

Lecture 8

**Aromatics Product Profile,
Ethyl Benzene & Styrene,
Cumene & Phenol, Bisphenol,
Aniline**

LECTURE 8

AROMATICS PRODUCT PROFILE, ETHYL BENZENE & STYRENE, CUMENE AND PHENOL, BISPHENOL, ANILINE

Aromatics are backbone of organic chemical industries. Aromatic hydrocarbons especially benzene, toluene, xylene (BTX), and ethyl benzene are major feedstock for large number of intermediates which are used in the production of synthetic fibers, resins, synthetic rubber, explosives, pesticides, detergent, dyes, intermediates, etc. Styrene, linear alkyl benzene, and cumene are the major consumer of benzene. Product profile of aromatics is shown in [Figure M-VII 8.1](#).

Global production and consumption of benzene in 2009 were between 36.4 and 36.6 million metric tons. Average global capacity utilization was 69.2percent in 2009, lower than in 2008. Global benzene consumption is estimated to have decreased by 3.8percent in 2009; however, it is expected to average growth of 4.7percent per year from 2009 to 2014, and 2.6percent per year from 2014 to 2019 [[Petrochemical overview, SRI consulting](#)]. Ethyl benzene/styrene monomer and cumene/phenol with demand shares of 52.6percent and 18.3percent respectively of the global benzene market respectively are the leading end-use segments for benzene in 2010. Other uses such as cyclohexane, nitrobenzene and LAB collectively consumed less than 15percent of global benzene demand in 2010 [[Styrene market & Asian demand to drive global benzene markets” Chemical weekly November 22, 2011, p.205](#)].

Global production and consumption of toluene in 2009 were each almost 18.4 million metric tons. Global capacity utilization was 64percent in 2009. Toluene consumption estimated to have decreased by almost 2percent in 2009. Demand is expected to grow on average 3.6percent per year from 2009 to 2014, and 2.2 percent per year from 2014 to 2019 [[Petrochemical overview, SRI consulting](#)].

Global production and consumption of mixed xylenes in 2009 were each approximately 41 million metric tons. Global capacity utilization was around 74percent in 2009. Xylenes consumption in 2009 is estimated to have increased by around 4.6percent from 2008; it is

expected to average growth of 5.2percent per year from 2009 to 2014, and 3.3percent per year from 2014 to 2019. Operating rates are expected to drop in 2010 but gradually increase afterward [[Petrochemical overview, SRI consulting](#)]. Product profiles of major aromatics-BTX are given in [Table M-VII 8.1](#).

Table M-VII 8.1: World Aromatic Petrochemicals Scenario

Product	Consumption 2002 ('000 tonnes)	Consumption Growth (in%)			Capacity 2002 ('000 tonnes)	Announced Capacity Due by 2012 ('000 tonnes)	Capacity Change Needed by 2012 2002 after Announcement	
		1997-2002	2002 - 2007	2007 - 2012			('000 tonnes)	(%)
Benzene	33,278	3.5	4.2	2.8	43,945	4,443	5,765	13
Toluene	16,688	1.9	3.5	2.4	24,642	1,184	900	4
Ethyl benzene	25,130	4.2	3.5	2.7	27,536	5,948	3,593	13
Styrene	22,188	3.9	3.5	2.7	23,742	6,087	6,647	28
Mixed Xylenes	29,187	5.7	5.1	4.1	36,784	6,640	9,775	27
Xylene	3,050	3.4	4.5	2.7	3,948	498	760	19
p-Xylene	18,701	6.2	5.8	4.6	20,605	7,359	7,320	36
Cumene	9,214	5.8	4.7	2.6	10,612	505	3,445	32
Phenol	7,166	5.2	4.4	1.7	7,843	1,262	2,078	26
Caprolactam	3,746	6.1	3.1	3.3	4,566	448	750	16
Terephthalic Acid	24,822	8.2	5.9	5.0	26,168	8,038	12,000	46
Phthalic Anhydride	3,488	3.5	4.1	2.5	4,374	358	700	16
Dimethyl Terephthalate	3,747	-3.7	1.5	0.5	4,710	53	65	1
TDI	1,383	3.9	4.1	3.7	1,809	932	0	0

Source: Chemistry Industry News, March 2004

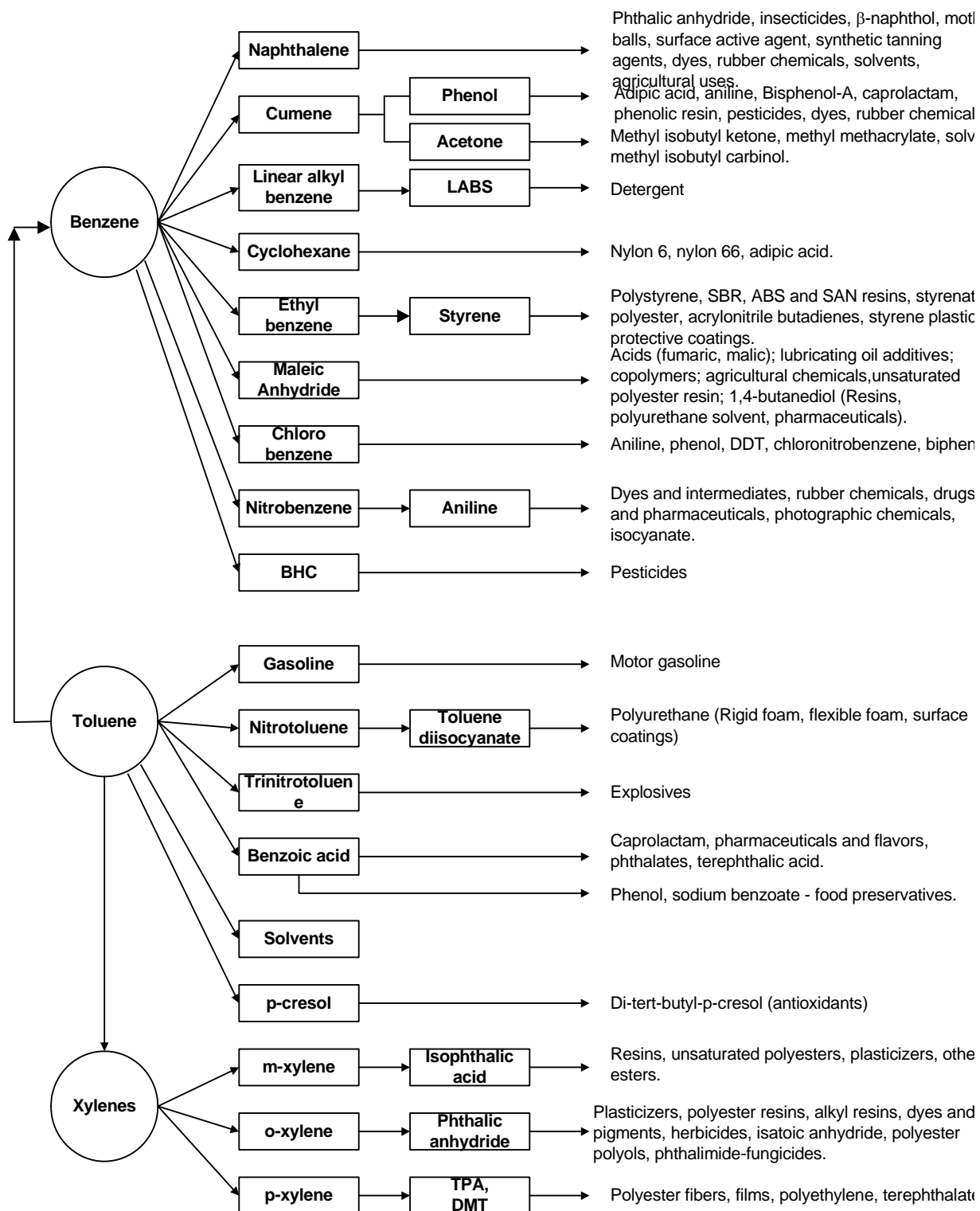


Figure M-VII 8.1: Product Profile of Aromatics

Global production and consumption of p-xylene in 2009 were each approximately 27.6 million metric tons. Global capacity utilization was 83percent in 2009, unchanged from 2008. p-Xylene consumption is estimated to have increased by approximately 4.7percent in 2009; it is expected to average growth of 5.5percent per year from 2009 to 2014, and 3.5percent per year from 2014 to 2019[Petrochemical overview, SRI consulting].

Global production and consumption of o-xylene in 2009 were approximately 3.7 million metric tons. Global capacity utilization was 66percent in 2009. o-Xylene consumption is estimated to have increased slightly in 2009; it is forecast to average growth of 3.2percent per year from 2009 to 2014, slowing to 2.4percent per year from 2014 to 2019. Average global utilization rates are expected to remain in the 70s range throughout the forecast period [Petrochemical overview, SRI consulting].

ETHYLY BENZENE AND STYRENE

Ethyl benzene and styrene are two important aromatics. Ethyl benzene is mainly used for making styrene. Styrene which finds application in synthetic rubber and polymer industry for the manufacture of SBR and polystyrene, ABS plastic.

Major route for styrene manufacture is dehydrogenation of ethyl benzene which is manufactured by alkylation of benzene. Styrene plant consists of two major units. The process involves:

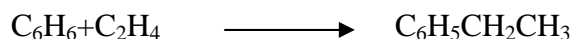
- Production of ethylene either from molasses route or by naphtha/natural gas cracking
- Production of ethyl benzene by alkylation of benzene
- Dehydrogenation of ethyl benzene to styrene

ETHYL BENZENE

Ethyl benzene is made by alkylation of benzene with ethylene. Ethylene can be produced from either from molasses route or naphtha/gas cracker. The convention alkylation catalysts are metal chlorides (BF₃, AlCl₃, etc) and mineral acids (HF, H₂SO₄). However, with development of zeolite, now the benzene alkylation I is done by using ZSM-5 catalysts using vapor-phase process [Mobil-badger Process] and liquid phase alkylation using MCM-22 azeolite proprietary catalyst based catalyst.

Vapour Phase Alkylation of Benzene: The process consists of vapor phase alkylation of benzene with ethylene using zeolite catalyst in a fixed bed catalytic distillation technology. Alkylation and distillation takes place in the alkylator. Unreacted ethylene, and benzene vapour are condensed and fed to the finishing reactor where the remaining alkylation is completed in the presence of a catalyst. The product stream goes to fractionating columns where ethyl benzene is separated from the higher ethylated benzene and heavy ends. Higher ethylated alkyl benzene is sent to the trans-alkylator where its trans-alkylated to produce additional ethyl benzene [Petrochemical Processes 2003” Hydrocarbon processing March1999, p.10]

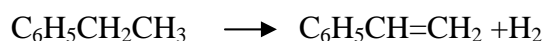
Liquid Phase Alkylation Of Benzene With Ethylene Using MCM-22 Catalyst:In this process alkylation of ethylene takes place in a liquid filled alkylator reactor containing multiple fixed beds of MOBIL MCM-22 catalyst. During alkylation Ethyl benzene and small quantity of polyethylbenzene are formed which is converted to ethyl benzene using trans-alkylation catalyst. The product streams from alkylator and trans-alkylator are sent to various fractionating columns for separation of product ethyl benzene, polyethylbenzene, benzene, gases and heavy ends.



STYRENE

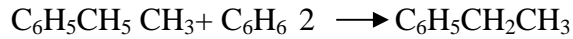
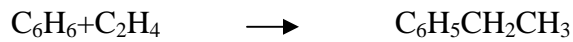
Styrene is one of the most important monomers for the production of polymers, resins and rubber. The biggest consumer of styrene monomer is polystyrene, other major derivatives are expanded polystyrene, Styrene butadiene(SB) latex, SB rubber, styrene block co-polymers (eg: ABS, MBS, SBS) [SNOW: an innovative technology for styrene synthesis, hydrocarbon asia,2007,p.42]

Styrene is made by catalytic dehydrogenation of ethyl benzene

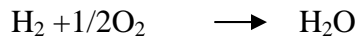


Styrene can be also directly recover from raw pyrolysis gasoline derived from cracking of naphtha, gas oils Using GT styrene process

Lumus/UOP EB One Process: Styrene is made by catalytic dehydrogenation of ethylbenzene in the presence of steam. In Lumus/UOP EB one process involves first alkylating benzene with ethylene followed by dehydrogenating the EB to form styrene. The benzene and recycled benzene are preheated the liquid phase reactor containing zeolite catalyst. The polyethylbenzene formed during alkylation is fed to another reactor for transalkylating with benzene. Transalkylation reaction is isothermal and reversible in distillation section. The reactor effluent from both reactions is sent to the distillation section for separating ethyl benzene from polyethylbenzene.



Ethyl benzene and recycled ethyl benzene are then dehydrogenated to styrene in the presence of steam at high temperature (550-680°C) under vacuum in a multistage reactor



During dehydrogenation stages air or oxygen is introduced to partly oxidize the hydrogen to preheat the process gas and to remove the equilibrium constraint for dehydrogenation reaction. [HC,1999]. Reactor effluents are cooled to recover waste heat and condensed, uncondensed gases are used as fuel. The condensed product containing styrene is sent to distillation columns for separating styrene monomer, unconverted ethyl benzene is recycled.

Toluene is formed during the process which is recovered



GT Styrene Process: Styrene can be also directly recovered from raw pyrolysis gasoline derived from cracking of naphtha, gas oils Using GT styrene process. Raw pyrolysis gasoline is fractionated into a heart cut C8 stream from which styrene is separated by extractive distillation.

Innovative SNOW Technology: The snow technology has been jointly developed by Snamprogetti and Dow represents a technological and economical breakthrough in styrene production and uses benzene and ethane as raw material which is dehydrogenated in the same reaction for EB dehydrogenation. SNOW reactor is rise type [SNOW: an innovative technology for styrene synthesis, hydrocarbon asia,2007, p.42].

PHTHALIC ANHYDRIDE

Phthalic anhydride first became commercially important during the nineteenth century as an intermediate for dyestuff industry. However, now phthalic anhydride is largely used for the manufacture of plasticizers, alkyd resins, and unsaturated polyester resins where about 95percent of the phthalic anhydride production is consumed. With an aggregate installed capacity of 267,200-tpa across India, major PAN producers include IG Petrochemicals Ltd and Thirumalai chemicals Ltd. Consumption pattern of PAN is shown in Figure M-VII 8.2. List of the phthalic anhydride manufacturer in India is given in Table M-VII 8.2.

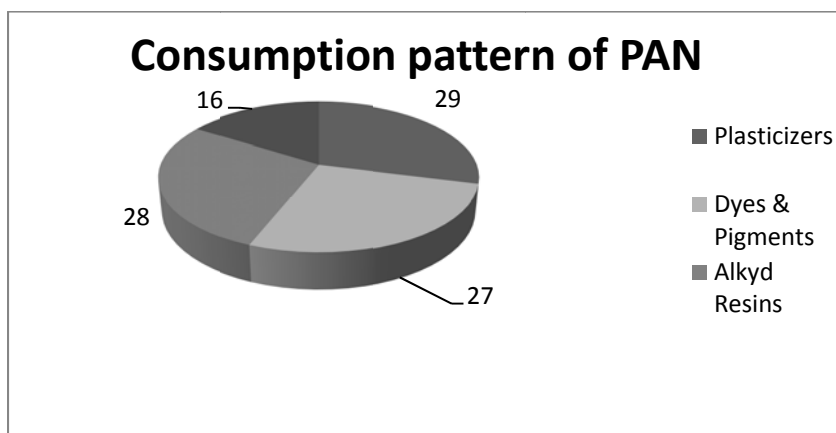


Figure M-VII 8.2: Consumption pattern of PAN

Source: Dutta, P.” Phthalicanhydride: A Techno-commercial Profile Part I: Indian Scenario, Chemical Weekly Jan1,2008 p.209

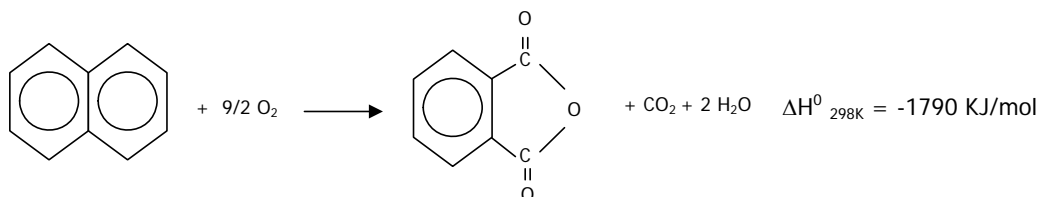
Table M-VII 8.2: Phthalic Anhydride Manufacturer in India

Company	Location	Installed Capacity (TPA)
I.G. Petrochemicals Ltd.	Taloja, Maharashtra	120,000
Thirumalai Chemicals Ltd.	Ranipet, Tamil Nadu	100,000
Asian Paints Ltd.	Ankleshwar, Gujarat	25,200
Mysore Petrochemicals Ltd.	Raichur, Karnataka	12,000
S.I. Group Ltd.	Thane, Maharashtra	10,000
Total		267,200

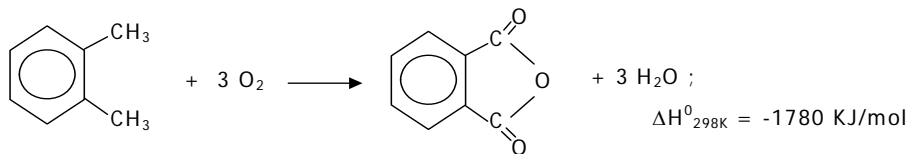
Source: Dutta, P." Phthalicanhydride:A Techno-commercial Profile Part I: Indian Scenario, Chemical Weekly Jan1,2008 p.209

The basic raw material for the manufacture of phthalic anhydride is naphthalene and o-xylene. Phthalic anhydride was manufactured from naphthalene. With the availability of large amount of o-xylene as a byproduct during p-xylene production, now phthalic anhydride is made from o-xylene. Both vapor phase and liquid phase oxidation of o-xylene are available.

Phthalic anhydride is produced by oxidation of naphthalene in the gas phase using vanadium pentoxide catalyst supported on silica or silicon carbide promoted with various other metal oxides, e.g. titanium oxide (wire) in either a fixed bed multiple reactors or fluidized bed reactor



Production of phthalic anhydride from o-xylene is similar to naphthalene route. Catalytic oxidation of o-xylene is done either in fixed bed catalytic reactor having multi tube or fluidised bed reactor in the presence of vanadium pentoxide and titanium oxide catalyst.



CUMENE

Cumene is made by alkylating benzene with propylene using zeolite catalyst. Following three major processes are available

Catalytic Distillation Technology: The process uses a specially formulated zeolite alkylation catalyst in a proprietary catalytic distillation (CD) process and a trans-alkylator reactor using zeolite catalyst. In CD column combines both reaction and fractionation takes place.

Liquid Phase Q-max Process: In this process, cumene is produced by liquid phase alkylation of benzene with propylene in presence of zeolite catalyst.

Cumene by Mobil Badger Process: The process produces cumene from benzene and any grade of propylene using a new generation of zeolite catalysts from Exxon m Mobil. The process includes a fixed bed alkylation reactor and a fixed bed trans-alkylation reactor and distillation section.

PHENOL

According to SRI consulting report 2010 global production and consumption of phenol were both around 8.0 million tones with global capacity utilization of 77percent. Phenol consumption is expected to average growth of 5.1percent per year from 2009 to 2014 and around 2.5percent from 2014-19. Phenol is consumed mainly for production of bisphenol A and phenolic resins which accounted for 42percent and 28percent respectively of total phenol consumption in 2009.

Various routes for Phenol:

- Phenol from Cumene
- Phenol from Benzoic acid
- Phenol from chlorobenzene
- Benzene Sulphonation

With the availability of propylene now phenol is made by cumene route with added advantage of acetone as by product

ANILINE

The process of aniline manufacture involves two stages: Company which produce aniline is given in [Table M-VII 8.3](#).

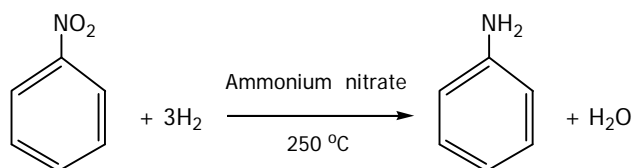
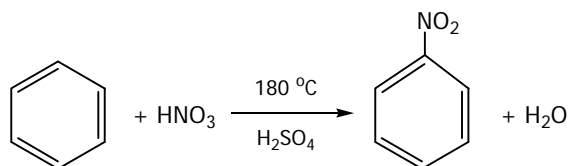
Table M-VII 8.3: Company-Wise Production of Aniline

Company	Years	Production	Sales Quantity	Sales Value
Gujarat Narmada Valley Fertilizers Ltd.	2008-09	27077	27090	1865
	2009-10	33848	33825	2167
	2010-11	39896	-	-
Hindustan Organic Chemicals Ltd.	2009-10	5538	5231	309
	2010-11	1833	1826	135

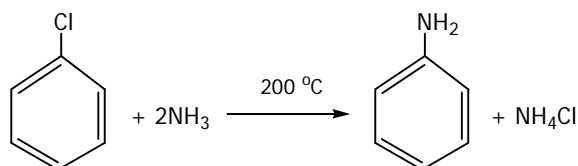
Source: Chemical Weekly January 24, P-198, 2012.

Nitrobenzene Route:

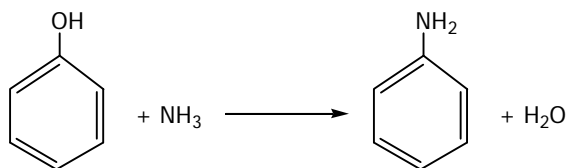
- Nitration of benzene with nitric acid
- Hydrogenation of nitrobenzene to aniline



Ammonolysis of Chlorobenzene



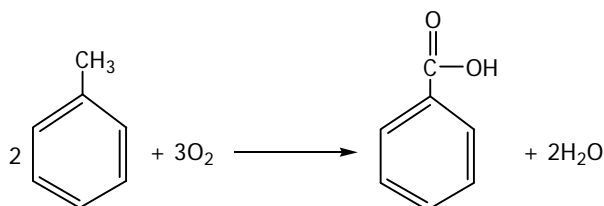
Ammonolysis of Phenol



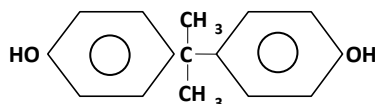
BENZOIC ACID (C₆H₅COOH)

Benzoic acid is the simplest member of the aromatic carboxylic acid. Benzoic acid, which is used in the manufacture of caprolactam, phenol, terephthalic acid and used as mordant, is manufactured by liquid phase catalytic oxidation of toluene in presence of cobalt acetate at 165 °C and 11.2 atm pressure. Major processing steps in the manufacture of benzoic acid consist of:

- Catalytic liquid phase air oxidation of toluene
- Stripping of unreacted toluene and light end precursors from the benzoic acid for recycle
- Distillation to recover benzoic acid as a pure overhead product



BISPHENOL



Bisphenol is an important building block and its measure use is in the manufacture of polycarbonate plastic and epoxy resins. Other uses include in flame retardants, unsaturated polyester resin and polyacrylate, polyetherimide and polysulphone resin [[Chemical weekly, 2008](#)].

India and Global demand of Bisphenol [[Chemical business, 2012](#)]

Demand of bisphenol in India during 2010-11 was 30,000 tonnes per annum

Global installed capacity: around 5.2 million tones

Global demand around 4.2 million tones

Global growth rate in demand 5 to 6percent

Polycarbonate resin are the largest and fast growing BPA market, consuming 60percent of the global production.

Process Technology

Various process technologies available for manufacture of bisphenol are:

- Condensation of phenol with acetone
- Condensation of phenol with alkenyl phenol
- Condensation of phenol with ethylene and acetylenes
- Condensation of phenol with alkyl benzene

Bisphenol From Phenol And Acetone: Bisphenol is synthesized by a condensation reaction between phenol and acetone using proprietary cation exchange resin-base catalyst (4PET) in a packed bed reactor. The catalyst has higher acetone conversion, higher BPA selectivity and longer life. Reactor effluents are process in series of distillation column for separation of product bisphenol, unreacted acetone, water, phenol. Phenol and acetone are recycled. Bisphenol is purified by crystallization where bisphenol crystals are separated from the impurities. Although the impurities are removed with mother liquor, however two stage crystallistion can lower the impurities captured in the crystal. Bisphenol is sent to prilling tower to get final bisphenol in the form of spherical prill.

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