

THE FIRST CATALYSTS

Efforts to develop processes using catalysts were vital to the growth of the chemical industry. For many years, the *first catalysts* were most probably the result of trial and error and were based on the observations of scientists. When Berzelius defined catalysis, the examples he quoted did not include any industrial applications. For example, no mention was made of the lead chamber process or the Phillips patent proposing the use of a platinum catalyst for sulfuric acid production.

When the chemical industry began to expand, BASF improved the contact process and, following Haber's investigations, introduced ammonia synthesis, which provided a practical basis for catalyst design.

However, as Miles noted in his book on the contact process, published by Gurney and Jackson in 1925, the secrecy surrounding new processes slowed down the release of technical information. Miles tried to reverse a situation in which no process was completely described until it was out of date!

Many changes have now been made to the first catalysts since they were introduced, but they are still being used and, with more recent introductions, are indispensable in the modern chemical, refining and petrochemical industries.

2.1. SULFURIC ACID

Large-scale production of sulfuric acid began in about 1740 when Joshua Ward burned sulfur and niter in glass bell jars with a capacity as high as 66 gal. This procedure was improved in 1746 by Dr John Roebuck and Samuel Gardner at

their Birmingham, UK, *vitriol manufactory*, where they burned the sulfur and niter in *lead houses*. This was the critical step in producing tonnage quantities of sulfuric acid for the first time.

Later, Roebuck's factory in Glasgow incorporated a suggestion by J. A. Chaptal (Napoleon's Minister for Agriculture) that the sulfur and niter should be burned in an external furnace. While this meant that the sulfur dioxide and the nitrogen dioxide catalyst were passed into the lead chamber with a current of steam, it was some time before the process became really continuous. The size of the lead chambers increased from about 200 ft³ in Roebuck's plants, producing about 25 lb of acid a day, to about 5000–10,000 ft³ by 1820.

Large-scale production led to the price of acid falling from about £30 per ton in 1790–1800 to £3.5 per ton in 1820, when UK production of sulfuric acid was about 10,000 tons a year. Removal of the UK salt tax in 1825 reduced the price still further to £1.25 per ton.

2.1.1. The Lead Chamber Process

At first it was not known that niter, which was an essential part of the lead chamber process, acted as a catalyst. When Lavoisier showed that sulfuric acid contained only sulfur, oxygen, and hydrogen (1772–1777) it was realized that niter was not a component of chamber acid. Operators then assumed that it either made the sulfur flame hotter or supplied oxygen to the sulfurous acid.

At that time, acid was still being made in batches and no air was added to the lead house during reaction. By 1793 Clement and Desormes had suggested that the continuous addition of air would improve reaction, and in 1806 they defined the action of niter, which was clearly essential to the process:¹

“ . . . nitric acid is only the instrument of the complete oxygenation of the sulfur: it is the base, nitric oxide, that takes the oxygen from the atmospheric air to offer it to the sulfurous acid in the state which suits it best . . . ”

Clement and Desormes were also the first to observe the formation of *chamber crystals* that evolved nitric oxide and formed sulfuric acid when added to water. The nitric oxide was then available for recycling.

The basis of the lead chamber process was, therefore, to combine sulfur dioxide with the oxygen in air in the presence of a relatively small amount of niter. Some details of the process development are summarized in [Table 2.1](#) and a typical lead chamber plant is shown in [Figure 2.1](#). Despite this conclusion, many UK producers continued to operate the process in batches until as late as 1820. The fact that it was difficult to transport sulfuric acid meant that many small, *on-site* plants supplied users directly. This, of course, eliminated competition and delayed technical developments. Even after the eventual introduction of the contact process during the 1920s, the lead chamber process was still widely

TABLE 2.1. Development of the Lead Chamber Process.

Innovator	Procedure	Comment
1666: Fevre and Lemery	Sulfur burned with saltpeter (KNO_3)	
1740: Ward, Richmond, UK	Rows of 66-gal glass jars. One part KNO_3 and eight parts sulfur burned in a horizontal glass neck.	Sulfur trioxide dissolved in water in jar. Sulfur burned until acid strength high enough for use or concentration.
1749: Roebuck and Garbutt, Prestonpans, Scotland. Used lead chambers.	1-lb KNO_3 with 7-lb sulfur every 4 hours on iron trays.	Air replenished between batches of sulfur. Acid gravity usually 1.250 (33%) after six weeks! Concentrated to almost 50%. Yield about 110% based on sulfur. Several hundred chambers used at each site 70,000 ft^3 (200 m^3) at Prestonpans.
1793: Clement and Desormes	Continuous flow of air limited amount of KNO_3 required.	Confirmed air was main (90%) oxidant and KNO_3 only an intermediate.
1807–1814: St Rollox, Scotland	Continuous sulfur burning—steam and air flowing through lead chambers.	
1827: Chaumy, Gay-Lussac tower	Nitrogen oxides absorbed at outlet of lead chambers to allow catalyst (oxides of nitrogen) recovery.	First use at Chaumy in 1842 and Glasgow in 1844. Little used until Glover tower became available.
1859: Glover tower	Nitrous oxides recovered from Gay-Lussac tower.	Slow acceptance. First use 1859 at Washington, Co Durham, UK.

used throughout the world until the 1950s—a typical example of industrial *catalytic* inertia.

Nitrogen oxides were lost to the atmosphere with the residual nitrogen during operation of lead chamber plants. This led Gay-Lussac to suggest in 1828 that effluent nitrogen be washed with chamber acid in a separate tower to dissolve the nitrogen oxides, which could then be recycled. Because it was difficult to liberate the nitrogen oxides without diluting the chamber acid, Gay-Lussac towers were not often used. Finally, in 1859, Glover passed the nitrous vitriol down through a second tower, where hot gas from the pyrites burner removed the nitrogen oxides, which were returned to the lead chambers.² This procedure was important as it also concentrated the acid. The combined Gay-Lussac and Glover towers were, therefore, the first catalyst recovery plants. A tower built in 1868 concentrated 73,000 tonnes of sulfuric acid to specific gravity 1.75 (80%

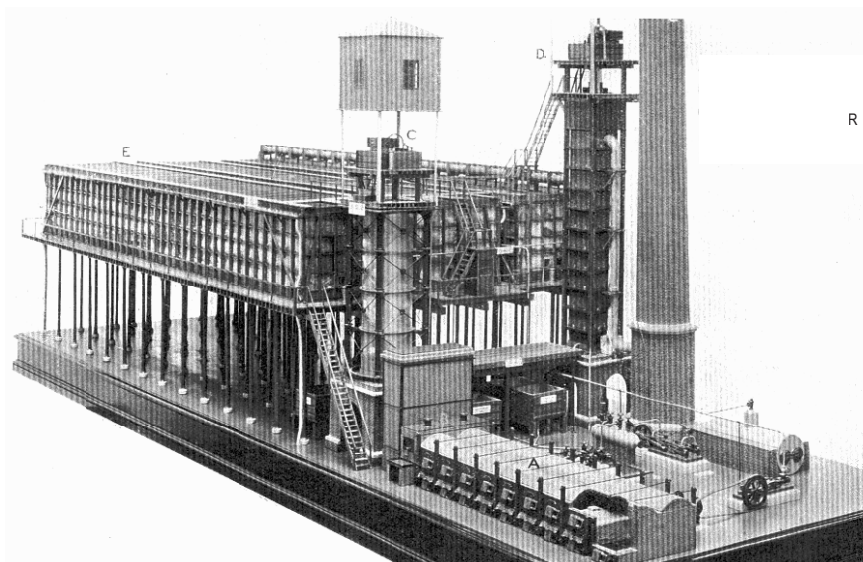


Figure 2.1. Lead chamber process for the manufacture of sulfuric acid. Reprinted with permission of the Science Museum, London.

H₂SO₄) from a total of 15,400 tonnes of pyrites. The tower cost £450 and annual repairs over a 6-year period cost only £11.³ Even so, despite the bargain prices, Glover towers were slow to gain acceptance, and by 1890 were used by only about half of US acid plants. Until the lead chamber process was fully developed, concentrated sulfuric acid could only be produced by evaporation in glass or platinum vessels.

2.1.1.1. *Chemistry of the Lead Chamber Process*

Lunge and Berl proposed the following mechanism for the oxidation of sulfur dioxide:⁴

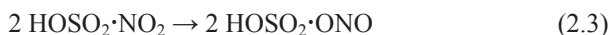
- Reaction with nitrous fumes:



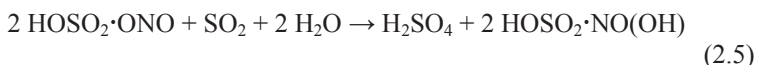
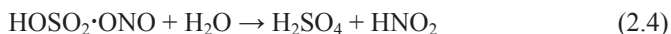
- Oxidation of hydroxynitrosulfuric acid:



- Isomerization of nitrosulfuric acid:



- Nitrosulfuric acid then forms sulfuric acid with steam or sulfur dioxide:



Process efficiency depended on gas mixing in the lead chambers. Major improvements in operating the lead chamber process were the use of packed towers by Gaillard-Parrish and Peterson, the introduction of conical towers by Mills and Packard, and process designs introduced by Kachkaroff.⁶ Chamber acid was dilute 65% sulfuric acid as produced but could be concentrated to 80% in the Glover tower.

2.1.1.2. *The Continuing Use of the Lead Chamber Process*

Lead chamber plants were used for many years after the introduction of the contact process in which small companies made acid for their own operations. [Table 2.2](#) shows that in both the United States and the United Kingdom production of chamber acid continued until well after the 1960s.

At least one lead chamber plant was still operating in the north of England in 1960. There were plumbers patching the lead chamber and carpenters regularly replacing the wooden ducting used to transfer acid from the chambers to the point of use.

TABLE 2.2. Gradual Introduction of Contact Process 1900–1975.

Year	United Kingdom		United States	
	Lead chamber	Contact	Lead chamber	Contact
1899	100%	—		New Jersey Zinc
1901	100%			General Chemical Co.
1920	More than 100 plants used	First contact process plant	Up to 80%	More than 20%
1929			About 65%	About 35%
1938	About 63%	About 37%	More than 90 plants remain	
1944	About 55%	About 45%		
1960	About 10%	About 90%	Few chamber plants remain	
1975	Small capacity lead chamber plants only. Contact acid > 96%.			

In fact new *lead chamber* plants were still being offered by a contractor in 1958.⁶ A description of the *Kachkaroff process* shows how the old plants operated. The burner, which produced reaction gas, was followed by four large cylindrical reaction vessels in which sulfur dioxide reacted with oxygen, catalyzed by the circulation of *nitrous vitriol* and gaseous nitrogen oxides. Nitrous vitriol was a solution of 10–15 wt% nitrogen oxides in sulfuric acid. Nitrogen oxide losses were made up as required by a small ammonia oxidation unit.

More than 80% of the sulfur dioxide was oxidized in the first reaction vessel. Reaction was rapid and the surface of the liquid was violently agitated. A consequence of this mixing was that as sulfuric acid was produced the gaseous nitrogen oxide catalyst dissolved to form more nitrous vitriol.

The circulation of nitrous vitriol through the final three reaction vessels was regulated to balance the conversion of the remaining sulfur dioxide. Inlet temperature to each reaction vessel was controlled by cooling the circulating acid solution. A volume of the nitrous vitriol equal to the sulfuric acid being produced was removed from the circulating liquid when the reaction was completed and pumped to a denitration tower linked to an acid concentration tower. During denitration of the nitrous vitriol in the first tower, the sulfuric acid was diluted from 80–85% to 60–68%. Cool acid was then concentrated by passing it down the second, concentration, tower, which also cooled the hot gases leaving the burner. Cooled burner gas then passed through the reaction vessels to continue the cycle.

Overall loss of nitrogen oxide catalyst was equivalent to about 0.15 tons of nitric acid per ton of sulfuric acid produced, which was lower than in the conventional, less sophisticated lead chamber process plants. Sulfuric acid could be obtained as either 77–82% or 60–80% solutions. An advantage of the more modern process was that the low-temperature operation allowed the use of PVC as piping, tower cladding, and storage tank linings.

2.1.1.3. *Raw Material for Sulfuric Acid Production*

During the nineteenth century, the main source of sulfuric acid was Sicilian sulfur and most US plants continued to import sulfur from Sicily until the 1890s. However, in 1838 the king of Sicily gave an export monopoly to a French company, which increased the price from £5 to £14 per ton, and most European companies considered it necessary to find an alternative raw material. Iron pyrites was known to burn forming sulfur dioxide and, despite the presence of arsenic impurities, was used from about 1825. Spain became the major supplier of pyrites in Europe and sulfuric acid production was often associated with copper smelting. By 1860, most European plants were using pyrites, although, later, as spent oxide (sulfide iron oxide) started becoming available from gas works, it, too, was used as a source of sulfur.

TABLE 2.3. Development of the Contact Process.

Innovator	Comment
1831: Peregrine Phillips	British patent 6096 (1881) described process of forming sulfur trioxide with a platinum catalyst. Used stoichiometric volumes of sulfur dioxide and oxygen. Inspired further research.
1837: Clement	Writing to Schneider felt that the contact process would be widely used within 10 years.
1844: Schneider	Demonstrated that a pumice catalyst could produce sulfuric acid without lead chambers. He did not claim use of platinum but this is probable [<i>Dingl Polyt J</i> 56 , 395 (1847); 69 , 354 (1860)].
1846: Jullion	British patent 11425 (1846) claimed a platinum catalyst supported on asbestos for the first time. Catalyst also used for a range of other reactions.
1852: Wohler and Mahla	Found that chromium and copper oxides oxidized sulfur dioxide. Copper metal inactive—the first comment on oxidation with oxide catalysts. Showed iron and copper were reduced and oxidized during reaction. Findings later applied to Mannheim process [<i>Ann. Chim. Pharm.</i> 81 , 255 (1852)].
1850s: Deacon	Patented use of copper sulfate in process and first to observe that reaction rate faster with an excess of oxygen.
1853: Robb	British patent 731788 (1853) protected the use of pyrites cinders as catalyst.
1853: Hunt	British patent 1919 (1853) protected the use of silica as a catalyst support.

Note: These processes could have reduced costs of niter and lead used in the lead chamber process while improving production rate. Development was slow owing to a lack of technical experience and innovation. Demand for acid, in particular, was still small.

Herman Frasch developed a process to recover cheap natural sulfur in 1891 that was used first in Louisiana and then in Texas, and eventually became the major source of supply, particularly in the United States. The recovery of refinery sulfur by the modified Claus–Chance process now provides a further enormous supply of pure sulfur throughout the world, and this has largely replaced the Frasch process.

2.1.2. Contact Process Development

The contact process was patented as early as 1831 by Peregrine Phillips, the son of a vinegar maker in Bristol.⁷ His process involved a heated porcelain tube containing finely divided platinum or wire to convert a stoichiometric mixture of sulfur dioxide and air to sulfur trioxide. The process was not commercial at that time for several reasons, including the engineering problems associated with circulating hot corrosive gases, the availability of acid resistant materials, and poisons in the sulphur dioxide. Table 2.3 shows the main developments leading

the granting of Phillips's patent in 1853 and demonstrate the interest in a new *contact* process.

By 1875 Squire and Messel had patented a form of the contact process that used dilute chamber acid as the raw material to avoid any problems with catalyst poisons.⁸ Chamber acid was decomposed by heating and the poison-free sulfur dioxide thus produced was oxidized in air using a platinized pumice catalyst. Sulfur trioxide could then be used to produce oleum, which was needed for the synthesis of alizarin by the newly developing dye industry. The same procedure is still being used to recover sulfur from sulfuric acid wastes. At about the same time Clemens Winkler set up a contact process plant in his factory at Freiberg using more or less the same process but did not apply for patent cover immediately.⁹ All of the processes up to the 1890s used the same exact ratio of sulfur dioxide and oxygen to provide sulfur trioxide. Efforts were made by Schroder and Hannich to use higher pressures.¹⁰ Messel also suggested burning sulfur in pure oxygen to avoid dilution of the reaction mixture with nitrogen.¹¹ A typical modern sulfuric acid plant is shown in [Figure 2.2](#) and the most important developments are described in [Table 2.4](#).



Figure 2.2. Modern sulfuric acid plant using the contact process.

TABLE 2.4. Introduction of the Contact Process for Oleum.

Innovator	Comment
1875: Clemens and Winkler <i>Dingl. Poly. J.</i> 218 , 128 (1875); 223 , 409 (1877).	Described experiments to produce oleum using 8.5% platinum on asbestos with pure oxygen (73.3% conversion) or air (47.4% conversion). Used stoichiometric ratio of SO_2/O_2 . Pure sulfur dioxide from decomposing sulfuric acid. Sulfur trioxide absorbed in water to form oleum. Their results were not thermodynamically possible—Ostwald later claimed it delayed developments [<i>Z. Electrochem.</i> 8 , 154 (1902)].
1875: Squire (and Messel)	British Patent 3278 (1875) resulted from high oleum price. Used a platinum catalyst supported on pumice with a stoichiometric mixture of SO_2/O_2 made from decomposing H_2SO_4 in a platinum still (70% recovery of SO_3). Plant at Silvertown produced three tons of SO_3 per week. Patent mentioned that this avoided catalyst deactivation with dust and, probably arsenic although <i>poisons</i> were not recognized.
1875–1880: Jacob	Operated a contact process oleum plant in Germany at first from decomposed chamber acid but later from sulfur burning (43% free SO_3). Jacob sold his plant to Meister, Lucius, and Bruning at Hoechst, who still made oleum in 1925.
1879: Thann Chemical Works, Alsace	Acquired an improved oleum process design from Squire. Burned Sicilian sulfur and washed gas at 4 atm pressure. Mixed SO_2 with stoichiometric volume of air and formed SO_3 using platinized asbestos. Output 1.5 tons of SO_3 per day and dissolved in concentrated H_2SO_4 .
1880s: BASF	Began to use the same process as Thann, producing such large volumes that the oleum price fell. Production increased from 18,500 tons during 1880 to 116,000 tons by 1900.

Further development of the contact process did not rely on a better catalyst but depended on better methods to remove poisons and clean the gases produced by roasting pyrites, which, by then, had replaced sulfur as the preferred source of sulfur dioxide. In attempting to overcome the difficulty, the Mannheim process used a bed of relatively inactive iron oxide to guard the main bed of a platinum catalyst. New Jersey Zinc and the General Chemical Company in the United States built plants of this kind in 1899 and 1901, respectively.

A 1901 lecture by Rudolph Knietsch¹² described the work carried out by BASF during the period 1880–1900.¹³ As might be expected, the early process developments he described were mainly empirical. They concerned washing of pyrite gas, determination of the most efficient sulfur dioxide/oxygen ratios with excess oxygen for use in the feed gas, and absorption of sulfur trioxide in 98% acid to produce sulfuric acid. This information had been confidential until the paper was published. Perhaps the most important detail, apart from the use of excess oxygen, was the cooling of the gas during reaction in tube-cooled reactors to improve conversion, which was not part of earlier processes.

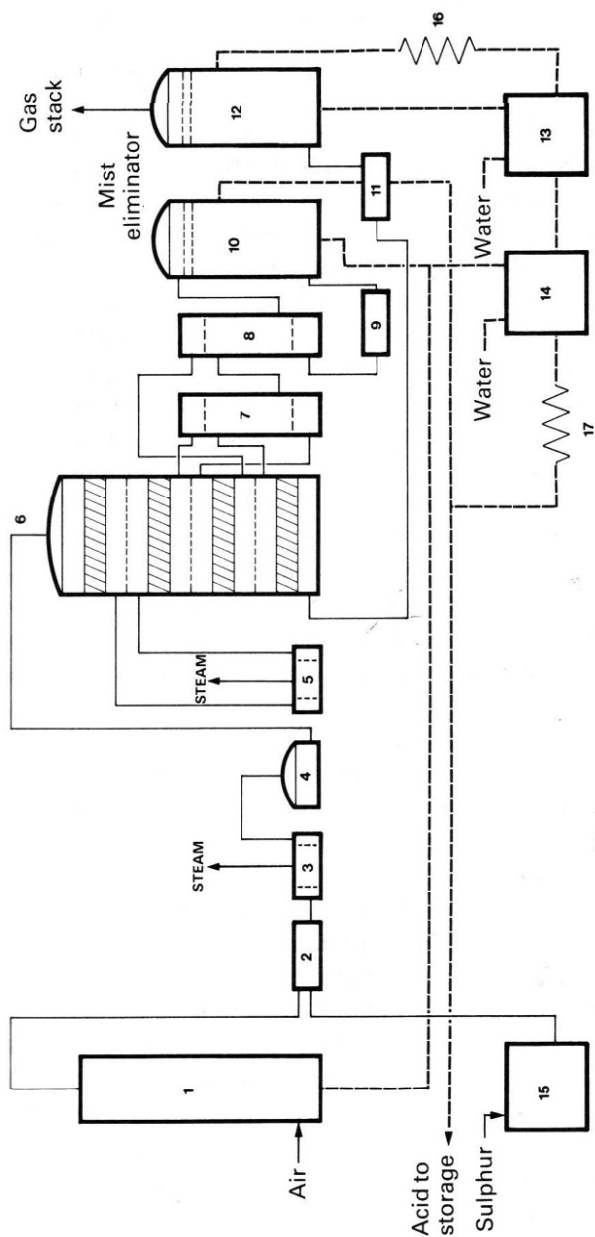
In a further significant advance, De Haen first demonstrated the use of vanadium pentoxide catalysts in 1900, following a suggestion by R. Meyers in Germany in 1898.¹⁴ There was little further progress at that time because the original vanadium pentoxide catalysts were relatively unstable and much less active than the platinum catalysts then available.

The contact process was developed as a matter of urgency during World War I because the effective nitration of toluene required the catalytic use of concentrated sulfuric acid to generate the active species, NO_2^+ . Nitration of toluene, of course, yields the military explosive, TNT. The increased demand for platinum could not be met economically, so that from 1914 on vanadium catalysts had to be introduced rapidly to expand sulfuric acid production. About one-third of German sulfuric acid at that time came from the contact process, but vanadium catalysts were not used extensively in other parts of the world until the mid-1920s.

Porous supports were used to make commercial platinum sulfuric acid catalysts. These included asbestos, kieselguhr, and silica gel. Rather surprisingly, water-soluble carriers such as magnesium sulfate were also successful and made platinum recovery more convenient. A flow sheet of a typical modern sulphuric acid plant is shown in Figure 2.3. Table 2.5 describes four typical industrial catalysts.

TABLE 2.5. Contact Process Catalysts Containing Platinum.

Producer	Comment
1898: BASF ¹⁵	Platinized asbestos produced by impregnating asbestos with platonic chloride solution followed by reduction with formaldehyde. Operated up to 10–12 years in several 10–20 cm layers. Contained 8–10% platinum. Tubular reactors were still designed for vanadium catalysts until 1950s. Agreement with Grillo up to 1898.
1902: Grillo Company	Grillo Company recovered sulfur dioxide from zinc blende smelters. Pre-1898 tightly packed tubes, using up to 15 layers of 8–10% platinum on asbestos converted 25% sulfur dioxide and 75% air. From 1898 used calcined magnesium sulfate sprayed with platonic chloride to give 0.1–0.3% platinum ¹⁶ on finished catalyst. Feed gas contained less sulfur dioxide. ¹⁷
1998–1999: Mannheim Tenterloff Process	First bed loaded with burnt pyrites containing copper. Second bed, with up to 200 tubes—about 12 cm diameter, full of asbestos sponge soaked with platonic chloride solution reduced with formaldehyde.
Davison Chemical Company	Used silica gel impregnated with ammonium chloroplatinate to give 0.1% platinum. Claimed to use less platinum than other catalysts and to resist arsenic poisoning.



The performance of platinum catalysts depended strongly on the form of the support, which influenced crystallite size. Operating life depended on the poisons present in the sulfur dioxide and was originally about two years. With process improvements to remove poisons, the catalyst life eventually increased to about 10 years. Most reactors contained tubes that were cooled by exchange with cold inlet gas. The Grillo reactor contained trays with a form of heat exchange.

Vanadium soon replaced platinum as the most economic catalyst for the contact process. The *strike* temperature at which reaction began was higher but, when necessary, a *striker* layer of platinum catalyst was used until better process designs were available. The big advantages of vanadium pentoxide were that it was both cheaper and less affected by common poisons such as halogens, phosphorus, arsenic, selenium, tellurium, and mercury. Platinum catalysts were probably replaced by vanadium sometime before 1930. Table 2.6 lists several of the early vanadium catalysts.

Sulfuric acid catalysts containing vanadium pentoxide are characterized by complicated recipes and manufacturing procedures.

Following the introduction of vanadium pentoxide by De Haen it was discovered empirically by Slama and Wolf that alkalis improved catalyst activity and these have been used in all the catalysts produced ever since. They were specified as important for stability by both BASF and the General Chemical Company. Vanadium pentoxide catalysts had been used for more than 20 years before Frazer and Kirkpatrick²² showed that the addition of alkali led to the for-

TABLE 2.6. Contact Process Catalysts Containing Vanadium Pentoxide.

Producer	Comment
1920: Slama-Wolf ¹⁸	Used by BASF from 1920 and in the United States by General Chemical Co. from 1927. Made by mixing ammonium metavanadate and potash with kieselguhr (50:56:316). Dried, granulated and calcined at 480°C in air and sulfur dioxide.
1932: Seldon Corporation ¹⁹	Ammonium metavanadate mixed with potash and potassium aluminate combined with a gel formed by sprinkling kieselguhr with potassium silicate (<i>zeolite</i>). Dried, pelleted (4–6 mm cylinders), calcined in air and SO ₂ to fuse V ₂ O ₅ . Used in tubes cooled with feed gas.
1933: Monsanto ²⁰	Silica gel with ammonium metavanadate and potassium hydroxide. The first of many catalysts made by Monsanto and used worldwide.
1932: General Chemical Co. ²¹	Developed by Joseph. A mixture of caustic soda, potash, and vanadium pentoxide added to wet mix of fine kieselguhr, potassium sulfate, and <i>tragacanth</i> gum. Dilute sulfuric acid added to neutralize alkalis. Mixture evaporated before granulation and extrusion. Calcined 600°C.

mation of an active liquid catalyst melt held in the pores of the support. This consisted of liquid potassium pyrosulfate with dissolved vanadium pentoxide. Catalyst activity is about the same for vanadium pentoxide contents in the range 2–10%, although higher levels give longer lives. Catalyst performance depends on the porosity and stability of the support, which controls and stabilizes the liquid melt to determine the life of the catalyst. Vanadium catalysts resist the effects of most poisons, although vanadium may be volatile in the presence of halogens.

The main cause of operating problems is related to the deposition of entrained dust on the relatively wide but thin layers of catalyst in the reactor. Dust, which is usually carried into a reactor with feed gases, can also form by catalyst disintegration and leads to an increase in pressure drop. Feed gas from the roasting of pyrite, anhydrite, or smelter gases is more likely to cause dust problems, but *pure* sulfur can also contain 0.5% ash, which should be reduced to less than 0.002% by filtering the liquid sulfur or using gas filters before the reactors.

If pressure drop through the catalyst beds (or *passes* as they are normally called) increases then the catalyst can be removed during a normal shut-down period and sieved before being examined and replaced for future use. Catalysts in the form of rings or other shapes have now been introduced in order to minimize pressure drop problems. A normal average life of a catalyst in sulfuric acid plants is usually more than 10 years.

2.1.3. Modern Sulfuric Acid Processes

Modern vanadium pentoxide catalysts have been developed on a more scientific basis than those discovered empirically during the 1920s. Following Slama and Wolf's use of alkali by to improve catalyst activity, Frazer and Kirkpatrick and then Kiyoura,²² realized that the catalyst was molten and filled the support pores during operation. Extensive investigation then led to an understanding of the ideal catalyst structure²³ and the reaction mechanism.

It is obvious now that the pores should be large enough to hold the melt as a thin film without being completely filled. Furthermore, since this is an equilibrium reaction that is adversely affected by higher temperatures, the solid catalyst should melt at a sufficiently low temperature to alleviate this equilibrium limitation. This was just about possible although the silica gel supports, prepared with an appropriate pore size and volume to increase low-temperature activity, tended to sinter at the operating temperature required in the first bed of a multi bed reactor.²⁴ It was often beneficial to use kieselguhr supports to increase operating stability, so some operators used a stable catalyst in the first bed with more active formulations in the remaining beds.

The catalyst melt contained vanadium compounds dissolved in a mixture of alkali pyrosulfates,²⁵ which melt at a lower temperature as the atomic number of the alkali metal increases. Potassium sulfate containing a small proportion of

sodium sulfate was usually chosen, because it was cheaper than the higher-atomic-weight alkali metals such as cesium. Satisfactory operation was therefore possible at a time when environmental controls were minimal and the price of sulfuric acid catalysts extremely low.

During the experimental work following the discovery that the sulfuric acid catalyst was actually a liquid held in the pores of the silica support, several observations were significant in understanding the way in which sulfur dioxide was oxidized:

- The vanadium pentoxide dissolved in melted alkali pyrosulfate.
- Activity and long life were associated with the reduction of pentavalent vanadium when alkali sulfates were used in catalyst production.
- Sulfate or pyrosulfate ions were not found in the melted catalyst and the degree of sulfation was normally in excess of that required to form pyrosulfate.

Fresh catalyst contains vanadium pentoxide, potassium/sodium sulfate, and silica in the ratios required for high activity and stability. During stabilization with sulfur dioxide it is likely that the vanadium pentoxide first dissolves to form pyrosulfate, which then reacts to give a mixture of polymeric ions. The melting point of the catalyst has been found to depend on the alkali metal/vanadium pentoxide ratio, up to about four, as well as the atomic weight of the alkali metal. The liquid state allows rapid formation of the polymeric ions, which are the active catalyst.²⁶ According to Boreskov, they correspond to specific compounds with a general composition $V_2O_5 \cdot nK_2O \cdot mSO_3$, where $n = 2, 3$, or 4 and m is approximately $2n$. Crystals with these compositions had been isolated from melted catalyst. At high sulfur dioxide concentration, melts also contain $K_2O \cdot V_2O_4 \cdot 3SO_3$. Polymers formed by direct absorption of sulfur trioxide or copolymerization of existing ions often have molecular weights that exceed 1000.

The redox mechanism of sulfur dioxide oxidation was first explained by Mars and Maesson,²⁷ who proposed that the oxidation to sulfur trioxide led to the reduction of pentavalent vanadium in the polymeric ions. The resulting tetravalent vanadium was then reoxidized by adsorption of molecular oxygen. On occasions when a catalyst is partially deactivated by process gas containing a high sulfur dioxide concentration and low oxygen concentration, it is possible to regenerate the catalyst simply by heating in air at about 450° – 500° C.

2.1.3.1. Catalyst Preparation

Catalyst is prepared by mixing a silica sol made from potassium silicate with vanadyl sulfate or ammonia metavanadate and precipitating with ammonia. The silica used can be either fresh or a solid such as kieselguhr. A sol mixed with

TABLE 2.7. Chemical Composition and Physical Properties of Modern Sulfuric Acid Catalyst.

Composition (wt%)	
V ₂ O ₅	6–8
K ₂ O	8–10
Na ₂ O	1–2
SO ₃	20–30
SiO ₂	55–65
Physical properties	
Bulk density	0.4–0.6 kg. liter ⁻¹
Attrition loss	< 10%
Dimensions	6-mm diameter extrusions
Surface area	2–5 m ² g ⁻¹
Pore volume	0.5–0.6 ml g ⁻¹

kieselguhr can react to give the *zeolite* support described by early catalyst producers. No filtering or washing is required and after drying the powder can be formed into shapes by the usual methods. Finished catalyst has the composition and physical properties shown in [Table 2.7](#).

A list of some US patents describing catalyst preparation between 1935 and 1981 was given by Donovan, in Leach: *Applied Industrial Catalysts*, Vol. 2, Ch. 7, Academic Press, 1983.

Before use the catalyst is generally pretreated in a stream of air containing a low concentration of sulfur dioxide. This sulfates the vanadium compounds and avoids an undesirable exothermic reaction when operation begins. However, final sulfation in the reactor does assist in start-up by increasing catalyst temperature faster than using heated feed gas and heat exchange between the beds.

2.1.3.2. Sulfuric Acid Plant Design

Conventional contact process sulfuric acid plants operate with four adiabatic catalyst beds, or passes. Heat of reaction is removed after each bed by heat exchange to generate steam or by quenching with cold air.

Up to the 1960s sulfur trioxide was recovered by a single absorption stage at the outlet of the fourth bed. A typical plant design limited the catalyst volume used in the first bed by the minimum inlet temperature of up to 420⁰C, at which the catalyst was active, and the approach to the equilibrium conversion of sulfur dioxide to sulfur trioxide at about 600⁰C. By coincidence, the maximum reasonable operating temperature to avoid deactivation in the first bed of catalyst was about 600⁰–650⁰C. Catalyst volumes in the final three beds were also designed to maximize conversion within the same limits of inlet temperature and equilibrium. This made it difficult to achieve more than 98.5% conversion consistently in four beds, even with large volumes of catalyst, as shown in [Table 2.8B](#).

Better conversion was achieved when double absorption plants were introduced on a large scale during the 1960s.²⁸ As shown in Table 2.8B, the first three beds were operated in the same way as in the conventional plants but when gases left the converter to be cooled they also passed through an intermediate sulfur trioxide absorber. On re-entering to the final bed, a better equilibrium conversion, in some cases up to 99.8%, was achieved as a result of the lower sulfur trioxide content. Double absorption is now widely used despite the extra cost of equipment. The process was even more useful as all of the new plants being built in the United States needed to use double absorption or stack scrubbing systems to comply with strict environmental regulations from 1966 introduced.

2.1.3.3. Cesium-Promoted Catalysts

The use of catalysts in which some of the potassium is replaced by cesium provided the more active catalyst anticipated from earlier development work.²⁹ A striking temperature as low as 320°C was reported in a full-scale four-bed plant, and operation was possible at a stable bed-1 inlet temperature of 370°C.

TABLE 2.8. Operation of Single Absorption and Double Absorption Sulfur-Burning Sulfuric Acid Plants.

	Bed 1	Bed 2	Bed 3	Bed 4
A: Four pass <i>single-absorption</i> converter.				
Production 250 tonnes.day ⁻¹ .				
Heat exchange cooling between beds 1–2, 2–3 and 3–4 with sulfur trioxide absorption after bed 4.				
Feed gas 9% sulfur dioxide and 10% oxygen. Catalyst loading 190 liters of catalyst per tonne of acid per day.				
Catalyst volume (m ³)	10	11	22	23
Inlet temperature (°C)	420	445	435	428
Outlet temperature (°C)	600	500	450	430
% Conversion SO ₂ to SO ₃	65–70	88–90	96	98.5
				(SO ₃ Abs.)
B: 1000 tonnes.day ⁻¹ <i>double-absorption</i> converter.				
Heat exchange cooling between beds 1–2 and 2–3 with sulfur trioxide absorption after bed 3 and bed 4.				
Feed gas 10.5% sulfur dioxide and 10.5% oxygen.				
Catalyst loading 165 liters of catalyst per tonne of acid per day.				
Catalyst volume (m ³)	30	42	42	50
Inlet temperature (°C)	414	440	440	425
Outlet temperature (°C)	613	500	495	440
% conversion SO ₂ to SO ₃	65–70	85–88	96	99.8
			(SO ₃ Abs.)	(SO ₃ Abs.)

Operation of the cesium catalyst at a much lower inlet temperature than the potassium-promoted catalyst achieved a sulfur dioxide conversion in the range 99.2–99.6%. This was comparable to a double-absorption plant but with a lower capital cost apart from increased heat exchange capacity and a slightly more expensive catalyst. It allows producers to use existing four-bed single-absorption units and meet environmental demands without the capital expense of a new plant.

2.1.3.4. *Sulfuric Acid Plant Operation*

Sulfuric acid plants are designed with optimized catalyst volumes and bed inlet temperatures to give a reasonable approach to equilibrium in each bed to achieve the maximum possible conversion of sulfur dioxide to sulfur trioxide. As shown by the examples in Table 2.8, this results in a significantly smaller volume in bed 1 than the remaining beds. The total catalyst volume used normally corresponds to a *loading* of 180–220 liters of catalyst per tonne of sulfuric acid produced per day although many plants use more, depending on conditions and the source of the sulfur dioxide. Lower volumes of catalyst are normally used in double-absorption units.

2.1.3.5. *Improved Catalyst Shapes*

The main problem in operating sulfuric acid plants using an extruded catalyst is usually increasing pressure drop through the reactor, which can result from dust or other impurities in process gas, which generally deposit at the top of the first bed. The catalyst must, therefore, be removed at intervals, screened to remove the accumulated dust, and replaced. On average the first bed has to be sieved at intervals of 1 to 3 years and the remaining beds at longer intervals. Catalyst life usually exceeds 10 years.

Modern catalysts are now supplied in a variety of shapes, all with the same composition. These allow longer continuous operation, at a lower pressure drop, by distributing the dust to prevent the formation of a crust. Shapes are available as rings of various diameters, often with fluted surfaces (ribs) and simple fluted extrudates.³⁰ Use of any shaped catalyst can also offer more than 30% reduction in pressure drop and, often, increased activity to allow more operating flexibility. The best combination of shapes to be used in particular plants is recommended by catalyst suppliers.

2.2. THE DEACON PROCESS

Scheele's discovery of chlorine in 1774 was soon followed by its use to bleach cotton and linen. The Deacon process, which made use of one of the first indus-

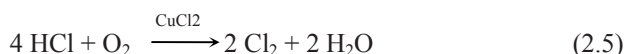
trial catalysts to be especially designed rather than discovered empirically,³¹ was used to produce chlorine from about 1870, until it was superseded by the electrolysis of brine.

2.2.1. The Process

In the Deacon Process, chlorine was produced from hydrochloric acid, the low-value by-product of the Le Blanc process, by catalytic oxidation with air. Deacon used a copper chloride catalyst that could combine with oxygen and hydrochloric acid and form chlorine through an oxidation/reduction cycle.

2.2.2. Operation

The overall reaction can be summarized as follows:



Hurter, in 1883, suggested that the reaction mechanism involved three stages:³²

- Thermal decomposition of cupric chloride by heating at 500°C in a stream of 40% hydrochloric acid and air:



- Oxidation of the cuprous chloride by air:



- Hydrolysis of the cupric oxychloride with hydrochloric acid:



The overall reaction is exothermic and controlled by equilibrium.

It was found that despite lower equilibrium yields, the optimum reaction rate was achieved in the temperature range 400⁰–450⁰C, giving only about 70% conversion of hydrochloric acid to chlorine.³³ Water formed during the reaction had to be removed from the gas leaving the first reactor and a second reactor included to increase conversion up to about 85%.

Operation at high temperatures led to catalyst problems because copper chlorides are volatile and chlorine corroded the equipment. It was reported in 1921 that the cost of copper lost per ton of *bleach* produced was one shilling!³⁴

At the same time, the low melting point of copper chloride meant that the catalyst operated as a liquid in the pores of the *baked clay* support. The process could not be used successfully on a large scale until the sulfur and arsenic impurities in the hydrochloric acid gas were removed by scrubbing with hot sulfuric acid, which is an early example of gas purification to remove catalyst poisons.³⁵

2.2.3. Catalyst Preparation

Deacon catalyst was prepared by impregnating a suitable porous and heat-resistant solid—firebrick and pumice could be used—with an aqueous solution of copper chloride. The final catalyst contained about 10 wt% of copper chloride.

2.2.4. Development

Although the Deacon process was only used for about 40 years, it is still of interest for two reasons: as an example of a catalyst selected by logical rather than empirical procedures and as an illustration of the need to remove poisons from process gases. Derivatives of the Deacon catalyst are still used in the production of ethylene dichloride, by the oxychlorination of ethylene.

2.3. CLAUS SULFUR RECOVERY PROCESS

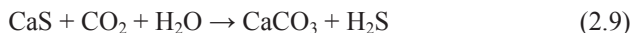
Sulfur recovery from sour natural gas or refinery off-gas streams is not only essential to avoid air pollution but also has become the main source of elemental sulphur, the key raw material for sulfuric acid production.

Claus sulfur recovery plants were reintroduced in about 1950, when a shortage of Frasch sulfur was anticipated. Subsequently, capacity was increased further with the need to process crude oils with high sulfur content. By the 1990s some two-thirds of US refineries, representing almost 90% of the crude oil treated, had acid gas treatment facilities to recover more than 60% of the total sulfur in the crude. This proportion will increase even further to meet new Environmental Protection Agency sulfur emission regulations, and virtually all refinery projects include new sulfur units or plans to expand existing facilities. The additional sulfur produced will result in the closure of Frasch sulfur capacity.

World production of Claus sulfur was about 22 million tonnes during 1998 (production capacity 45 million tonnes)—an important contribution from such a relatively uncomplicated catalytic process.

2.3.1. The Claus Process

The Claus process to recover and recycle sulfur in the Le Blanc process, based on the procedure suggested by C. F. Claus in 1883,³⁶ was introduced in 1887 by A. M. Chance. *Alkali waste* containing calcium sulfide was suspended in water, and hydrogen sulfide was generated by pumping carbon dioxide through the slurry:



Sulfur could then be recovered by passing the hydrogen sulfide, in a stream of air, through a kiln containing an iron catalyst.

The modern two-step process converts hydrogen sulfide mixed with a stoichiometric volume of air to sulfur. In theory, one-third of the hydrogen sulfide is oxidized to sulfur dioxide in a carefully designed furnace, while the remaining hydrogen sulfide reacts with the sulfur dioxide to produce sulfur in two or more reactors containing a suitable catalyst.



In practice, up to 70% of the reaction can take place in the furnace before the gas is passed directly to the reactors.³⁷ During the 1950s Claus plants operated at 90–95% conversion and tail gas containing the residual sulfur compounds was passed into the refinery fuel gas system.³⁸

Complete conversion of hydrogen sulfide cannot be achieved in Claus plants because the reaction is limited by equilibrium, and unavoidable side reactions in the furnace lead to the formation of carbon disulfide and carbon oxysulfide, which are difficult to remove. Recent environmental legislation has required that the overall conversion of hydrogen sulfide should now exceed 99%. To achieve this requirement, new processes have been developed which can be added on to the tail of existing Claus plants, to meet the new target.

2.3.2. Claus Plant Operation

Sulphur often occurs in crude petroleum as a complex mixture of organo-sulphur compounds, such as sulfides, thiophenes and benzthiophenes. These are fairly intractable compounds and need to be converted to hydrogen sulfide prior to separation using the Claus Process. This is usually achieved by hydrogenolysis of the sulphur derivative over cobalt/molybdenum or nickel molybdenum catalysts. Hydrogen sulfide is then separated from hydrocarbons by absorption in diethanolamine solution, but is usually contaminated with carbon dioxide.

Acid gas from refinery streams contains 70–90% hydrogen sulfide, whereas acid gas recovered from natural gas is often more diluted. The hydrogen sulfide content of feed gas to the furnace has a significant effect on both plant and catalyst operation.

With hydrogen sulfide concentrations greater than 60% the flame temperature is stable and all the acid gas and air pass directly to the furnace. With concentrations less than 60% it may be necessary to preheat the gas mixture or even to split the stream so that 37% of the hydrogen sulfide burns in the furnace and the remainder goes directly to the first catalytic reactor.

During combustion, some 60–70% of the hydrogen sulfide is converted directly to sulfur. Flame temperature depends on the hydrogen sulfide content of the feed gas and can reach almost 1300°C with more than 90% hydrogen sulfide.

Careful furnace and burner design is essential to maximize sulfur formation and to ensure complete combustion of hydrocarbon impurities that would otherwise damage the catalyst. Residual oxygen in gas from the furnace can also poison the catalyst. A significant excess of air must be avoided. At the temperature of the flame, nitrogen and oxygen will combine to form a small amount of nitric oxide. This will catalyse the oxidation of sulphur dioxide to the trioxide, which will form sulfates on the catalyst and lead to deactivation. Side reactions affecting the process also take place in the furnace. For example:

- Carbon disulfide forms by reaction of sulfur with hydrocarbons:



Both reactions are rapid and the carbon disulfide concentration at equilibrium reaches a maximum of almost 20 ppm at 950°C. Carbon disulfide formation becomes negligible as the furnace temperature approaches 1300°C.

- Hydrogen sulfide cracks to form hydrogen, which produces carbon monoxide by the reverse water gas shift reaction with the carbon dioxide. Carbon oxysulfide is formed by reaction of the carbon monoxide with sulphur:



- Carbon oxysulfide and carbon disulfide also form by reaction of hydrogen sulfide with carbon dioxide:



The concentration of carbon oxysulfide reaches a maximum of 10–15 ppm at about 1100°C but then declines as the flame temperature reaches about 1300°C. Because the flame temperature is proportional to the hydrogen sulfide content of the acid gas, both carbon disulfide and carbon oxysulfide concentrations are more significant when treating gases containing lower concentrations of hydrogen sulfide, particularly in the range 50–75%.

A typical modern Claus sulphur recovery plant uses several reactors to achieve the equilibrium conversion of hydrogen sulfide. The complex gas mixture from the furnace is cooled to condense sulfur and then reheated before it enters the first catalyst reactor. There are generally three catalytic reactors in series containing a catalyst in series, with coolers at each reactor outlet to condense sulfur as it forms. Typical operating conditions are shown in Table 2.9. Inlet and outlet temperatures in each reactor are controlled at levels high enough to prevent condensation of sulfur on the catalyst.

Owing to the equilibrium limitation, it is not possible to achieve 100% conversion simply by adding more reactors and catalyst to the plant. Overall con-

TABLE 2.9. Operation of Claus Sulfur Recovery Plant.

Capacity	35 tonnes day ⁻¹ sulfur		
Flow rate	1100–1400 Nm ³ h ⁻¹ acid gas H ₂ S content 92% in feed; 7.5% entering reactor 1		
Fuel gas composition	H ₂ S: ~ 0.35% SO ₂ : ~0.16% COS/CS ₂ : ~ 20 ppm		
	Reactor 1	Reactor 2	Reactor 3
Catalyst volume (m ³)	4.6	4.6	4.6
Inlet temperature (°C)	240	215	200
Outlet temperature (°C)	320	235	204
H ₂ S in outlet gas (%)	2	1	0.3
Overall conversion %			98.0–98.4
Equilibrium conversion (%)			98.8

Note: The Reactor 1 conditions are a compromise between the need for a temperature as high as 350°C for a maximum conversion of COS/CS₂ and a lower temperature to achieve better approach to equilibrium for H₂S/SO₂. The reaction rate in Reactor 2 is low owing to the lower H₂S/SO₂ concentration. Only a small amount of remaining H₂S/SO₂ is converted in Reactor 3.

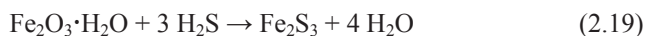
version increases gradually within the following ranges as the number of reactors is increased: two reactors 94–96%; three reactors 96–98%; four reactors 97–98.5%.

A number of tail gas treatments have been developed to increase sulfur recovery efficiency to more than 99%.³⁷

- *Cold bed absorption* involves adding two additional Claus reactors in parallel, operating below the dew point of sulphur at 120⁰–140⁰C. The equilibrium conversion to sulphur is favoured at the lower temperature, but sulphur condenses in the pores of the catalyst, leading to temporary deactivation. Thus, when one bed is saturated, flow is switched to the parallel bed while the first is regenerated at 300⁰C. Up to 99% conversion can be achieved.
- All residual sulfur compounds in tail gas are hydrogenated in a bed of cobalt/molybdate/alumina catalyst, operated at 300⁰C, after the addition of a suitable volume of hydrogen to the Claus reactor tail gas. The hydrogen sulfide formed can then be recycled to the Claus process furnace. This treatment improves conversion up to 99.9%.
- Alternatively, after hydrogenation of sulfur compounds, the residual hydrogen sulfide can be selectively oxidized to sulfur. A suitable catalyst is 5–6% ferric oxide supported on low-surface-area, high-pore-volume silica. During reaction the iron oxide is converted to ferrous sulfate. Conversions of up to 99.9% are possible, but if the hydrogenation step is omitted, only the residual hydrogen sulfide is oxidized and overall sulphur recovery depends on the volume of residual carbon oxysulfide and carbon disulfide in tail gas.

2.3.3. Claus Process Catalysts

The Claus plants built by A. M. Chance in 1887 used firebrick impregnated with an iron salt as the catalyst. Claus' original idea probably originated from the use in the United Kingdom of bog iron ore, a form of hydrated iron oxide, to remove hydrogen sulfide from town gas. During use, the bog iron ore was converted to a mixture of iron sulfides and free sulfur. Additional free sulfur could then be formed by exposing a partly spent oxide absorbent to air in a series of regenerations. After several *revivifications*, spent oxide contained up to 50 wt% sulfur, which blocked gas flow through the bed. The mass could then be used as a source of sulfur in sulfuric acid production:



Overall this corresponded to the Claus reaction:



Claus felt that the cyclic process could be simplified if the hydrogen sulfide were converted to sulfur by an iron catalyst in a kiln. It was later found that dried Weldon process mud or bauxite would operate as a catalyst at a lower temperature than ferric oxide. This not only extended the life of the kiln but also increased sulfur yield.³⁹ Problems with blocked beds were overcome as technology evolved and proper reactors containing solid catalyst particles were developed. Thus, the modern Claus sulfur recovery process originated from the statutory obligation to remove sulfur from town gas in Victorian gas works.

Different catalysts were used when the Claus process was reintroduced in refineries in 1940–1950. Bauxite, for example, which was already available in refineries to hydrodesulfurize straight-run naphthas, is a variable mixture of gibbsite and boehmite with iron and silica impurities. When calcined to activate the alumina, it is converted to a catalyst with about 1–12% ferric oxide supported on γ -alumina. Bauxite catalysts were successfully used in the Claus process, giving a sulfur conversion greater than 90%.³⁸

Eventually, sulfur recovery was introduced on a larger scale, particularly in Canada, and higher conversion was required to limit sulfur emission.⁴⁰ Pure activated alumina catalysts were then introduced in the form of strong spheres that improved gas flow and reduced pressure drop. Alumina catalysts are still the most widely used and give excellent results under normal conditions. However, more stable and active catalysts are needed in some plants,⁴¹ where they have been shown to operate more successfully in the presence of residual oxygen and to be particularly active for the conversion of carbon oxysulfide and carbon disulfide.⁴²

The formation of carbon oxysulfide and carbon disulfide in the furnace leads to problems when high overall conversion is required. Alumina catalysts are not sufficiently active to convert carbon disulfide and oxysulfide in the first *reactor* unless a high temperature is reached at the bottom of the bed. When this is not possible, the bottom third of the bed can be loaded with either an iron-promoted alumina or a newer titania catalyst. Cobalt/molybdate/alumina catalysts were also tested in early attempts to hydrogenate the impurities, but it was found that conditions in the first reactor favored sulfur dioxide hydrogenation instead. All of the catalyst types used in Claus sulfur recovery plants are described in [Tables 2.10](#) and [2.11](#).

2.3.4. Catalyst Operation

Typical Claus plant operating conditions are shown in [Table 2.9](#). Temperature in the first reactor is a compromise between the need to remove any carbon oxy-

TABLE 2.10. Catalysts Used for Claus Sulfur Recovery.

	Standard alumina	Oxygen-sulfation guard
Al ₂ O ₃ (wt%)	93–95	~91
Na ₂ O (wt%)	0.3–0.35	Traces
SiO ₂ (wt%)	0.02–0.03	0.4
Fe ₂ O ₃ (wt%)	0.02	8
Loss on ignition (wt%)	4.5–6.5	Loss free basis
Bulk density (kg liter ⁻¹)	0.6–0.7	Less than 1
Surface area (m ² g ⁻¹)	340–380	225–275
Pore volume (ml g ⁻¹)	0.5–0.6	0.5
X-ray diffraction	γ-Al ₂ O ₃	γ-Al ₂ O ₃
	Standard titania	
TiO ₂ (wt%)	85–95	
NiO (wt%)	0–6	
Bulk density (kg liter ⁻¹)	0.9	
Surface area (m ² g ⁻¹)	100–140	
Pore volume (ml g ⁻¹)	0.3	

sulfide and carbon disulfide that may be present and achieve maximum hydrogen sulfide conversion. High temperatures favor the removal of carbon sulfides and lower temperatures favor sulfur formation.

There are several typical catalyst operating problems. The most common is the deposition of elemental sulfur in the catalyst pores at low temperature. Alumina catalysts are soon saturated with sulfur if the operating temperature is less than 270°C. The *macro* pore volume of catalysts should, therefore, be high, and have the smallest particle size possible, consistent with a reasonable pressure drop at maximum space velocity. This increases the rate of diffusion in and around the catalyst particles. Operating temperature in the first reactor should also be high enough to increase the rate of reaction and avoid sulfur deposition.

TABLE 2.11. Catalysts Used for Claus Plant Tail Gas Treatment.

Tail gas hydrogenation		Tail gas incineration	
CoO (wt%)	3.0–4.0	Fe ₂ O ₃ (wt%)	5–6
MoO ₃ (wt%)	12.0–14.0	SiO ₂ (wt%)	Balance
SiO ₂ (wt%)	< 1		
SO ₄ (wt%)	< 2		
Al ₂ O ₃ (wt%)	Balance		
Loss on ignition (%)	1.5		
Surface area	250 m ² g	Surface area	40–45 m ² g ⁻¹
Pore volume	0.6 ml g ⁻¹	Pore volume	0.8 ml g ⁻¹
Form	Extrusions 3 × 6 mm	Form	Granules
Bulk density	0.6 kg liter ⁻¹	Bulk density	< 1.0 kg liter ⁻¹

Coke is deposited in the first reactor, particularly when the flame temperature is low, if hydrocarbons are not completely oxidized in the furnace. This can be avoided with proper furnace design. Hydrothermal sintering of the catalyst is

During normal operation the first reactor catalyst will not normally contain more than about 5–10 wt% of sulfur.

possible during start-up or shut-down if the temperature exceeds 500°C in the presence of water, and this will reduce activity. If sulfur trioxide forms in the furnace from oxidation of sulfur dioxide, it will react with the catalyst to form aluminum sulfate, which also reduces catalyst activity.

The catalyst can also be sulfated at lower temperature by a complex series of reactions with sulfur dioxide, and the catalyst can contain up to 3% of combined sulfur under normal operating conditions. It has been suggested that sulfur dioxide is strongly chemisorbed by surface hydroxyl groups to give a sulfite intermediate. This reacts with sulfur vapor to give a thiosulfate intermediate that reacts, in turn, with a neighboring hydroxyl to form sulfate. This does not necessarily deactivate the catalyst.

The presence of even a few hundred parts per million of oxygen, however, can cause immediate catalyst deactivation. Sulfate is produced on the active sites,⁴² by interaction with sulfur dioxide resulting in an affect similar to that of sulfur trioxide. The effect of sulfation is more severe in the second or third beds, which operate at a lower temperature.

Oxygen *poisoning* can be reduced to a certain extent by placing a layer of alumina containing iron or nickel oxide above the catalyst in the first reactor. This converted oxygen to water but at high oxygen levels ferrous sulfate was formed. A further benefit of these guard catalysts was that a higher proportion of any carbon disulfide and carbon oxysulfide in the gas could be converted.

Sulfation was more effectively controlled by the use of titania catalysts, which were not affected by oxygen concentrations of several thousand parts per million. This was partly because the thiosulfate intermediate on titania is unstable above 100°C, and because surface sulfates on titania are more easily reduced with hydrogen sulfide.⁴³ This means that a titania surface is free from sulfate, whereas sulfate blocks an alumina surface. Further advantages of using titania are that it can operate at a higher space velocity than alumina and convert a greater proportion of any carbon disulfide and carbon oxysulfide present.

2.4. AMMONIA SYNTHESIS

Ammonia, or alkaline air, was isolated by Priestley in 1724, who found that it could be decomposed by electric sparks to give an increased volume of an inflammable gas. Later, it was shown that the decomposition product was a mixture of hydrogen and nitrogen and that the reaction was reversible because 100% decomposition was not achieved at the elevated temperature required.⁴⁴

Ammonia could be formed when a mixture of nitrogen and hydrogen was exposed to electric sparks. Ramsay and Young also found that traces of ammonia formed when hydrogen and nitrogen were passed over a heated plati-

num/titania catalyst on a porous support. Hlavati and the Christiania Minekompanie in Norway both produced some ammonia using a supported titanium catalyst, with or without platinum, and disclosed the use of supported catalysts containing the oxides of antimony and bismuth, and alkali or alkaline earths containing small amounts of platinum.⁴⁵ Dufresne (alias Charles Tellier) demonstrated the production of ammonia in a cyclic process by heating spongy *titaniferous* iron alternately with nitrogen and hydrogen and suggested operation at 10 atm pressure.⁴⁶ A similar cyclic process, devised by De Motay, reacted red-hot titanium nitrides alternately with hydrogen and nitrogen.⁴⁷

Le Chatelier began to work on the high-pressure formation of ammonia in 1901, but discontinued his experiments following a serious explosion.⁴⁸ By 1900 it was thought that it should be possible to synthesize ammonia from its elements, but it was not yet known whether a suitable industrial process using catalysts could be developed.

2.4.1. Sir William Crookes

Both Liebig, in the book he published in 1840,⁴⁹ and Lawes, in his work at Rothamsted in 1845,⁴⁹ recognised that nitrogenous substances such as ammonia or nitrate were essential for healthy plant growth. Lawes, in particular, stressed that additional nitrogen in the form of mineral fertilisers would be required. The *nitrogen* problem had become widely recognised as a serious issue towards the end of the nineteenth century, since by 1890, it was clear that the available quantities of sodium nitrate from Chile, Chile saltpeter, would not be sufficient to meet the anticipated future demand. It was equally clear that other sources of supply would soon be required.

It is therefore not surprising that Sir William Crookes chose this subject for his presidential address to the British Association for the Advancement of Science in Bristol in 1898.⁵⁰ He had already demonstrated his *flame of burning nitrogen* in 1892 by combining the nitrogen and oxygen in air to form nitrogen oxides at high temperatures. He appealed to chemists for other, more economic and practicable methods to fix atmospheric nitrogen to supply the fertilizers needed to produce feed for a growing world population.

The direct production of nitric oxide from air at high temperatures in an electric arc by the Birkeland and Eyde or Cyanamide processes was feasible, but could only be used in locations with abundant and cheap hydroelectric power. This clearly was not the long term answer, and a series of significant advances initiated by Ostwald at Leipzig, following discussions with William Pfeffer, soon followed. Ostwald, himself, worked on the catalytic synthesis of ammonia, and its oxidation to nitric acid.

TABLE 2.12. Rates of Growth in World Population and Ammonia Production.

	World population (billions)	Synthetic ammonia capacity (million tonnes year ⁻¹)
1804	1	—
1927	2	~ 1
1960	3	1.6
1974	4	80
1987	5	145
1999	6	175

Note: Only approximately 70–80% of ammonia used as fertilizer.

Since the introduction of the more economic Haber process in 1913, it has been interesting to compare the worldwide increase of ammonia production with the increase in world population. Details are shown in [Figure 2.4](#) and in Table 2.12.

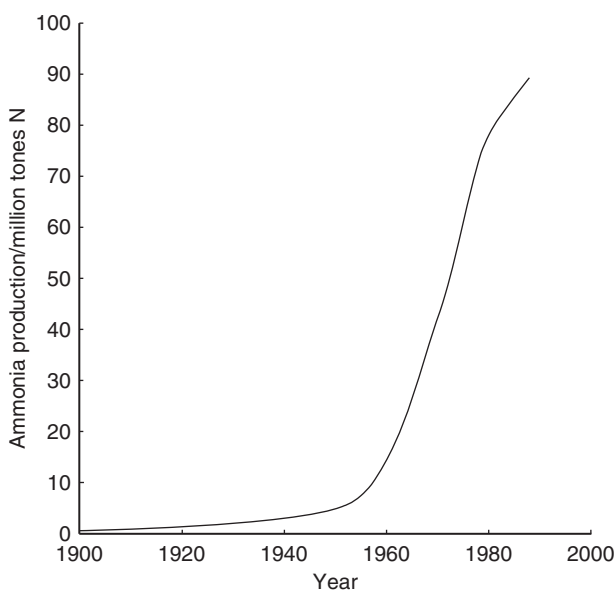


Figure 2.4. The growth of world ammonia production. Reprinted from *Catalyst Handbook*, 2nd ed., Ed. by M. V. Twigg, Wolfe Publishing, LTD., London, England, 1989, by kind permission of M. Twigg.

2.4.2. Development of the Ammonia Synthesis Process

Despite all the preliminary investigations, the production of ammonia using catalysts on an industrial scale was not possible until 1913 at Oppau, because it was not until then that the reaction was properly understood, a practical catalyst had been developed and suitable equipment available. The ammonia process resulted from the theoretical and experimental work of Ostwald, Nernst, and, particularly, Haber, who, with a number of associates, began a systematic investigation of the reaction over a wide range of temperatures and pressures to determine the equilibrium constants. Haber also measured the activity of a number of different catalysts.⁵¹

Ammonia synthesis has been described as the first example where the knowledge of thermodynamics led research to the most practicable industrial process.⁵² We now know from the thermodynamics of the reaction that the formation of ammonia is favoured by low temperatures and high pressures. It was thus possible to devise the conditions required for economic operation at low equilibrium conversion and then to develop a catalyst and the high-pressure equipment that was not available at the time.

Ostwald produced ammonia in laboratory experiments at atmospheric pressure using an iron wire catalyst and claimed that he obtained a relatively high yield.⁵³ He had, however, nitrated the iron during its pretreatment with ammonia and withdrew his patent application. From about 1904, Haber and a group of co-workers, funded by the Margulies brothers from Vienna, began to investigate the equilibrium conversions in the ammonia synthesis reaction using an iron catalyst at the Technical University of Karlsruhe. Although the conversion at atmospheric pressure was too low for an industrial process, it was known that conversion could be increased at higher pressure. Nernst, who used theoretical calculations to query some of Haber's early experimental results, experimented with Jost at pressures up to 75 atm.⁵⁴ He used catalysts including iron and manganese, but felt that the process would still not be commercially attractive because the conversion to ammonia was less than 1%. Haber, however, was more optimistic due to his experience with osmium and uranium carbide catalysts. He realised that despite the low equilibrium constant, the process could work at high pressures, and he achieved up to 6% ammonia in the gas stream in experiments at 200 bar. This suggested that a process could be feasible provided that the synthesis gas was recycled continuously in a loop and that the product ammonia was removed from the synthesis gas after each cycle through the catalyst. The patents, which were issued in 1908 and 1909, had many of the features of the modern process, including the recirculation of synthesis gas and the use of heat exchange between the gases leaving and entering the reactor.⁵⁵

2.4.3. Commercial Application of Ammonia Synthesis Catalysts

The commercial process was developed after 1910 when Haber began his collaboration with BASF. Carl Bosch, who was in charge of the development, began to look for an efficient, cheaper catalyst. Osmium could be operated successfully at 550⁰–600⁰C and 175–200 atm giving an ammonia conversion up to 6%. It was, however, expensive, poisonous, unstable in air, and, more important, almost unobtainable. These were not the qualities required for an industrial catalyst. Furthermore, the iron reactor then available was found to suffer from hydrogen embrittlement under operating conditions and could explode. Uranium, the other active catalyst favored by Haber, was also expensive and, unfortunately, was rapidly poisoned by traces of water and oxygen in the synthesis gas.

One of the first innovations made by Bosch was the introduction of a comprehensive program of catalyst testing using thirty specially designed laboratory units. These are described as using only 2g of catalyst—a tremendous achievement in those days. Alvin Mittasch was in charge of the testing program.⁵⁶

It was thought that iron would be the best catalyst, despite its relatively poor activity in earlier investigations. In one of the fortunate coincidences that are typical of industrial developments, a particular kind of magnetite from Sweden that Mittasch found in his laboratory was used in the tests. It gave excellent results and, even now, is used for industrial catalyst production. It will continue to be so until a better catalyst is discovered or the particular deposit in Sweden is exhausted.⁵⁶

An intensive investigation of catalyst promoters was then undertaken, and by 1910 an alumina-promoted iron catalyst was produced that had the same activity as the previously favored osmium and uranium types. This was followed in 1911 by an alumina/potash-promoted iron catalyst that was more stable.⁵⁷ Finally, a few years later, calcium oxide was discovered to be a third promoter.

During tests full-scale operating procedures were worked out and catalyst poisons, including sulfur compounds, chlorides, phosphates, arsenic, and relatively common oxygen compounds such as water and carbon monoxide, were identified. By 1922, when several full-scale ammonia plants were operating, a total of about 20,000 tests had been completed!⁵⁸

Despite the novelty of the new process, a small pilot plant was rapidly constructed in 1909 so that metallurgical and operating problems could be investigated. The first full-scale, 30-tons.day⁻¹, ammonia plant was then built at Oppau in 1912 and was operating by 1913. By 1916 production had been increased to 250 tonnes.day⁻¹ and a further plant was operating at Leuna with a capacity of 36,000 tonnes.year⁻¹, which had increased to 240,000 tonnes.year⁻¹ by 1918. An early ammonia synthesis converter is shown in [Figure 2.5](#).

2.4.4. The Haber–Bosch Synthesis Reactor

The development of a high-pressure synthesis reactor was difficult because the carbon steel available for fabricating the shell quickly burst as a result of decarbonization (hydrogen embrittlement) as hydrogen diffused through the steel and removed carbon to form methane. Problems with decarbonization were overcome by the use of a soft iron lining in the carbon steel shell. The outer shell was also drilled so that any hydrogen passing through the liner could escape.

The ammonia synthesis reaction is exothermic, but as a result of the low conversion heat loss from the small early reactor exceeded the heat of reaction.

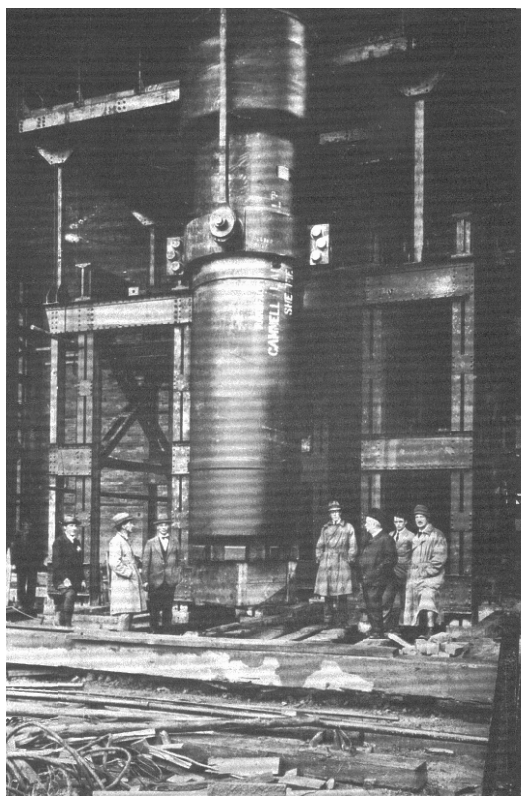


Figure 2.5. An early ammonia synthesis converter. Reprinted with permission from the Imperial Chemical Industries PLC.

Therefore, additional heat had to be supplied to the catalyst bed and this was done in a number of ways:

- In early units the reactor was heated externally, by gas burners, although this had the disadvantage of further weakening the shell.
- A special air burner at the top of the catalyst bed could increase the gas temperature and was used until 1922, despite the poisoning effect of water on the catalyst.
- Larger reactors only used a gas heater at start-up with reverse gas flow to avoid catalyst poisoning.
- From 1920 better steel alloys that resisted embrittlement became available.

By 1925, new reactors had been developed by using improved chromium/vanadium steel alloys and internal heat exchangers. The outer shell was protected from overheating by passing the cold synthesis gas down the annular space between the shell and the catalyst basket as it entered the vessel. A typical plant was operated with the catalyst temperature in the range $500^{\circ}\text{--}650^{\circ}\text{C}$ and at a higher pressure, up to 300–350 atm, which allowed higher conversion and easier ammonia removal by water scrubbing. While these conditions should give a theoretical conversion in the range 8–11%, the actual conversion was only 7–9%.

A reactor, producing $20\text{ tons}\cdot\text{day}^{-1}$ of ammonia weighed about 70 tonnes, was 12 m long, and held a basket of 80 cm internal diameter. It took about 3 days to change a deactivated catalyst and restart operation. In those days, in order to increase production, typical ammonia plants operated with several small reactors rather than a single large one.

2.4.5. Conclusion

The production of ammonia during the early 1900s stimulated the increasing use of industrial catalysts. Development of the synthesis catalyst set a pattern for all other catalysts subsequently used in chemical and refining processes.

Theoretical and experimental effort had shown that the process was feasible. This was followed by the development of practical equipment and full-scale operation. A relatively cheap and reliable catalyst was thoroughly tested and produced economically in what were then large volumes. Finally, both the process and catalyst were gradually improved as the scale of operation expanded.

The pioneering work of Haber, Bosch, and Mittasch led to a process which has survived in more or less the same form as it is used today. Their achievement led to the introduction of chemical engineering, high pressure technology and consolidated the ideas of unit processes. New materials were developed for use with hydrogen at high pressures.

From 1940, when synthesis gas first was produced from natural gas rather than coal, single-stream ammonia plants were developed and the process was subject to an ongoing series of improvements. Improved catalysts based on the same natural magnetite were made as the internal structure of magnetite and the function of the promoters could be investigated with modern analytical procedures. Catalyst life with purer synthesis gas can now exceed 15 years.

Although better reactor designs were introduced, the use of almost 200 tonnes of catalyst in a single vessel led to problems with packing, activation, and pressure drop. Furthermore, spent catalyst is very pyrophoric and large volumes of spent catalyst are difficult to deal with. Catalyst reduction could last for almost a week, so the first modern catalyst innovation was prereduction and stabilisation of the catalyst before it was loaded into the converter. This made plant start-up more efficient. Attempts to provide a more uniform, pelleted catalyst were not successful and crushed granules are still used.

Since the early 1980s there have been several catalyst developments, including the use of cobalt oxide with magnetite to increase activity. The most significant, however, is the successful use of a ruthenium catalyst supported on a special carbon and promoted with cesium and barium. Although still expensive, cost and availability should not restrict the use of ruthenium in the way that osmium was excluded by Bosch, provided that the metal is recycled.

2.5. COAL HYDROGENATION

2.5.1. The Bergius Process

Bergius began his experiments on the high-pressure hydrogenation of coal using small autoclave reactors as early as 1911. His aim was to increase the yield of liquid products from coal carbonization and, like Ipatieff, he worked at the time that BASF was developing its new high-pressure ammonia process. By 1921 he had built a small, continuous, semitechnical unit at Reinau/Mannheim with horizontal stirred reactors and was obtaining encouraging results. These units operated until 1927.⁵⁹

In the plant, a slurry of coal and heavy oil was hydrogenated using about 4 wt% luxmasse as the catalyst. Luxmasse, which is rich in iron with some titania, is the residue from bauxite after alumina extraction. Hydrogenation conditions were in the range 450–480°C and 100–150 atm of hydrogen, yielding 40–50 wt% of liquid hydrocarbons, depending on the type of feed used. Residual solids and heavy oils could be recycled.

Bergius certainly recognised the relationship between his work and the catalytic hydrogenation of heavy crude oil fractions, relative to the newly introduced thermal cracking.⁶⁰ Thermal cracking of crude oil fractions was first used in refineries around 1911–1912 to increase the yield of gasoline. By about 1924 the

thermal cracking process was an essential part of refinery operation, particularly in the United States, where more than 25 million motor vehicles were registered. The attraction of a more efficient catalytic process was obvious and led big oil companies such as Royal Dutch Shell, who apparently funded some of Bergius' work, and Standard Oil, who later worked with I. G. Farben, to take a keen interest at a time when crude oil reserves were thought to be declining.

2.5.2. Commercial Development by I. G. Farben

In 1920 after the war, demand for synthetic ammonia had fallen and Bosch felt that the high-pressure ammonia plant at Leuna might be converted to hydrogenate coal. Experimental work began at Oppau, and the Bergius patent rights were acquired in 1925, at the time that I. G. Farben was formed. Soon afterward I. G. Farben decided to convert the plant at Leuna to produce 100,000 tons.year⁻¹ of oil products. Operation started in June 1927, but it was some time before the technical problems were sorted out and the plant could be operated successfully. Costs were therefore extremely high and operation was stopped. The plant was restarted in 1931, when plans were made to treble capacity and to build three more plants in other parts of Germany in 1935.⁶¹

I. G. Farben needed to develop efficient, sulfur-resistant catalysts and to improve the process. Two converters were operated in series. Light oils formed in the first converter were removed by distillation before further hydrogenation of the residue took place in the second converter.

2.5.3. Cooperation between I. G. Farben and Standard Oil

I. G. Farben and Standard Oil began to talk about coal hydrogenation in 1925, and in 1927 they signed an agreement to cooperate in the research and development of oil hydrogenation. At that time, Standard Oil decided to build two gas oil hydrogenation units, each with a production capacity of 40,000 tons.year⁻¹ of petrol, solvents, lube oil, and kerosene at Baytown, New Jersey, and Baton Rouge, Louisiana.⁶² Hydrogen for these plants was to be made in the first commercial hydrocarbon steam reformers using a process and catalyst developed by I. G. Farben. Standard Oil planned to use the low-molecular-weight waste gases from the hydrogenation process as the hydrocarbon feed to the steam reformers. Standard Oil acquired the world rights to oil hydrogenation in 1928.

2.5.4. Commercial Developments by ICI

There was, of course, a worldwide interest in producing gasoline by coal hydrogenation, and those companies which developed ammonia processes were able to establish production facilities. In 1927, ICI acquired the patent rights of

the British Bergius syndicate and started to work independently on the coal hydrogenation process. To suit local conditions it was decided to modify operation and produce gasoline from bituminous coal. Coal was chosen because tar, the preferred feed, was not readily available in the quantities needed. A large pilot plant was built by 1929 and was in operation until 1931, by which time it had been established that at least 60 wt% of gasoline could be produced from coal. A full-scale plant was then designed to start operating in 1935 to produce a nominal 100,000 tons.year⁻¹ of gasoline.⁶³

2.5.5. International Cooperation

In 1931 the four major companies interested in the hydrogenation process—I. G. Farben, Standard Oil (New Jersey), Royal Dutch Shell, and ICI—became associated in the International Hydrogenation Patents Company to pool their patent rights and exchange technical information.⁶³

2.5.6. Coal Hydrogenation Processes

Coal hydrogenation processes were being developed at a time when there was no known theory of catalysis. High-pressure equipment was not generally available and was, therefore, very expensive. For special applications, potential operators had to design reactors and valves themselves. For these reasons progress in developing coal hydrogenation in the 1920s was fairly slow. However, because of the continuing fears that crude oil supplies would decline, work on the project went ahead and a range of new catalysts was developed. The most active chemical companies in Europe were I. G. Farben in Germany and ICI in the United Kingdom, and they were also working on a wide range of other catalytic processes at the time. Similarly, the international oil companies Standard Oil of New Jersey and Royal Dutch Shell were also introducing new catalytic processes for use in refineries.

These activities made significant contributions to both sides during World War II for the production of aviation gasoline. Subsequently rapid developments led to many other chemical and refinery processes based on catalysts. These are listed in [Table 2.13](#).

[Table 2.14](#) shows the total production of oil products in Germany and aviation gasoline in the United Kingdom by catalytic hydrogenation of coal or creosote from 1935 to 1946.

It was found during pilot plant testing that maximum yields of liquid hydrocarbons could only be obtained if the coal, or later tar and creosote, was partly

TABLE 2.13. Processes Developed from Coal Hydrogenation

Direct	Indirect
Coal hydrogenation	Hydrocarbon steam reforming
Tar/creosote hydrogenation	Liquid/gas phase reactors Catalyst sulfiding Hydrodenitrogenation
Gas oil hydrogenation	Hydroforming (catalytic reforming) Hydrotreating Hydrocracking

hydrogenated as a slurry in one reactor and the conversion completed by vapor phase hydrogenation in a second reactor. Operating conditions and the catalysts used depended on the feed to the process and whether the product required was a mixture of oil products or simply gasoline.

2.5.6.1. *The I. G. Farben Process*

The I. G. Farben process was used to produce mixed oils.⁶⁴ Originally the coal, slurried with heavy oil and a molybdenum catalyst, was hydrogenated at 400°C and 200 atm. Light and middle oils were then separated. The residue was again hydrogenated at 450–470°C and 200 atm, this time with a cobalt sulfide catalyst, to produce more light and middle oils. Residual heavy oil was recycled as a slurry with more coal. About 75% of the coal was converted into useful light and middle oils. Eventually I. G. Farben used sulfided iron catalysts at 700 atm to achieve higher conversion.

TABLE 2.14. Production of Oil and Gasoline from Coal, 1935–1946.

Year	Feed		
ICI (high-octane gasoline) ^a	Coal	Creosote	Gas oil
1935–1939: total tons	170,000	320,000	—
1940–1946: total tons	—	630,000	~ 1.2 million
Germany (liquid oil products)	Coal	Tar/pitch	Brown coal
By 1945: tons.year ⁻¹	740,000	910,000	~ 2 million

Note: Operation was at different pressures owing to the different catalysts used by ICI.

^aIso-octane production by ICI from waste C4 gases was about 10,000 tons.year⁻¹ from 1941 and 60,000 tons.year⁻¹ from 1943.

2.5.6.2. *The ICI Process*

ICI produced gasoline.⁶⁵ Coal was slurried with heavy oil (bp > 400°C) and 2% of an iron oxide catalyst (later an improved stannous oxalate catalyst was used) and hydrogenated at 420°C and 250 atm. During operation in the tall, narrow reactor the slurry was agitated by the upward flow of hydrogen. The ratio of hydrogen to slurry was about 1000, with a residence time of up to 2 h.

The liquid product was separated into gasoline (< 200°C), middle oil (200–300°C), and heavy oil (> 300°C) fractions. Heavy oil was recycled with more coal to the first reactor for further hydrogenation. Middle oil was then hydrogenated in a second, vapor phase reactor at 480°C and 250 atm with 1 m³ of hydrogen per kg of oil at a residence time of 3 min. The catalyst was pelleted tungsten sulfide. Gasoline was again separated and the residual middle oil recycled. The yield from both stages exceeded 60 kg of gasoline per 100 kg of coal. ICI operated two stages at 240–260 atm: stage 1 to convert either coal, a heavy oil slurry, or heavy creosote to middle oil that was then cracked in stage 2 to produce gasoline. Details are shown in Table 2.15.

TABLE 2.15. Coal and Creosote Hydrogenation Process and Catalysts.

Conditions		Reactor details		
First stage (liquid phase)	47% coal/heavy oil slurry	Creosote > 375°C		
Catalyst/ton feed	Tin oxalate (0.02%) NH ₄ Cl (0.2%)	Tin oxalate (0.01%) CCl ₄ (0.04%) iodine (0.02%)		
Temperature (°C)	465	445–475		
Product:				
heavy oil (%)	6	—		
middle oil (%)	43 (to second stage) ^a	70 (to second stage)		
gasoline (%)	11	11		
C ₁ –C ₄ (%)	20	17		
		Early operation with one reactor	Later operation with two reactors	
			No. 1: 1939–1945	No. 2: 1939–1942 No. 2: 1942–1945
Feed ton ⁻¹ catalyst	1.1		1.2	1.0
Temperature (°C)	420		385	370
Conversion (%)	54		Removes nitrogen	55
Yield (%)	92		Fed to No. 2	85–75
Octane	68	—	75	85–75

Note: One of the first catalysts was sulfided ZnO/MgO/MoO₃, which gave low yields. Replaced with WS₂, which produced low-octane gasoline. Two vapor phase reactors in series used WS₂ in the first, with either WS₂ on Terrana clay (fuller's earth) or 10% FeF₃ on kieselguhr in the second to produce high-octane gasoline.

^aSecond stage = vapor phase.

2.5.7. Catalysts for Coal Hydrogenation

Originally Bergius felt that coal hydrogenation could not be catalyzed because the large quantities of sulfur present would poison the catalysts. He added luxmasse simply to absorb sulfur from the products although, coincidentally, the combination of iron oxide with titania and alumina was an excellent choice of catalyst. Since his first tests, however, the industrial use of the process has depended on catalysts that were developed more or less empirically. It was soon realized that the processes involved in hydrogenating coal were more complex than the simple reactions described by Sabatier and Ipatieff. Different catalysts such as iron oxide or iron sulfide, probably with traces of other metal oxides, were required. These catalysts could be used in the presence of sulfur and were, in fact, even more active when sulfided.⁶⁶ Several studies reported that iron, nickel, cobalt, tin, zinc, and copper chlorides were effective catalysts and claimed that ammonium molybdate was particularly active.

An early I. G. Farben patent⁶⁴ used a molybdenum catalyst in the first stage of the hydrogenation, probably based on a 31 ZnO:15 MgO:54 MoO₃ mixture, and a cobalt sulfide catalyst in the second stage. At about the same time ICI used an iron oxide or tin-plated iron catalyst in the first, liquid phase reactor.⁶⁵ ICI subsequently used stannous oxalate in their first reactor with the addition of ammonium chloride to neutralize the alkaline ash and maintain catalyst activity. Alkalinity was a common problem with all coal feeds and, eventually, I. G. Farben plants opted to increase operating pressure to 700 atm, which allowed them to use a simple iron catalyst which was more resistant to alkali. Later they also used sulfuric acid to neutralize the alkalinity. Until 1935 the preferred vapor phase hydrogenation catalysts used in the second reactor seemed to be the zinc oxide/magnesia/molybdena catalyst. This could only operate at high temperatures and gave relatively low liquid yields with correspondingly high levels of gas formation.

By 1930 I. G. Farben had introduced a new tungsten sulfide catalyst that was extremely active in both the cracking and hydrogenation stages of the process and produced high yields with all feeds. A disadvantage was that often sulfur had to be added to resulfide the catalyst. Despite the higher proportion of gasoline produced compared with early catalysts, the octane number (68–70) was low, because the use of tungsten sulfide results in a decreased aromatic content. When higher-octane gasolines were required, the pure tungsten sulfide catalyst was modified to 10% tungsten sulfide supported on activated montmorillonite (Terrana clay). The new catalyst was just as active but produced gasoline with an increased octane number.

It was found, however, that the catalyst was poisoned by feeds containing more than 5 ppm of nitrogen. This meant that it could only be used directly with crude oil fractions and not with coal or coal tars. Nitrogen poisoning could be avoided by partial hydrogenation of the feed over tungsten sulfide at a low tem-

perature before the final hydrogenation step with supported 10% tungsten sulfide. This produced some low-aromatic gasoline in the first reactor, which was removed by distillation before the final hydrogenation in the second reactor which produced high-octane gasoline. In order to achieve a somewhat higher octane number, at the expense of yield, in the 1940s ICI began to use an iron fluoride catalyst supported on hydrogen fluoride- activated superfiltrol.

2.5.8. Creosote and Other Feeds

The ICI plant was converted to use creosote feed during the war years. This was originally for safety reasons but later coal became too expensive and was in short supply. Creosote could be easily hydrogenated and gave reliable operation in a plant producing more than 100,000 tonnes.year⁻¹ of 100-octane aviation gasoline (Figure 2.6).

Gas oil was another readily available alternative to coal and required only half of the amount of hydrogen needed compared with creosote. It was used in a second hydrogenation plant operated by Shell, ICI, and Trinidad Leaseholds, Ltd. (Trimpell, Ltd) to produce more than 300,000 tonnes.year⁻¹ of 100-octane gasoline. Butane, a by-product from both plants, was converted by the new UOP



Figure 2.6. ICI creosote hydrogenation plant. Reprinted with permission from Johnson Matthey.

process to iso-octane for use in gasoline (Figure 2.7). In May 1940 the 10,000-tonnes.year⁻¹ iso-octane plant at Billingham was the first in the world to use the process.

While coal hydrogenation was not a commercial success it was certainly a wartime strategic necessity for Germany and the United Kingdom. It is probable that the introduction of catalytic refinery processes would have been delayed if Standard Oil, Shell, and ICI had not used the coal hydrogenation catalysts for gas oil hydrogenation and developed the other *refinery-type* processes mentioned previously in Table 2.13.

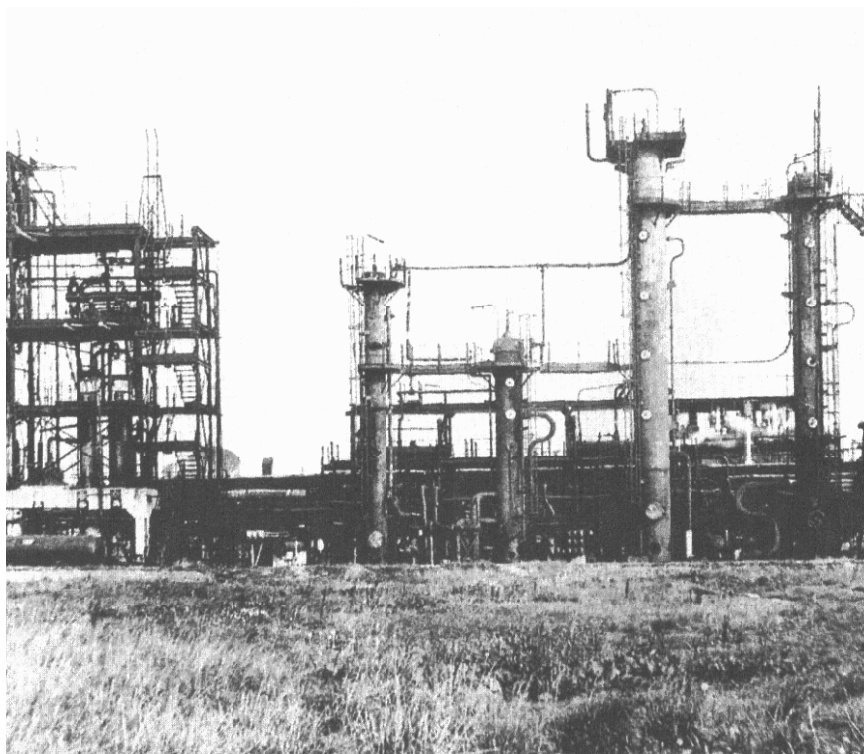


Figure 2.7. First UOP iso-octane plant at ICI. Reprinted with permission from Johnson Matthey.

2.6. THE FISCHER–TROPSCH PROCESS

The possibility of producing fuels from carbon monoxide and hydrogen (synthesis gas) was investigated as far back as 1913 using alkali-activated cobalt and osmium oxide catalysts supported on asbestos. A mixture of alcohols, aldehydes, ketones, and fatty acids with some aliphatic hydrocarbons was produced at 300⁰–400⁰C and 100–200 atm. The work was, of course, also stimulated by the development of high-pressure equipment and the production of synthesis gas by BASF.⁶⁷ From 1923 Franz Fischer and Hans Tropsch continued work on what they called the *Synthol* process at the Kaiser Wilhelm Institute at Mulheim-Ruhr. Using alkalized iron turnings as a catalyst, they were able to produce *Synthin*, an oily liquid at 400⁰–450⁰C and 100–150 atm. At high pressures the oil produced by the Synthol catalyst consisted mainly of oxygenated compounds but further experiments at about 7 atm did provide a mixture of olefins and paraffins. Nickel and cobalt catalysts also produced methane and higher hydrocarbons at atmospheric pressure and 200⁰–250⁰C, but the catalysts were quickly deactivated under these conditions. As all the tests with nickel and cobalt catalysts were carried out at atmospheric pressure, on the assumption that this gave the most desirable product, iron catalysts, which operated more effectively at higher pressure, were excluded.

Full reviews of the early work are given by Robert Anderson⁶⁸ and H. H. Storch.⁶⁹ The synthesis of hydrocarbons from hydrogen and carbon monoxide *synthesis gas* by Fischer, Tropsch, and their associates became known as the Fischer–Tropsch process. This has been used and developed extensively since 1955 by Sasol, in South Africa, where it is still known as the Synthol process.

Fischer and Tropsch went on to test a number of catalysts based on nickel and cobalt supported on thoria and kieselguhr, which were considered more promising than iron. Their experimental work is a classic example of catalyst and process development that has probably since been followed by many other investigators.

Catalyst preparation evolved through the use of the mixed metal oxides, the decomposition of mixed metal nitrates, and the precipitation of carbonates and hydroxides from solutions of metal salts. Because powders were difficult to handle, granules and pellets were produced using binders and tested in a variety of shapes and sizes.

The first promising catalyst was introduced by 1931 and contained a high proportion of nickel oxide supported on a mixture of thoria and kieselguhr. The convention widely used at the time was to describe composition as 100 parts nickel, 18 parts thoria, 100 parts kieselguhr. Catalysts made with cobalt rather than nickel were more effective but could not be considered commercially at that time because cobalt was not available in sufficiently large quantities. The same problem had, of course, faced Haber and Bosch in the replacement of osmium by iron oxide for the ammonia synthesis catalyst.

A disadvantage with the nickel catalyst, which was active but less selective than cobalt in the reaction, is its short operating life. One reason for this may have been the need to activate the catalyst by reduction at 450°C before use. The reason for this short lifetime is that nickel silicates are formed during catalyst preparation by reaction of the nickel compound with kieselguhr. These can only be reduced at the relatively high temperature of 450°C. Nickel crystallites are very prone to sintering at this temperature and the catalysts are somewhat deactivated even before they are charged to the reactor. Silicate formation during catalyst preparation has been a continuing problem with nickel/kieselguhr hydrogenation catalysts. A small amount of copper was added to allow catalyst reduction at a temperature closer to the operating level of 178°C. Unfortunately, the copper also sintered and catalyst activity was actually decreased.

Subsequent work included attempts to use less of the more expensive materials in the catalyst recipe and to replace them with cheaper *diluents*. This was done empirically adding manganese oxide, magnesia, and more kieselguhr. Although it was a novel approach at the time, it is now a routine procedure in cutting the cost of a catalyst!

Ruhrchemie built a large pilot plant in 1934 and tested a 100Ni:25MnO:10Al₂O₃:100 kieselguhr formulation. This approach demonstrated another important stage in catalyst development, namely that small-scale atmospheric pressure tests do not highlight full-scale operating problems. In this case the problem was the need for efficient heat removal from exothermic reactions. The pilot plant also confirmed that although nickel was not very selective, deactivation could be partly restored by regeneration in air and rereduction in hydrogen at 400°C. A further problem was an unacceptable loss of nickel during operation, presumably as a result of nickel carbonyl formation.

Roelen⁷⁰ took over the responsibility for catalyst development in 1934 and began further testing of the previously successful cobalt catalyst used by Fischer. He decreased the quantity of expensive materials and also investigated the effects of copper on reduction temperature. The catalyst developed by Roelen, 100Co:5ThO₂:8 MgO:200 kieselguhr, was used in the four large plants built by Ruhrchemie in 1936 and operated during the war. By the end of the war nine plants were using the catalyst with a capacity of about 700,000 tonnes of hydrocarbons per year.

The introduction of magnesia to what seems an already complicated mixture is interesting mainly because it was also included in other nickel catalysts such as the raschig-ring catalysts for steam reforming. It is now realized that the molecular dimensions of magnesia are similar to those of cobalt and nickel oxides, and that magnesium can replace cobalt and nickel in solid solution within a crystalline lattice. This can make catalyst reduction easier and result in the formation of smaller, more stable metal crystallites.

Research on precipitated iron catalysts continued while the first commercial plants were being built as part of the program to find a cheaper catalyst. Results

were not encouraging until the operating pressure was raised to 15 atm.⁷¹ This increased both the hydrocarbon yield and the catalyst life. Several catalysts, including a typical fused ammonia synthesis catalyst, were compared in 1936 in a government competition at Schwarzheide. Different promoters were tested, and potash was found to increase activity and selectivity. Later, in 1940 Pichler and Buffeg tested supported ruthenium catalysts at pressures up to 1000 atm and obtained high-molecular-weight waxes.⁷²

2.6.1. Postwar Development of the Synthol Process by Sasol

There was no further full-scale operation of the wartime plants after 1946. However, experimental work continued in the United States and the United Kingdom as well as in Germany because of possible future oil shortages. The lack of oil in South Africa had led Anglovaal to take out a license for the construction of a Fischer–Tropsch plant in 1935,⁷³ but owing to various delays the plant was not actually built until 1955, when Sasol, which was owned by the South African Government, went ahead with the project. The Sasol 1 plant, at Sasolburg, produced up to 200,000 tonnes·year⁻¹ of hydrocarbons using two processes. The first, licensed by Lurgi and Ruhrchemie, used fixed bed tube-cooled ARGE reactors, containing a precipitated iron/copper/silica catalyst to provide heavy liquid hydrocarbons and waxes. The second, licensed by Kellogg, operated with a circulating fluid bed of crushed fused iron catalyst and made hydrocarbon gases and gasoline.⁷⁴

The fixed bed process worked well. It was not easy, however, to circulate the fluidized dense iron catalyst through the reactor and back through the separator without further development. Good operation was eventually made possible and the process was successful in the Sasol *Synthol* reactor. Typical product distributions for the two processes are shown in [Table 2.16](#).

Early catalysts used in the Synthol process were produced as follows:⁷⁴

- a) Ruhrchemie catalyst for the in fixed bed tubular reactor:
 - Solutions of cobalt, thorium, and magnesium nitrates were added to a sodium carbonate solution up to pH 7.
 - Kieselguhr was added and the slurry filtered, dried, washed, and calcined.
- b) Alternative recipe used by Sasol:
 - Precipitation of basic carbonates and hydroxides from copper and ferric nitrate solutions with sodium carbonate solution.
 - Filter and wash precipitate before slurring the solid with potassium silicate solution to give 25 g SiO₂ per 100 g iron.
 - Wash with dilute nitric acid to remove any excess potassium leaving 5 g K₂O per 100 g iron.
 - Filter and extrude partly dried filter cake. Dry to less than 10% water.
 - Add other promoters.

TABLE 2.16. Product Distribution from the Fisher–Tropsch Process.

Product	Fixed bed	Fluid bed
C ₁ –C ₄	13	43
C ₅ –C ₁₁ (gasoline)	18 (ON35)	40 (ON65)
C ₁₂ –C ₁₈ (diesel)	14 (CN75)	7 (CN55)
C ₁₉ –C ₂₃ (jet fuel)	7	—
C ₂₄ –C ₃₅ (medium wax)	20	> C ₁₉ 4
> C ₃₅ (hard wax)	25	—
Water soluble neutral	3	5
Acid	0.2	1

Note: Light gas + LPG reformed to hydrogen and cracked to ethylene. α -Olefins separated for use in polyethylene or detergents. Alcohols and ketones extracted.

c) Fused magnetite catalyst used in transported fluid bed reactors:

- Fuse magnetite, such as mill-scale, with potash, alumina, silica, and other promoters at 1500°C.
- Chill cast molten mass and mill to required size grade.
- Oxides such as Al₂O₃, MgO, TiO₂, and CrO₃ were claimed to form solid solutions whereas K₂O and SiO₂ remained on crystal boundaries. The composition was not published.
- Catalyst must be reduced before use.

Following the successful development of the Synthol process, Sasol went ahead and built two larger plants at Secunda, Sasol 2 and Sasol 3, which were based on coal. A further plant using the Synthol reactor but with natural gas as feed was built at Mossul Bay by Moss gas.

The atmospheric pressure adiabatic reactors used during the war by Ruhrchemie were not very efficient, and although research on reactor design continued, nothing could be done at the time to make any improvements. Metal plates, 7 mm apart, were stacked vertically in the reactor. During operation, the catalyst between the plates was cooled by water running through horizontal tubes passing through the plates. This arrangement was inefficient at the low gas hourly space velocity through the catalyst.⁷⁵

At the time Ruhrchemie made some minor improvements by using concentric tubes in the medium-pressure reactors, with catalyst in the annular space and cooling water flowing around the tube and through the inner space. This was still inefficient at low gas space velocity. The ARGE reactors used by Sasol in 1955 were conventional boiling water tubular reactors with gas recycle to limit heat evolution. A typical wartime reactor contained 1250 tubes, whereas the early Sasol reactor used more than 2000 tubes.

Present-day reactor design is much more efficient and, as a result, catalyst operation has been improved. The nonadiabatic reactor recently developed by UOP is similar to the original Ruhrchemie design, with the catalyst packed be-

tween the vertical plates of a heat exchanger.⁷⁵ This allows the feed and coolant to flow in any direction to control the temperature more efficiently in both exothermic and endothermic reactions. Pressure drop through the catalyst bed can also be selected. The advantages are a better approach to reaction equilibrium at high rates with better selectivity and less recycle. Nonadiabatic reactors provide a good example of how interesting ideas in catalytic processes could not be developed even 50 years ago because the technology was not available.

Fluid bed operation proved to be difficult in the original trials held by Standard Oil and Hydrocarbon Research Incorporated in the United States.⁷⁷ The main problems were obtaining a uniform density throughout the bed and proper gas mixing. The circulating fluid bed used by Kellogg and developed at Sasol eventually operated very well. Operating conditions for both Sasol processes are summarized below:⁷⁴

a) Fixed bed tubular reactor:

- Reactor with more than 2000 tubes, each 12 m long, containing 20 liters of catalyst per tube.
- Operating pressure 27 atm, temperature 220–250°C. Fresh feed (1.8 H₂ : 1 CO) at space velocity 500 h⁻¹.
- Initial conversion 40% per pass.
- Catalyst life less than 1 year, depending on operating severity (e.g., to produce high-molecular-weight wax.) The catalyst sinters in the presence of water. Prereduction provides preshrinkage of the catalyst. Preshrinkage is also possible by heating the catalyst in liquid wax.

b) Transported fluid bed:

- Reactor 46 m high (original design 2.3 m internal diameter).
- Operating pressure 22 atm; reactor outlet temperature about 340°C. Fresh feed 100,000 m³ h⁻¹ (6 H₂ : 1 CO).
- Initial conversion 85% per pass.
- Catalyst life was originally 40 days but now increased.
- Reduction of catalyst in hydrogen before use at high linear velocity.
- Catalyst is carbided during reaction with some reoxidation by water produced during the reaction. Potash promotes carburization and retards oxidation. Alumina increases surface area and activity.
- Catalyst can be added or removed during operation to improve operation.

Slurry bed reactors using heavy oil to support the catalyst have been tested and can operate over a wider range of operating conditions and feed gas compositions than the fluid beds.⁷⁷ Sasol has now developed an improved Sasol advanced Synthol (SAS) reactor to produce high-grade distillate. The Sasol slurry phase distillate process (SSDP) has been tested in a demonstration plant at Sasol 1 since 1993. The SAS reactor is said to use an iron-based catalyst similar to the one used in its original plants, whereas the SSDP process uses a cobalt catalyst.

The Sasol processes are of interest now that the conversion of synthesis gas-to-liquid products is being developed by a number of companies. The gas-to-liquid (GTL) process is of particular interest in the production of sulfur-free distillates.

2.6.2. The Importance of Gas-to-Liquids as Gasoline Prices Increase

The major developments of gas-to-liquids (GTL) technology have arisen due to the availability of cheap by-product natural gas or associated gases in remote areas. The capital expense of new plants can be offset against future increases in crude oil prices. An advantage of the GTL products is the low content of sulfur, metals, and other impurities. GTL plants that are currently operating on a large scale; the Moss gas process using natural gas, was reported to be using the largest steam-reforming train in the world.

Since the end of the 1990s several companies have been developing processes to supply liquid hydrocarbons. Synthesis gas is produced and treated in variations of the Fischer–Tropsch process. High-boiling C_{10} – C_{40} liquid and wax products can be converted to sulfur-free, low-boiling products in the C_{10} – C_{20} range by hydrocracking. Since 1955 only the Sasol processes have been tested extensively.

Sasol produces synthesis gas from coal by partial oxidation or from natural gas by steam reforming. The first version of the Synthol process was upgraded to use the advanced Synthol reactor. Both Synthol processes use fluid catalyst beds. A new SSDP has now been introduced and should soon be operating. Distillates and waxes can be produced (25 atm; 240°C).

Shell operated its middle-distillate synthesis process (SMDS) in Malaysia from 1993 to 1997, but closed the facility in 1997 while better Fischer–Tropsch catalysts were being developed for future operation. Synthesis gas produced by the Shell partial oxidation process was converted to distillates and waxes in a tubular high-pressure Fischer–Tropsch reactor. A slurry phase reactor using an improved catalyst is being developed (40–46 atm; 120–130°C).

Exxon developed an advanced gas conversion process (AGC-21) that produces synthesis gas by combined partial oxidation and steam reforming in a fluidized bed. A multiphase, slurry Fischer–Tropsch reactor has also been developed. Syntroleum uses an autothermal air/natural gas reformer to produce synthesis gas. A fluidized bed Fischer–Tropsch reactor has been developed (20–35 atm; 190–230°C).

The catalysts likely to be used in those processes are listed in [Table 2.17](#). It is clear that although many innovations will be included, the catalysts will, as far as possible, be well-tested types already operating in other processes.⁷⁸ So far only Shell, which is using a cobalt/metallocene catalyst, seems to have developed something new. Following recovery of the low-boiling, liquid products, the

TABLE 2.17. Catalysts Used in Gas-to-Liquids Production

	Synthesis gas	FT conversion
Sasol	Conventional steam-reforming catalysts.	1. ARGE process. Iron catalyst. 2. Advanced Synthol. Iron catalyst. 3. SSPD process. Cobalt or iron catalyst.
Shell	No catalysts in partial oxidation except purification of feed.	Proprietary metallocene catalyst to provide better product range.
Exxon	Conventional reforming catalysts.	Proprietary cobalt-based catalyst.
Syntroleum	Autothermal reforming using a ceramic membrane (as catalyst?)	Proprietary cobalt-based catalyst.

high-molecularweight hydrocarbons and waxes will be upgraded in hydrocracking units. Gas-to-liquid process plants will, of course, be expensive and in order to be profitable will have to be built on a large scale. However, the recent surges in the price of crude oil suggest that more of these processes will become necessary in the future.

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