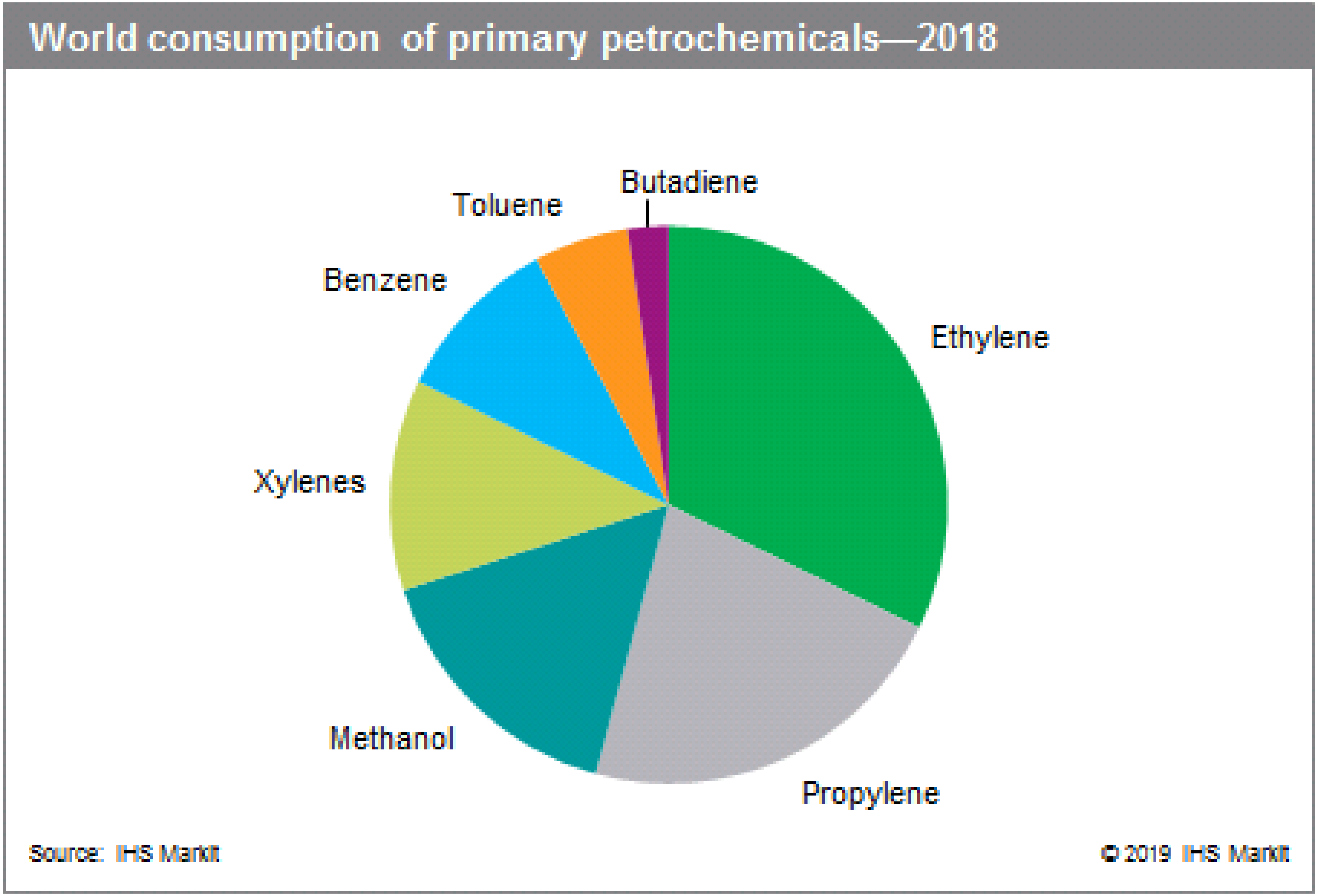
Benzene derivatives

Dr. Ákos Fürcht

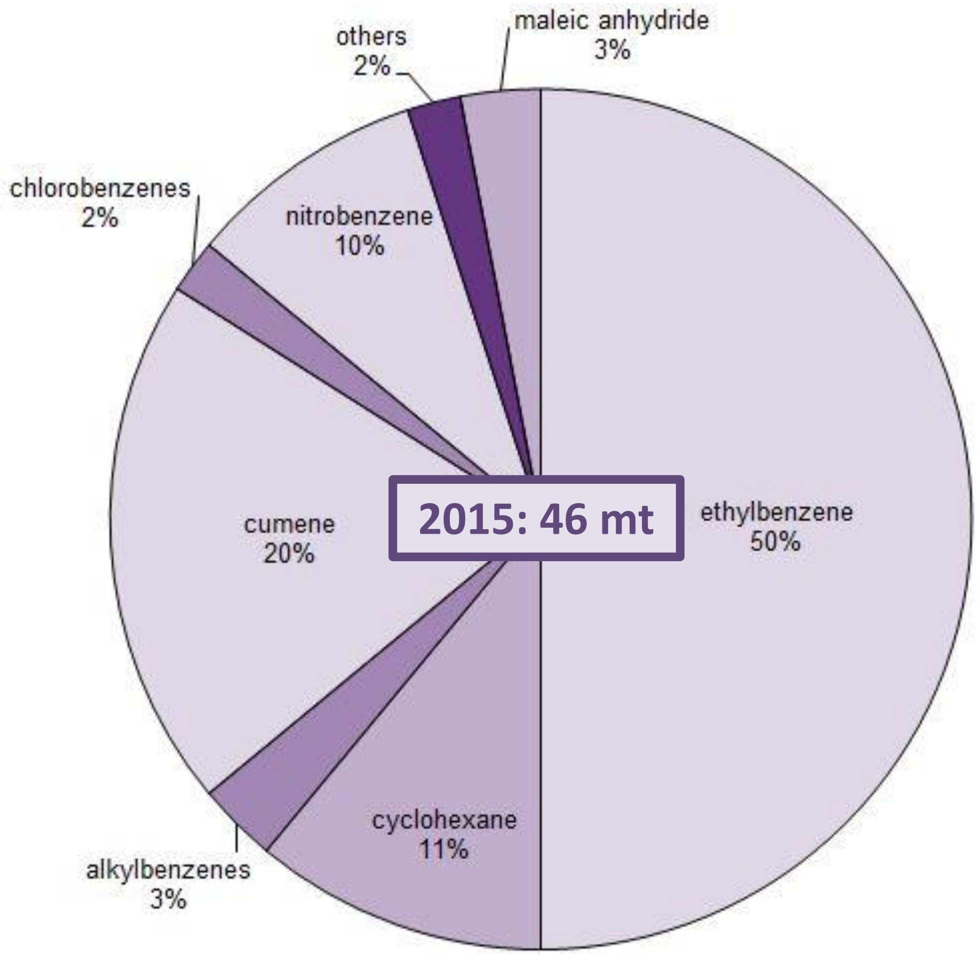
2019

BME



Source: https://ihsmarkit.com/products/petrochemical-industry-chemical-economics-handbook.html

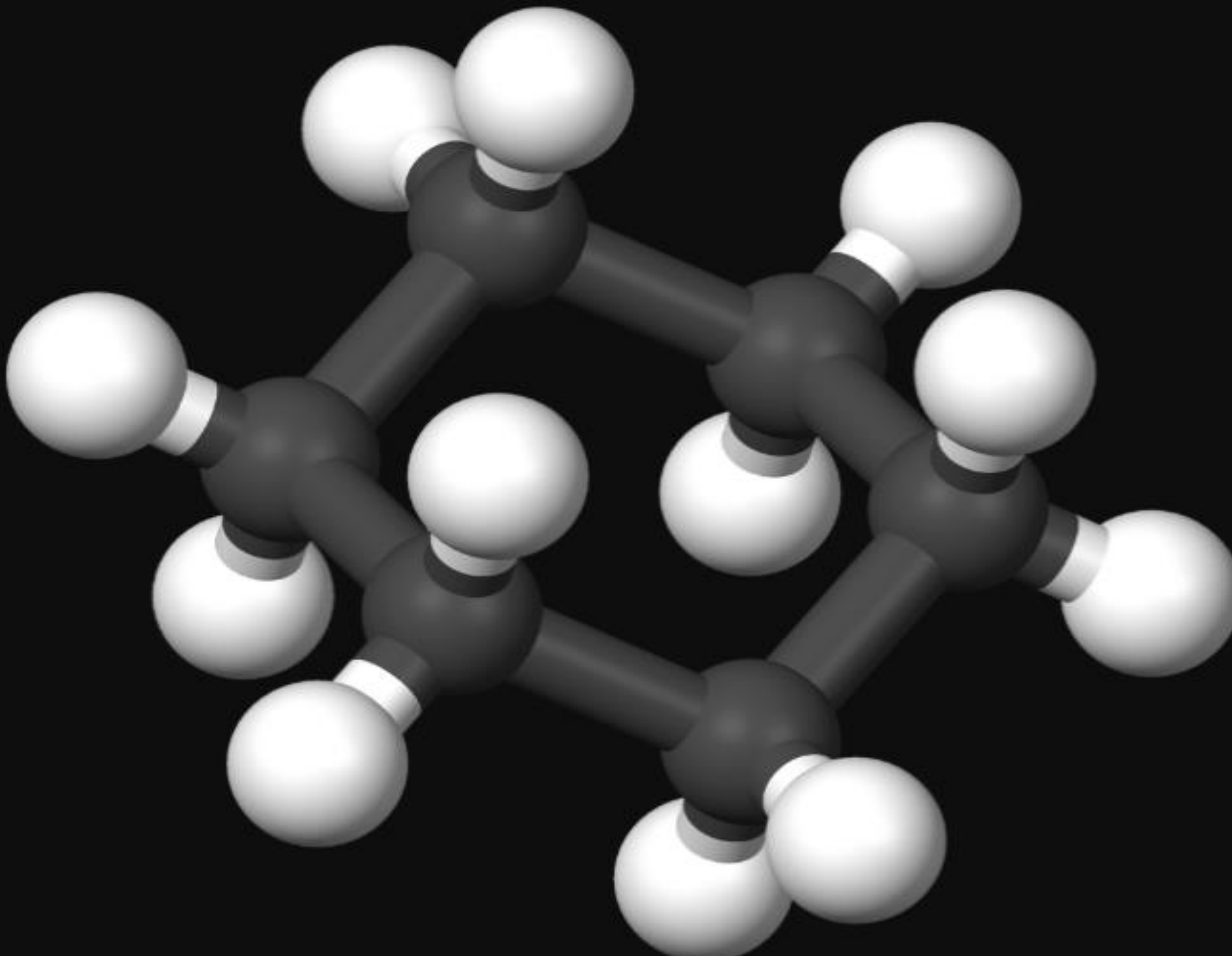
Primary derivatives



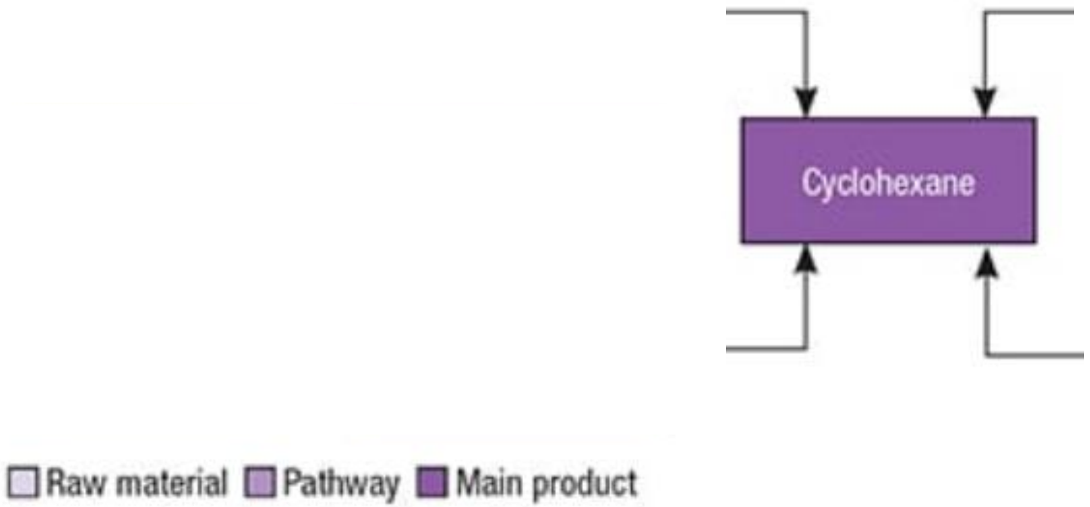
- Ethylbenzene → polystyrene (PS)
- Cumene → epoxy polymers
- Cyclohexane → polyamides (PA)
- Nitrobenzene → polyurethanes (PU)
- Alkylbenzenes → surfactants
- Maleic anhydride
- Chlorobenzenes

Source: http://www.essentialchemicalindustry.org/chemicals/benzene.html

Cyclohexane production



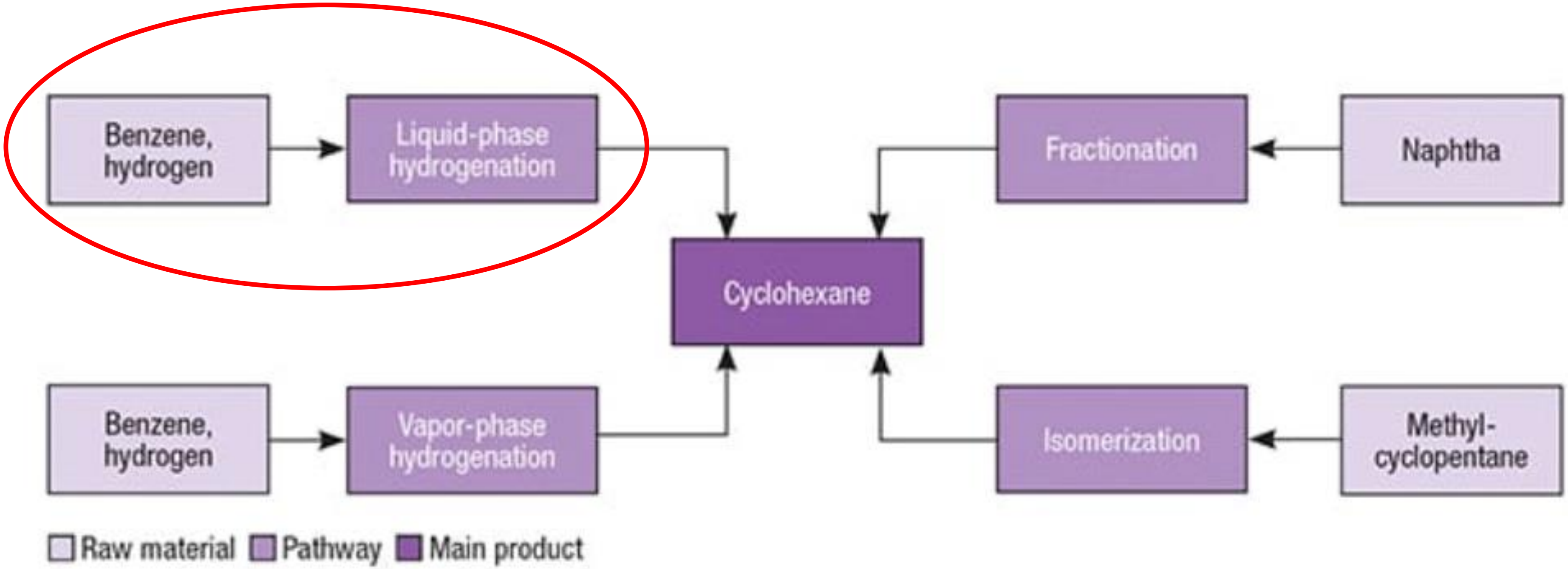
Production pathways



- Most crude oils contains cyclohexane in concentration well below 1%
- Methyl-cyclopentane is not available in huge quantities
- Vapor phase reaction is substantially more expensive and the flow scheme is more complicated

Source: Polyestertime (https://www.polyestertime.com/cyclohexane-production-benzene-hydrogen/)

Production pathways



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- Methyl-cyclopentane is not available in huge quantities
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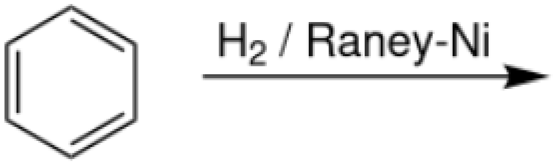
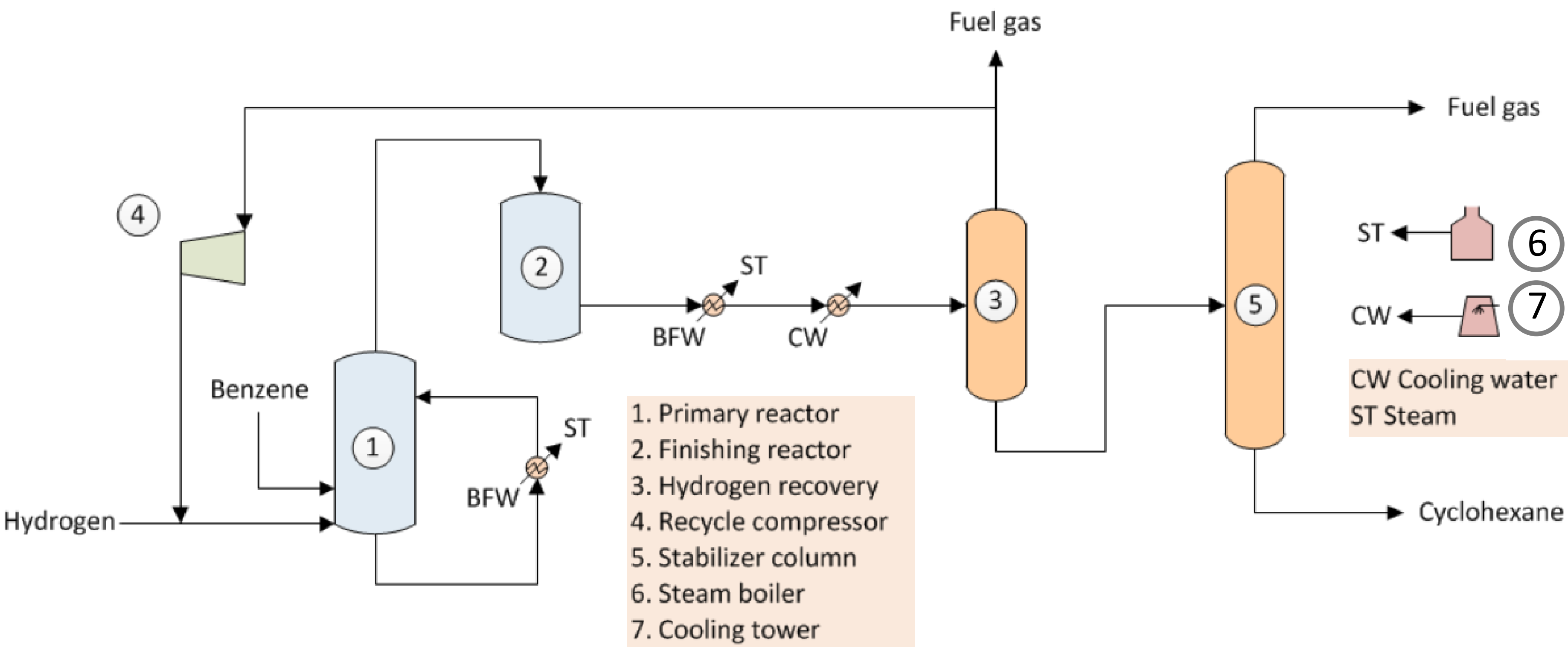
Chemistry



ΔH = -216 kJ/mol

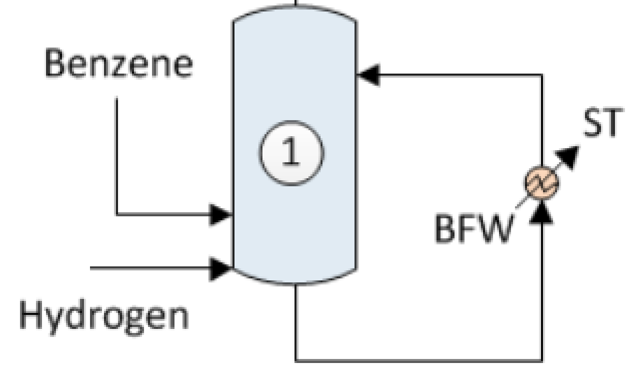
- Feed is pure
  - Benzene (refinery source)
  - Hydrogen (steam reformer source)
- Catalyst: **Raney-Ni**
- Reaction is highly exothermic
  - **Heat removal is the main concern**
- Liquid or vapor phase reaction is possible

Liquid-phase hydrogenation: Process flow



Source: Intratec (https://www.intratec.us/free-tools/how-to-make/cyclohexane-manufacture-technology)

Main reactor features



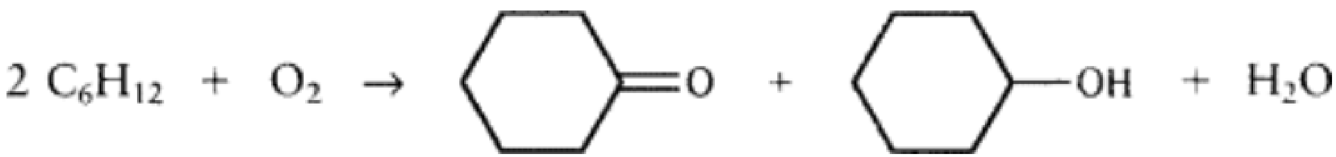
- The hydrogenation reaction is carried out in the main reactor – **liquid-phase reaction**
- The Raney-Ni catalyst is maintained in **suspension** with the aid of an external circulation loop
- **Most of the reaction heat** is removed by the vaporization of the product stream
- The remaining reaction heat is removed in the external loop – this is to **maintain and control** a stable reaction temperature
- Due to the liquid phase environment, thermodynamically favored **low reaction temperature** might be applied
- In case of catalyst deactivation, the catalyst slurry is easily **removed and replaced with fresh catalyst** in the external loop

Finishing reactor and stabilizer

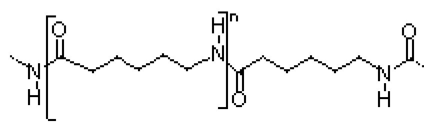
- The hydrogenation is carried out in **gas phase** in the finishing reactor
- In this **fixed bed** reactor **Ni/Al_2O_3 catalyst** is used
- The catalytic hydrogenation of residual benzene is completed
- In the stabilizer the **light ends** (by-products due to unwanted cracking reactions) are separated
  - Benzene bp: 80.5 °C
  - Cyclohexane bp: 80-81 °C
- The cyclohexane quality **may reach 99.9% purity**

Uses

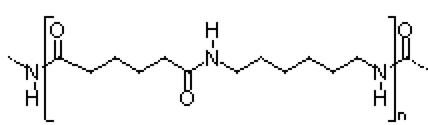
- Over **90% of cyclohexane** is used for the production of Nylon-6 and Nylon 66
- First step is the **oxidation with air** in the presence of cobalt catalyst to produce cyclohexanone and cyclohexanol



- The two polymer has similar, but still different structure
  - Nylon-6

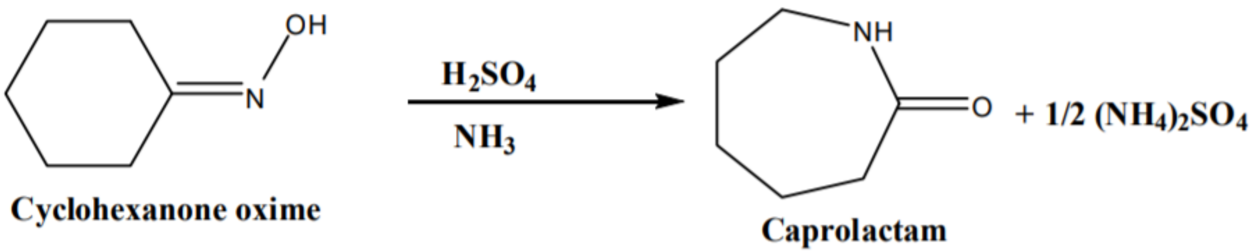


  - Nylon-66

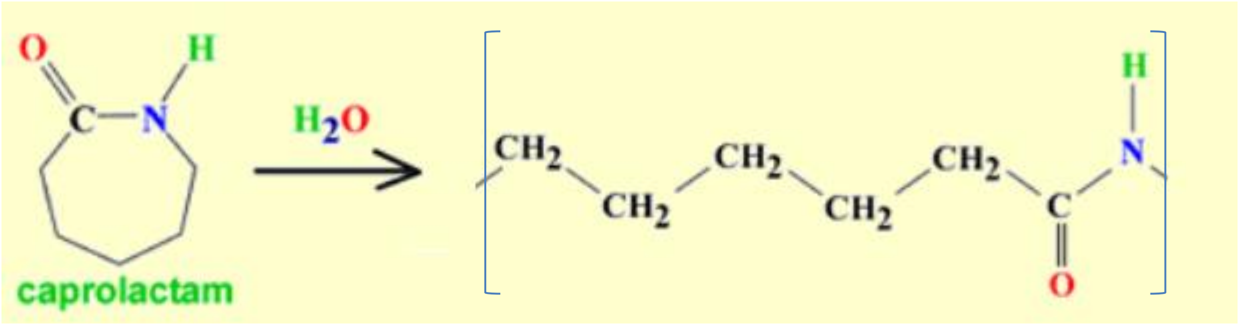


Nylon-6

- Nylon-6 is made by polymerization of caprolactam
  - which has several production pathways from cyclohexane
  - the final step being the Beckmann rearrangement of cyclohexanone oxime to caprolactam



- The caprolactam polymerization is catalysed by water to nylon-6



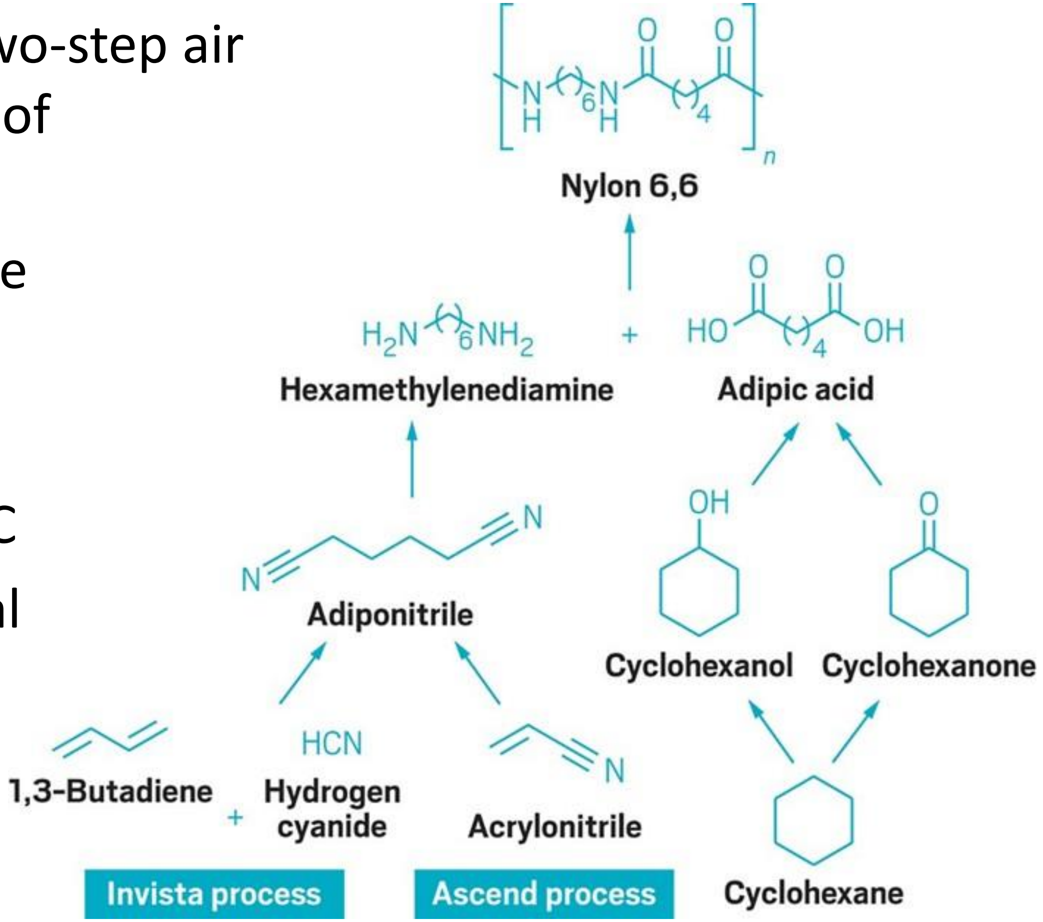
Nylon-66

- Nylon-66 is made by polymerizing equal quantities of adipic acid and hexamethylene diamine (HMDA)
  - Adipic acid is made by two-step air and nitric acid oxidation of cyclohexane
  - HMDA is produced by the reduction of adiponitrile

Source: C&EN (https://cen.acs.org/materials/polymers/chemical-industry-bracing-nylon-66/96/i40)

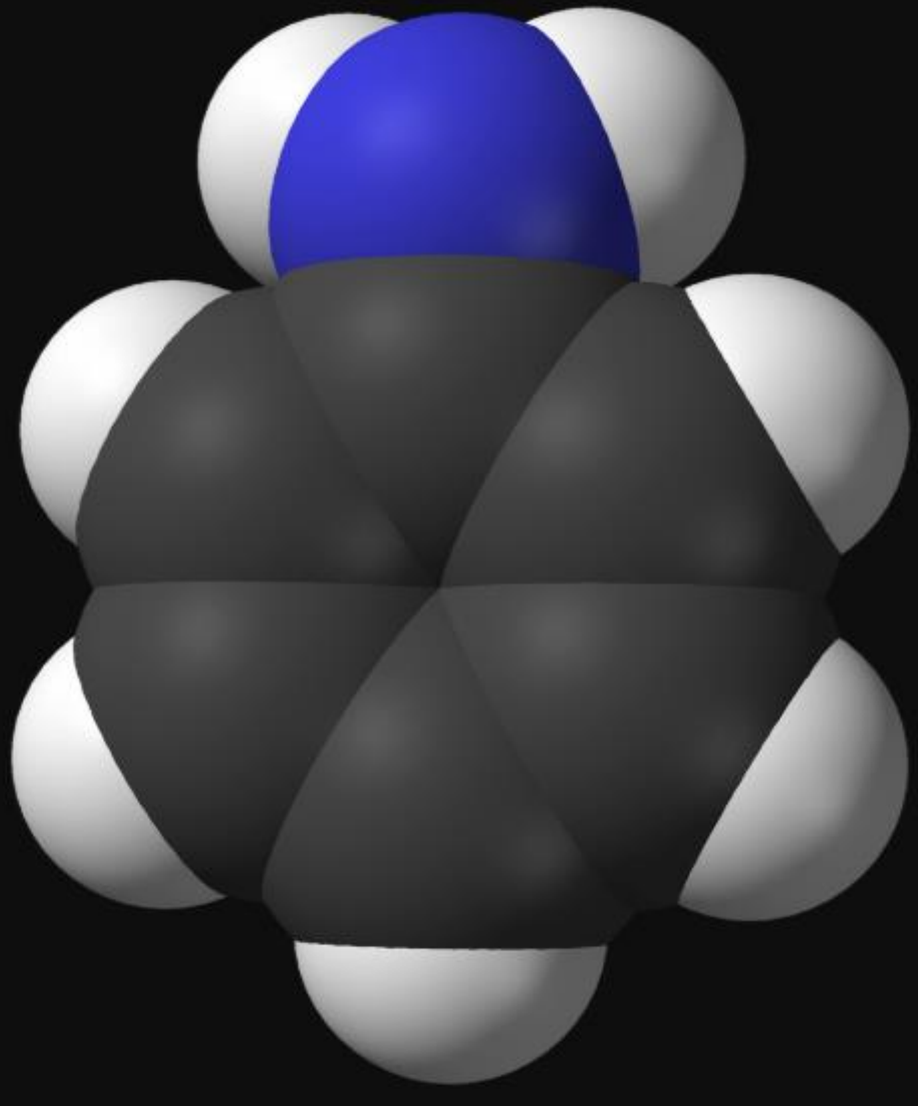
Uses – Nylon-66

- Nylon-66 is made by polymerizing equal quantities of adipic acid and hexamethylene diamine (HMDA)
  - Adipic acid is made by two-step air and nitric acid oxidation of cyclohexane
  - HMDA is produced by the reduction of adiponitrile
- Nylon-66
  - starts to deform at 260°C
  - has outstanding chemical resistance
  - low tendency to absorb moisture and expand



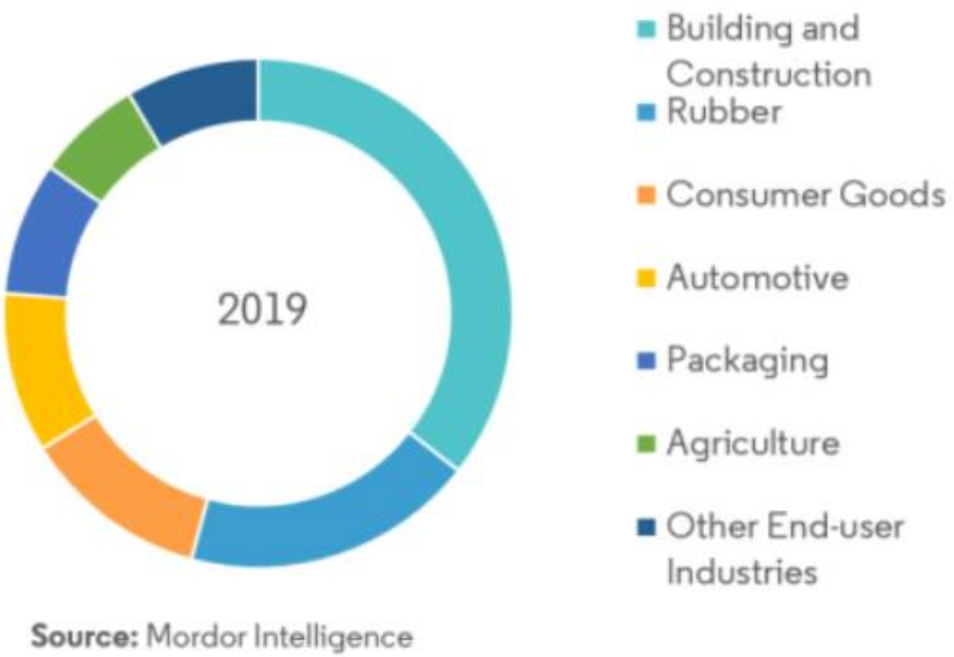
Source: C&EN (https://cen.acs.org/materials/polymers/chemical-industry-bracing-nylon-66/96/i40)

Nitrobenzene – Aniline – MDI production line



Aniline market

- Main application areas:
  - MDI → PU
  - Rubber processing chemicals
  - Agricultural chemicals
  - Dye and pigments
  - Specialty fiber
  - Other applications

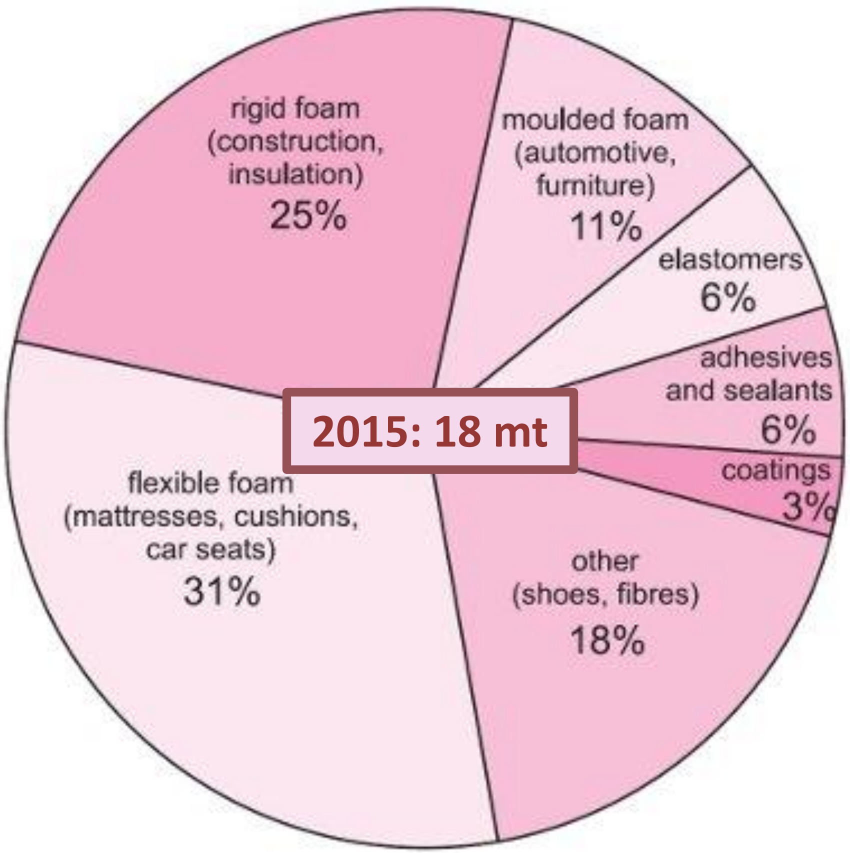


Market share by End-User industy

- Borsodchem to built a new 200.000 t/y aniline plant at Kazincbarcika (planned start-up in 2021)

Source: Mordor Intelligence (https://www.mordorintelligence.com/industry-reports/aniline-market)

Polyurethane applications

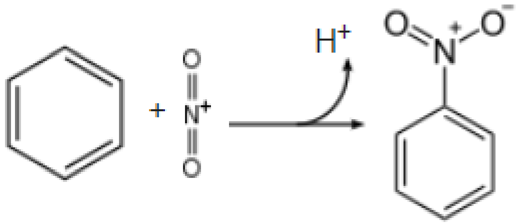


- Aniline is used in manufacturing polyurethane, which finds its application in
  - durable plastics (construction)
  - spray polyurethane foams (insulation)
  - polyurethane flexible foams (construction, automotive industry)
  - polyurethane based binders

Source: http://www.essentialchemicalindustry.org/chemicals

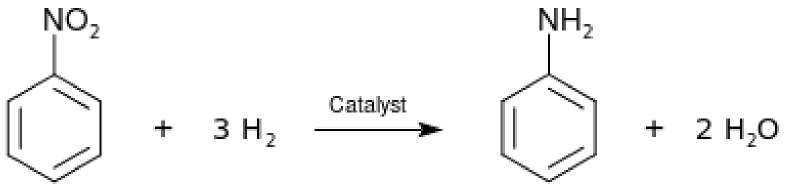
Chemistry

- First, nitrobenzene is produced via **nitration of benzene**



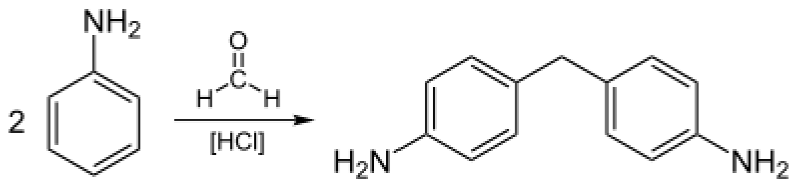
$\Delta H = -117$ kJ/mol

- Second, nitrobenzene is **reduced to aniline**

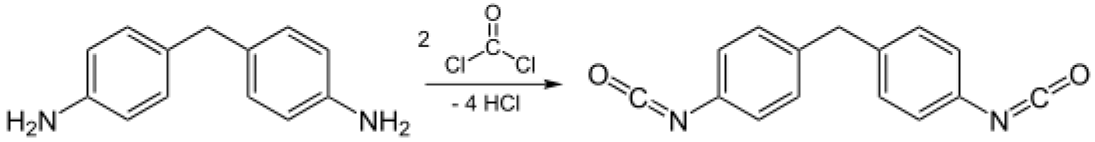


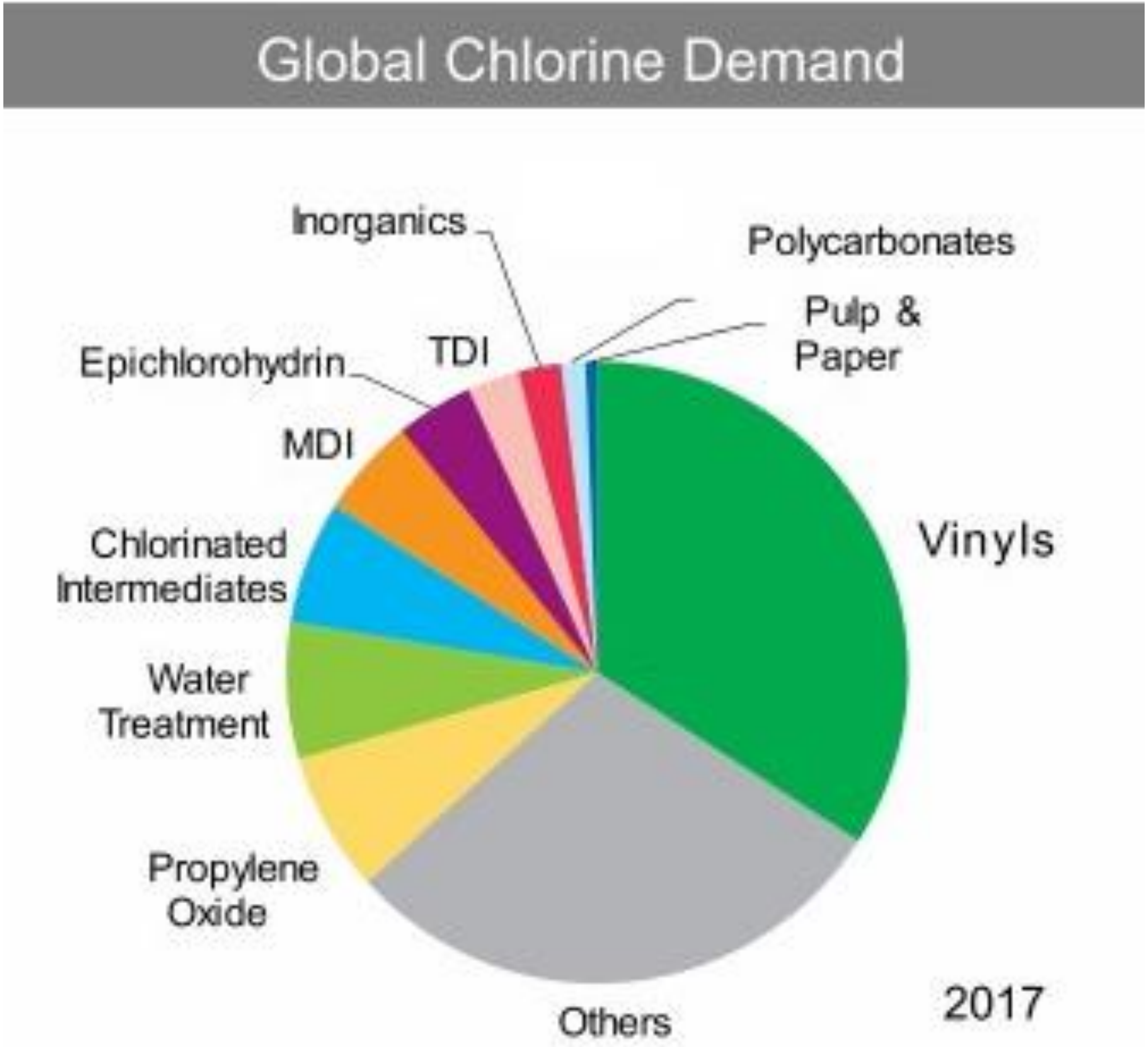
Chemistry

- Third, aniline is converted to **methylenedianiline**



- Fourth, methylenedianiline is reacted with phosgene **to yield MDI** (Methylene diphenyl diisocyanate)





Source: IHS Markit

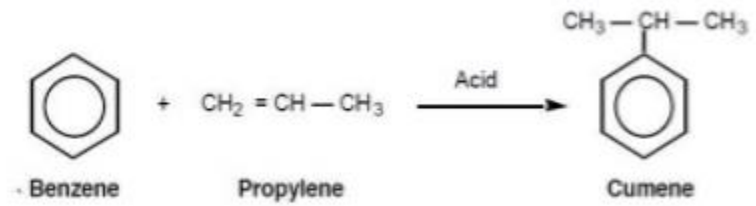
Cumene and Phenol

Cumene Hydoperoxide uses

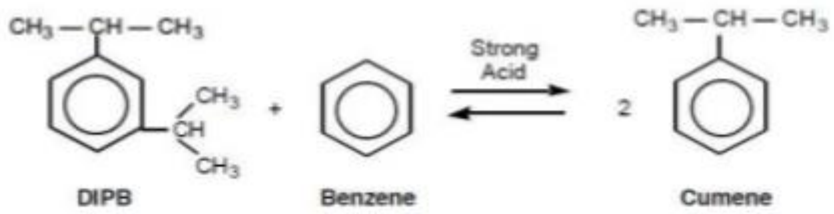
- Cumene hydroperoxide is used for different purposes, principally but not limited to the phenol/acetone route (via BPA – bisphenol-A)
  - Epoxy resin curing
  - Epoxy coatings
  - Polycarbonates
  - Laminates
  - Resins (wind turbines)
  - Organic synthesis
    - Polymerization initiator (e.g. ABS polymers)
    - Organic peroxide production (as polymerization inhibitor)
    - Oxidizing agent

Cumene chemistry

- Cumene is produced by alkylation of benzene

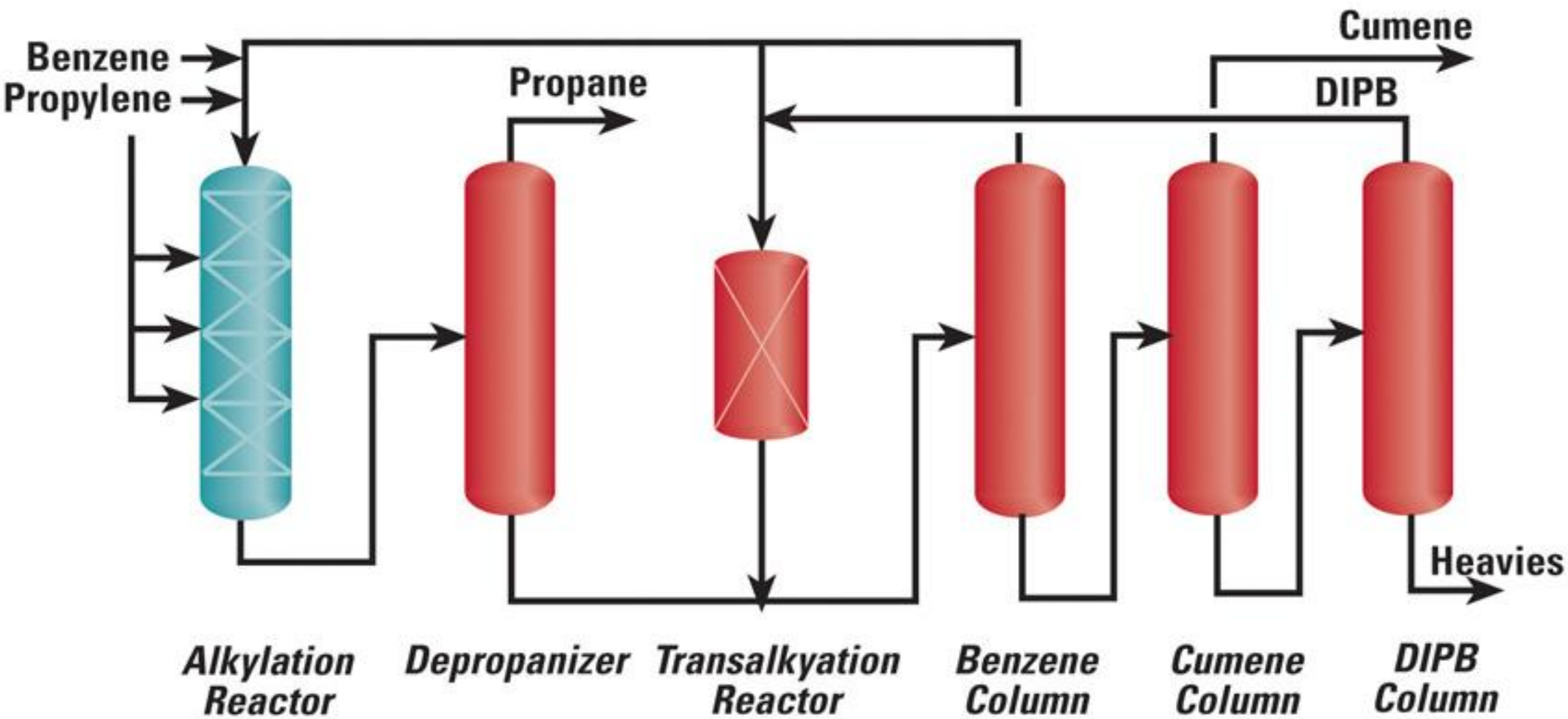


- or by transalkylation of polyizopropylbenzene (PIPB)



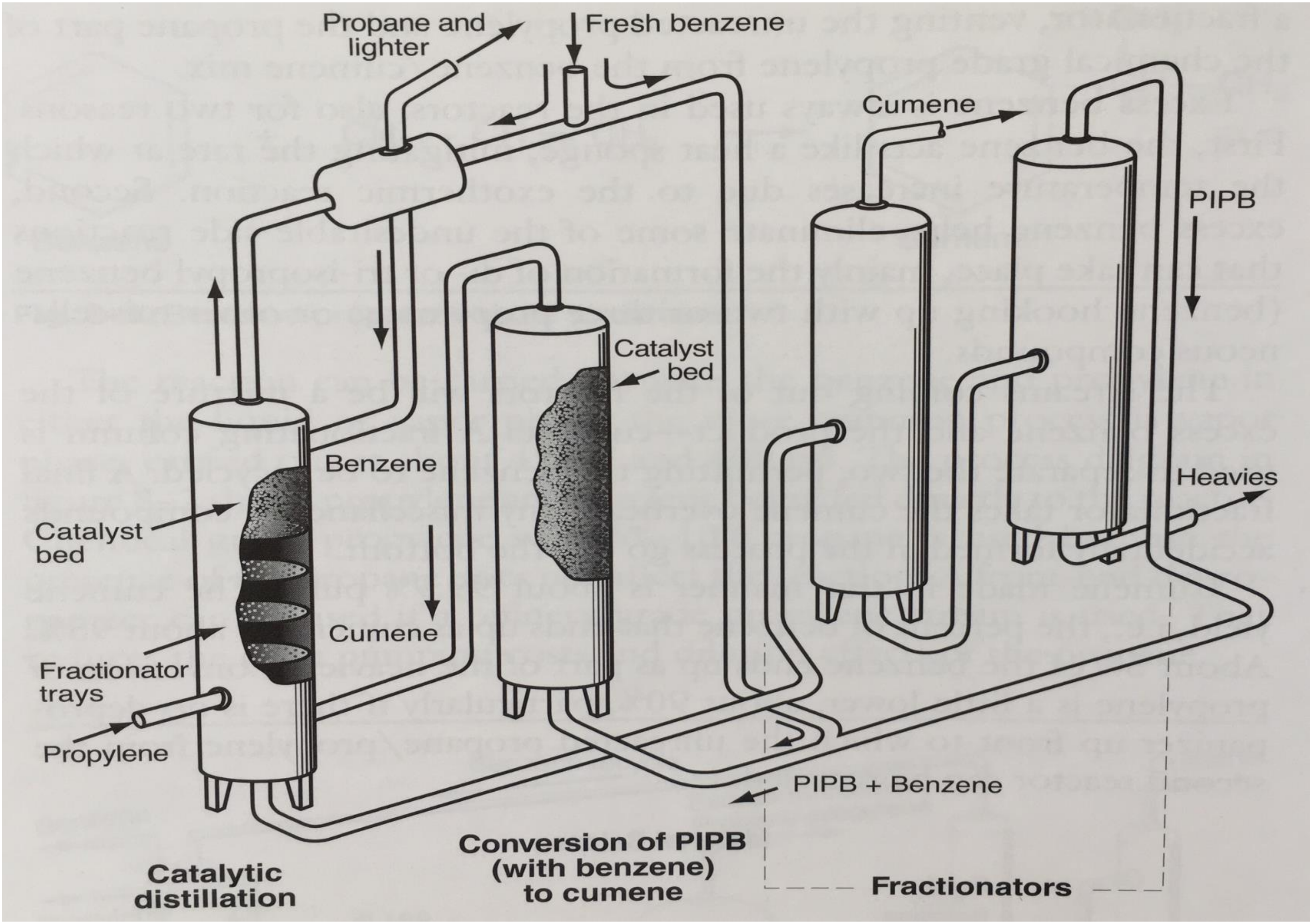
Fixed bed process

- UOP QMax process



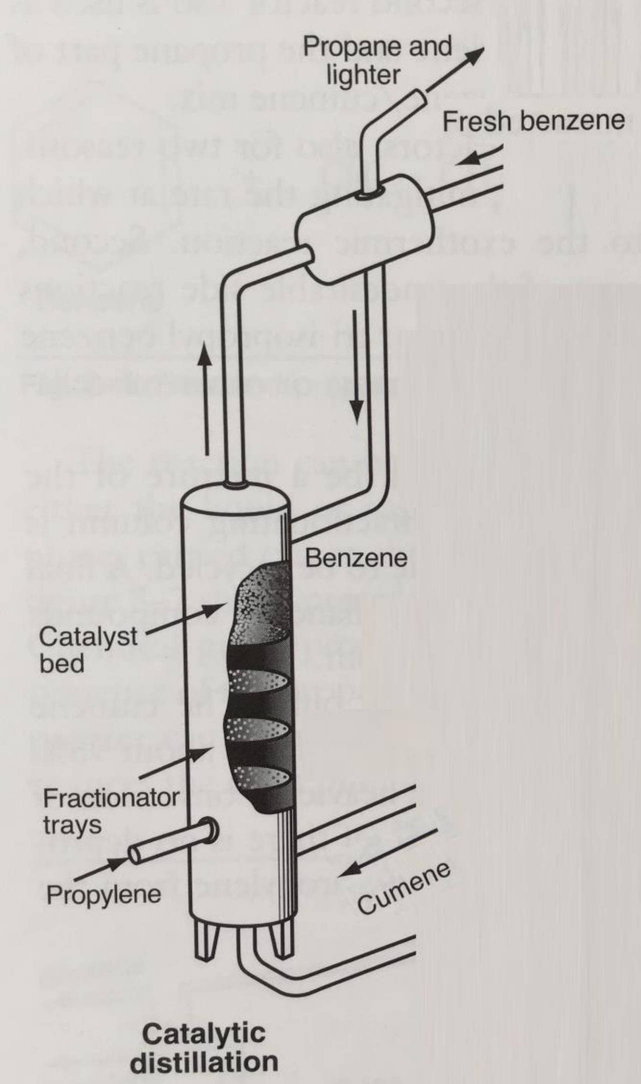
Source: UOP (https://www.uop.com/cumene-qmax/)

Catalytic distillation process



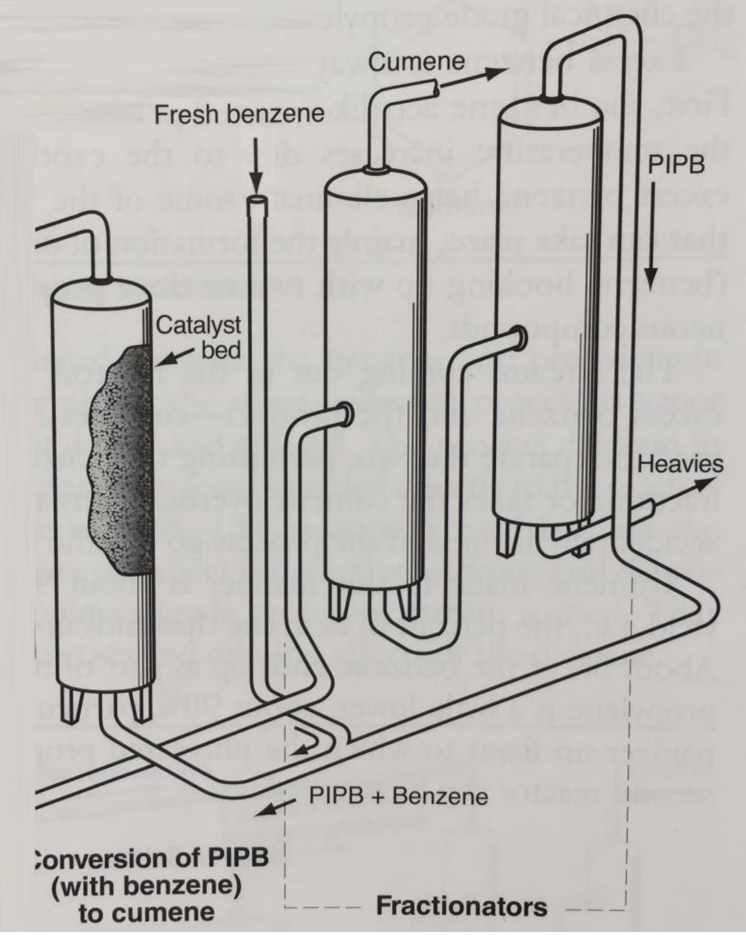
Main reactor features

- The **catalytic distillation column** combines a fixed bed reactor with a fractionator
- **Chemical grade propylene** is introduced in the lower section of the column as a vapor (and moves upward), while **pure benzene** at the top as liquid (and flows downward)
- **Direct alkylation** will occur on the surface of the **zeolite based catalyst**, as the two stream countercurrently mix with each other
- Heavier **cumene** product and by-product PIPB **leaves the bottom**, being stripped by the hot propylene vapor (lighter components, e.g. benzene are evaporated)



- Light fraction leaves the top. Propane and lighter components are removed, while **unreacted benzene is recovered** and combined with fresh benzene

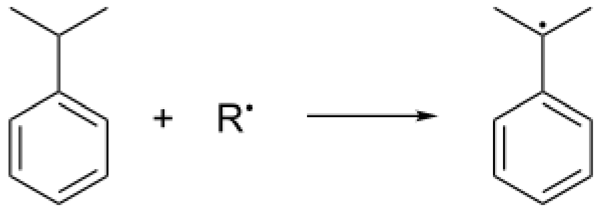
Fractionation and PIPB reactor



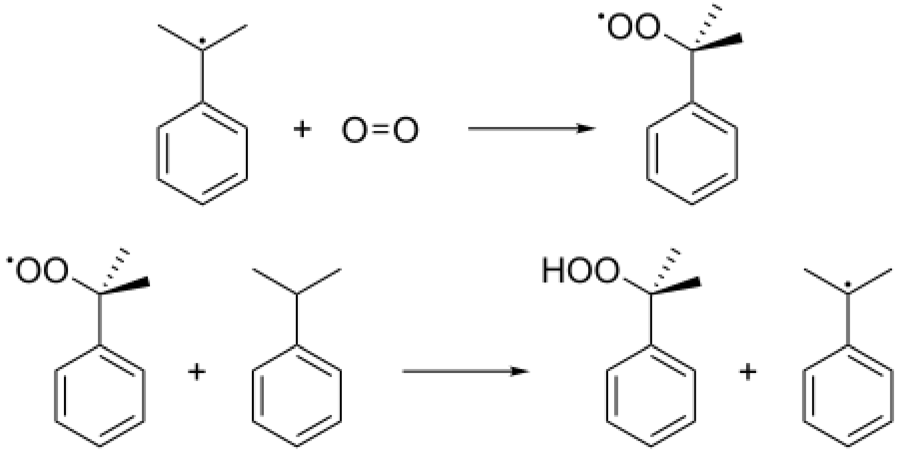
- **Cumene is recovered** from the first distillation column at the top, the rest entering the second column
- The by-product **PIPB is** recovered from the top and is **recirculated** to the PIPB conversion reactor
- It the PIBP reactor fresh benzene is used to facilitate the **transalkylation** of PIPB, thus yielding additional cumene
- The second reactor effluent will enter the catalytic distillation column bottom to join the main stream cumene
- The product purity may reach **99.5-99.8%**

Phenol chemistry

- Cumene radical is formed first,

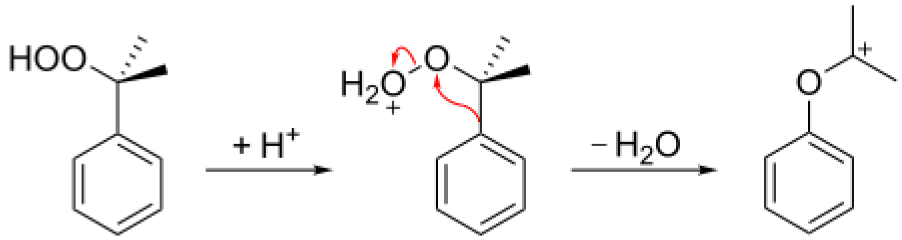


- which will converted to cumene hydroperoxide, while reacted with air

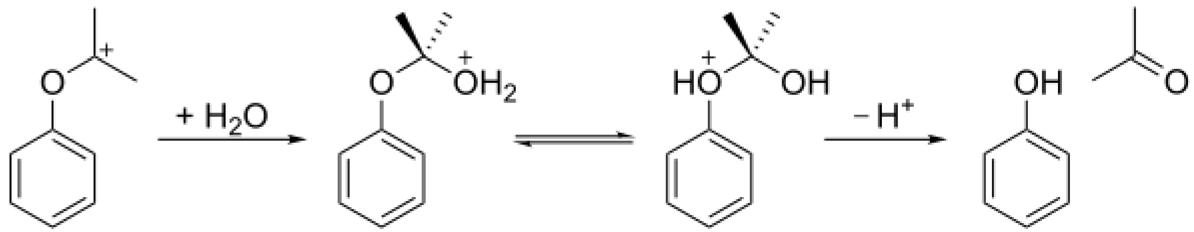


Phenol chemistry

- Cumene hydroperoxide is protonated and rearranged

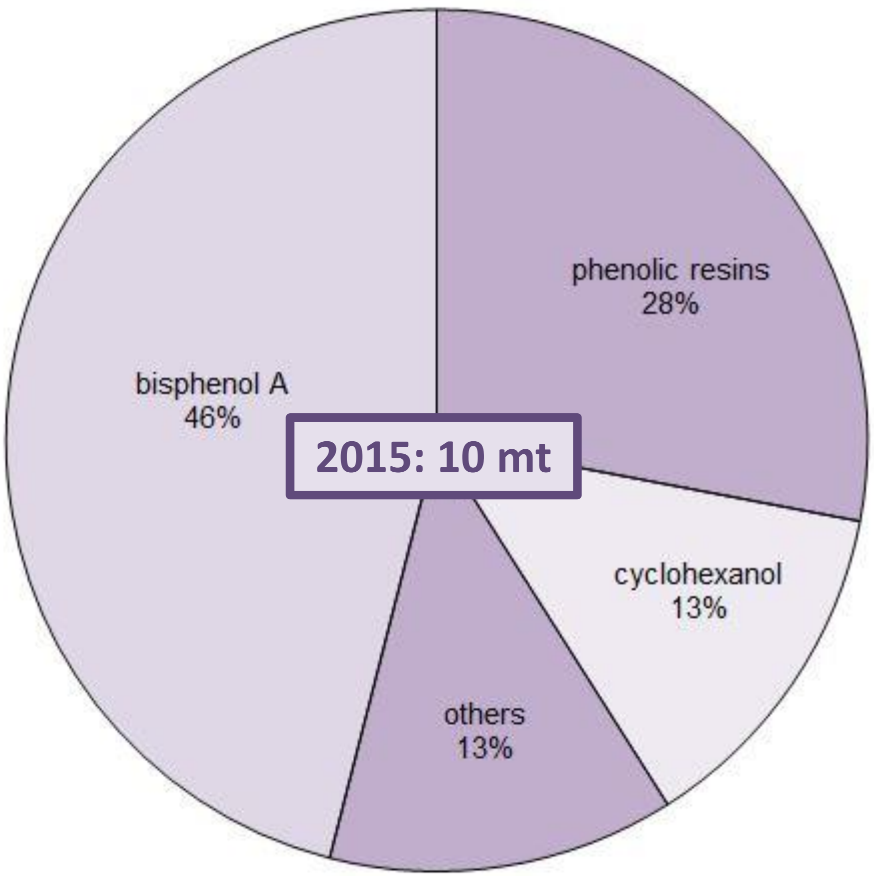


- The carbocation is reacted by water to phenol and acetone



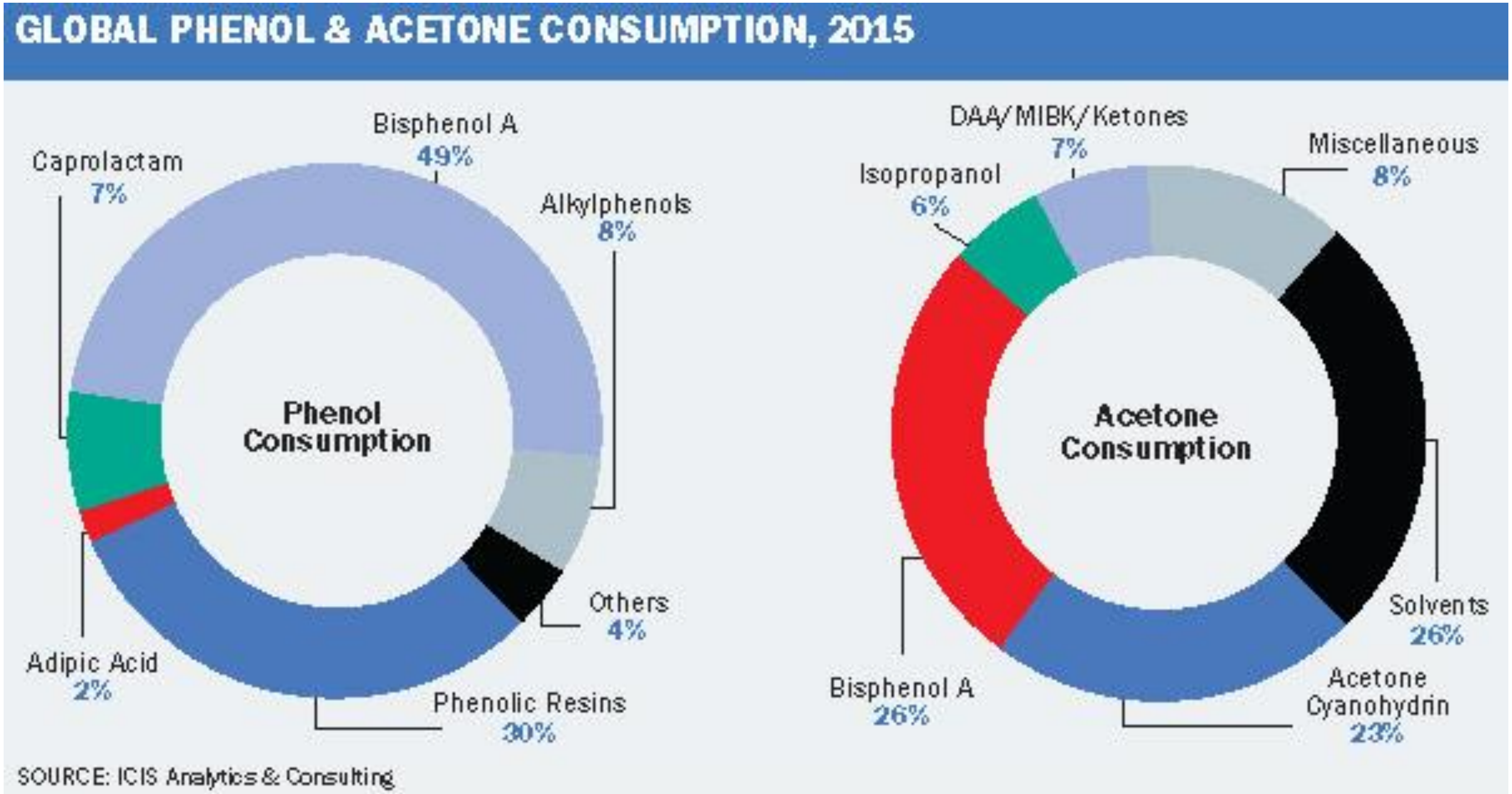
- The two **co-products are produced in different quantities**, with around 1.5 tons of phenol manufactured for each tons of acetone, but **the economics of the process requires demand for both acetone and phenol**.

Phenol applications



- Phenol is used principally to produce bisphenol-A (BPA)
  - which in turn is used to produce polycarbonates (70%)and epoxy resins (20%)
- Phenolic resins are thermosetting polymers
  - once reacted with formaldehyde (PF resins)
  - used as wood adhesive in plywood manufacturing
- Could be reduced to cyclohexanol
  - to be further processed to Nylon-6 or Nylon-66

Source: http://www.essentialchemicalindustry.org/chemicals



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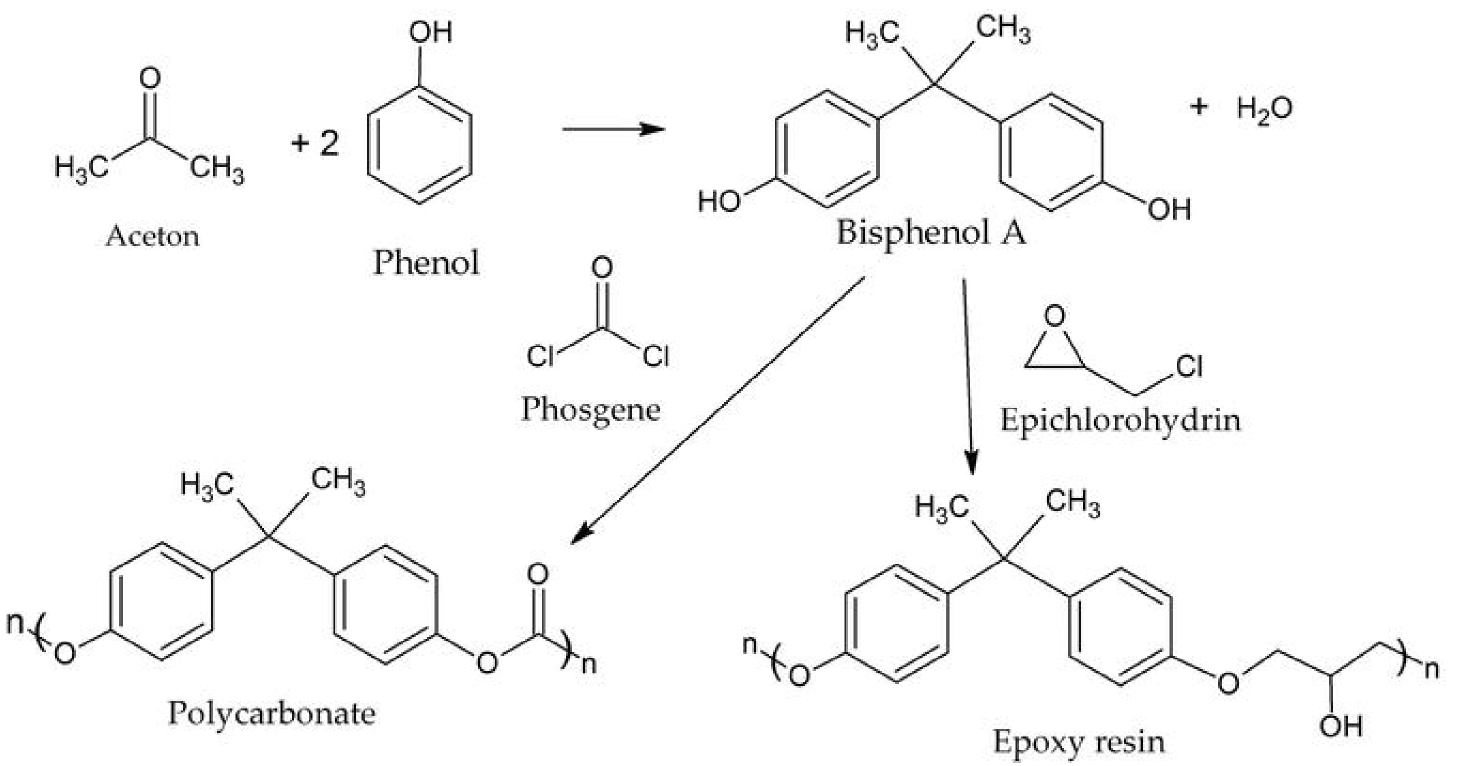
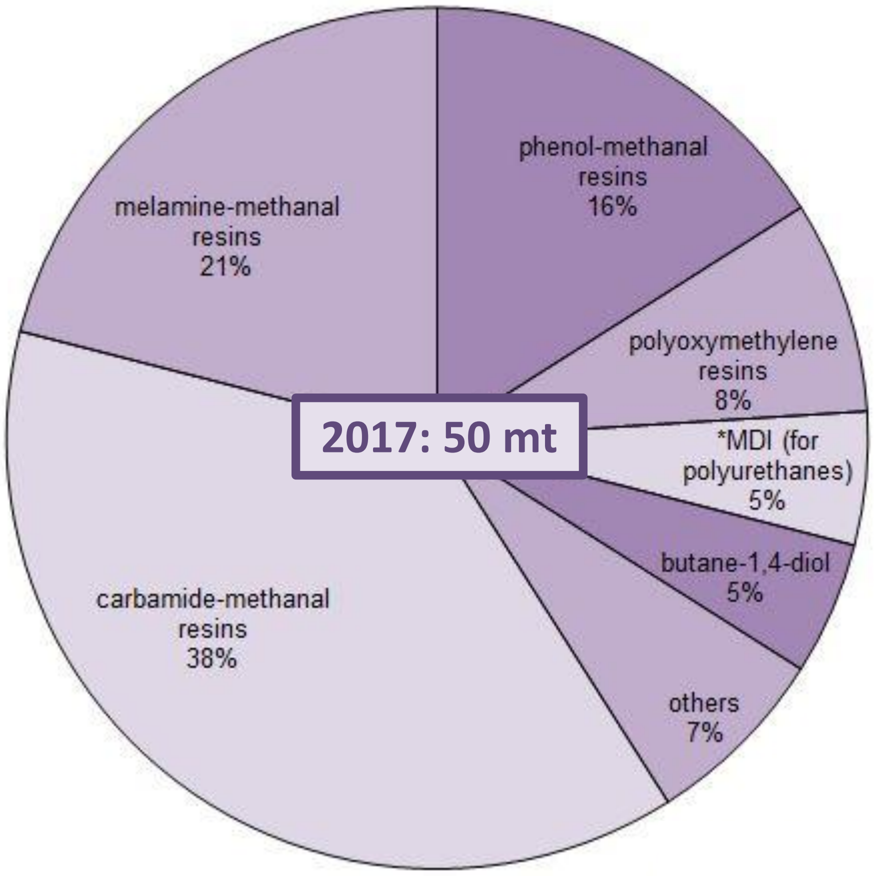
Source: https://www.icis.com/explore/resources/news/2016/06/09/10006764/market-outlook-phenol-acetone-markets-are-under-ressure-icis-consulting/

Bisphenol-A chemistry



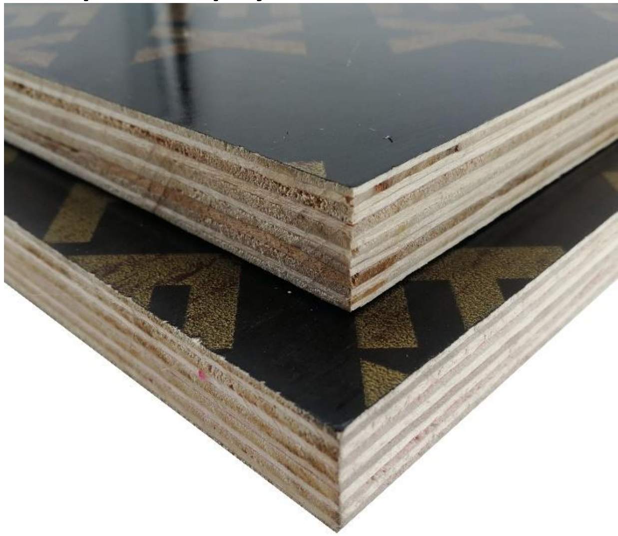
- **Polycarbonate plastics** may be encountered in many products, especially in food and drink containers, while **epoxy resins** are frequently used as inner liners of metallic food and drink recipients with the aim to prevent corrosion.

Phenol-formaldehyde (PF) resins



World formaldehyde production

- PF resins are used for
  - Bakelite production
    - Billiard balls production
    - Telephone
    - Etc.
  - Laminates
  - Weather proof plywood
  - Etc.



Source: http://www.essentialchemicalindustry.org/chemicals

Tischfernsprecher W 38 by Siemens & Halske from 1938

Literature

- D.L. Burdick, W. Leffler: Petrochemicals in nontechnical language, 4th edition, PennWell, 2010
- W. Leffler: Petroleum Refining in nontechnical language, 4th edition, PennWell, 2008