Nitrobenzene/
Aniline/
MDI

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Report Abstract
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For further information about these reports, please contact the following:

Dr. Alexander Coker, Global Manager, PERP Program: phone: + 44-207-950-1570, e-mail: acoker@nexant.com
Mrs. Heidi Junker Coleman, Global Support Manager, Multi-Client Programs phone: + 1-914-609-0381, e-mail: hcoleman@nexant.com
Dr. Y. Larry Song, General Manager, Nexant China phone: +86 21 6182 6791, e-mail: ylsong@nexant.com

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INTRODUCTION
Practically all nitrobenzene is consumed as feedstock for aniline production, while about 80 percent of aniline is used in the production of methylene diphenyl diisocyanate (MDI).

MDI is a white to yellow solid at room temperature. It is predominantly produced as the 4,4’-MDI isomer, but the 2,4 and 2,2 isomers are also formed in small quantities.

MDI is a high volume, high value chemical, with demand in terms of millions of tons per annum. Capacity growth rates are predicted to be double digit in China between 2011 and 2016. Some new MDI production is also expected to come on stream in South Korea and the Middle East in the next five years.

With a high MDI demand growth expected, the effect on demand for the whole value chain will be considerable. Therefore Nexant has taken a thorough look at the market dynamics, production routes and process economics.

COMMERCIAL TECHNOLOGY

Nitrobenzene
The chemistry behind nitrobenzene production is relatively simple and the production technology is mature. The nitration of benzene by mixed acid (also called nitrating acid), proceeds by the formation of nitronium ion, \( \text{NO}_2^+ \). The nitronium ion is formed by the reaction of the mixed acids (nitric acid with concentrated sulfuric acid) as shown below:

\[
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-
\]

The nitronium ion formed in this way is then attacked by the aromatic ring to give nitrobenzene:

\[
\text{C}_6\text{H}_4 + \text{NO}_2^+ \rightarrow \text{C}_6\text{H}_4\text{NO}_2 + \text{H}^+
\]

The following nitrobenzene production processes are discussed in the report:
Nitrobenzene/Aniline/MDI

- NORAM technology
- Chematur technology
- Meissner technology
- Dupont technology

Aniline

Aniline is produced commercially by catalytic hydrogenation of nitrobenzene. (A route involving phenol amination was previously used but is no longer employed; Sunoco Chemical shut down its U.S. plant in 2002 due to mechanical problems and Mitsui in Chiba, Japan closed its plant in 2009 due to poor economics.)

The highly exothermic catalytic hydrogenation of nitrobenzene (heat of reaction about 544 kilojoules per mol) is carried out commercially in the presence of excess hydrogen in both the vapor phase and the liquid phase.

\[
\text{NO}_2 + 3\text{H}_2 \rightarrow \text{NH}_2 + 2\text{H}_2\text{O}
\]

The use of purer grades of hydrogen serves to reduce reactor and recycle compressor sizes, vent losses, and energy requirements.

Vapor-phase processes may employ either fixed-bed (e.g., Bayer) or fluidized-bed reactors (e.g., BASF). Copper or palladium on activated carbon or an oxidic support, in combination with other metals (lead, vanadium, phosphorous, and chromium) as modifiers/promoters, has been shown to be an effective catalyst for vapor-phase hydrogenation, achieving high activity and selectivity.

The following aniline production processes are discussed in the report:

- Vapor-phase process technology including overviews of the processes developed by BASF, Bayer, BorsodChem/Yantai Wanhua, and Sinopec
- Liquid phase process technology including overviews of the processes developed by Dupont, Huntsman, Chematur, and Bechamp

MDI

MDI is produced in monomeric and polymeric forms by the acid-catalyzed, liquid phase condensation of aniline and formaldehyde, followed by the liquid phase phosgenation of diphenylmethane diamine (MDA) to MDI.

The process chemistry and technology for production of MDA and MDI are discussed, including overviews of the technologies owned by BASF, Bayer, Chematur, Dow, Huntsman, and Yantai Wanhua.
The vapor phase phosgene route to MDI is briefly discussed.

DEVELOPMENTS IN NON-PHOSGENE TECHNOLOGY

Phosgene is an extremely toxic chemical that requires rigorous process design standards to protect the health and safety of workers. Investment requirements are increased by the need for close analytical monitoring and control, equipment designs for lethal service, and treatment of vent streams by caustic scrubbing or incineration. Toughening of worldwide environmental restrictions has added impetus to the search for a non-phosgene route to isocyanates.

This section of the report reviews potential non-phosgene routes for MDI production. Most of the proposed routes are via the intermediate product, dimethyl methylene diphenyl 4,4’-dicarbamate (MDC), which then undergoes thermal decomposition into MDI and methanol, although Asahi proposed a route via ethyl phenylcarbamate (EPC) in the early 1980s.

MDC can be produced via the reaction of methyl-N-phenyl carbamate (MPC) and formaldehyde, or through the reaction MDA (an intermediate in the traditional phosgene route) and with dimethyl carbonate (DMC).

An alternative non-phosgene route was proposed by Asahi in the 1980s, via ethyl phenyl carbamate (EPC). The chemistry and a process flowsheet are also presented in this section, to compare with routes via MDC.

In all the non-phosgene methods proposed, the carbamate is thermally decomposed to produce MDI and byproduct methanol, by-passing the phosgenation step.

PROCESS ECONOMICS

Process economics have been developed for the following:

- Nitrobenzene cost of production via benzene nitration using NORAM technology
- Nitrobenzene cost of production via benzene nitration using Chematur technology
- Aniline production via liquid phase hydrogenation of nitrobenzene using DuPont technology
- Aniline production via liquid phase hydrogenation of nitrobenzene using Chematur technology
- Aniline production via the vapor phase hydrogenation of nitrobenzene using BASF technology
- MDI production via acid catalyzed condensation of aniline with formaldehyde to MDA followed by liquid phase phosgenation of MDA to MDI using generic process technology (large scale)
- MDI production via acid catalyzed condensation of aniline with formaldehyde to MDA followed by liquid phase phosgenation of MDA to MDI using Chematur process technology (small scale)
The above cost estimates highlight the different process performances as they are all compared on a same capacity and United States Gulf Coast (USGC) location basis. However, other regions are important. Therefore, Nexant has also developed a regional analysis for the production of all processes on China, Middle East and Western Europe bases.

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate (a simple nominal return on capital is also included).

COMMERCIAL MARKET REVIEW

Applications

Nitrobenzene is used almost completely (97 percent) in the production of aniline. The remaining three percent of nitrobenzene goes into a variety of miscellaneous uses, including explosives, dyes and pigments, pesticides, drugs, and solvent use.

Aniline, in turn, is used primarily (75 to 85 percent depending on world region) for the production of methylene diphenyl diisocyanate (MDI). The next largest end use is as an intermediate for rubber-processing chemicals, such as vulcanization accelerators, antioxidants, antiozonates, and stabilizers. A smaller end use is as an intermediate for pesticides (fungicides), herbicides, and other agricultural chemicals. Dyes and pigments were at one time the most important use for aniline, but now represent only a few percent of the total. Miscellaneous uses for aniline include cyclohexylamine (boiler water treatment, rubber chemicals), pharmaceuticals, textile chemicals, photographic developers, amino resins, explosives, and specialty fibers (Kevlar, Nomex). An emerging specialty use for aniline is in the preparation of fuel cell membranes.

Polymeric MDI is primarily used for polyurethane foams such as rigid foams for construction, insulation and packaging. Monomeric MDI which accounts for less than 25 percent of production output is used in coatings, adhesives, sealants and elastomers (CASE) applications. Small quantities of ortho-MDI (OMDI) and liquefied-MDI (LMDI) are also produced. MDI producer capacity share is illustrated in the figure below.
Figure 1  Global MDI Capacity Share by Producer

Regional Market Review
The following is presented:

- Nitrobenzene global capacity, with a list of each nitrobenzene plant showing specific plant capacities, owning company, location and annual tonnage produced.
- Nitrobenzene new plant builds expected to come on stream between 2012 and 2016.
- Aniline global capacity, with a list of each nitrobenzene plant showing specific plant capacities, owning company, location and annual tonnage produced.
- Aniline new plant builds expected to come on stream between 2012 and 2016.
- MDI global capacity, with a list of each nitrobenzene plant showing specific plant capacities, owning company, location and annual tonnage produced.
- MDI new plant builds expected to come on stream between 2012 and 2016.
- MDI global supply, demand, and trade with forecast to 2015 with breakdown for regions of North America, Western Europe, China, Japan and Rest of World.
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