

CHEMSYSTEMS PERP PROGRAM

Developments in Toluene Diisocyanate (TDI) Process Technology

Comparison of Production Costs & Technology for Bayer's Gas-Phase Phosgenation (GPP) process, EniChem's Urethane Pyrolysis (Non-Phosgene), and Conventional Liquid-Phase Phosgenation Routes. Regional Supply/Demand Forecasts.

PERP07/08S9

October 2008

6 Nexant

CHEMSYSTEMS PERP PROGRAM

PERP07/08S9

Developments in Toluene Diisocyanate (TDI) Process Technology

October 2008



44 South Broadway, White Plains, New York 10601, USA Tel: +1 914 609 0300 Fax: +1 914 609 0399

The ChemSystems Process Evaluation/Research Planning (PERP) program is recognized globally as the industry standard source for information relevant to the chemical process and refining industries. PERP reports are available as a subscription program or on a report by report basis.

Nexant, Inc. (www.nexant.com) is a leading management consultancy to the global energy, chemical, and related industries. For over 38 years, ChemSystems has helped clients increase business value through assistance in all aspects of business strategy, including business intelligence, project feasibility and implementation, operational improvement, portfolio planning, and growth through M&A activities. Nexant has its main offices in San Francisco (California), White Plains (New York), and London (UK), and satellite offices worldwide.

For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: http://www.chemsystems.com.

Copyright © by Nexant Inc. 2009. All Rights Reserved.

1. INTRODUCTION

Toluene diisocyanate (TDI) is an important intermediate in the production of polyurethanes. TDI is based on toluene as the primary hydrocarbon feedstock. Amine functionality is introduced by di-nitration of the toluene, followed by hydrogenation. The resulting diamine is converted to the corresponding diisocyanate, usually by reaction with phosgene.

The main application for TDI is in polyurethane foams. The other component of polyurethane foams is polyols (polyhydric alcohols) that are made by polymerizing alkylene oxides (primarily propylene oxide, though some ethylene oxide is also used) with a range of initiator compounds. Depending on the components selected and how they are combined, end products with diverse properties can be produced.

Demand is driven by the main TDI application in flexible polyurethane foams (used in furniture, automotive seating, carpet underlay, and bedding), which accounted for about 85 percent of global consumption in 2008, as seen in the figure below. The balance of demand is accounted for by coatings, adhesives, sealants, and urethane elastomers.

Polyurethane elastomers are valued particularly for their toughness, flexibility, and abrasion resistance and find use in premium applications such as automotive bumper covers and fascias, industrial rollers, sport soles and boots, and mechanical goods. Polyurethane coatings compensate for their relatively high cost with excellent durability, resistance to corrosion and abrasion, and flexibility. They are typically used in high-performance applications such as automotive refinishing, wood finishing, and corrosion protection.



Global TDI Demand by End-Use

Q308_00101.0008.4117-Charts.xls\F7.1

ChemSystems PERP report on TDI deals with the technological, economic, and commercial aspects of TDI production. Conventional and developing processes, including Bayer's new gas-phase process, are discussed and evaluated.

2. CHEMISTRY

Toluene diisocyanate (TDI) is currently produced via a three-step process:

- Nitration of toluene to dinitrotoluene (DNT)
- Reduction of dinitrotoluene to toluene diamine (TDA)
- Phosgenation of TDA to TDI

The majority of TDI manufacturing is carried out on integrated plant sites, combining all three process operations.

2.1 Nitration

Toluene is nitrated in two steps, the first producing the three isomers of mononitrotoluene. In the second step, the mixed mononitrobenzene isomers are further nitrated resulting in dinitrotoluene isomers. The production of 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) are favored in this step.

Current technology uses a mixture of two acids, typically strong sulfuric acid and nitric acid, for the nitration reaction. The concentration of mixed acid is carefully controlled so that very little trinitrotoluene is produced. Spent acid is recovered, purified, and reconstituted with nitric acid for recycle back to the nitration reaction. The use of only nitric acid instead of a sulfuric/nitric acid mixture is discussed in this report.

2.2 Reduction

Dinitrotoluene (80/20 weight percent of 2,4-DNT/2,6-DNT) produced in the nitration step is dissolved in methanol and reduced continuously by reaction with hydrogen in the presence of a suitable catalyst.

The DNT isomers are reduced to their corresponding diamines in approximately the same proportion (no isomerization takes place, although a small amount of degeneration occurs), thus the final product is usually identified as 80/20 TDA.

One of the features of this report is a discussion of the variations in process by different manufacturers. Brief outlines are as follows:

It has been reported that Bayer uses a modified Raney catalyst, produced by treating an alloy made up mainly of aluminum, nickel and/or cobalt, and a modifying material with an alkali metal. This catalyst permits reaction at a higher temperature, allowing for recovery of the exothermic heat of reaction in the production of low-pressure steam. The catalyst is separated from the TDA product and the methanol solvent is subsequently removed by distillation. Conversion of DNT to TDA is essentially quantitative.

Meanwhile, BASF has developed a preparation method using a small amount of carbon monoxide in the hydrogen feed to the reactor. Excellent yields are reported

Mitsui Toatsu has developed a continuous process whereby TDA containing some water is used as the solvent. Excellent conversion is reported.

2.3 Phosgenation

The 80/20 TDA produced by any of the above processes is converted to diisocyanate by reaction with phosgene:



Q308_00101.0008.4117-1.cdx

Batch phosgenation process: A 10 to 20 percent solution of the TDA isomers is prepared in monochlorobenzene, *ortho*-dichlorobenzene, or other suitable solvent, and is mixed at ambient temperature with excess liquid phosgene or a solution of phosgene in the same solvent.

Continuous phosgenation process: The same raw materials are reacted at ambient temperature to produce a slurry of toluene dicarbamoyl chloride isomers. This slurry is then pumped into a single (or series) reactor where carbamoyl chloride is converted to isocyanate at elevated temperatures.

BAYER GAS-PHASE PROCESS: Bayer has developed a gas-phase phosgenation (GPP) process for the production of TDI from TDA. The main difference from conventional TDI processes is in the use of gas-phase reaction of TDA and phosgene, as opposed to these reactants being handled as dilute solutions in a solvent such as *ortho*-dichlorobenzene.

The gas-phase phosgenation technology results in significant savings on solvents, leading to operating cost savings due to a reduction in energy consumption required to process the much smaller volume of solvent during distillative recovery. The much shorter residence time of TDA and phosgene in the reactor reduces the required phosgene process inventory considerably. Further benefits are significantly greater reactor throughput per unit time (space-time yield) and the ability to downsize key plant components. These size reductions, lead to additional investment cost savings. The gas-phase technology also provides improved reaction selectivity, generating fewer byproducts. Process safety is vastly improved by the reduction in both phosgene and solvent inventories within the process. A further safety enhancement is the ability to start up and shut down the gas-phase process quickly.

EniChem Urethane Pyrolysis (Non-Phosgene) Process: Here, oxidative carbonylation of methanol is used to produce dimethyl carbonate (DMC). DMC is then reacted with TDA to give a urethane intermediate which is then cracked at high temperature and low pressure to give TDI.



3. ECONOMIC COMPARISON

The economics (investment, cost of production and sensitivity to plant capacity) for the following TDI processes are compared and evaluated:

- The Bayer Gas-Phase Phosgenation route
- The Conventional Liquid-Phase Phosgenation route and
- The EniChem Urethane Pyrolysis (Non-Phosgene) route

Under the pricing scenario used, economic comparisons for these TDI processes indicate that the gas-phase phosgenation route to TDI shows an advantage over the conventional liquid-phase phosgenation route. Similarly, the liquid-phase phosgenation route shows an advantage over the non-phosgene route utilizing TDA and DMC as feedstocks.

4. MARKET OVERVIEW

Some of the items discussed in the market review include:

- Global TDI demand forecast for 2008-13.
- Supply by region and producer.
- Supply/Demand balance (operating rates/capacity)





Nexant, Inc.

San Francisco London Tokyo Bangkok New York Washington Houston Phoenix Madison Boulder Dusseldorf Beijing Shanghai Paris

www.chemsystems.com