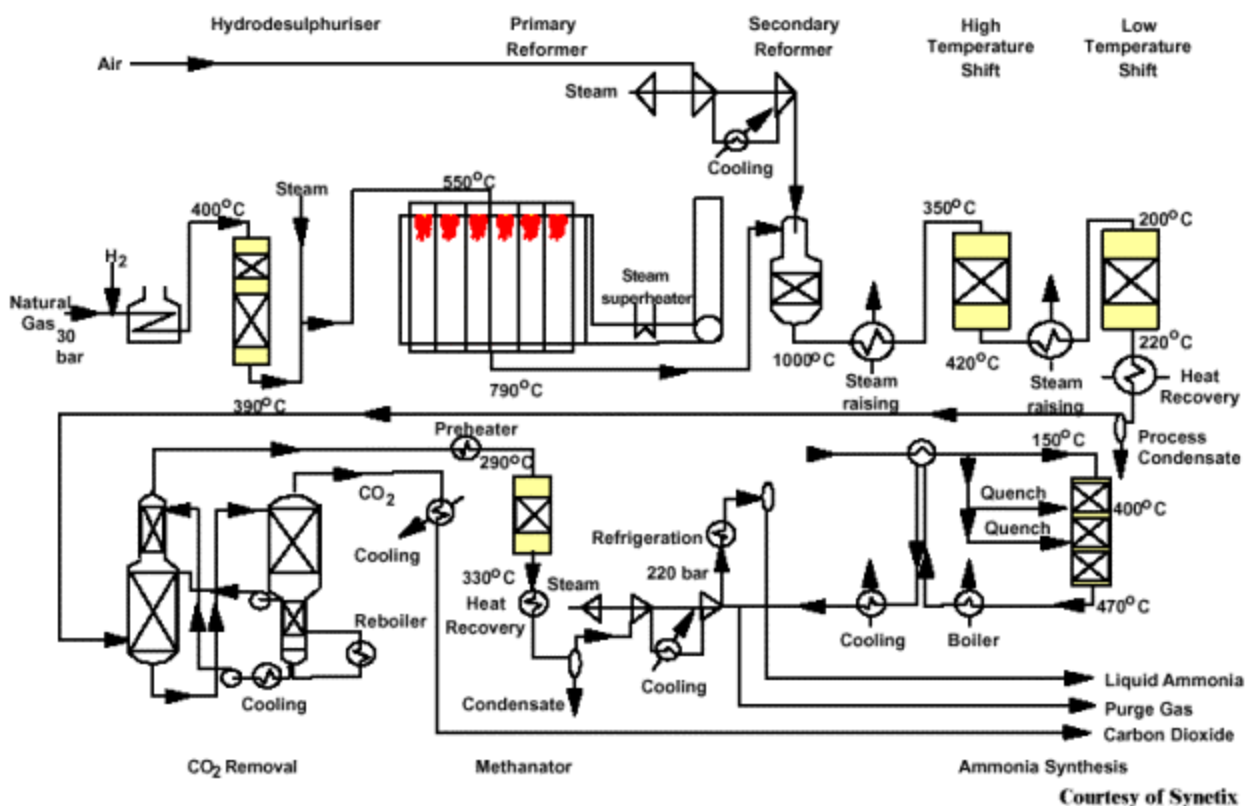


## Ammonia: The Next Step

Steam reforming of hydrocarbons for ammonia production was introduced in 1930. Since then, the technology has experienced revolutionary changes in its energy consumption patterns. Ranging from an early level of 20 Gcal/tonne (79.4 MBtu/tonne) to about 7 Gcal/tonne (27.8 MBtu/tonne) in the last decade of the 20th century. The energy intensive nature of the process is the key driving force for improving the technology and reducing the overall cost of manufacturing.



**Figure 1: Overall Layout of a Steam Reforming Plant for Ammonia Synthesis**

Looking further ahead, we'll review some potentially significant developments and concepts that may impact the manner in which ammonia is produced. Some of these manufacturing routes are being tested or employed at a few plants around the world, but have yet to be fully developed into commercial processes. We'll also review more traditional approaches to ammonia manufacturing along the way.

## Developments

### 1. Reforming Section

In the conventional process, steam reforming is carried out in a fired furnace of the side fired or top fired type. Both need large surface areas for uniform heat distribution along the length of the catalyst tubes. This process has several disadvantages. For example, it is a thermally inefficient process (about 90% including the convection zone) and there are mechanical and maintenance issues. The process is difficult to control and reforming plants require a large capital investment.

#### A. Gas Heated Reformers

Future technologies include the use of Gas Heated Reformers (GHR), which are tubular gas-gas exchangers. In the GHR, the secondary reformer outlet gases supply the reforming heat. Though it is not presently being used widely, GHR has certain advantages over fired furnaces. Table 1 shows a list of these advantages. Kellogg's Reforming Exchanger System is an example of GHR technology. Although GHR results in reduced energy consumption, a comprehensive energy conservation network should be established to maximize the benefits of a GHR system.

**Table 1: Advantages of Gas Heated Reformers**

<b>Fired Furnace</b>	<b>Gas Heated Reformers</b>
Large volumes	Smaller volumes
Larger surface area and heat loss	Reduced surface area and heat loss
Complex instrumentation	Simplified instrumentation
High maintenance costs	Low maintenance costs
Large convection zone	No convection zone
Stack losses	No stack losses
High fixed capital costs	Low fixed capital costs
Reduced catalyst tube loss from high temperature and uneven heat distribution	Longer tube life due to uniform heat distribution
Increased downtime required for shut down	Reduced downtime required for shut down
Well established process	Yet to gain wide acceptance

## B. Hydrogen Separation

Lechatelier's Principle states that a reaction equilibrium can be shifted by applying external forces. This offers a means of removing products from the reaction mixture to increase the conversion per pass. In reforming, experiments have been performed up to 500 OC (932 OF) and 20 bar (294 psig) using a palladium membrane to remove the product hydrogen. These experiments have results in a significant increase in methane conversion as can be seen by the following case study.

### **Case Study on the Membrane Separation Process**

The separation of hydrogen from the product gas of the reforming process can result in significant productivity gains when compared to the current processes being employed. The base case for this study is a conventional steam reforming plant based on natural gas operating at 1750 tonnes per day. The operating conditions of the plant are assumed to be the same as those typically employed today and the only modification is the introduction of hydrogen separation. The tests for the membrane separation have been carried out at 500 OC (932 OF) and 20 bar (294 psig), these conditions will function as upper limits for the process to be considered in this study. Membrane units will be considered after the primary reformer (at 60% hydrogen separation), after the secondary reformer (at 60% hydrogen separation), and after the High Temperature Shift (HTS) converters (at a 50% hydrogen separation)

The following assumptions are made in this case study:

1. The natural gas feed at the primary reformer is the same for both cases.
2. The primary reformer exit temperature is the same for both units.
3. The primary reformer operating pressure is the same for both units.
4. The process air is fed to the secondary reformer at optimal conditions and any remaining nitrogen that is required is supplied through an Air Separation Unit (ASU) and is available at 0.1 kg/cm<sup>2</sup> (1.42 psig)
5. Any extra energy consumption in the ASU is considered for the revamp case.
6. All of the heat from the process gas from the primary reformer to the carbon dioxide removal section is used in a steam network.

7. No changes in the carbon dioxide removal system are considered.
8. The pressure drop across the front end of the process is kept constant for both systems, thus the synthesis gas compressor suction pressure remains constant.
9. The loop pressure is the same for both processes and is controlled by changing the purge gas quantity.
10. The existing compressors are capable of handling any additional loads.
11. No scheme changes are considered in the synthesis loop.
12. All hydrogen from the membrane separation unit is available at 9.0 kg/cm<sup>2</sup> (128 psig)
13. The productivity analysis is carried out on the ammonia plant only (the urea plant is excluded)
14. A complete steam balance is included on both processes. Changes in the steam balance are considered for:

Steam generation from the front end of the processes

Steam generation from the back end of the processes

Additional steam in the carbon dioxide removal section caused by a reduction in the heat available from the process gas

Additional power for the synthesis compressor due to changes in flow and composition

Additional power in the ammonia refrigeration compressor

Reduced load on the process air compressor

Additional power for low pressure hydrogen separated through membranes

Additional power for nitrogen compression

Additional power for the air compressors of the ASU

Small changes in other drives and small equipment

**Comparison Between Conventional Reforming and Reforming with Hydrogen Separation**

Production rise from 1750 to 1854 tonnes per day	<b>+6.0% rise in capacity</b>
<b>Process Change</b>	<b>Energy Change (Gcal/tonne)</b>
Gain in feed and fuel including steam superheater	+0.36
Loss in steam generation (front end)	0.00
Loss in steam generation (back end)	-0.02
Loss in additional steam for carbon dioxide removal	-0.27
Gain in energy in synthesis gas compressor	+0.01
Extra energy in refrigeration compressor	0.00
Gain in energy in process air compressor	+0.16
Extra power in hydrogen compressor	-0.22
Extra power for nitrogen from ASU	-0.12
Steam savings in primary reformer	+0.08
Other rotary drives and equipment	+0.04
<b>Total Gain</b>	<b>+0.02</b>

It is evident from these results that the major losses occur in the carbon dioxide removal section of the plant. These losses are the result of consuming additional steam and compression energy for hydrogen separation. With additional minimization of these losses, additional savings can result. For a production gain of 6% over the base case, the energy saving is **0.02 Gcal/tonne (0.08 MBtu/tonne)**.

This development could yield savings by increasing methane conversion in reformers and increasing the carbon monoxide conversion in shift reactors. The energy savings can be as high as 0.50 Gcal/tonne (1.98 MBtu/tonne) depending on the adopted process configuration. Hydrogen separation technology can also result in increased ammonia plant capacity as illustrated in the above case study.

The reduced air requirement (about 80% of conventional plants) in the secondary reformer is required with a 60% hydrogen removal rate in the reformer. This will also require an additional source of nitrogen. Therefore, the technologies in which nitrogen is being added separately, either from an Air Separation Unit (ASU) or from any other sources, will become more important in this case.

### C. Isobaric Manufacturing

The primary hurdle in the isobaric method of manufacturing ammonia is the poor conversion of methane at elevated pressure. The bottleneck is the maximum permissible temperature range due to metallurgical constraints in the reformer tubes. Synthesis pressures are no longer an issue with the development of the Kellogg Advanced Ammonia Process (KAAP), which utilizes a ruthenium-based catalyst operating at 90-100 ata (1470 psia). Thus, if the methane conversion can be increased by hydrogen separation, the process can be operated at higher isobaric pressures.

The synthesis compressor can be reduced to one small compressor at the natural gas feed. The power consumption in this compressor will be 3.0 MW for an isobaric pressure of 100 ata in the front end because of reduced gas flow and reduced differential pressure. The gas flow in synthesis compressor remains near 200,000 Nm<sup>3</sup>/h (117,715 scfm) while the flow will be reduced to near 45,000 Nm<sup>3</sup>/h (26,485 scfm) in natural gas compressor. The differential pressure in the synthesis compressor is 175 kg/cm<sup>2</sup>a (from 25 kg/cm<sup>2</sup>g to 200 kg/cm<sup>2</sup>g), while the differential pressure is only 60 kg/cm<sup>2</sup>a in natural gas compressor (from 40 kg/cm<sup>2</sup>g to 100 kg/cm<sup>2</sup>g). The power consumption is around 3.0 MW in the conventional recirculator. This will result in a total power consumption of 6.0 MW in raising the pressure of synthesis gas. Presently, the power consumption in the synthesis gas compressor is around 25.0 MW for a conventional ammonia plant at same load. This, however, requires the process air compressor to be operated at a discharge pressure of 100 ata (1470 psia) compared with a pressure of 34-35 ata (510 psia) in the conventional plant. The net energy saving in the isobaric process can be near 0.5 Gcal/tonne (1.98 MBtu/tonne). Moreover, it will also save the energy in CO<sub>2</sub> compressor of the urea plant because the CO<sub>2</sub> from the ammonia plant will be available at a much higher pressure.

## 2. Shift Section

The water-gas shift reaction is favorable for producing carbon dioxide which is used as a raw material for urea production. Presently, most plants use a combination of conventional High/Low Temperature Shift (HTS/LTS) or High/Medium/Low Temperature Shift (HTS/MTS/LTS) technology. Another option is a combination of HTS/LTS/Selectoxo technology. While not as common as the other combinations, this arrangement offers advantages that will be discussed later. The most important objectives for this section are a low pressure drop and efficient heat recovery from the process gas.

### A. Selectoxo Unit

The Selectoxo unit offers several advantages for grass root designs as well as for revamps. Selectoxo (or selective catalytic oxidation) was developed by Engelhard for oxidizing carbon monoxide while not oxidizing hydrogen. The Selectoxo process provides good energy efficiency because it minimizes carbon monoxide "slip" (only about 0.03%), improved process flexibility, and higher productivity in revamps when compared to other oxidation options. The Selectoxo unit is capable of increasing a plant's capacity by 1.5-2.0%.

The Selectoxo unit can also help in a grass root plant by maintaining carbon dioxide/ammonia production ratios which is favorable for full conversion of ammonia to urea. The economics of this option are to be considered against the extra cost of carbon dioxide production by other means (either from the flue gas of the primary reformer or through back burning of extra synthesis gas).

## 3. Carbon Dioxide Removal Section

The removal of carbon dioxide has been performed via solvent absorption and distillation since the inception of ammonia technology processes. This section of the ammonia plant is the largest consumer of energy after the cooling water system. The energy consumption is due to thermally inefficient distillation, dissipation of huge amounts of low level heat into the cooling water via product carbon dioxide, and pressurization and depressurization of absorbents.

### A. Isobaric Manufacturing

Chemical absorption in the isobaric manufacturing of ammonia can be unattractive because of the very high pressure (100 ata). Therefore, major changes in the existing carbon dioxide removal technologies may be necessary. Replacement technologies may include cryogenic condensation or pressure swing absorption (PSA).

Carbon dioxide separation through PSA is offered in the Low Cost Ammonia Process (LCA). PSA is scalable and may be more economical because of efficient carbon dioxide recovery at higher pressures. However, further development in this direction is essential for the recovery of high purity carbon dioxide as desired in urea production.

Carbon dioxide separation via condensation may also become more attractive due to an increased concentration of carbon dioxide which can be realized with successful hydrogen separation through membranes. This would allow the concentration of carbon dioxide to be increased by 18 to 36 mole percent. This would allow carbon dioxide concentrations in the gas to be reduced to 15% by chilling of the 100 ata front end gases. This method also provides high pressure carbon dioxide for urea production which will reduce the power consumption in the carbon dioxide compressor of the urea plant substantially. The remaining product carbon dioxide gas can be recovered via PSA. A combined PSA and condensation process may solve the problem of carbon dioxide purity from the PSA process.

#### 4. Final Purification of Synthesis Gases

The conventional methanation process can result in the loss of hydrogen. Minimizing this loss is of prime concern when examining the process used to purify the syngas.

##### A. Pressure Swing Absorption (PSA) Unit

PSA represents an effective means of reducing the hydrogen loss in the methanator. In this process, the product hydrogen is separated out from the raw synthesis gas and then nitrogen is added. The other benefit is the production of pure synthesis gas, which saves on recycle compression and the elimination of the losses through the purge gas stream by way of eliminating the purge itself.

##### B. Cryogenic Separation Process

Cryogenic separation of inert gases from the raw synthesis gas is a commonly used approach. This unit is integrated into the purge gas recovery loop from the back to the front end of the ammonia unit. It serves to recover hydrogen from the purge stream and feed it back to the ammonia synthesis loop after recompression.

In this separation process, inerts in the synthesis gas are removed through cryogenic condensation. Typically, the composition of conventionally prepared synthesis gas is about 74% hydrogen, 0.8-1.0% methane, 0.32% argon with the balance being nitrogen. In this process, nearly all of the methane is removed along with half of the argon present, thus it produces "cleaner" synthesis gas for ammonia production. Moreover, the hydrogen to nitrogen ratio of the synthesis gas can be controlled independently without affecting the performance of front end. Traditionally, this ratio is controlled by varying the process air flow to the secondary reformer which makes the system reactive between front end and the back end. A cryogenic separation unit eliminates the dependence of the back end on the performance of the front end.

However, this process does not contribute to energy savings. Rather, it represents a good option for revamps after achieving the limits of capacity using conventional revamps. The cryogenic separation process creates additional margin in the front end by allowing more methane slip and by reducing the total quantity of inerts in the loop.

## 5. Ammonia Synthesis

Several developments in ammonia synthesis have been made in the past, these developments revolve around the basic principles of reaction, heat recovery, cooling, production ammonia separation, and recycling of synthesis gas.

### A. Synthesis Catalyst

After almost 90 years of a monopoly in the ammonia synthesis market, iron catalyst has not been replaced by a precious metal (ruthenium) based catalyst used in the KAAP developed by Kellogg. The KAAP catalyst is reported to be 40% more active than iron catalysts.

Research work on low temperature and low pressure catalysts to produce ammonia at 20-40 kg/cm<sup>2</sup>g and 100 °C is being performed at Project and Development India Ltd. (PDIL) according to their in-house magazine. The catalyst being studied is based on cobalt and ruthenium metals and has exhibited few encouraging results.

### B. Ammonia Separation

The removal of product ammonia is accomplished via mechanical refrigeration or absorption/distillation. The choice is made by examining the fixed and operating costs. Typically, refrigeration is more economical at synthesis pressures of 100 ata or greater. At lower pressures, absorption/distillation is usually favored. A comparison of these two methods is presented in Table 2.

**Table 2: Comparison of Ammonia Separation Techniques**

<b>Condensation</b>	<b>Absorption</b>
High energy costs at lower loop pressures (below 100 ata)	Almost constant energy costs independent of pressure, and less than condensation separation below 100 ata
Higher fixed costs below 100 ata	Almost constant fixed costs independent of pressure, and less than condensation separation below 100 ata
Economical at higher operating pressures (above 100 ata)	Economical at lower synthesis pressures in comparison to condensing process
Energy consumption in refrigeration cycles	Inefficient energy consumption in the distillation process
Simple process with condensers and separators	More complex process with absorber, distillation column, pumps, reboilers, condensers, and reflux accumulators. Associated instrumentation is also complex
No chance of catalyst poisoning	Chance of catalyst poisoning due to oxygen in the absorbents

Minimizing the amount of ammonia in the recycle gas of an ammonia process presents an interesting scenario. Usually the ammonia concentration of the recycle is 3-4%, but reducing this amount to 1.5% can increase plant capacity by about 2.5%. However, the additional separation can often represent a significant addition to the capital cost of the plant and may not be economical for retrofitting (depending on operating pressure). However, reduced ammonia concentration in the recycle can be reviewed for a grass root project where capacity gains can be realized with an additional investment.

Decreasing the ammonia concentration in the recycle stream of existing plants is usually hampered by the high energy cost required for water absorption. Norsk Hydro (Norway) developed a method of reducing the recycle ammonia concentration to near 0.5% via absorption in glycol (DEG). This process can be installed in a high pressure loop (>100 ata) and in combination with a condensation unit. The installed cost is said to be lower than a comparable mechanical refrigeration system.

The separation of product ammonia within the converter using liquid or solid adsorbent can increase the system efficiency significantly. The regenerated adsorbent is fed to the converter and contacts the reaction mixture. Product ammonia is absorbed and removed from the converter. The product ammonia can be recovered either by changing the pressure or temperature depending on process economics. This method would eliminate the need for a synthesis loop and the recycling of synthesis gas. This concept is still being investigated in academic research.

## 6. Final Word

The developments discussed here such as isobaric manufacturing, the use of gas heat reformers, hydrogen separation, carbon dioxide removal technology, product ammonia separation, and high activity synthesis catalyst can result in a significant reduction in energy consumption when compared with traditional technology.

Global demand, increased competition, and ingenuity have fueled efforts to enhance existing ammonia technology. In an industry where change is often accepted reluctantly, these technological advancements will have to prove themselves worthy before receiving industry-wide attention.

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