

# The Haber-Bosch Heritage: The Ammonia Production Technology



Haber



Bosch



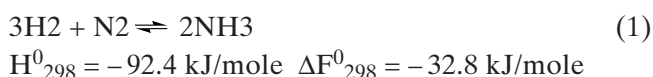
Mittasch

Max Appl

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# Introduction

Based on the fundamental research work of **Fritz Haber, Carl Bosch** and his engineering team developed the ammonia synthesis to technical operability using the promoted iron-based catalyst found by **Alwin Mittasch** and co-workers. Since then there has been no fundamental change in the synthesis reaction itself. Even today every plant has the same basic configuration as this first plant. A hydrogen-nitrogen mixture reacts on the iron catalyst (today's formula differs little from the original) at elevated temperature in the range 400–500 °C (originally up to 600 °C), operating pressures above 100 bar, and the unconverted part of the synthesis gas is recirculated after removal of the ammonia formed and supplemented with fresh synthesis gas to compensate for the amount of nitrogen and hydrogen converted to ammonia.



Of course, progress made in mechanical and chemical engineering and increased theoretical knowledge have led to improvements in efficiency, converter design and energy recovery in the synthesis section, but really dramatic changes happened over the years in the technology of synthesis gas generation.

As the synthesis is the very heart of every ammonia production and is also from an historical point of view the most interesting section, it is probably appropriate to start our review with this section.

## The synthesis

### The ammonia equilibrium and the recycle concept

The reaction proceeds with a reduction in volume and is also exothermic, so the equilibrium concentrations of ammonia are higher at high pressure and low temperature, but at the turn of the last century a quantitative knowledge of chemical equilibrium was not available, and this might explain why early experiments aimed at the ammonia synthesis were unsuccessful. A famous victim of the lack of thermodynamic data was **Wilhelm Ostwald**. He offered in 1900 BASF a process in which nitrogen and hydrogen were passed over heated iron wire at atmospheric pressure, claiming several percent of ammonia, a concentration

which was far beyond equilibrium. BASF found the reason for his erroneous data and – irony of history – he withdraw his patent application, not knowing how important that application could have been later when indeed iron became the basis of the commercial ammonia synthesis catalyst.

First systematic measurements were made by Haber in 1904/05 but they yielded too high figures as a consequence of problems with exact analysis of the low concentrations values attained at atmospheric pressure and 1000 °C using iron for catalysis. As this figures did not comply with the Heat Theorem, **W. Nernst** made own measurements at 75 bar, which were actually the first experiments at elevated pressure. From the results he concluded that a technical process, which he probably anticipated as a once-through process, should not be feasible as the much higher pressures needed in this case seemed to be beyond the technical possibilities of the time. Haber continued with his investigations now also including pressure experiments.

From the more reliable equilibrium data now available it was obvious that at normal pressure the reaction temperature should be kept well below 300 °C in order to obtain even a small percentage of ammonia. For this temperature level no catalyst was

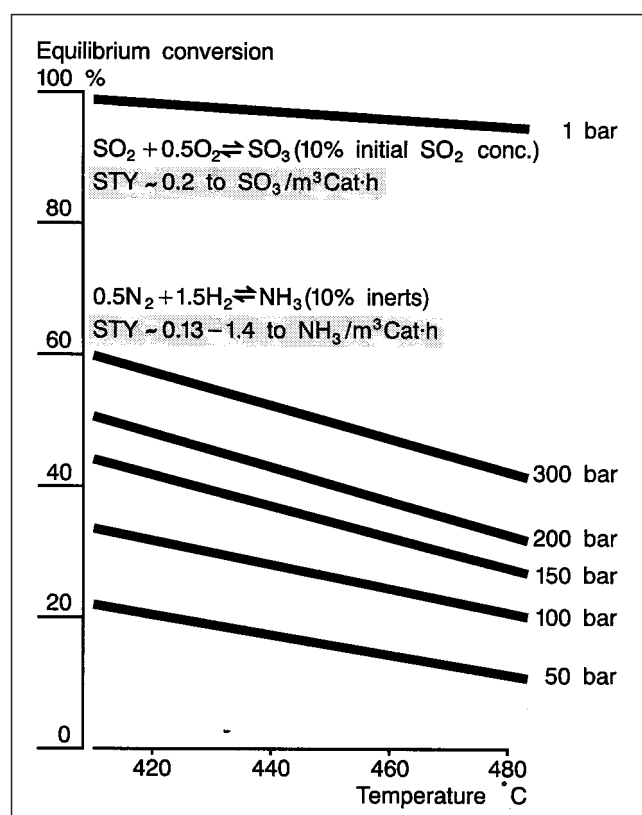


Figure 1: Equilibrium conversion and space time yield for NH<sub>3</sub> and SO<sub>3</sub> production

available. By increasing the pressure for example to 75 bar the equilibrium conditions were improved, but with catalysts active at 600 °C only low ammonia concentrations were attained. So Haber concluded that much higher pressures had to be employed and that, perhaps more importantly, a recycle process had to be used, an actually new process concept at that time, and thus he overcame his colleagues' preoccupation which resulted from the unfavorable equilibrium concentrations and the concept of a once-through process.

The amount of ammonia formed in a single pass of the synthesis gas over the catalyst is indeed much too small to be of interest for an economic production. Haber therefore recycled the unconverted synthesis gas: after separating the ammonia formed by condensation under synthesis pressure and supplementing it with fresh synthesis gas to make up for the portion which was converted to ammonia, the gas was recirculated by means of a circulation compressor to the catalyst containing reactor.

Haber's recycle idea changed the static conception of process engineering in favor of a more dynamic approach. For the first time reaction kinetics were considered as well as the thermodynamics of the system. In addition to the chemical equilibrium Haber recognized that for the technical realization reaction rate was a determining factor. Instead of simple yield in a once-through process he concentrated on space time yield. Figure 1 illustrates this consideration of equilibrium concentration in combination with space time yield by a comparison of the ammonia synthesis with the SO<sub>2</sub> oxidation process.

Also anticipated by him was the preheat of the synthesis gas to reaction by heat exchange with the hot effluent gas from the reactor. In 1908 Haber approached the BASF to find support for his work and to discuss the possibilities for the realisation of a technical process. Early in 1909 he discovered in finely distributed osmium a catalyst which yielded 8 Vol% of ammonia at 175 bar and 600 °C. A successful demonstration in April 1909 of a small lab-scale ammonia plant convinced the representatives of BASF and the company's board decided to pursue the technical development of this process with all available resources.

In BASF then Carl Bosch, entrusted with extraordinary authority, became project leader and succeeded together with a team of dedicated and very able

co-workers to develop in an unprecedented effort a commercial process in less than five years. The production facilities for 30 t/d were erected on a new site near the village Oppau (now a part of the city of Ludwigshafen), the first production was in September 1913 and full capacity was reached in 1914.

## The ammonia catalyst

In BASF Alwin Mittasch was responsible for the catalyst search. Osmium, used by Haber showed excellent catalytic activity but was difficult to handle, the main disadvantage, however, was that the world's stock of this rare material was only a few kilograms. Mittasch started a systematic screening program, covering nearly all elements of the periodic table. Until 1910 more than 2500 different formulas were tested in 6500 runs. For these experiments special small test reactors containing easily removable cartridges holding about 2 g of catalyst were developed.

In November 1909 a sample of magnetite from a place in Sweden showed exceptionally good yields, which was surprising because other magnetite types were total failures. Mittasch concluded that certain impurities in this Gallivara magnetite were important for

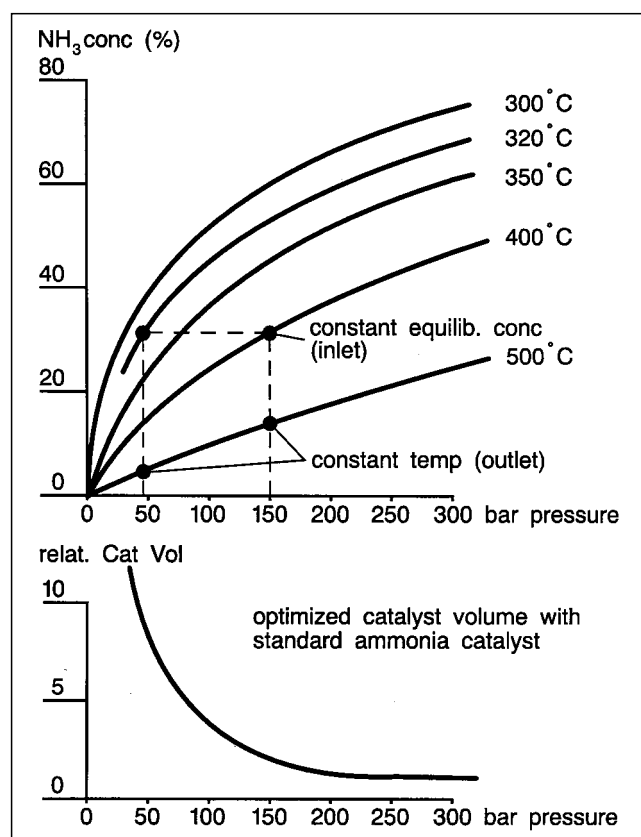


Figure 2: Ammonia equilibrium and catalyst volume

its good performance. So he investigated the influence of various individual additives, which in today's terminology are called promoters. By 1911 the catalyst problem had been solved. Iron with a few percent alumina and a pinch of potassium yielded a catalyst with acceptable reproducibility and performance and tolerable lifetime.

But the research program was continued until 1922 to be certain about the optimum composition. The only additional result was that the further addition of calcium gave a certain improvement. All magnetite based catalysts on the market today have a similar composition to that of the original BASF catalyst. Also the **catalyst preparation** remained practically the same: Melting natural magnetite from Sweden with addition of the various promoters, cooling the melt, breaking the solidified melt into small particles followed by screening to obtain a fraction with suitable particle size.

From these early days until today an enormous amount of academic research was dedicated to elucidate the mechanism of the synthesis, to study the microstructure of the catalyst and to explain the effect of the promoters. Besides the scientific interest there was of course some hope to find an improved catalyst, which could operate at far lower temperatures and thus at lower pressures saving compression energy, which is in a modern plant still 300 kWh/t NH<sub>3</sub>. In principle one can operate with the classic magnetite catalyst at 35–45 bar in the temperature range of 350 to 450 °C, but needing a trainload of catalyst – about 450 m<sup>3</sup> (1300 t) for a plant of 1350 t/d NH<sub>3</sub> – to achieve very low ammonia concentrations which would require removal by water-scrubbing instead of condensation by refrigeration. M. W. Kellogg proposed such a process in the early 1980s, but didn't succeed with commercialization. For a real low pressure catalyst operating at front end pressure to need no compression, an operation temperature well below 300 °C would be required. To illustrate this situation figure 2 shows ammonia equilibrium and catalyst volume.

With the modern spectroscopic tools of **Surface Science** rather detailed information on the **reaction mechanism at the catalyst surface** was obtained. Kinetics of nitrogen and hydrogen adsorption and desorption were investigated and adsorbed intermediate species could be identified. The results allowed to explain, for the most part, the mechanism of ammo-

nia synthesis in the pressure range of industrial interest. This success has many fathers, outstanding contributions were made by **Brill, Ertl, Somorjai, Boudard, Nielsen, Scholtze, Schlögl** and many others. The rate determining step is the dissociative adsorption of the nitrogen at the catalyst surface and the most active sites are the crystal faces (111) and (211), which is probably caused that these are the only surfaces which expose C7 sites, which means iron atoms with seven nearest neighbors.

The primary **function of the Al<sub>2</sub>O<sub>3</sub>** is to prevent sintering by acting as a spacer between the small iron platelets and it may in part also contribute to stabilize the Fe(111) facets. The promoting **effect of the potassium** is probably based on two factors. One is the lowering of the activation energy of the dissociative adsorption of nitrogen by an electronic charge transfer effect from potassium to iron which increases the nitrogen bond strength to the iron and weakens the nitrogen-nitrogen bond. The other factor consists in reducing the adsorption energy of ammonia thus easing the desorption of the formed ammonia which avoids blocking the surface and hindering the nitrogen adsorption.

Commonly the term ammonia catalyst is used for the oxidic form consisting of magnetite and the promoters. Actually this is only the catalyst precursor, which is transformed into the active catalyst consisting of  $\alpha$ -iron and the promoters by reduction with synthesis gas. In the 1980s pre-reduced ammonia catalysts found acceptance in the market as they avoid the relatively long in-situ reduction which causes additional downtime and considerable feedstock consumption without production. These catalysts are reduced at the vendor's facilities and subsequently passivated at temperatures around 100 °C using nitrogen with a small amount of air.

A notable improvement of the magnetite system was the introduction of **cobalt as an additional component** by ICI in 1984. The cobalt enhanced formula was first used in an ammonia plant in Canada using ICI Catalco's AMV process with a synthesis pressure of 90 bar. With similar kinetic characteristics, the volumetric activity is about two times higher than that of the standard iron catalyst.

In October 1990 Kellogg commercialized the Kellogg Advanced Ammonia Process using a catalyst composed of **ruthenium on a graphite support**, which is

claimed to be 10–20 times as active as the traditional iron catalyst. According to original patents assigned to **BP**, the new catalyst is prepared by subliming ruthenium-carbonyl  $\text{Ru}_3(\text{CO})_{12}$  onto the carbon-containing support which is impregnated with rubidium nitrate. The catalyst has a considerably higher surface than the conventional catalyst and, according to the patent example, it should contain 5% Ru and 10% Rb by weight. This catalyst works best at a lower than stoichiometric H/N ratio of the feed gas and it is also less susceptible to selfinhibition by  $\text{NH}_3$  and has an excellent low pressure activity.

The potential of ruthenium to displace iron in new plants will depend on whether the benefits of its use are sufficient to compensate the higher costs. In common with the iron catalyst it will also be poisoned by oxygen compounds. Even with some further potential improvements it seems unlikely to reach an activity level which is sufficiently high at low temperature to allow an operation of the ammonia synthesis loop at the pressure level of the syngas generation.

## The ammonia converter and the synthesis loop configuration

With the catalyst at hand, the next step was to construct somewhat larger test reactors for catalyst charges of about 1 kg. Surprisingly, these reactors ruptured after only 80 hours. Further studies showed that the internal surface had totally lost its tensile strength. This phenomenon had apparently propagated from the inner surface outward until the residual unaffected material was so thin that rupture occurred.

With the aid of microscopic investigations by thin section technique Bosch found the explanation. Decarbonization of the carbon steel had occurred, but, surprisingly, the result was not soft iron but rather a hard and embrittled material. Hydrogen diffusing into the steel caused decarbonization by methane formation. This methane, entrapped under high pressure within the structure of the material, led to crack formation on the grain boundaries which finally resulted in embrittlement. Systematic laboratory investigations and material tests demonstrated that all carbon steels will be attacked by hydrogen at high temperatures and that the destruction is just a matter of time.

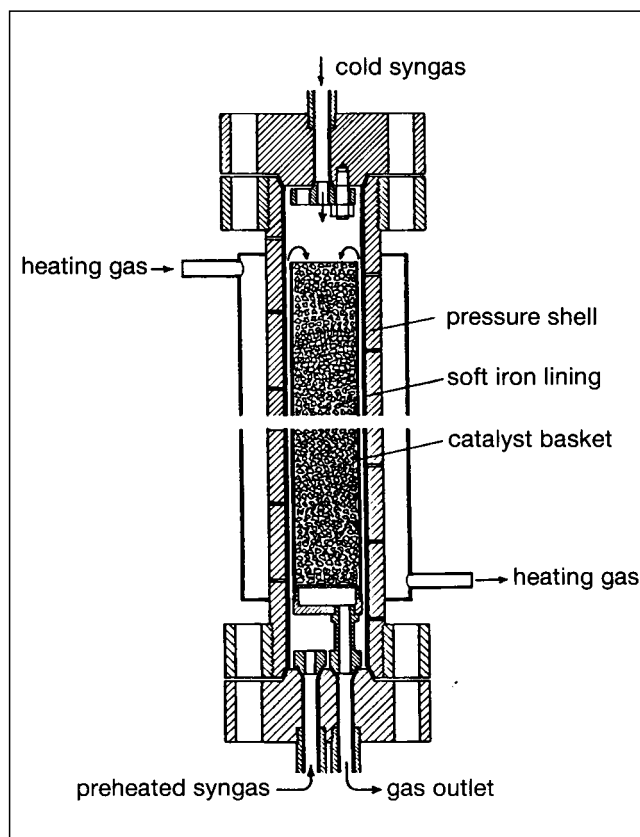


Figure 3: First pilot plant converter with soft iron lining and external heating

**Bosch's unconventional solution to the embrittlement problem** was to use a carbon steel pressure shell with a **soft iron liner**. To prevent the hydrogen which had penetrated this liner from attacking the pressure shell, measures had to be taken to release it safely to normal pressure. This was achieved by providing small channels on the outer side of the liner which was in tight contact with the inner wall of the pressure shell and by drilling small holes, later known as "**Bosch-Holes**", through the pressure shell, through which hydrogen could escape to the atmosphere. These holes had no effect on the strength of the shell and the resulting losses of hydrogen were negligible. Figure 3 gives a sketch of such a pilot plant converter.

Bosch did not content himself with his liner/hole concept but looked further for alternative solutions for the embrittlement problem. He initiated in the late 1920s research in the steel industry to develop steels resistant to hydrogen under pressure. Special alloy components as for example molybdenum, chromium tungsten and others form stable carbides and enhance the resistance of steel against this sort of attack considerably. This problem and the related physical hydrogen attack is not restricted to the synthesis but has to be considered carefully also in the synthesis gas production section because of the temperatures and

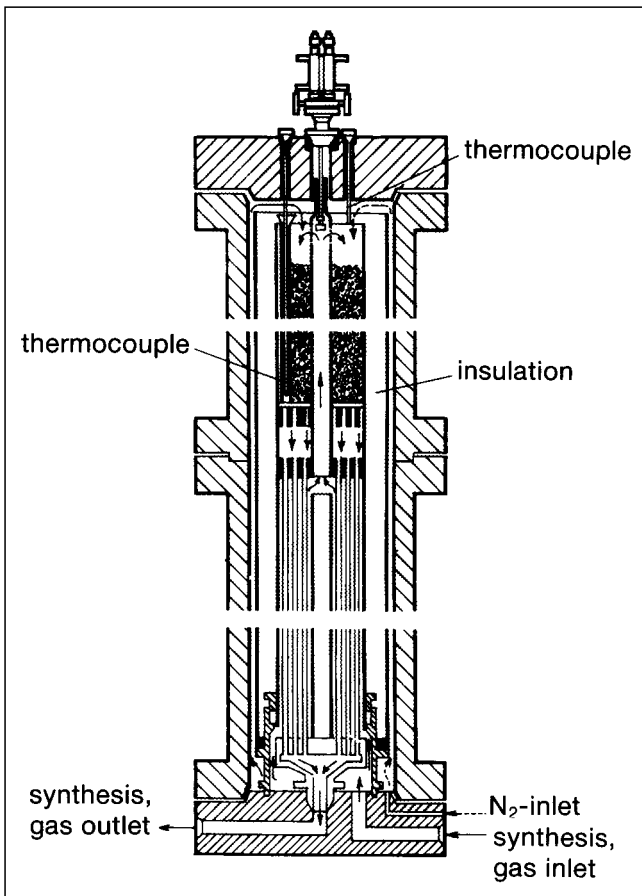


Figure 4: Converter with pressure shell cooling by nitrogen

hydrogen partial pressures involved there. Extensive research and careful evaluation of operation experiences have made it possible to prevent largely hydrogen attack in modern ammonia plants by proper selection of hydrogen-tolerant alloys with the right content of metals which form stable carbides. Of fundamental significance in this respect was the work of **Nelson**, who produced curves for the stability of various steels as a function of operation temperature and hydrogen partial pressure.

In the small reactors heat losses predominated and continuous direct external heating by gas was necessary and this led to deterioration of the pressure shells after short operation times even without hydrogen attack. With increasing converter dimensions in the commercial plant heating was only necessary for start up.

Bosch developed an internal heating by the so-called inverted flame, introducing at the top of the reactor a small amount of air, igniting with an electrically heated wire. Later this was replaced by an electric resistance heater. Subsequently introduced flushing with nitrogen as shown in figure 4 and later with cold

synthesis gas kept the pressure vessel walls cool and rendered the liner-hole concept redundant.

Subsequent reactor designs in the technical plant included internal heat exchangers and later the catalyst was placed in separate tubes which were cooled by the feed gas. Another improvement was the introduction of an externally insulated catalyst basket. Because of the low concentrations aqueous ammonia was separated from the loop by water scrubbing. Converters with catalyst tubes had a better temperature control and this led together with an increased pressure to higher ammonia concentrations which now allowed from 1926 onwards the direct production of liquid ammonia. In 1942 the first quench converter was installed and this design gradually has replaced then the converters with the catalyst tubes.

Soon after the first world war development started also in other countries, partly on basis of BASF's pioneering work. **Luigi Casale** built 1920 the first plant in Italy, and based on developments by **M. G. Claude** the first French plant started to produce in 1922. Both the Casale and the Claude process operated under extreme high pressure. In contrast to this **Uhde** constructed a plant based on coke oven gas, operating under extreme low pressure. (**Mont Cenis process**). Further developments were by G. Fauser who worked together with Montecatini. During the 1920s several plants were built in the USA, some based on European some on American Technology. The successful US company was Nitrogen **Engineering Corporation (NEC)**, the predecessor of Chemicco.

Mechanical design was now already rather advanced but for the process design of converter and loop so far empirical data in form of charts were used as no suitable mathematical expressions for the reaction kinetics were at hand. When better experimental data for the reaction kinetics and other process variables became available in the 1940s and 1950s lay-out of converters received a better quantitative chemical engineering basis. Figure 5 shows reaction rate of ammonia formation and equilibrium. When the temperature is increased (under otherwise constant conditions), the reaction rate increases to a maximum, to decrease with further temperature increase and becomes zero when reaching equilibrium temperature. Joining these points will result in a line giving, for each  $\text{NH}_3$  concentration, the temperature for the maximum rate. This curve runs about parallel to the

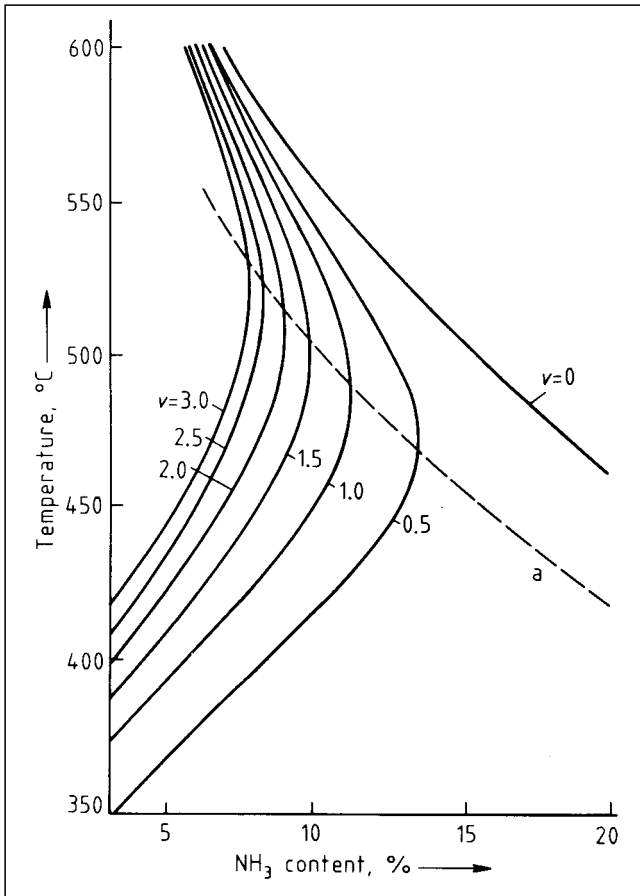


Figure 5: Reaction rate of ammonia formation

equilibrium line and at a about 30 – 50 °C lower temperature. To maintain the maximum ammonia formation rate, the reaction temperature must decrease as the ammonia concentration increases.

For optimal catalyst usage the reactor temperature profile (after a initial adiabatic heating zone in the

first part of the catalyst) should follow this ideal line. For a long time converters were always compared to this “ideal” for optimum use of high-pressure vessel volume. Today the objective is rather to maximize heat recovery (at the highest possible level) and to minimize investment costs for the total synthesis loop. In any case it is necessary to remove the heat of reaction as the conversion proceeds to keep the temperature at an optimal level. For the removal of the reaction two principal configurations are possible:

**Tubular converters** have cooling tubes within the catalyst bed through which the cooling medium, usually cooler feed gas, flows co-currently or counter-currently to the gas flow in the catalyst bed. Alternatively the catalyst can be placed within tubes with the cooling medium flowing on the outside. The tube cooled converters dominated until the early fifties, but are largely outdated today. Well known examples were the TVA converter (counter-current) and the NEC/Chemico design (co-current, with best approximation to the maximum rate curve). An interesting revival of this principle is the **ICI tube cooled converter** used in the LCA process and also for methanol production.

In the **multi-bed converters** the catalyst volume is divided into several beds in which the reaction proceeds adiabatically. Between the individual catalyst layers heat is removed either by injection of colder synthesis gas (quench converters) or by indirect cooling with synthesis gas or via boiler feed water heating or steam raising (indirectly cooled multi-bed converter).

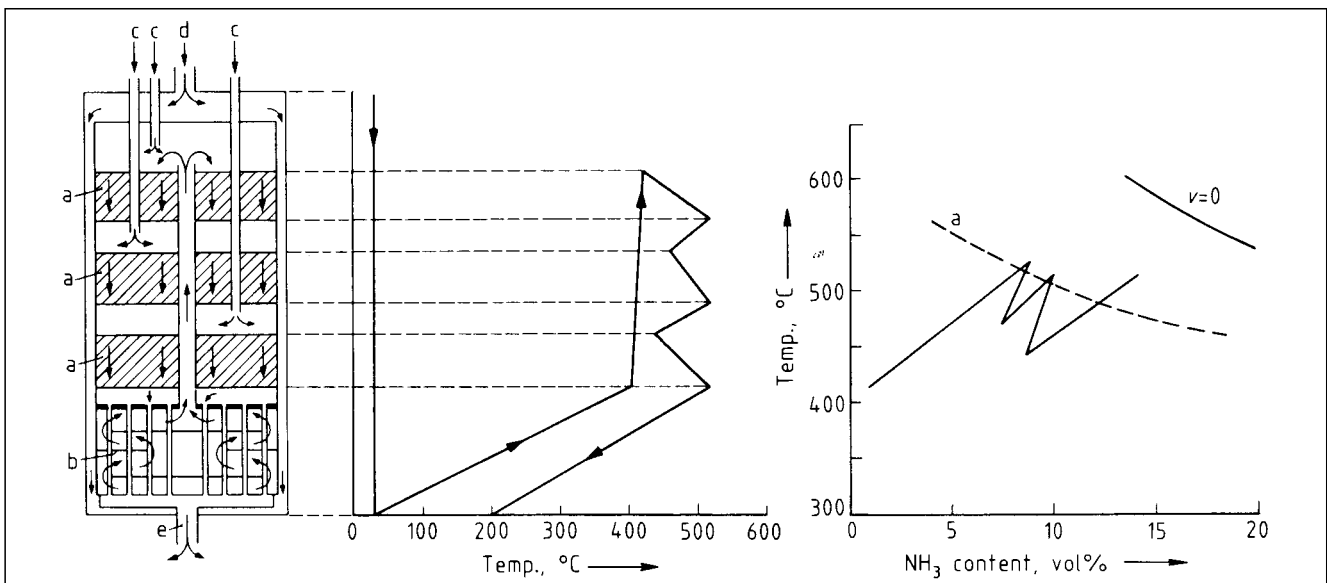


Figure 6: Quench converter

In the **quench converters** only a fraction of the recycle gas enters the first catalyst layer at about 400 °C. The catalyst volume of the bed is chosen so that the gas will leave it at around 500 °C. Before entering the next catalyst bed, the gas temperature is „quenched” by injection of cooler (125 – 200 °C) recycle gas. The same thing is done at subsequent beds. In this way the reaction profile describes a zig-zag path around the maximum reaction rate line. A schematic drawing of a quench converter together with its temperature/location and temperature/ammonia concentration profile is presented in figure 6. The catalyst beds may be separated by grids designed as mixing devices for main gas flow and quench gas (cold shot), or be just defined by the location of cold gas injection tubes as for example in the ICI lozenge converter.

A disadvantage is that not all of the recycle gas will pass over the whole catalyst volume with the consequence that a considerable amount of the ammonia formation occurs at higher ammonia concentration and therefore at reduced reaction rate. This means that a larger catalyst volume will be needed compared to an indirect cooled multi-bed converter. On the other hand, no extra space is required for inter-bed heat exchangers, so that the total volume will remain about the same as for the indirect cooled variant.

As the quench concept was well suited for large capacity converters it had a triumphant success in the early generation of large single stream ammonia plants constructed in the 1960s and 1970s. Mechanical simplicity and very good temperature control contributed to the widespread acceptance.

**Multibed converters with indirect cooling.** In converters of this category the cooling between the individual beds is effected by indirect heat exchange with a cooling medium, which may be cooler synthesis gas and/or boiler feed water warming and steam raising. The heat exchanger may be installed together with the catalyst beds inside one single pressure shell but an attractive alternative, too, preferentially for large capacities, is to accommodate the individual catalyst beds in separate vessels and have separate heat exchangers. This approach is especially chosen when using the reaction heat for raising high pressure steam. The indirect cooling principle is applied today in almost all large new ammonia plants, and also in revamps an increasing number of quench converters are modified to the indirect cooling mode.

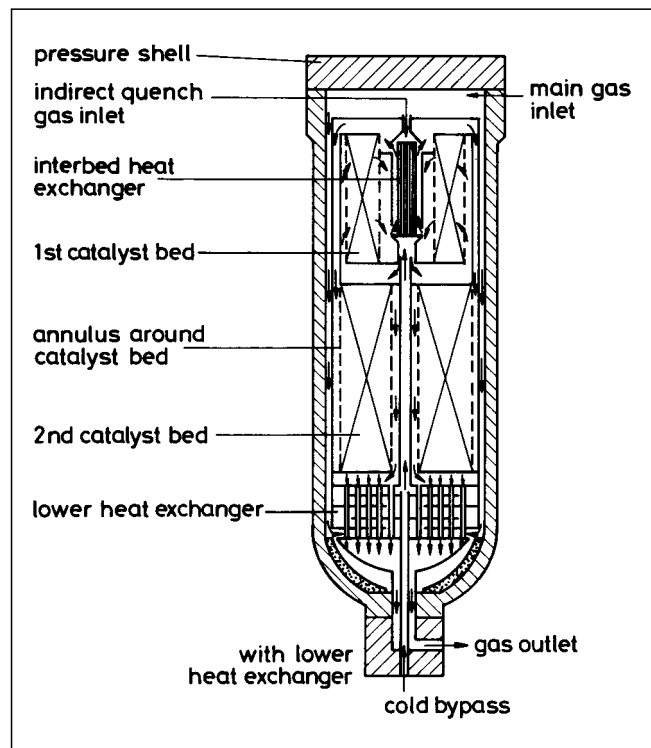


Figure 7: Topsoe Series 200 indirect cooled converter (radial flow)

Axial flow through the catalyst in the converters as exclusively used until the early 1970s face a general problem: With increasing capacity the depth of the catalyst beds will increase, as for technical and economical reasons it is not possible to enlarge the pressure vessel diameter above a certain size. In order to compensate for the increasing pressure drop axial flow converters with usual space velocities of 10 – 15000 h<sup>-1</sup> have to use relatively large catalyst particles and a particle size of 6 – 10 mm has become standard. But this grain size has compared to finer catalyst a considerably lower activity, which decreases approximately in a linear inverse relation. Two factors are responsible for the lower activity of the larger particles. Firstly, the larger grain size retards on account of the longer pores the diffusion from the interior to the bulk gas stream and this will inhibit the dissociative nitrogen adsorption and by this the reaction rate. Secondly, the reduction of an individual catalyst particle starts from the outside and proceeds to the interior. The water formed by removing the oxygen from the iron oxide in the interior of the grains will pass over already reduced catalysts on its way to the outer surface of the particle. This induces some recrystallization leading to the lower activity. The effect is considerable: going from a particle size of 1 mm to one of 8 mm, the inner surface will decrease from 11 – 16 to 3 – 8 m<sup>2</sup>/g.



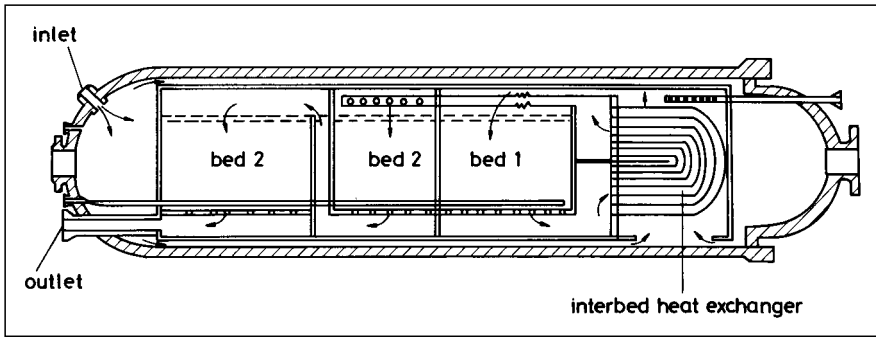


Figure 8: Indirect Cooled Horizontal Converter of M. W. Kellogg

**Haldor Topsøe's** company solved the dilemma with the pressure drop and small catalyst particles with a **radial flow** pattern, using a grain size of 1,5–3 mm (Figure 7). **M.W. Kellogg** chose another approach with its **horizontal crossflow converter** (Figure 8). The catalyst beds are arranged side by side in a cartridge which can be removed for catalyst loading and unloading

through a full-bore closure of the horizontal pressure shell.

Today each new world-size ammonia plant employs the indirect cooling concept raising high pressure steam up to 125 bar. Generally after the first bed an inlet-outlet heat-exchanger is placed and after the second or further beds the reaction heat is used to raise high pressure steam.

**Brown and Root (formerly C. F. Braun)** or **Uhde** (Figure 9) accommodate the catalyst in several vessels. Figure 9 is a simplified flow sheet of Uhde's synthesis loop. Actually the concept of separate vessels for the catalyst beds, with heat exchange after the first and waste heat boiler after the

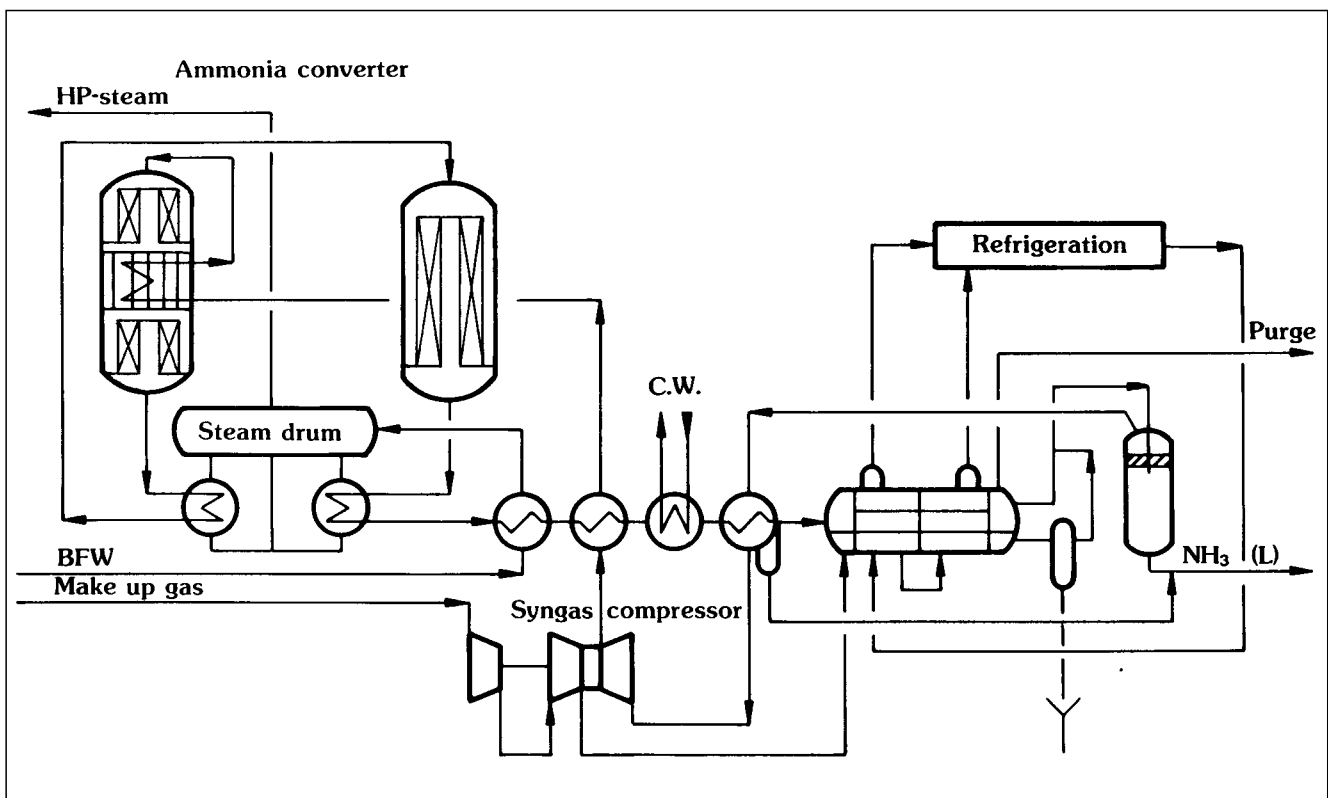


Figure 9: Uhde's synthesis loop with two pressure vessels and three catalyst beds

second (nowadays they use also a third one followed by a boiler, too) was already introduced by C. F. Braun at time when most plants still used quench converters.

The **Ammonia Casale ACAR Converter** has a mixed flow pattern. In each catalyst layer the gas flows through the top zone predominantly axially but traverses the lower part in radial direction. This simplifies the design by avoiding special sealing of the top end of the bed to prevent by-passing.

Today **computerized mathematical models** are used for **converter and loop lay-out**. In principle, these models use two differential equations which describe the steady state behavior of the reaction in the converter. The first gives a concentration-location relationship within the catalyst bed for the reactants and the ammonia. It reflects the reaction kinetic expression. The second models the temperature-position relationship for the synthesis gas, catalyst and vessel internals. The form of this equation is specific to the type of the converter.

The **kinetics of the intrinsic reaction**, that means the reaction on the catalyst surface without any mass transport restrictions, are derived from measurements

on very fine catalyst particles. The first useful expressions for engineering purposes to describe the reaction rate was the **Temkin-Pyshew** equation, proposed in 1940. It was widely applied, but today there are improved versions and other equations available. Additional terms are included to model the influence of oxygen-containing impurities on the reaction rate. Although oxygen-containing compounds may be regarded as a temporary poison, severe exposure for an extended period of time leads to permanent damage. For practical application these equations have to be modified to make allowance for **transport phenomena** (heat and mass transfer), and this is done by so-called **pore effectiveness factors**.

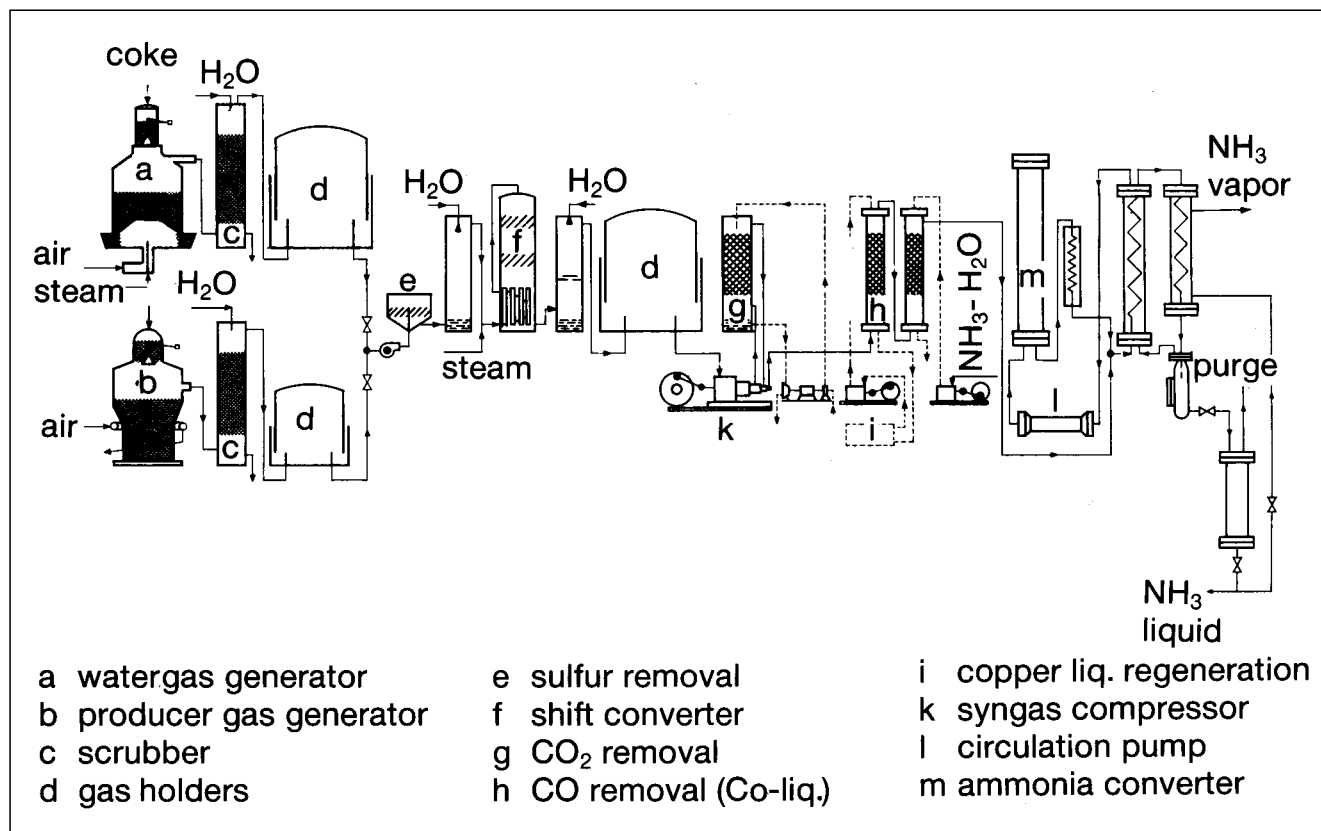


Figure 10: Simplified flow sheet of a coke-based ammonia plant

# Synthesis Gas Preparation

## The classical route based on coke

The pilot plant experiments at BASF for the ammonia synthesis were based on hydrogen from the chlorine-alkali electrolysis. When the capacity of this gas source was exhausted, water gas served as an independent hydrogen feedstock using the cryogenic Linde-Fränk process for the separation. In this process carbon monoxide is condensed out of the water gas at  $-200\text{ }^{\circ}\text{C}$  and 25 bar. Nitrogen was provided by an air separation unit and nitrogen was also used in an indirect liquid nitrogen circulation system in the cryogenic hydrogen separation. The residual content of 1.5 % CO in the hydrogen was removed by conversion to sodium formate in a gas scrubber operated with a 10 % sodium hydroxide solution and at  $230\text{ }^{\circ}\text{C}$  and 200 bar.

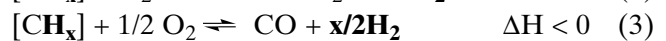
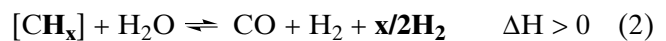
The initial operation of the commercial plant commissioned in September 1913 was based on hydrogen and nitrogen produced by this cryogenic separation, but after a few months on line, it became apparent that the Linde refrigeration process was not reliable and economic enough for the production on large scale. A new catalytic process, the **shift conversion**, was introduced. In this reaction, found by **W. Wild** in BASF already in 1912, the gas is passed together with a surplus of steam over an iron oxide/ chromium oxide catalyst at about 350 to 450  $^{\circ}\text{C}$ . The carbon monoxide reacts with water to form hydrogen and carbon dioxide. The use of the shift reaction permitted a great simplification of the synthesis gas preparation. Instead of using the refrigeration processes, producer gas (a mixture of 60 % nitrogen and 40 % carbon monoxide) was generated by reacting air with red hot coke and mixed with the parallel generated water gas supplied by the alternating air blowing and steaming process and this mixture was converted in the shift reaction to yield a gas consisting of hydrogen, nitrogen, carbon dioxide and a small amount of residual carbon monoxide. The carbon dioxide could then be removed satisfactorily by water scrubbing at 25 bar. The removal of the residual carbon monoxide by scrubbing with hot caustic soda solution with formation of sodium formate used in the initial cryogenic route was corrosive and troublesome. It could now be replaced by copper liquor scrubbing. Water gas production from lignite started in 1926 in Leuna using a process developed by Winkler. This process, in which coal is gasified continuously with oxygen and steam in a

fluidized bed, was a spin-off of the research work on the removal of sulfur from ammonia synthesis gas. Figure 10 is a simplified flow sheet of a coke based Haber-Bosch plant as it was operated in the 1930s and 1940's at BASF and elsewhere. In the 1950s BASF developed and introduced continuously operated water gas generators using oxygen or oxygen enriched air from which the slag could be withdrawn in liquid form.

## A new age with hydrocarbons

The plants continued to be based on coal for synthesis gas generation until the 1950s. With growing availability of cheap **hydrocarbon feedstocks** and novel cost saving gasification processes a new age dawned in the ammonia industry. The development started in the USA where steam reforming was introduced, a process, originally developed in the 1930s by BASF and greatly improved by ICI which extended it also to naphtha. Before natural gas became available in large quantities in Europe, too, partial oxidation of heavy oil fractions was used in several plants, with process technology developed by Texaco (1940) and Shell (1950). After several oil crisis coal gasification research and development was resumed with the result that for this route a few technically proven processes are available today.

The chemical reaction of water, oxygen, air or any combination of these reactants with fossil feedstocks is generally described as **gasification**. In a simplified way it can be viewed as the reduction of water by means of carbon and carbon monoxide. It yields a gas mixture made up of carbon monoxide and hydrogen in various proportions along with carbon dioxide and, where air is introduced, some nitrogen.



Reaction (2) is endothermic and needs an external source of energy supply, whereas reaction (3) is exothermic and can be carried out adiabatically. For the initial carbon dioxide content in the raw gas from the gasification the shift reaction equilibrium is responsible which at the high temperature is rather on the CO side.



This shift reaction, in which actually CO reduces water to yield additional hydrogen, is favored by low temperature and is therefore purposely made to proceed on a catalyst in a separate step at a temperature lower than the preceding gas generation step.

With coke the reaction (2) corresponds to the non-catalytic **classic water gas process**. With light hydrocarbons reaction (2) is called **steam reforming** and is made to proceed over a nickel catalyst. The reaction (3) is commonly called **partial oxidation** and in principle applicable for any fossil feedstock, from coal to natural gas. As can be seen from the stoichiometric equation, the hydrogen contributed by the feedstock itself increases with its hydrogen content, which ranges from a minimum of [CH<sub>0,1</sub>] in coke to a maximum of CH<sub>4</sub> in methane.

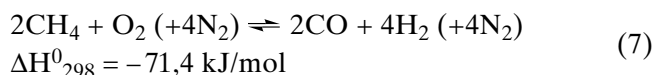
## Syngas preparation via steam reforming

The steam reforming process is restricted to light hydrocarbons ranging from natural gas (methane) to light naphtha. For higher hydrocarbons, such as fuel oil or vacuum residue this technology is not applicable on account of impurities as sulfur and heavy metals which would poison the sensitive nickel catalyst. In addition cracking reactions are more likely to occur on the catalyst, depositing carbon which might block the catalysts pores and also restrict the gas flow. As the nickel catalysts are highly sensitive to sulfur compounds, these catalysts poisons have to be removed prior to the reforming reaction. For this purpose any organic sulfur compounds contained in the hydrocarbon feedstock are first hydrogenated on a cobalt-molybdenum catalyst to hydrocarbon and hydrogen sulfide, which is then absorbed with zinc oxide to form zinc sulfide.

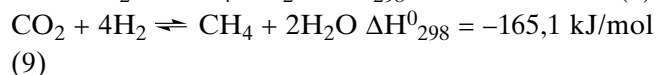


For ammonia production the steam reforming is performed in two steps: First the hydrocarbon /steam mixture is passed through high-alloyed nickel-chromium tubes filled with a catalyst containing finely dispersed nickel on a carrier. The heat needed for the endothermic reaction is supplied by gas burners in a furnace box. The reaction in this **primary reformer** is controlled to achieve only a partial conversion of around 65 % , leaving about 14 % methane (dry basis) content in the effluent gas at a temperature of 750 to

800 °C. The gas is then introduced into the so-called **secondary reformer** – a refractory lined vessel also with a nickel catalyst – where it is mixed with a controlled amount of air introduced through a burner. This raises the temperature sufficiently to complete the reforming of the residual methane adiabatically. It also introduces the right amount of nitrogen to achieve the correct stoichiometric ratio in the final synthesis gas. The overall reaction in the secondary reformer may be described as some sort of a partial oxidation, but the stoichiometric equation (7) does not give a clue to the actual reactions taking place.



The gas leaves the secondary reformer at 950 to 1000 °C and a methane content of 0,3 to 1.5 %. It is cooled down to 350–400 °C using the removed heat for high pressure steam generation. In the first steam reforming based plants the shift conversion used only the classical chromium-iron catalyst achieving around 2 % residual CO. For CO<sub>2</sub> removal in this early plants the traditional water scrubbing was applied and the final purification was still performed by copper liquor. In the early 1960s **copper-zinc-alumina catalysts** became available for a **second conversion step** at temperatures of about 200 °C, whereby the residual CO concentration could be lowered to 0.2–0,3 %. This allowed to eliminate the copper liquor scrubbing, removing the residual concentrations of CO and CO<sub>2</sub> by **methanation**. In this highly exothermic reaction which is performed at about 300 °C on a nickel catalyst, hydrogen reacts with carbon monoxide to methane and water; it is the reverse of the steam reforming reaction of methane (equation 8 and 9).



With aqueous **monoethanolamine (MEA)** a new solvent for CO<sub>2</sub> removal was introduced in 1943. This process has been used extensively in many ammonia plants until hot potash and other solvents with lower heat requirement were developed. The plants with capacities up to 300 t/d used reciprocating compressors for compression.

As natural gas is usually delivered under elevated pressure and because the reforming reaction entails an

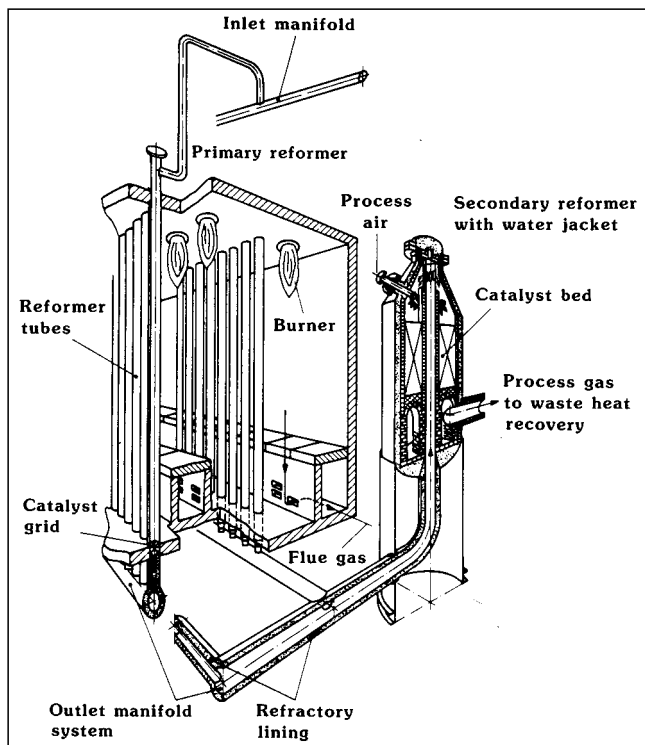


Figure 11: Top-fired primary reformer and secondary reformer (Uhde design)

increase in total volume, significant savings of compression energy are possible if the process is performed under higher pressure. But there is also a disadvantage in raising the pressure level of reforming as the equilibrium is shifted to lower conversions, which can be compensated by higher temperatures. As all the heat in the primary reformer has to be transferred through the tube wall, the wall temperatures will rise and approach the material limits. Originally **HK 40 tubes** with a content of 20 % nickel and 25 % chromium were commonly used. With new grades as **HP modified** with higher nickel content and stabilized with niobium and the recently introduced **Micro Alloys** which additionally contain titanium and zirconium higher wall temperatures and thus higher pressures up to 44 bar in the primary reformer have become possible. The steam surplus applied in the reformer could thus also be reduced from a steam to carbon ratio of 4 and higher to about 3 or slightly below, and this was assisted by improved catalysts with enhanced activity and better heat transfer characteristic. For naphtha reforming a higher steam surplus is necessary.

Fancy catalyst shapes as “wagon wheels, six-shooters, shamrock or four-hole” have replaced the old Raschig rings. The stability of the **standard catalyst supports** as **calcium aluminate**, **magesium aluminate** and  $\alpha$ -alumina has been improved and it has become a widely accepted practice to install in the first third of the catalyst tube where the bulk of the reforming reaction takes place, a **potassium promoted catalyst** which was developed by **ICI originally for naphtha** steam reforming in order to prevent carbon deposition by cracking reactions. From the various **primary reformer** designs the **top fired concept** with a single radiation box dominates in the larger plants, the **side-fired design** in which only 2 tube rows can be accommodated in the radiation box, allows only a linear extension and additional fire boxes connected to a common flue gas duct. The **secondary reformers** have been optimized regarding hydrodynamics and burner design using **computational fluid dynamics**. Figure 11 shows an example of a top-fired reforming furnace together with the secondary reformer.

The **reduction of the steam-to-carbon ratio** was a bigger problem for the **HT shift** than in the reformer step, as the gas mixture became a higher oxidative potential and tended to over-reduce the iron-oxide from magnetite to FeO and in extreme cases partially to metallic iron. Under these conditions the **Boudouard reaction** will become significant and carbon accumulation in the catalyst particles leads to breaking. In addition the **Fischer-Tropsch** reaction leads to the formation of methane and higher hydrocarbons. Copper promotions of the iron catalyst suppresses these side reaction. The nasty problem of methanol and amine formation in the **LT shift** is largely solved by

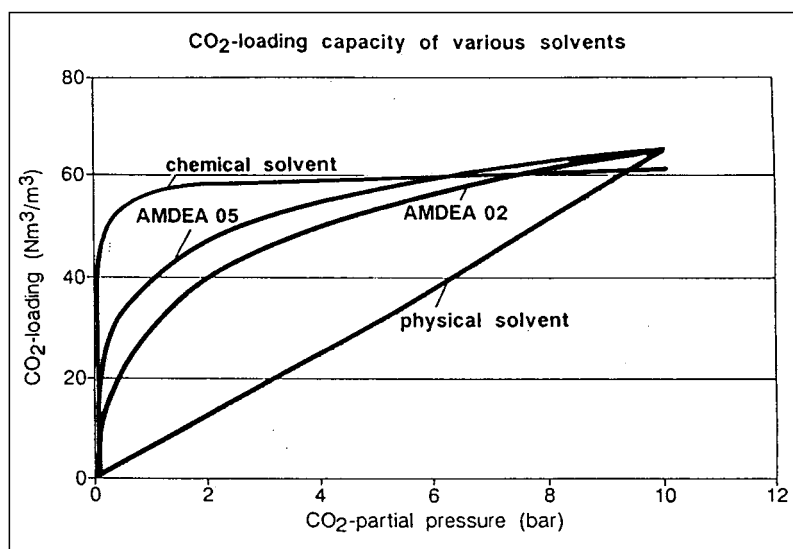


Figure 12: CO<sub>2</sub> Loading characteristics of various solvents

improved formulations of the copper/zinc/alumina, and a new development is the **intermediate temperature shift** catalyst, operated quasi isothermal in a tubular reactor, for example in the ICI LCA ammonia process or the Linde ammonia process (LAC).

Large progress in the **CO<sub>2</sub> removal systems** was made in the last decade. The original MEA systems had a heat consumption for solvent regeneration over 200 kJ/kmol, a corrosion inhibitor system called amine guard III brought it down to about 120 kJ/kmol, but this is still nearly 5 times as high as the most advanced system, the **BASF aMDEA Process**, which uses an aqueous solution of monomethyl-diethanolamine together with a special promotor which enhances the mass transfer. Other low energy systems are the **Benfield LoHeat Process**, which is a hot potash system or the **Selexol Process**, which uses a mixture of glycol dimethylethers, a pure physical solvent. In physical solvents, a prominent example was water in the old plants, the solubility of the CO<sub>2</sub> is according to Henry's law direct proportional to the CO<sub>2</sub> partial pressure and regeneration can be achieved by flashing, without application of heat.

In contrast to this the MEA is a chemical solvent, the solubility is only slightly dependent on the CO<sub>2</sub> partial pressure and approaches a saturation value. MEA forms a stable salt with the carbon dioxide and a high amount of heat is required in the stripper to decompose it. BASF's aMDEA Process is about in between, the characteristic can be adjusted in a flexible way by the concentration of the activator, so that the major part of the dissolved carbon dioxide can be released by simple flashing and only a smaller proportion has to be stripped out by heat. Figure 12 shows CO<sub>2</sub> loading characteristics of various solvents.

The tubular steam reformer has become a very reliable apparatus and the former problems with tube and transfer line failures and catalyst difficulties are largely history. But the tubular furnace and its associated convection bank is a rather expensive item and contributes substantially to the investment cost of the total ammonia plant. So in some modern concepts the size was reduced by shifting some of the load to the secondary reformer necessitating an overstoichiometric amount of process air. The surplus of nitrogen introduced in this way, can be removed downstream by the use of a cryogenic unit. **C.F. Braun** was the first contractor which introduced this concept in the so-called **Purifier Process**. Some contractors have gone so far to by-pass some of the natu-

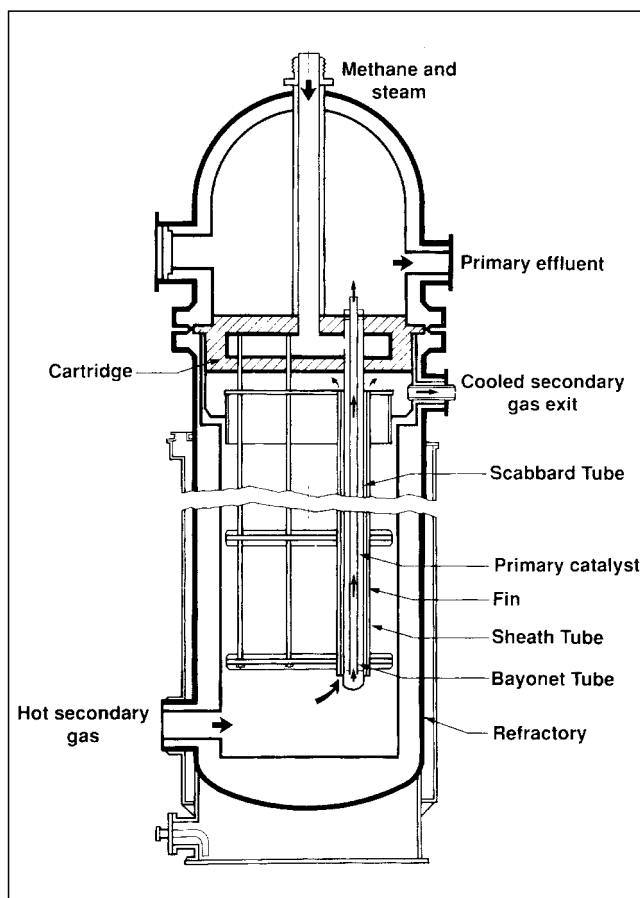


Figure 13: ICI Gas-Heated Reformer

ral gas around the tubular reformer and feeding it directly to the secondary reformer which likewise needs surplus of process air or oxygen enriched air.

But there are additional reasons for breaking away further from the fired furnace concept. The temperature level of the flue gas from a traditional reformer is usually higher than 1000 °C and the process gas at the outlet of the secondary reformer is also around 1000 °C. It is thus from a thermodynamic point of view wasteful to use this high temperature level simply to raise and superheat high pressure steam. The boiling point of HP steam is only 325 °C and the first heat exchanger in the flue gas duct preheats process air in the conservative plants to only 500 °C (600–700 °C in more modern installations). Recycling high-level heat from the secondary reformer and making use of it for the primary reforming reaction is thermodynamically the better option. Concepts which use this heat in an exchanger reformer have been successfully developed and commercially demonstrated. The first to come out with this concept in a real production plant was **ICI** with its **GHR (Gas Heated Reformer)**. The hot process gas from the secondary reformer is the sole heat source. A surplus of process air of around 50 % is needed in the sec-

dary reformer to achieve a closed heat balance. Figure 13 is a simplified drawing of the ICI Gas-Heated Reformer.

Quite recently ICI has come out with a modified design, the **AGHR**, with the “A” standing for advanced. The bayonet tubes are replaced by normal tubes attached to a bottom tube sheet using a special packing which allows some expansion. Thus the delicate double tubesheet is now eliminated.

In the **Kellogg Exchanger Reformer System**, abbreviated **KRES**, the gas flow pattern is different. The tubes are open at the lower end and the reformed gas mixes with the hotter effluent of the secondary reformer. The mixed gas stream flows up-ward on the shell side to heat the reformer tubes. Thus primary reforming and secondary reforming reaction proceed in parallel in contrast to the ICI concept where the two reactions proceed in series. The Kellogg process uses enriched air. The complete elimination of the fired tubular furnace leads to a drastic reduction of  $\text{NO}_x$  emission, because there is only flue gas from much smaller fired heaters required for feed and process air preheat. An even more progressive exchanger reformer presently operating in a demoplant is **Uhde’s CAR (Combined autothermal reformer)** which not only replaces the catalytic secondary reforming step by a non catalytic partial oxy-

lation step but also combines this with the exchanger reformer in one single vessel.

## Syngas from heavy oil fractions via partial oxidation

In partial oxidation heavy oil fractions react according to equation (2) with an amount of oxygen insufficient for total combustion. The reaction is non-catalytic and proceeds in an empty vessel lined with alumina refractory. The reactants, oil and oxygen, along with a minor amount of steam, are introduced through a nozzle at the top of the generator vessel. The nozzle consists of concentric pipes so that the reactants are fed separately and react only after mixing at the burner tip in the space below. The temperature in the generator is between 1200 and 1400 °C. Owing to the insufficient mixing with oxygen, about 2% of the total hydrocarbon feed is transformed into soot, which is removed by water scrubbing. The separation of the soot from the water and its further treatment differs in the **Shell** and the **Texaco Process** – the two commercially available partial oxidation concepts. The gasification pressure can be as high as 80 bar.

After gas cooling by further waste heat recovery, the hydrogen sulfide formed during gasification is removed along with carbon dioxide by scrubbing with chilled methanol below -30 °C in the **Rectisol** pro-

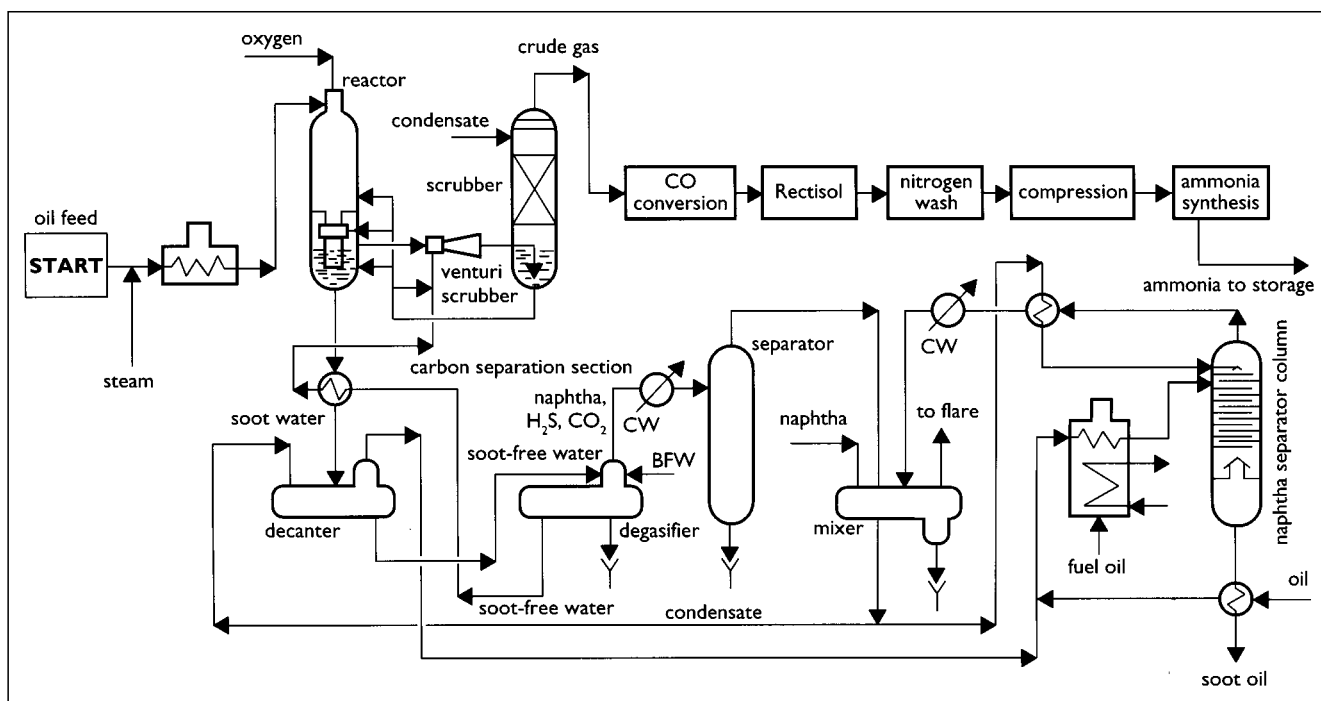


Figure 14: Ammonia syngas by partial oxidation of heavy hydrocarbons (Texaco)

cess. Then, as in the steam reforming route, the gas undergoes the CO shift reaction. Because of the higher carbon monoxide content much more reaction heat is produced, which makes it necessary to distribute the catalyst on several beds with intermediate cooling. The carbon dioxide formed in the shift conversion is removed in a second stage of the Rectisol unit; both have a common methanol regeneration system. The H<sub>2</sub>S-rich carbon dioxide fraction from the first stage of the regenerator is fed to a **Claus plant**, where elemental sulfur is produced. In the final purification, the gas is washed with **liquid nitrogen**, which absorbs the residual carbon monoxide, methane and a portion of the argon (which was introduced into the process in the oxygen feed). The conditions in this stage are set so that the stoichiometric nitrogen requirement is allowed to evaporate into the gas stream from the liquid nitrogen wash. The process needs, of course, an air separation plant to produce oxygen, usually around 98.5 % pure, and to supply the liquid nitrogen. Figure 14 is a simplified flowsheet of synthesis gas preparation by partial oxidation of heavy fuel oil using the Texaco Syngas Generation Process. The Shell process uses of a waste heat boiler for raw gas cooling whereas Texaco prefers for ammonia plants a water quench for this purpose which has the advantage that this introduces the steam for the subsequent shift conversion which – different from Shell – is performed without prior removal of the sulfur compounds using a **sulfur tolerant shift catalyst**.

Besides some optimizations there are no fundamental new developments in the individual process steps. Some proposed changes in the process sequence, for example methanation instead of liquid nitrogen wash, or the use of air instead of pure oxygen are not realized so far. Though other CO<sub>2</sub> removal systems as Selexol or Purisol (N-Methylpyrrolidone) and alternative

sulfur recovery processes are suitable too, Rectisol and Claus Process remain the preferred options.

## Synthesis gas by coal gasification

There is no chance for a wide-spread use of coal as feedstock for ammonia in the near future, but a few remarks should be made regarding the present status of coal gasification technology. Proven gasification processes are the **Texaco Process**, the **Koppers-Totzek Process**, and the **Lurgi Coal Gasification**. The **Shell gasification**, not yet in use for ammonia production, but successfully applied for other productions is an option, too. Texaco's concept is very similar to its partial oxidation process for heavy fuel oil feeding a 70 % coal-water paste into the generator. Koppers-Totzek is an entrained flow concept, too, but feeding coal dust. In the Lurgi process, the coarse grounded coal is gasified in a moving bed at comparably low temperature using higher quantities of steam as the others. Shell's process differs considerably from its oil gasification process in flow pattern and feeds coal dust. Texaco, Lurgi, and Shell operate under pressure, whereas the Koppers-Totzek gasifier is under atmospheric pressure, but a pressure version, called PRENFLOW<sup>®</sup> is presently tested in a demoplant. Continuous slag removal either in solid or mol-

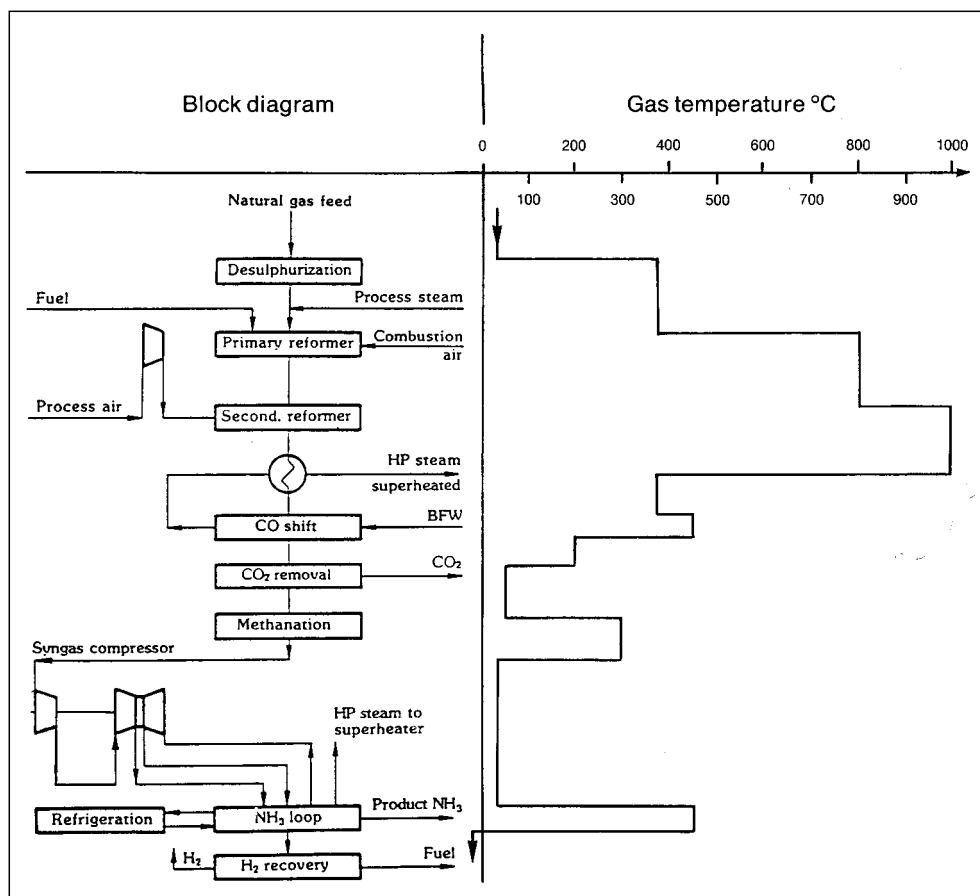


Figure 15: Ammonia plant temperature profile



ten form is, indeed, the fundamental technical problem with coal-based systems and the technical solutions differ considerably. Gas cooling is achieved by quench and or waste heat boiler, entrained coal dust is removed by water scrubbing. The following process steps for shift conversion, CO<sub>2</sub> removal and final purification are largely the same as in partial oxidation of heavy fuel oil.

## Energy integration and ammonia plant concept

### The integrated steam reforming ammonia plant

In the old days an ammonia plant was more or less just a combination with respect to mass flow and energy management was handled within the separate process sections, which were often sited separately, as they usually consisted of several parallel units. A revolutionary break-through came in the mid of the 1960s with the steam reforming ammonia plants. The new impulses came more from the engineering and contractor companies than from the ammonia plant industry itself. Engineering contractors have been working since the thirties in the oil refining sector. The growing oil demand stimulated the development of machinery, vessel and pipe fabrication, instrumentation and energy utilization leading to single-train units of considerable size.

By applying the experience gained in this field it was possible to create within a few years in the mid 1960s the modern large-scale ammonia concept. To use a single-train for large capacities (no parallel lines) and to be as far as possible energetically self-sufficient (no energy import) through a high degree of energy integration (with process steps with surplus supplying those with deficit) was the design philosophy for the new steam reforming ammonia plants pioneered by M. W. Kellogg and some others. It certainly had also a revolutionary effect on the economics of ammonia production, making possible an immense growth in world capacity in the subsequent years. The basic

**Table 1: Main energy sources and sinks in the steam reforming ammonia Process**

Process section	Originating	Contribution
Reforming	Primary reforming duty	Demand
	Flue gas	Surplus
	Process gas	Surplus
Shift conversion	Heat of reaction	Surplus
CO <sub>2</sub> removal	Heat for solvent regeneration	Demand
Methanation	Heat of reaction	Surplus
Synthesis	Heat of reaction	Surplus
Machinery	Drivers	Demand
Unavoidable loss	Stack and general	Demand
Balance	(Auxiliary boiler or import)	Deficit
	(Export)	Surplus

reaction sequence has not changed since then. Figure 15 shows the process sections and the relevant gas temperature levels in a steam reforming ammonia plant.

High-level surplus energy is available from the flue gas and the process gas streams of various sections, while there is a need for heat in other places such as the process steam for the reforming reaction and in the solvent regenerator of the carbon dioxide removal unit (Table 1). Because a considerable amount of mechanical energy is needed to drive compressors, pumps and fans, it seemed most appropriate to use steam turbine drives, since plenty of steam could be generated from waste heat. As the temperature level was high enough to raise HP steam of 100 bar, it was possible to use the process steam first to generate mechanical energy in a turbine to drive the synthesis gas compressor before extracting it at the pressure level of the primary reforming section.

The earlier plants were in deficit, and they needed an auxiliary boiler, which was integrated in the flue gas duct. This situation was partially caused by inadequate waste heat recovery and low efficiency in some of the energy consumers. Typically, the furnace flue gas was discharged up the stack at unnecessarily high temperatures because there was no combustion air pre-heat and too much heat was rejected from the synthesis loop, while the efficiency of the mechanical drivers

was low and the heat demand in the carbon dioxide removal unit regenerator was high.

A very important feature of this new concept was the use of a centrifugal compressor for synthesis gas compression and loop recycle. One advantage of the centrifugal compressors is that they can handle very large volumes which allows also for the compression duties a single line approach. The lower energetic efficiency compared to the reciprocating compressors of which in the past several had to be used in parallel is more than compensated by the lower investment and the easy energy integration. In the first and also the second generation of plants built to this concept, maximum use was made of direct steam turbine drives not only for the major machines such as synthesis gas, air and refrigeration compressors but even for relatively small pumps and fans. The outcome was a rather complex steam system and one may be tempted to describe an ammonia plant as a sophisticated power station making ammonia as a by-product. The plants produce more steam than ammonia, even today, the most modern plants still produce about three times as much. In recent years electrical drives have swung back into favor for the smaller machines.

In most modern plants total energy demand (feed/fuel/power) has been drastically reduced. On the demand side important savings have been achieved in the carbon dioxide removal section by switching from old, heat-thirsty processes like MEA

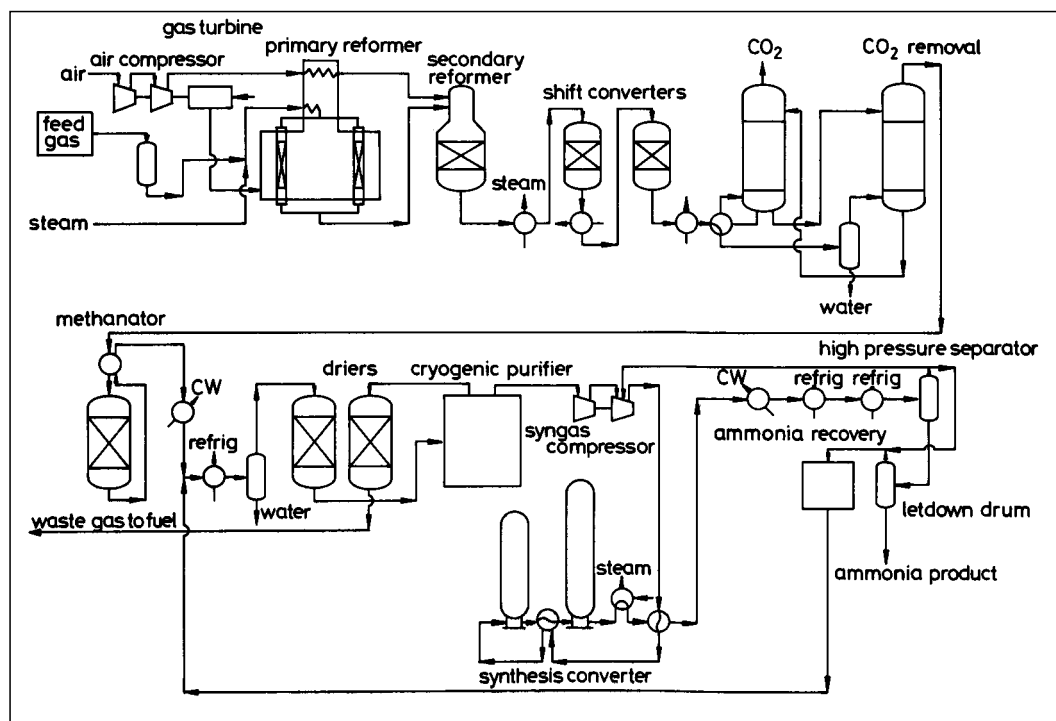


Figure 16: Simplified flow sheet of a modern steam reforming ammonia plant (C.F. Braun Purifier Process)

scrubbing to low-energy processes like the newer versions of the **Benfield process** or **amDEA**. Fuel is saved by **air preheat** and feed by **hydrogen recovery** from the purge gas of the synloop by cryogenic, membrane or pressure swing adsorption technology. In the synthesis loop the mechanical energy needed for feed compression, refrigeration and recycle has been reduced, and throughout the process catalyst volumes and geometry have been optimized for maximum activity and minimum pressure drop.

On the supply side, available energy has been increased by greater heat recovery, and the combined effect of that and the savings on the demand side have pushed the energy balance into surplus. Because there is no longer an auxiliary boiler, there is nothing in the plant that can be turned down to bring the energy situation into perfect balance; therefore the overall savings have not, in fact, translated into an actual reduction in gross energy input to the plant (in the form of natural gas); they can only be realized by exporting steam or power, and it is only the net energy consumption that has been reduced. But under favorable circumstances this situation can be used in a very advantageous way. If there is a substantial outlet on the site for export steam, it can be very economic (depending on the price of natural gas and the value assigned to steam) to increase the steam export deliberately by using additional fuel, because the net energy consumption of the plant is simultaneously reduced).

It is only possible to reduce the gross energy demand – that is, to reduce the natural gas input to the plant – by reducing fuel consumption, because the feedstock requirement is stoichiometric. So the only way is to cut the firing in the reforming furnace by shifting reforming duty to the secondary reformer, as we had already discussed earlier or to choose a more radical approach by the use of an exchanger reformer instead of the fired furnace: ICI's Gas-Heated Reformer (GHR) system, the KRES of M. W. Kellogg and the **Tandem Reformer (now marketed by Brown & Root)**, or the even more advanced Combined Autothermal Reformer (CAR) of Uhde. But none of these designs necessarily achieves any significant improvement over the net energy consumption of the most advanced conventional concepts under the best conditions.

For the cases in which export of steam and/or power is welcome there is the very elegant possibility of integrating a **gas turbine** into the process **to drive the air compressor**. The hot exhaust of 500 – 550 °C contains well enough oxygen to serve as preheated combustion air for firing the primary reformer. The gas turbine does not even have to be particularly efficient, because any heat left in the exhaust gas down to the flue gas temperature level of 150 °C is used in the furnace. Thus an overall efficiency of about 90 % can be achieved.

Boiler makers provide today largely reliable designs for **high-duty waste heat boilers** after secondary reformer and in the synthesis loop, in which up to 1.5 t steam/t NH<sub>3</sub> are produced, corresponding roughly to a recovery of 90 % of the reaction enthalpy of the synthesis. **Centrifugal compressors** have become much more reliable, though their efficiency has not increased spectacularly in recent years. Some improvements were made in turn-down capability in improving the surge characteristic. New developments are **dry seals** instead of oil seals and another potential improvement, already successfully introduced in non-ammonia applications, is the **magnetic bearing**.

So from a mere thermodynamic point of view, in an ideal engine or fuel cell heat and power should be obtained from this reaction. But because there is a high degree of irreversibility in the real process a considerable amount of energy is necessary to produce the ammonia from methane, air and water. The stoichiometric quantity of methane derived from the foregoing equation is 583 Nm<sup>3</sup> per mt NH<sub>3</sub>, which corresponds to 20.9 GJ (LHV) per tonne of ammonia, which with some reason could be taken as minimum value. Of course, if one assumes full recovery of the reaction heat, then the minimum would be the heating value of ammonia, which is 18.6 GJ (LHV) per mt NH<sub>3</sub>.

**Energy and exergy analysis** (First and Second Law of Thermodynamics respectively) identify the process steps in which the biggest losses occur. The biggest energy loss is in the turbines and compressors, whereas the exergy loss is greatest in the reforming section, almost 70 %. Based on exergy the thermodynamic efficiency for the ammonia production based on steam reforming of natural gas is almost 70 %.

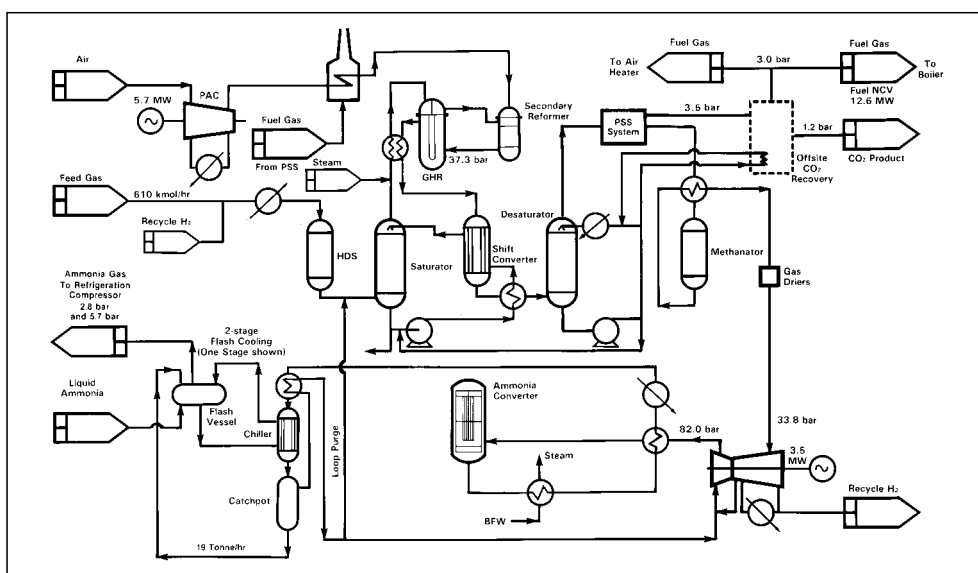
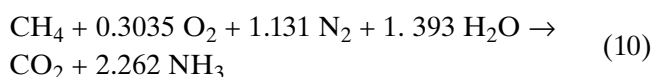


Figure 17: Flow diagram of ICI's LCA Ammonia Process (Core unit) for 450 mtpd

Although the introduction of the single-train integrated large plant concept in the 1960s revolutionized the energy-economics of ammonia production, it is surprising that since then the total consumption has been reduced by about 30 %, from roughly 40 to 28 GJ/t. An example of a modern plant shows Figure 16.

From this enormous reduction in energy consumption the question may come up, what is the **theoretical minimum energy consumption** for ammonia production via steam reforming of natural gas. Based on pure methane, we may formulate the following stoichiometric equation:



$$\Delta H_{298}^0 = -86 \text{ kJ/mol}; \Delta F_{298}^0 = -101 \text{ kJ/mol}$$

It has become rather common to measure modern ammonia concepts above all by their energy consumption. Yet these comparisons need some caution in interpretation; without a precise knowledge of design bases, physical state of the produced ammonia and state of the utilities used, e. g. cooling water temperature, nitrogen content in natural gas, or conversion factors used for evaluating imported or exported steam and power, misleading conclusions may be drawn. In many cases, too, the degree of accuracy of such figures is overestimated.

The best energy consumption values for ammonia plants using steam reforming of natural gas are around 28 GJ/tNH<sub>3</sub>. Industrial figures reported for plants with high-duty primary reforming and stoichiometric process air and for those with reduced primary reforming and excess air show practical no difference.

## New steam reforming ammonia process configurations

The **ICI Leading Concept Ammonia Process LCA** – a radical break-away from the philosophy of the highly integrated large plant which has been so successful for more than 25 years – had its industrial debut in 1988 at ICI's own location in Severside, England. The process consists of a core unit with all the essential process steps (Figure 17) and a separate utility unit which comprises utility boiler and electric generator, CO<sub>2</sub> recovery, cooling water system, demineralized water and boiler feed water conditioning and ammonia refrigeration.

Feed gas is purified in a hydro-desulfurization operating at lower than usual temperatures and passes a saturator to supply a part of the process steam, the balance is injected as steam. Heated in an inlet/outlet exchanger to 425 °C the mixed feed enters the ICI Gas Heated Reformer (GHR) at 41 bar, passing to the secondary reformer at 715 °C. The shell side entrance temperature of the GHR (secondary reformer exit) is 970 °C falling to 540 °C at the exit of the GHR. Methane levels exit GHR and secondary reformer are 25 % and 0.67 % respectively (dry basis). Overall steam to carbon ratio is 2.5 to 2.7. The gas, cooled down to 265 °C in the inlet/outlet exchanger, enters a single stage shift conversion, using a special copper-zinc-alumina based catalyst operating in quasi-isothermal fashion in a reactor with cooling tubes, circulating hot water, whereby the absorbed heat is used for the feed gas saturation as described above. CO<sub>2</sub> removal and further purification is effected by a PSA System, followed by methanation and drying. The synthesis operates at 82 bar in a proprietary tubular converter loaded with a cobalt enhanced formula of the classical iron catalyst. Purge gas is recycled to the PSA unit and pure CO<sub>2</sub> is recovered from the PSA waste gas by an mDEA wash. Very little steam is generated in the synloop, and from waste gases and some natural gas in an utility boiler in the utility section (60 bar) and all drivers are electric. The original intention was to design a small capacity ammonia plant which can compete with modern large capacity plants in consumption and specific investment, and to achieve with lower energy integration a higher flexibility for start up and reduced load operation, needing a minimal staffing. The basic plant features (GHR, isothermal shift and synthesis) can principally be applied for larger capacities, too. The flow sheet energy consumption is 29.3 GJ/t NH<sub>3</sub>.

In the context of the LCA process some discussion on the **economics of scale** came up. Within the same sort of process configuration specific investment will be reduced by increasing capacity, at least to a point where limitations for equipment size and transport might play a role and specific investment would then increase again after having reached a minimum. In any case for the traditional modern steam reforming ammonia plant, a capacity of 2000 t/d is not beyond the optimum. On the other hand it cannot be excluded that concepts as the LCA with no elaborate steam system and a modular and prefabrication construction may come close to the specific investment of world size plants, but with regard to the other fixed costs, e. g. staffing, some question marks remain.

**Kellogg** has combined the ruthenium catalyst based synthesis loop (KAAP) with its exchanger reformer system (KRES) to an optimized integrated ammonia plant concept (**Ammonia 2000**) intended for the use in world-scale single-train plants in the 1850 t/d range. Desulfurized gas is mixed with steam and then split into two streams in approximate proportion 2:1. These streams are separately heated in a fired heater. The smaller of the two enters the exchanger reformer at 550–550 °C, while the remainder is passed directly to the autothermal reformer at 600–640 °C. The exchanger reformer and the autothermal reformer use conventional nickel-based primary and secondary reforming catalysts respectively. To satisfy the stoichiometry and the heat balance, the autothermal reformer is fed with enriched air (30 % O<sub>2</sub>). The required heat for the endothermic reaction in the tubes of the exchanger reformer comes from the gases on the shell side, comprising a mixture of the effluent from the autothermal reformer and the gas emerging from the tubes. The shell side gas leaves the vessel with 40 bar. The synthesis proceeds at about 90 bar in a 4-bed radial-flow converter (hot wall design) with inter-bed exchangers. The first bed is charged with conventional iron-based catalyst for bulk conversion and the other beds with Kellogg's high activity ruthenium-based catalyst, allowing to attain an exit ammonia concentration in excess of 20 %. The other process steps are more along the traditional lines. The overall energy claimed for this process can be as low as 27.2 GJ/t NH<sub>3</sub>.

Another recently launched process is the **Linde Ammonia Concept** (LAC) which consists essentially of a hydrogen plant with only a PSA unit to purify the synthesis gas, a standard cryogenic nitrogen unit and

an ammonia synthesis loop. The concept is similar to **KTI's PARC process** for small capacities. The first project with a capacity of 1350 t/d is presently executed in India. The single isothermal shift conversion uses Linde's spiral-wound reactor, which has been successfully used for methanol plants and hydrogenation in ten plants around the world. In the loop a Casale three bed converter with two interbed exchangers is used. As in ICI's LCA process, pure carbon dioxide can be recovered by scrubbing the off gas from the PSA unit, for which Linde also uses the BASF aMDEA process. The process consumes about 28.5 GJ/t NH<sub>3</sub>, or, with inclusion of pure CO<sub>2</sub> recovery 29.3 GJ/t NH<sub>3</sub>.

## The status of ammonia plants based on heavy fuel oil and coal

For lack of economic incentive, not much optimization and development work has been dedicated in the last few years to the field of **partial oxidation of higher hydrocarbon** fractions. The gasification of these plants usually does not consist of a single line. Compared to

a steam reformer furnace there are more production interruptions because of periodic burner changes and cleaning operations in the gasification units. For this reason most installations have a standby unit. In addition to that the maximum capacity of single gas generator corresponds only to 1000-1100 t/d of ammonia. Therefore world size ammonia plants have 3–4 partial oxidation generators. Generally the degree of energy integration is lower than in the steam reforming process because, in the absence of a large fired furnace, there is no large amount of hot flue gas and consequently less waste heat is available. So in this process route a separate auxiliary boiler is usually necessary to provide steam for mechanical energy and power generation. Nevertheless, in modern concepts some efforts have been made to bring the energy consumption down. Whereas older plant concepts had values of around 38 GJ/t NH<sub>3</sub>, for a concept with the traditional use of 98.5%+ oxygen quite recently a figure of 33.5 GJ/t NH<sub>3</sub> was claimed in a commercial bid.

To reduce investment cost and energy consumption it has been recommended to use air or enriched air

**Table 2: Comparison of ammonia production 1940–1990**

		Multi-line plant BASF 1940	Modern Single Train 1991
Feedstock		Coke	Natural gas
Capacity	t/d	800	1800
Plot size	m <sup>3</sup>	35 000	18 000
Steel	t	30 000	13 000
Personal		1800	100
Investment (1990)	Mio DM	1000	300
Energy consumption	GJ/t NH <sub>3</sub>	88	28

**Table 3: Ammonia production cost from various feedstock in 1996 in NW Europe (1800 t/d, new plant)**

Feedstock		Natural gas	Vacuum residue	Coal
Process		Steam Reforming	Partial Oxidation	Partial Oxidation
Feedstock price	DM/GJ	4.3	3.0	2.7
Total energy consumption	GJ/t NH <sub>3</sub>	28.5	38	48.5
Feedstock & energy costs	DM/t NH <sub>3</sub>	123	114	131
Other cash costs	DM/t NH	50	65	100
Total cash costs	DM/t NH <sub>3</sub>	173	179	231
Capital-related costs	DM/t NH <sub>3</sub>	100	143	260
Total cost	DM/t NH <sub>3</sub>	273	322	491
Investment	Mio DM	350	500	900

*For capital-related costs a debt/equity ratio of 60:40 is assumed. With 6% depreciation, 8% interest on debts and 16% ROI on equity, total capital-related charges are 17.2% on investment.*

instead of pure oxygen. **Topsøe** proposed the use of enriched air (43 %) and methanation instead of liquid nitrogen wash. For CO<sub>2</sub>/H<sub>2</sub>S removal Selexol is applied. The shift reaction proceeds over a sulfur-resistant catalyst in a three-bed configuration, bringing the residual carbon monoxide content down to 0.55 %. For the loop a Series 200 converter is chosen. The partial oxidation step can be designed according to either the Texaco or the Shell process. An overall consumption of 34.8 GJ/mt NH<sub>3</sub> is stated.

**Foster Wheeler** suggests the use of highly preheated air in a Texaco generator operating at 70 bar. The gas purification train comprises soot scrubbing followed by shift conversion, acid gas removal and methanation. The gas is dried by molecular sieves and finally fed to a cryogenic unit to remove the surplus nitrogen and residual methane, argon and carbon monoxide traces. The rejected nitrogen is expanded in a turbine, which helps to drive the air compressor. A special design consideration was the following: Conventional air separation uses fractional distillation of oxygen and nitrogen at a difference in boiling points of only 13 °C. In the cryogenic unit of the Foster-Wheeler process a lesser quantity of nitrogen (because the stoichiometrically needed proportion remains in the gas) is separated from hydrogen at a much higher boiling point differential (57 °C). This should save capital investment and energy consumption against the traditional approach. A figure of 35.6–37.6 GJ/mt NH<sub>3</sub> is given for heavy oil feedstock.

For **coal based plants** the economic incentive for extensive R&D is even lower than with fuel oil. The major part of coal fed ammonia plants -most of them of rather small size – are located in China and use still the water gas route. A few ammonia plants based on more modern coal gasification processes as the Texaco Process, the Koppers-Totzek Process, and the Lurgi Coal Gasification are of larger size and operate in South Africa, India and Japan. Also in coal based ammonia plants the gas generation consists of several lines. Depending on the gasification process the maximum capacity of a single gasifier corresponds to an ammonia production between 500 t/d (Koppers-Totzek, Texaco) and 800 t/d (Lurgi gasifier). Regarding the degree of energy integration the situation is at best as in the partial oxidation of fuel oils, but in any case much lower than in a steam reforming plant. **Lurgi's** moving bed gasification produces a gas with a rather high content of methane, which after separation in the cryogenic step is processed in a small

steam reforming unit. Shift conversion, Rectisol unit, liquid nitrogen wash are the other essential steps in the synthesis gas preparation. The gasification needs 32–34 GJ/t NH<sub>3</sub>, power and steam generation consumes 18–22 GJ/t NH<sub>3</sub>, resulting in a total energy consumption of 50-56 GJ/t NH<sub>3</sub>. For the **Koppers-Totzek** route a figure of 51.5 GJ/t is reported. Ube Industries commissioned a 1000 t/d ammonia plant in 1984 using **Texaco's coal gasification** process. An energy consumption of 45.5 GJ/t NH<sub>3</sub> is stated, which is lower than the normally quoted figure of 48.5 GJ/t NH<sub>3</sub> for this technology.

## Economics of ammonia production

The enormous technical and economical progress made from the old plants using coke and water gas technology to the modern steam reforming ammonia plant with natural gas feedstock may be seen from the table 2. Table 3 gives an estimate for ammonia production in 1996 cost in northwest Europe for different feedstocks using today's best and proven technological standards for each process.

From table 3 it is obvious that at present there is no chance for the other feedstocks to compete against steam reforming of natural gas. Only under very special circumstances – in cooperation with a refinery, for example – partial oxidation of heavy oil fractions might be economically justified. It should be noted, however, that the average energy consumption of the steam reforming plants presently in operation is noticeable higher than the example of the modern low-energy concept used in table 3.

The combined cost of feedstock and energy for a steam reforming plant – both are natural gas – is the principal determinant of the overall production costs. The price of gas – and, by extension, the price of ammonia – is to a greater or lesser extent linked to the price of crude oil. The present interfuel relationship between gas and oil pricing might be distorted by the need for cleaner and less polluting fuels resulting from increasing environmental awareness. In this respect, natural gas is so advantageous in relation to other fossil fuels that demand could well be pushed up in the coming years.

The received opinion is that, although gas supply can be increased, upward pressure on prices is necessary to make that happen. The forecast is for higher production costs in Western Europe and the USA. In the low gas cost areas such as the Arab Gulf, Trinidad and Indonesia, competing usages for natural gas are not expected to grow to any great extent, and in such locations feedstock costs for the ammonia producers are expected to rise only moderately. The biggest share of the proven world reserves of natural gas have former USSR, followed by the Middle East.

In the very long term, coal has prospects which might be drawn from consumption and world reserves of fossil feedstocks. At present consumption rates coal will cover the demand for 235 years, natural gas for 66 years and oil for 43 years. But at least for the medium term natural gas can continue as preferred feedstock.

## **Future perspectives for the ammonia production technology**

Albeit world population and thus the demand of fertilizers is increasing – 87 % of the ammonia production is consumed in this sector – building of new ammonia plants did not keep up adequately with this. Of course, the main increase of demand is in the developing countries, but in most cases there is not sufficient capital available for the investments needed. In the industrial countries with sufficient food supply the fertilizer consumption is at best stagnant for ecological concerns presently exercising the collective minds in the Western World. The sometimes from environmentalists propagated ecological agriculture is no alternative as manure and biomass are not sufficient in effect and quantity to supply the necessary nitrogen and in addition they have the same problem with nitrate run-off.

Direct biological fixation is presently restricted to the legumes by their symbiotic relationship with the Rhizobium bacteria, which settle in the root nodules of the plants. Intensive genetic engineering research has provided so far a lot of insights in the mechanism of this biological fixation but a real breakthrough for practical agricultural application has not yet happened. The enzyme nitrogenase practically performs an ammonia synthesis in the bacteria, and for the synthesis of the nitrogenase the so-called NIF gene is responsible. One option, for example, would be to broaden the host spectrum of the Rhizobium bacteria by genetic manipulation. Other possibilities are to transfer the NIF gene to other bacteria which have a broader host spectrum but have no own nitrogen fixation ability or to insert the NIF gene directly into plants. One important point to consider especially with the option of constructing a nitrogen fixing plant, is the energy balance of the plant. Because of the low efficiency, a considerable amount of the photosynthesis product would be consumed to supply the energy needed. This would consequently lead to a reduction in yield, which is estimated by some researchers to be as high as 18 %.

The possibility of converting atmospheric nitrogen into ammonia in homogeneous solution using metal-organic complexes was first raised around 1966. The prospects for this route are not judged to be very promising in terms of energy consumption and also with respect to the cost of these very sophisticated cat-



alyst systems. Photochemical methods of producing ammonia at ambient temperature and atmospheric pressure in the presence of a catalyst have been reported, but the yields are far too low to be economically attractive.

So for the foreseeable future we have to rely on the conventional ammonia synthesis reaction, combining hydrogen and nitrogen using a catalyst at elevated temperature and pressure in a recycle process, as conceived in laboratory by Fritz Haber and made operable on an industrial-scale by C. Bosch, and on the use of the known routes to produce the hydrogen and nitrogen needed (which are in fact, what consumes all the energy).

In conclusion it is possible to sum up the prospects by the following broad predictions:

- Natural gas will remain the preferred feedstock for at least the next 15 years. Coal gasification will not play a major role in ammonia production in that period.
- The present ammonia technology will not change fundamentally, at least in the next 15 years. Even if there are radical, unforeseeable developments, they will take time to develop to commercial introduction. With the available concepts, the margins of additional improvements have become rather small after years of intensive research and development. Thus only minor improvements of individual steps, catalysts and equipment might be expected.
- A further significant reduction in the energy consumption of the natural gas-based steam reforming ammonia process is unlikely; figures between 27 and 28 GJ/t NH<sub>3</sub> are already close to theoretical minimum.
- In the medium term the bulk of ammonia production will still be produced in world-scale plants of 1,000–2,000 t/d NH<sub>3</sub>. Small capacity plants will be limited to locations where special logistical, financial or feedstock conditions favor them.
- New developments in ammonia technology will mainly reduce investment costs and increase operational reliability. Smaller integrated process units (e. g. exchanger reformer, CAR) contribute to this reduction and give additional savings by simplify-

ing piping and instrumentation. Improved reliability may result from advances in catalyst and equipment quality and from improved instrumentation and computer control.

- It is very likely that genetic engineering will succeed in modifying some classical crops for biological nitrogen fixation and that application in large scale will occur predominantly in areas with still strongly growing population to secure the increasing food demand. This development may be pushed by the fact that compared to the classical fertilizer route less capital and less energy would be needed. This may happen within the next 20 years, but time estimates are always risky. (A famous example: “Man will not fly for 50 years, Wilbur Wright 1901”). But even with the introduction of this new approach, traditional ammonia synthesis will continue to operate in parallel, because it might be necessary to supplement the biological nitrogen fixation with classical fertilizers. In addition, the existing ammonia plants represent a considerable capital investment and a great number of them may reliably operate for at least another 20–30 years from a mere technical point of view.

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