | 9.2 | 75.72 |
| Coal | 0.66 t | 9.2. | 57.31 |

-----------------------------------------------------------

a.  From reference (12)--------------- SPL

For the base case, a 1,000 tpd plant operating at about-90%
capacity (300,000 tpy) using natural gas at $ 0.078/m3, the
estimated production cost is about $162/ton of $NH_3$ and the
gate sale price is $217.8 (see table 6).

For comparison the world market price is t $100-105/ton of
$NH_3$ (Fertilizer Market Bulletin (FMB) March 1992). This is
much higher than the estimated production cost but
considerably lower than the estimated gate sale price. Some
factors that might lead to a price lower than that estimated
in table 5 are (1) the average feedstock price may be less
than $0.53/$m^3$ (2) the return on investment may be less than
10% and (3) majority of plants were built at a time when
plant construction costs were lower than at present and are
partially depreciated. thus the capital investment is lower.
It will be noted that capital related costs are about 38% of
the production cost and 49% of the gate sale price.

Unfortunately, low cost natural gas is available only in
remote locations where construction costs are high. A grass-
roots plant in an industrial location of a developed country

is estimated to cost $165 million (base case), whereas, the same plant in a developing country is likely to cost 25%-50% more. Perhaps more importantly, it is usually necessary to provide more auxiliary and supporting facilities, since services and supplies that are readily available in developed countries may be unavailable. Also, infrastructure improvements are likely to be needed, it may be debatable how much of the infrastructure improvements should be charged to the plant. However, the fact remains that the plant could not function efficiently without them.

### TABLE 6 ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA FROM NATURAL GAS.

FEEDSTOCK: NATURAL GAS
CAPACITY: 1000 tpd, CAPACITY UTILIZATION: 90%
ANNUAL PRODUCTION: 300,000 tons
LOCATION: U.S. GULF COAST
PLANT COST: 165 $ MILLIONS

| Item | Quantity | | Unit price, $ | $/ton of NH3 |
|------|----------|---|--------------|--------------|
| Natural gas | (7.37 Gcal) | 704 Nm3 | 0.079 | 55.62 |
| Catalyst and chemicals | | | | 2.60 |
| Miscellanea, supplies | | | | 1.50 |
| Steam export | (0.49 Gcal) | 0.65 mt | 7.74 | (5.06) |
| Electricity | | 33 kWh | 0.036 | 1.19 |
| Cooling water | | 177 m3 | 0.0164 | 2.90 |
| Boiler feed water | | 1.43 m3 | 0.6 | 0.86 |
| Labor | | 0.176 man-hour | 23.98 | 4.22 |
| Overhead | | 100% of labor | | 4.22 |
| Chemical control | | 20% of labor | | 0.84 |
| Maintenance | | 3% of plant cost | | 16.50 |
| Taxes and insurance | | 2% of plant cost | | 11.00 |
| Depreciation | | 6.67% | | 36.68 |
| Interest | | 4% | | 22.00 |
| Subtotal | | | | 155.07 |
| Adm. and misc. expense 5% of subtotal | | | | 7.75 |
| Production cost | | | | 162.82 |
| ROI, 10% | | | | 55.00 |
| Gate sale price | | | | 217.82 |

Note: effective heating consumption 7.37 - 0.49 = 6.88 Gcal/ton of NH3

Whatever the reasons, it is not uncommon for the total project cost in a developing country to be twice as much as in an industrialized developed country.

The previous comparisons have been based on a capacity utilization of about 90% (annual production 300 times daily rated capacity). Some plants have achieved several-year records of 100% capacity utilization, which is generally assumed to be 330 times daily capacity, or even higher, but many plants do not attain 90% annual capacity utilization for a variety of reasons such as interruptions in feedstock supply, lack of market demand, or technical difficulties. In particular, many ammonia plants in developing countries have operated well below 90% of rated capacity even when fertilizer was in short supply. There are some outstanding exceptions, and the average for developing countries is improving.

Since ammonia production is highly capital intensive, the percentage of capacity utilization has an important effect on production cost and profitability.Operating at 100% rather than 90% of capacity would decrease the production cost and the gate sale price.However, operating at 75% rather than 90% capacity would increase the production cost and the gate sale price For higher cost plants, the effect is larger. Thus, the advantage of locating a plant where low-cost feedstock is available can be lost by a combination of higher capital cost and lower capacity utilization.

Even though minimizing the capital cost is important, it should not be done at the expense of reliability. In general extra money spent in improving plant reliability will be repaid in improved capacity utilization. lower production cost, and greater profitability. In locations where feedstock costs are low, some saving in capital costs can be made by less elaborate heat and energy recovery facilities. The extra equipment that is required to improve efficiency is important when feedstock costs improve efficiency is important when feedstock costs are high but much less important where low-cost natural gas is available. In addition, the extra equipment tends to complicate plant operation and increase maintenance cost. Some other means for reducing capital costs are (1) choose a standard design. (2) select reliable and capable contractors. and (?) minimize construction time.

The choice of feedstock affects the production cost in that it affects plant cost, as previously discussed. by influencing raw material costs and other operating costs. The choice of feedstock may also affect plant reliability, although there are no precise data on this point. Coal-based plants have a poor record for reliability although production rates up to 90% of capacity have been reported. If production of ammonia from coal becomes popular, it is

likely that equipment design will be improved and standardized so that more dependable operation can be expected.

Estimated production costs and gate sale prices for a 1,000 tpd ammonia plant located in a developed country using naphtha, fuel oil, and coal are shown in Table 7, 8 and 9

### TABLE 7 ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA FROM NAPHTHA

FEEDSTOCK: NAPHTHA
CAPACITY: 1000 tpd, CAPACITY UTILIZATION: 90%
ANNUAL PRODUCTION: 300,000 tons
LOCATION: U.S. GULF COAST
PLANT COST: 188 $ MILLIONS

| Item | Quantity | Unit price, $ | $/ton of NH3 |
|------|----------|---------------|--------------|
| Naphtha | (7.45 Gcal)  0.724 mt | 185 | 133.94 |
| Catalyst and chemicals | | | 3.47 |
| Miscellanea, supplies | | | 1.50 |
| Electricity | Self sufficient | 0.036 | 0.00 |
| Cooling water | 203 m3 | 0.0164 | 3.33 |
| Boiler feed water | 1.18 m3 | 0.6 | 0.71 |
| Labor | 0.196 man-hour | 23.98 | 4.70 |
| Overhead | 100% of labor | | 4.70 |
| Chemical control | 20% of labor | | 0.94 |
| Maintenance | 3% of plant cost | | 18.80 |
| Taxes and insurance | 2% of plant cost | | 12.53 |
| Depreciation | 6.67% | | 41.80 |
| Interest | 4% | | 25.07 |
| Subtotal | | | 251.49 |
| Adm. and misc. expense 5% of subtotal | | | 12.57 |
| Production cost | | | 264.06 |
| ROI, 10% | | | 62.67 |
| Gate sale price | | | 326.73 |

## TABLE 8 ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA FROM HEAVY OIL.

FEEDSTOCK: FUEL OIL
CAPACITY: 1000 tpd, CAPACITY UTILIZATION: 90%
ANNUAL PRODUCTION: 300,000 tons
LOCATION: U.S. GULF COAST
PLANT COST: 264 $ MILLIONS

| Item | Quantity | | Unit price, $ | $/ton of NH3 |
|---|---|---|---|---|
| Fuel oil | (8.56 Gcal) | 0.88 mt | 86 | 75.68 |
| Catalyst and chemicals | | | | 0.90 |
| Miscellanea, supplies | | | | 1.50 |
| | | | | |
| Electricity | Self sufficient | | 0.036 | 0.00 |
| Cooling water | | 270 m3 | 0.0164 | 4.43 |
| Boiler feed water | | 1.45 m3 | 0.6 | 0.87 |
| | | | | |
| Labor | 0.264 man-hour | | 23.98 | 6.33 |
| Overhead | 100% of labor | | | 6.33 |
| Chemical control | 20% of labor | | | 1.27 |
| | | | | |
| Maintenance | 3% of plant cost | | | 26.40 |
| Taxes and insurance | 2% of plant cost | | | 17.60 |
| Depreciation | 6.67% | | | 58.70 |
| Interest | · 4% | | | 35.20 |
| | | | | |
| Subtotal | | | | 235.21 |
| Adm. and misc. expense 5% of subtotal | | | · | 11.76 |
| | | | | |
| Production cost | | | | 246.97 |
| ROI, 10% | | | | 88.00 |
| | | | | |
| Gate sale price | | | | 334.97 |

## TABLE 9 ESTIMATED PRODUCTION COST AND GATE SALE PRICE OF AMMONIA FROM COAL

FEEDSTOCK: COAL
CAPACITY: 1000 tpd, CAPACITY UTILIZATION: 90%
ANNUAL PRODUCTION: 300,000 tons
LOCATION: U.S. GULF COAST
PLANT COST: 330 $ MILLIONS

| Item | Quantity | | Unit price, $ | $/ton of NH3 |
|---|---|---|---|---|
| Coal | (9.2 Gcal) | 1.508 mt | 38 | 57.30 |
| Catalyst and chemicals | | | | 0.90 |
| Miscellanea, supplies | | | | 1.50 |
| | | | | |
| Electricity | | 372 kWh | 0.036 | 13.39 |
| Cooling water | | 247 m3 | 0.0164 | 4.05 |
| Boiler feed water | | 0.06 m3 | 0.6 | 0.04 |
| | | | | |
| Labor | | 0.508 man-hour | 23.98 | 12.18 |
| Overhead | | 100% of labor | | 12.18 |
| Chemical control | | 20% of labor | | 2.44 |
| | | | | |
| Maintenance | | 3% of plant cost | | 33.00 |
| Taxes and insurance | | 2% of plant cost | | 22.00 |
| Depreciation | | 6.67% | | 73.37 |
| Interest | | 4% | | 44.00 |
| | | | | |
| Subtotal | | | | 276.35 |
| Adm. and misc. expense 5% of subtotal | | | | 13.91 |
| | | | | |
| Production cost | | | | 290.26 |
| ROI, 10% | | | | 110.00 |
| | | | | |
| Gate sale price | | | | 400.26 |

It is probably not realistic to assume that a coal-based
ammonia plant can be operated at the same percentage of
rated capacity as a natural gas or naphtha based plant, and
this factor should be taken into account. However, there is
not enough experience with coal based plants to establish
what average capacity utilization can be expected. If it
were assumed that the coal-based plant would operate at an
average capacity utilization of 10% less than a gas based
(80- versus 90%, for example), the production cost and the

gate sale pricedifferential would be increase.

It seems unlikely that coal-based ammonia plants using present technology can produce ammonia at or near the world market price. In the past, coal-based plants have been built in situations where coal was the only indigenous feedstock and where the advantages of domestic production (security, foreign exchange savings etc.) outweighed the higher cost. In the future, some developed countries may undertake ammonia production from coal as their natural gas supplies become exhausted, particularly if improved technology becomes available.

In developing countries as a group, natural gas reserves are equivalent to 1360 yrs' use at current production rates (6). While the production rate is increasing, more reserves are being discovered. Moreover, gas and oil reserves seem to be more widely distributed than coal; 70 countries including 45 developing countries reported reserves of natural gas or petroleum or both, while only 19 countries including 5 developing countries reported coal reserves. It appears, therefore that natural gas is likely to be the dominant feedstock on a worldwide basis for the remainder of the 20th century, probably well into the 21st century, and possibly throughout the 21st century depending on the rate of discovery.

## Economics of Small-Scale Ammonia Plants

Evaluation of the economics of small ammonia plants (100-300 tpd) is difficult because relatively few of them have been built in recent years and because their advantages depend on specific conditions that are hard to generalize. Some situations in which a small plant can be considered are:

1.   When there is a local market that would be difficult or expensive to supply from larger, distant paints.

2.   When the location is such that it would be difficult to transport large heavy equipment to the plant site or to erect it.

3.   When there is a limited supply of feedstock at a favorable cost, such as a small pocket of natural gas or a small supply of byproduct hydrogen.

Assuming that the capital cost of a 200-tpd plant is 60% greater per ton of capacity than that of a 1,000 tpd plant, the capital related production costs would be about $27/ton greater, using the standard method of calculation used in this chapter. This cost differential could readily be offset by lower-cost feedstock, more reliable supply of feedstock, and savings in import or distribution cost.

There have been numerous proposals for small ammonia or
ammonia-urea plants in developing countries, especially for
remote countries of remote regions of larger countries. For
example, Snamprogetti has proposed 150-tpd integrated urea-
ammonia plants (see chapter IX) and estimated that 10 such
plants would cost about 46% more than one 1,500-tpd plant
(35). However, it was estimated that the delivered cost of
the urea at the farm level would be substantially less.

A proposal for numerous small plants rather than one large
one would involve the question of feedstock supply. There
are not many countries where feedstock is available at a
large number of locations. However, the feedstock problem
could be solved if processes for production successfully on
a scale sufficiently large for a small ammonia plant.

Small ammonia (and urea) plants are available in a
standardized design consisting of skid-mounted preassembled
units that can be set up and connected with relatively
little on site construction labor (36). Thus, the
construction time can be quite short. As a result, there is
less interest on capital during construction. In addition,
shortening the period from inception to completion would
help to minimize the uncertainties that are inherent in
long-range planning.

Maintenance costs for small plants could be minimized by use
of a standardized design with interchangeable spare parts so
that spare parts could be quickly obtained from a central
location.

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( More references to be included)