Nexant Chem Systems

PERP Program - Ammonia
New Report Alert
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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Ammonia (05/06S11)***. To view the table of contents or order this report, please click on the link below:
http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

Ammonia Process Overview

Commercial synthetic ammonia production started in 1913 and has become a large industry by chemical standards; 2005 world production approached 143 million metric tons. Commercial ammonia synthesis chemistry and catalyst are still based directly on the original developments by Haber and Bosch; variations in reaction equipment, operating conditions, and process schemes, however, have proliferated through the years.

Most of the world's ammonia output is synthetic material manufactured by combining hydrogen and nitrogen over a catalyst according to the following equation:

$$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$$

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The following sections summarize the feedstocks and methods commonly used in the preparation of synthesis gas (containing hydrogen and nitrogen in a 3:1 mole ratio), that is then fed to a converter where it is catalytically transformed into ammonia.

Feedstocks for Ammonia Synthesis

Air is the ultimate source of nitrogen, and methane or heavier hydrocarbons are usually the main source of hydrogen. Of the hydrogen feedstock sources - natural gas, coal, and petroleum fractions - natural gas is the most often employed in commercial ammonia plants, representing about 90 percent of world production. A few commercial plants exist (one in Zimbabwe) that produce hydrogen for ammonia by electrolysis of water; this route requires extremely inexpensive electric power and is rarely used.

Natural gas is favored for several reasons: its availability and ease of delivery as an inexpensive feedstock, its high hydrogen content, and the simplicity and relative lack of expense of plants designed for natural gas. As inexpensive natural gas becomes more available in developing, export oriented regions, the percentage of natural gas based plants will rise even higher. Most ammonia is produced from gas, although other feedstocks are used, such as coal in China.

Hydrogen Production

Hydrogen is produced by steam reforming of natural gas (mainly methane) and is schematically represented by the following reaction:

$$CH_4 + H_2O \xrightarrow{+\text{ Heat}} CO + 3H_2 \qquad (1)$$

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A large amount of heat must be supplied to force reaction 1 in the desired direction. In the primary reformer, heat is externally supplied by burning fuel at an efficiency of about 30 to 40 percent in the radiant zone. In the secondary reformer, heat is generated by partial oxidation of reactants by mixing compressed air with the primary reformer effluent. The oxygen in the air burns some of the process gas and releases heat at efficiency close to 100 percent. At the same time, the nitrogen required for ammonia synthesis is introduced to the process with the air.

As shown in equation 1, carbon monoxide is also produced. The next step in hydrogen production is to react carbon monoxide with water to produce hydrogen. This step is called the water/gas shift conversion and is represented by the following reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 + \text{Heat} \qquad (2)$$

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The purpose of reactions 1 and 2 is to produce a synthesis gas ("syngas") that contains hydrogen, nitrogen and carbon dioxide. However, neither equation 1 nor 2 ever goes completely to the products shown on the right hand side. So, there is always some unreacted methane and carbon monoxide left in the synthesis gas. The argon and other inerts that enter the secondary reformer with the air will also be present in the syngas produced.

Synthesis Gas Purification

The raw syngas leaving the hydrogen production section must be purified before it is suitable as feed to an ammonia synthesis reactor. The impurities in the syngas include carbon dioxide, carbon monoxide, water, methane, and argon.

The first purification step is carbon dioxide removal. This step is accomplished through one of a variety of processes that are available, such as Benfield and activated MDEA. Typically, these processes reduce the carbon dioxide content of the syngas from about 20 percent to less than 0.1 percent. This is done by contacting the syngas with a liquid that either chemically reacts with, or physically dissolves, the carbon dioxide.

The syngas leaving the carbon dioxide removal step contains traces of unreacted carbon monoxide from reaction 2 and residual carbon dioxide from the previous step. Since oxygen bearing compounds would poison the ammonia synthesis catalyst, they must be removed. The process step that removes the carbon oxides is methanation. This chemical reaction converts carbon oxides to methane via the two equations shown below:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad (3)$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad (4)$$

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At this point in the purification sequence, the remaining impurities in the syngas are methane, water, and argon. These impurities may be removed by a variety of techniques, such as by cryogenic treatment or purged out from the downstream ammonia synthesis section.

Ammonia Synthesis

The synthesis gas leaving the purification section is compressed before feeding it to the ammonia synthesis loop where it is combined with recycle gas. This mixture is fed directly to the ammonia converter, where ammonia is formed according to the reaction:

$$3H_2 + N_2 \longrightarrow 2NH_3 \qquad (5)$$

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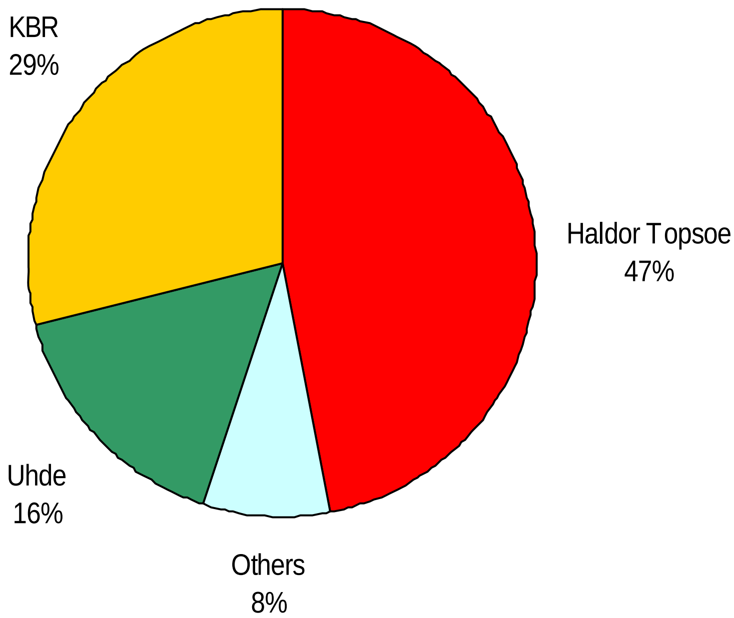
The synthesis reaction is favored by high pressure, but the conversion per pass is limited by reaction equilibrium constraints resulting in unreacted synthesis gas leaving the ammonia converter.

The effluent from the ammonia converter is cooled to condense and separate liquid ammonia from unreacted syngas. Part of this cooling duty is supplied by either air or water cooling, and the balance is provided by a mechanical refrigeration system. The separated unreacted syngas is returned to the ammonia converter as the recycle gas referred to above.

Commercial Ammonia Process Technology Licensors

This section reviews the technical features of modern low energy processes offered by the major licensors of ammonia technology. The following companies (listed in alphabetical order) represent the main suppliers of ammonia technology and cover the full spectrum of process variations: Haldor Topsoe, KBR, Linde, Lurgi AG, and Uhde. These licensors account for more than 92 percent of all ammonia plants being built worldwide. Historically, Kellogg Brown and Root (KBR), Uhde and Haldor Topsoe have had the major share of new greenfield plants. Licensor share since 1990 are shown in Figure 1.

Figure 1
Ammonia Licensor Market Share
(plants built since 1990)



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Production Cost Estimates

Around 90 percent of current global production of ammonia is based on natural gas feedstock, with the remainder coming from older technology based on coal, fuel oil, naphtha etc. Gas based producers have enjoyed the most favorable production economics for some time, and nearly all new ammonia capacity under consideration is based on natural gas. There are some projects in China which use coal as a feedstock. Access to low priced gas feedstock has therefore led to the concentration of new plants in Latin America, the Middle East, and some parts of Asia.

Several cases have been considered for the production of ammonia and presented in this report:

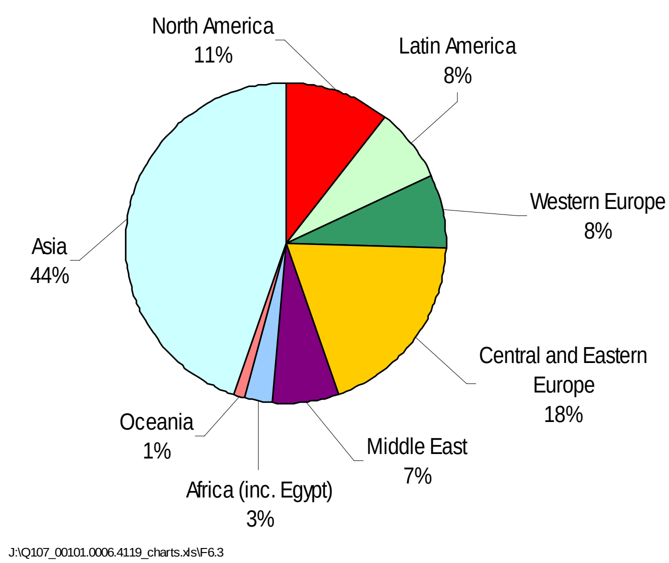
- Conventional process, USGC, 2,000 mtpd
- Conventional process, Middle East, 2,000 mtpd
- Conventional process, Middle East, 3,000 mtpd
- Coal-based process, China, 2,000 mtpd
- KBR Purifier™ Process, Middle East, 2,000 mtpd

Market Overview

Ammonia end use markets are not very diverse, with ammonia being used mainly as a source of nitrogen in fertilizer applications. The highest ammonia market is found in fertilizer applications with urea being the largest end use for ammonia at 49 percent of demand, followed by the use of ammonia in non-fertilizer industrial applications at 16 percent.

Ammonia global capacity has risen at an average annual growth rate of 1.9 percent from 2000 to 2005, approximately from 126 million tons N in 2000 to 139 million tons N in 2005. In 2005, Asia was the largest producer of ammonia (62.3 million tons N) followed by Europe (37 million tons N). Most new ammonia plants are currently being built in areas where natural gas costs are low. Regional distribution of ammonia capacity is illustrated in Figure 2.

Figure 2
Global Ammonia Capacity by Region, 2005



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