A new industry benchmark for ammonia production

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Through dedication and intelligent research, Haldor Topsøe’s name has become synonymous with efficient and profitable ammonia production and has set the standard for ammonia catalysts and technology. We build upon this legacy with the introduction of an ammonia synthesis catalyst that delivers the highest performance ever – KM 111. KM 111 is a magnetite-based catalyst developed for optimal performance in the lower beds of the ammonia converter. Using KM 111 in conjunction with our industry-leading catalyst KM1 increases the profitability of ammonia production through record high production levels as well as savings in energy consumption.

INTRODUCTION

Ammonia is widely known as an important industrial chemical, used in the manufacture of products ranging from fertilizers to plastics and fibers, and its production is one of the highest of all inorganic chemicals. Over 80% of the ammonia produced worldwide is currently utilized in fertilizers for food production, and these demands on the ammonia industry will only continue owing to the current trend of global population growth. At the same time, the current global economy and regional fluctuations in feedstock prices are putting pressure on ammonia producers to cost-optimize their operations. These factors together stress the need for constant improvements in the production process and the importance of selecting technology and catalyst solutions that maximize production as well as efficiency.
Topsøe has long valued the importance of high-quality products that deliver performance and efficiency. Fundamental and applied research efforts have been a cornerstone of the company since its founding, and these efforts have led to the introduction of numerous industry-leading products, such as Topsøe’s KM ammonia synthesis catalyst. The KM catalyst is the most successful ammonia synthesis catalyst on the market, known throughout the world for its superior performance. Over 1,200 charges of the catalyst have been sold since its introduction, and it is used in the production of over half of the world’s ammonia.

Improving synthesis catalyst properties is crucial to ammonia plant performance. Plant capacities are increasing beyond levels previously restricted by logistics related to storage and transportation, and energy consumption is approaching the theoretical minimum. Therefore, further improvements in energy utilization are expected to depend heavily on catalyst development and the process changes associated with new catalysts. Recognizing this need, Topsøe has dedicated years of meticulous and thorough research in the effort to produce an ammonia synthesis catalyst that would lead to both record high and energy-efficient production. The result is the new KM 111 synthesis catalyst.

100 YEARS OF MODERN AMMONIA SYNTHESIS

Nitrogen has long been recognized as one of the most critical nutrients for promoting plant growth. In the 1800s, saltpeter was discovered in South America and was mined extensively due to its proven performance as a fertilizer. However, due to an increasing awareness that the existing agricultural production rate would not keep pace with the projected exponential population growth, scientists raced to find a commercially viable synthetic fertilizer. An obvious method was the fixation of nitrogen gas abundantly available in air, but the difficulty lay in the inert nature of triple-bonded N₂. The breakthrough came in 1908, when Fritz Haber patented the high-pressure, catalytic process that combines atmospheric nitrogen with hydrogen gas to form ammonia:

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

In 1913, Carl Bosch and his team of engineers realized the industrial-scale potential of Haber’s discovery and built the first ammonia plant. This first installation successfully contained the high pressures and temperatures required for the process. It was commissioned with a capacity of 30 MTPD but by 1916, the capacity was increased to 250 MTPD. In 1917, a second plant was commissioned in Germany and by the end of the First World War, it was producing over 600 MTPD using the Haber-Bosch process.

By the time of the Second World War, it was generally believed that ammonia synthesis technology was mature, and that no significant further developments could be expected. This was to a certain extent true, since many of the features that characterize modern technology – including catalyst type, operating conditions, and converter designs – were already proven in industrial applications. However, ammonia plants looked very different at that time from what we know today. In early plants, effluent from the ammonia converter was cooled with cooling water without any heat recovery. Parallel trains were often used. Synthesis gas was compressed in reciprocating compressors, which had limited capacities corresponding to approximately 300–400 MTPD ammonia.

The mid-1900s saw a steep increase in ammonia production, as natural gas replaced coke as the preferred feedstock. Technological developments favored this shift in feedstock. Cost-saving improvements in processes such as steam reforming were quickly implemented, including Topsøe’s first side-fired tubular reformer in 1957. The result of the developments leading up to the 1960s was the large-capacity single-stream ammonia plant, which is still the dominating concept in the industry [1]. The basic process sequence has remained unchanged over the years:

- Feed purification
- Primary and secondary reforming
- Shift conversion
- CO₂ removal
- Final purification of synthesis gas
- Compression and ammonia synthesis
- Ammonia recovery and refrigeration
With the introduction of the large-capacity single-stream ammonia plant, a veritable explosion occurred in the industry. Within a decade, more than one hundred plants were constructed, and the installed capacity nearly tripled [2]. The steep production increase can be seen in Fig. 1, which also shows global population growth. It has been claimed that the introduction of synthetic fertilizers for food production facilitated the population growth from 1 billion in 1900 to its current level at approximately 7 billion. For this reason, the development of technology based on the Fritz-Haber process has been described as the “detonator of the population explosion” [3].

**Fig. 1:** Production of ammonia and population growth since 1900.

**THE TOPSØE LEGACY**

Optimizing the production of ammonia requires a delicate balance of operating conditions that take a large number of considerations into account. Among these are the reaction kinetics and thermodynamics, as well as synthesis catalyst properties. Therefore, one of the many difficulties facing ammonia converter design is the control of bed temperatures. Many converter designs were developed in an attempt to obtain better temperature control while simultaneously reducing energy costs by maximizing heat recovery.

The common characteristic of earlier converters was axial flow, but given the ever-increasing plant capacities, this flow type required catalyst beds so tall that the subsequent increase in pressure drop demanded larger catalyst sizes. Large particles, however, lower the effective catalyst activity due to the longer diffusion pathway to the interior of the catalyst. Topsøe solved this problem with the development of the radial flow converter in 1966. Not only did this converter type reduce pressure drop, it also allowed a significant decrease in catalyst particle size, resulting in much higher ammonia production. Ten years later, Topsøe further improved this design by introducing radial flow converters with indirect cooling between catalyst beds – the 2-bed **Topsøe S-200**. This converter type has since been used in more ammonia plants than any other type. More than 270 Topsøe-designed radial flow converters have been supplied worldwide, and Topsøe is recognized as the leading ammonia technology supplier with approximately 50% of all new ammonia plants designed using Topsøe technology.

In a world-scale ammonia plant, the pressure shell weighs typically between 500–700 tons, so any reduction in converter size is extremely beneficial, both for cost considerations and for transport and handling purposes. **Topsøe’s latest radial flow converter design, the S-300**, is an excellent example of a compact ammonia converter. In the S-300, the catalyst volume has been reduced by nearly 20% compared to its predecessor. Additional advantages of the S-300 converter include its ability to cope with issues such as nitriding and hydrogen attack. Such benefits are not only relevant for new plants but can also be valuable through revamps of existing plants. Topsøe has a successful history of partnering with customers to transform aging converters to modern, high-performance equipment that greatly increases profitability through improvements in production and energy consumption.

Over the years, the ammonia industry has seen a steady increase in plant capacities, and Topsøe’s designs are no exception. The first generation of large Topsøe ammonia plants was constructed in 1971,
and by 2000, Topsøe was commissioning plants with capacities over 2,000 MTPD. In 2009, Topsøe completed the design of a 2,600-MTPD ammonia plant as well as a 3,500-MTPD ammonia loop based on the use of a single S-300 converter.

**The KM1 catalyst**

Designing a compact yet efficient ammonia converter requires extensive knowledge about converter internals as well as knowledge about catalyst kinetic behavior. The synergy between technology and catalyst is crucial for the optimization of plant performance, and Topsøe is unique in being both a technology licensor and a catalyst supplier. Catalyst properties that can significantly affect the range of possible operating conditions include:

- Thermal stability
- Particle size and shape
- Pore system
- Mechanical strength
- Change in properties during activation and/or operation

The magnetite-based promoted catalyst is the most widely used type of ammonia synthesis catalyst today. It was first discovered in the early 1900s by Alwin Mittasch after an exhaustive search for the most viable industrial-scale catalyst. His eventual solution came from a particular sample of natural magnetite (Fe₃O₄), which had certain impurities, or promoters, that provided the necessary catalytic qualities.

Topsøe optimized the magnetite-based ammonia synthesis catalyst for the specific conditions of the synthesis reaction and introduced its first version of the ammonia synthesis catalyst in 1947. Over the following 65+ years, Topsøe’s ammonia synthesis catalysts have proven to be one of the most stable of all industrial catalyst types, capable of high mechanical strength, high poison resistance, and excellent thermal stability despite exposure to harsh operating conditions. Their superior activity has also been tested and confirmed over the decades. Today, KM1 and its prereduced equivalent are used to produce over half of the world’s ammonia. More than 1,200 charges have been sold since initial production, with 248 charges of the catalyst currently in operation worldwide (Fig. 2).

![Fig. 2: Current reference map of KM1.](image)

The unique characteristics of KM1 have resulted in an extensive track record of very long catalyst lifetimes achieved in industrial operation. Numerous plants worldwide have achieved KM catalyst lifetimes of more than 20 years, with the average lifetime well above 10 years. Typically, the KM1 catalyst is replaced in connection with plant revamps or installation of new converter internals, and not as a consequence of activity loss. This track record, proven by industrial experience, is a testament to the unsurpassed long-term stability of KM1.

One of the characteristics of KM1 is its resistance to poisons. Synthesis gas in modern ammonia plants typically has a high purity, but plant upsets may occur during which the synthesis catalyst is exposed to poisons such as chlorine, sulfur, or oxygen compounds. The inherent high activity of KM1 enables it to
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withstand exposure to high levels of poisons and in most cases allows for continued production. Industrial experience shows that the KM1 catalyst regains full activity even after severe oxygen poisoning.

THE NEW AMMONIA CATALYST

The magnetite-based catalyst is one of the most thoroughly investigated catalysts in the industry. Countless studies have probed its properties, searching for a way to further improve its activity. Throughout the decades, Topsøe’s scientists have been a part of these efforts, using advanced research techniques to expand our knowledge. The result was the development of a groundbreaking new magnetite-based catalyst with properties that exceed expectations. This new catalyst is Topsøe’s KM 111.

Produced with a new manufacturing method, the KM 111 catalyst possesses an activity that significantly surpasses the market-leading activity of KM1 (Fig. 3). The higher activity is achieved without compromising the excellent thermal and mechanical stability of its predecessor, KM1.

![Fig. 3: Comparison of catalyst activity for KM1 and KM 111. (Activity of KM1 is based on hundreds of charges; data points are therefore not shown.)](image)

The catalyst activity is optimized for operation at the higher ammonia concentrations inherent in the lower ammonia converter beds. With a more active catalyst, the kinetics of the ammonia synthesis reaction is improved, which allows for reductions in temperature. This is a critical advantage, since chemical equilibrium favors higher conversion at lower temperatures. Consequently, customers who select the combination of KM1 and KM 111 or their prereduced equivalents (Fig. 4) to catalyze their ammonia production can expect a considerable increase in capacity.

![Fig. 4: Schematic of ammonia synthesis converter with KM1 (or KM1R) in the top bed and KM 111 in the lower beds.](image)

A modern ammonia plant equipped with an S-300 converter can, for example, achieve production increases greater than 15,000 tonnes per year, when comparing with production from a full load of the benchmark catalyst KM1. After only five years of operation, this would yield an extra month of effective production. In other words, the payback time is very short for the premium catalyst.
An additional benefit of the higher conversion with KM 111 is a savings in plant operating costs. At existing plants, energy consumption can be reduced by operating at lower loop pressures and lower converter inlet flows while maintaining the same production levels achieved with other synthesis catalysts. In the case of a 2,100-MTPD ammonia plant, loop pressure can be decreased by 2% when switching from a full load of KM1.

For grassroots plants and for new ammonia converters at existing plants, KM 111 can meet capacity requirements with a smaller volume of catalyst, allowing customers to reduce reactor size and save in capital expenditures.

Another feature of KM 111 is its initiation of reduction at lower temperatures, which translates to shorter reduction times. As for all magnetite-based catalysts, reduction of iron oxide to metallic α-Fe is required for catalyst activation:

\[ \text{Fe}_3\text{O}_4 + 4 \text{H}_2 \rightleftharpoons 3 \text{Fe} + 4 \text{H}_2\text{O} \]

The removal of oxygen without shrinkage of the crystal lattice results in a porous structure with a surface area nearly 1,000 times greater than the unreduced pellet. For KM 111, in-situ x-ray powder diffraction studies (Fig. 5) indicate that the reduction time of the new KM 111 catalyst in an industrial-sized converter is approximately 10 hours faster than that of KM1.

The above benefits of the catalyst combination of KM1 and KM 111 together translate into maximum profitability through record high, energy-efficient ammonia production sustained over the long catalyst lifetime.

**Fig. 5: Comparison of reducibility from Fe_3O_4 to Fe for KM1 and KM 111.**

**PARTNERING WITH TOPSØE**

At Topsøe, catalysts and technology go hand in hand, and the benefits of the new catalyst combination are maximized when used in conjunction with Topsøe-designed ammonia technology. Our technology is available for both grassroots and revamp projects, and we have extensive experience in providing customers with tailor-made solutions that optimize plant performance.

Topsøe’s ammonia synthesis technology is based on the radial flow converter that we pioneered in the 1960s. Today, we offer three converter types: the S-200, the S-300, and the S-50. All of the converter types have the following benefits:

- 100% radial flow through the catalyst bed(s) to obtain low pressure and high conversion with small-size catalysts
- Indirect cooling of the gas in the heat exchangers between the catalyst beds instead of quenching to avoid dilution of the converted gas
- Full utilization of the total installed catalyst volume
- Stable operation with great flexibility in operating range
- Simple temperature control
The S-200 is a two-bed converter with indirect cooling between the catalyst beds and exists in two versions. The first has a built-in feed-effluent heat exchanger below the second bed, allowing the heat from the reaction to be used for preheating of the boiler feed water downstream of the converter. The second version is designed without a lower heat exchanger; the outlet gas from the second bed passes directly to a boiler for production of high-pressure steam.

The three-bed S-300 converter is Topsøe’s recommended converter selection for all new plants. It offers higher conversion or alternatively a reduced catalyst volume compared to the S-200. The S-300 basket design has been well received by the industry, with over 40 references since its first installation in 1999.

The S-50 is a single-bed converter added downstream of the main converter to increase the ammonia conversion and to improve steam generation. This utilizes the heat from the reaction after the last bed in the first converter.

Topsøe is active both in supplying technology to new plants and in helping proprietary and out-of-house plants transform their existing converters to modern pieces of high-performance equipment. Numerous revamp options are available, ranging from basic process design to complete equipment supply. Amongst Topsøe’s revamp options is an in-situ option that is well suited for bottle-shaped converters. It requires little to no modification of the existing pressure shell, allowing the shortest implementation time. As part of the complete revamp solution, installing Topsøe’s new combination of KM1 in the top converter bed and KM 111 in the lower beds maximizes the benefits to the customer, resulting in increased production and lower energy consumption.

**SUMMARY**

The new KM 111 is Topsøe’s next-generation ammonia synthesis catalyst and is the latest addition to our extensive portfolio of catalysts used in the production of ammonia. It is a state-of-the-art solution to the growing need for more cost-effective ammonia production, which depends heavily on catalyst performance. Topsøe has a strong legacy in high-quality catalysts and technology, and we have used our knowledge and expertise to develop a catalyst that will give customers an exceptional competitive advantage.

The benefits of KM 111 are optimized under the higher ammonia concentrations inherent in the lower converter beds. These benefits include the following:

- More ammonia production due to superior catalyst activity
- More energy-efficient conversion
- Smaller catalyst volumes
- Exceptional stability, resulting in sustained high performance
- Minimal plant downtime due to long catalyst lifetime
- Faster start-up due to shorter reduction times

At the forefront of technology, the catalyst combination of KM1 in the top bed and KM 111 in the lower bed(s) will outperform other catalysts on parameters such as energy efficiency, reliability, and on-stream performance. The advantages become even more pronounced for plants also operating with Topsøe ammonia synthesis technology, most significantly with the industry-leading S-300 basket.

**References**

