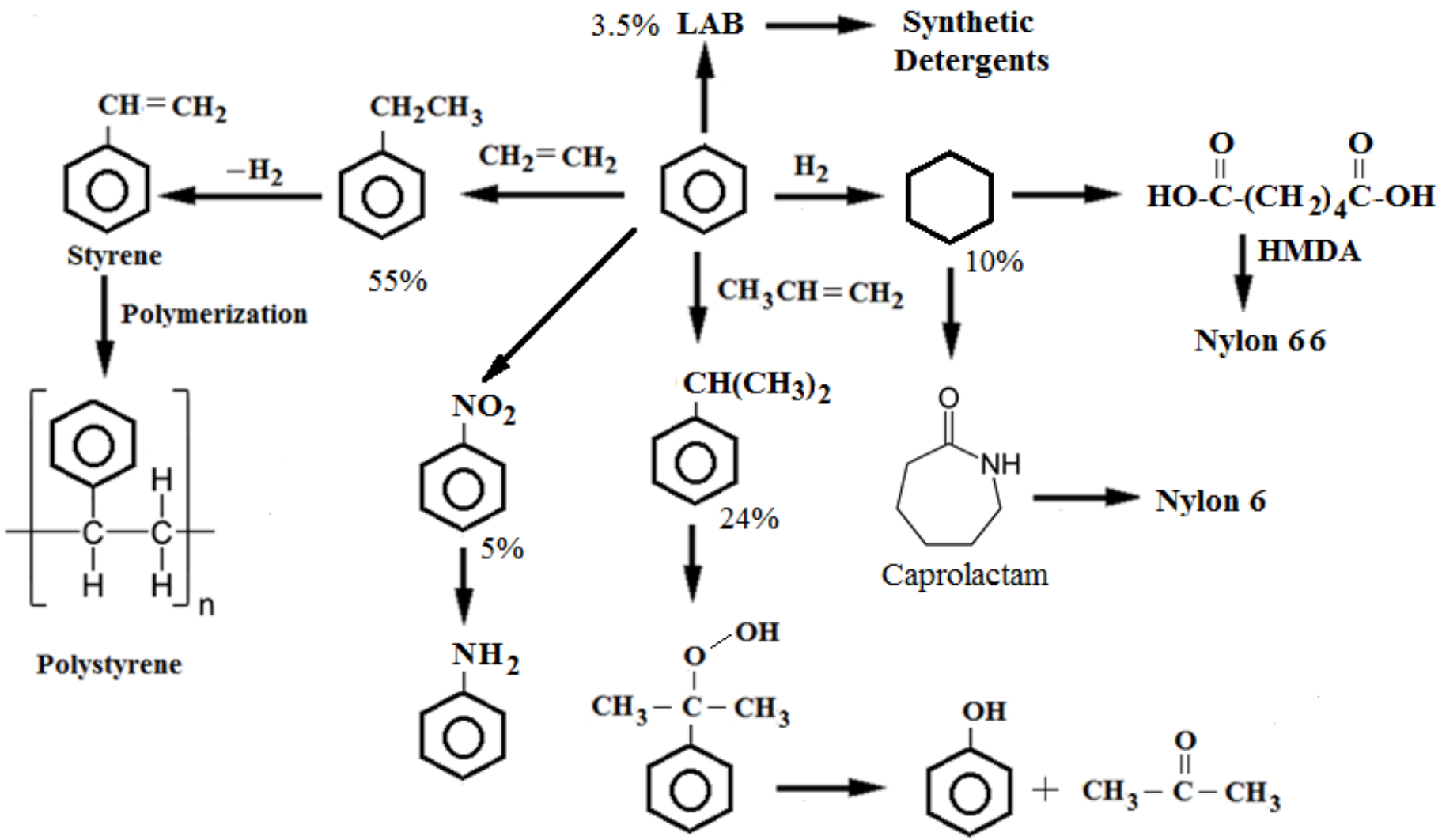
Petrochemical Technology

Chemicals from Benzene

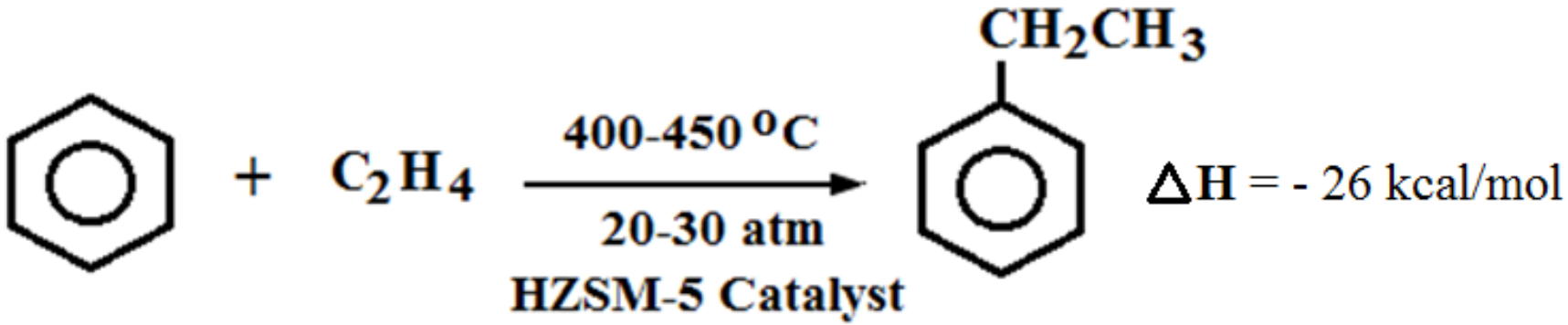
Major Chemicals from Benzene

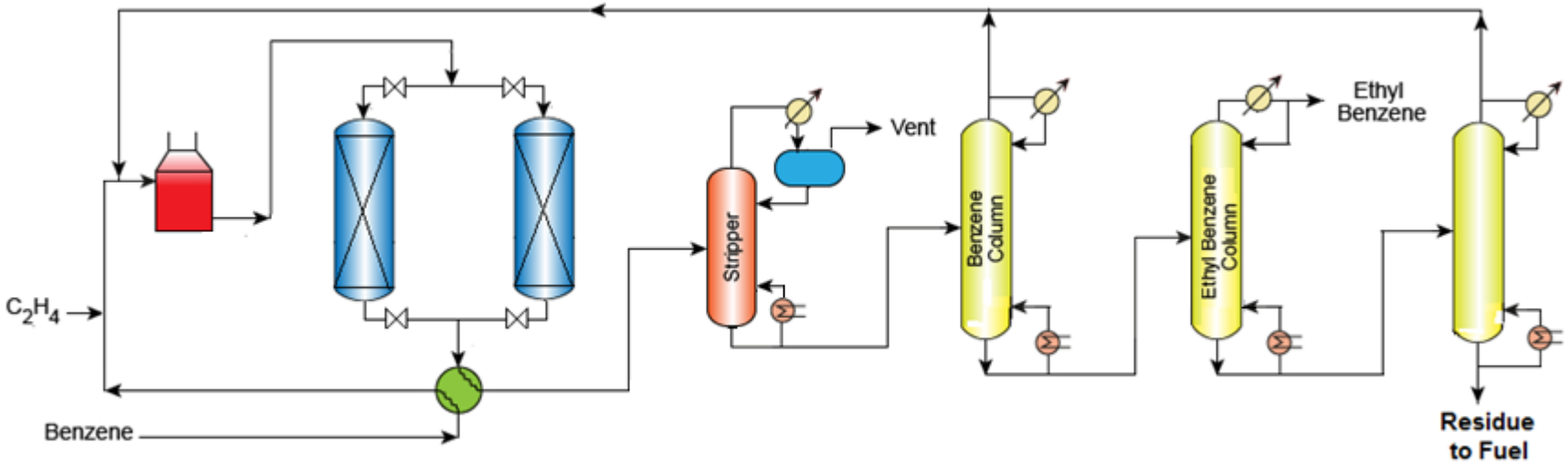
Global Benzene market stood at 52.94 Million Tonnes in 2022 and is forecast to reach 78.0 Million Tonnes by 2032, growing at a healthy CAGR of 4.32% until 2032.



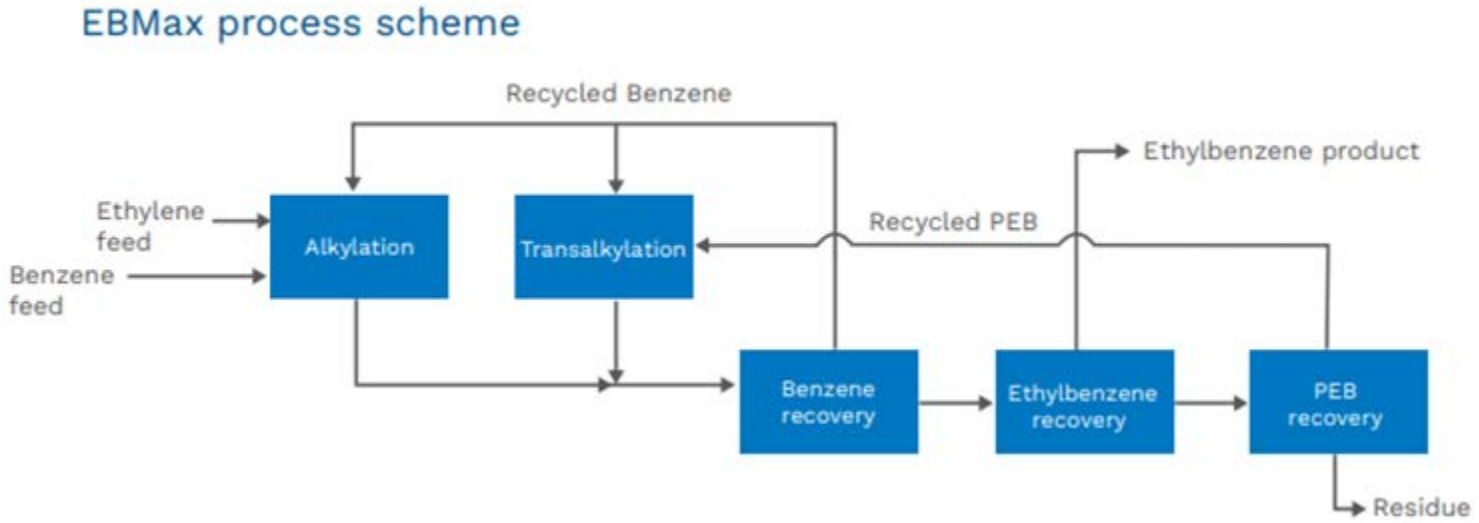
Production of Ethylbenzene and Styrene

Mobil-Badger Process for Ethylbenzene





Production of Ethyl Benzene

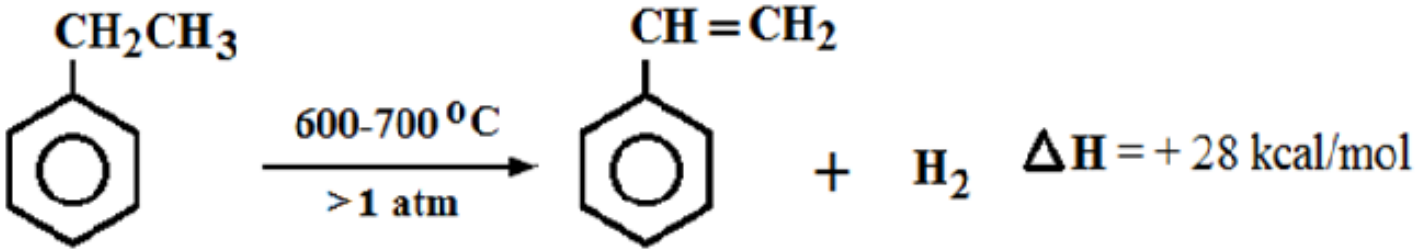


- ExxonMobil's proprietary zeolite alkylation catalyst does not age due to coking caused by ethylene oligomerization, resulting in long, uninterrupted EBMax unit operation.

- The alkylation catalyst is highly selective to monoalkylation, which has allowed operation at design benzene-to-ethylene molar feed ratios as low as 1.6-to-1.

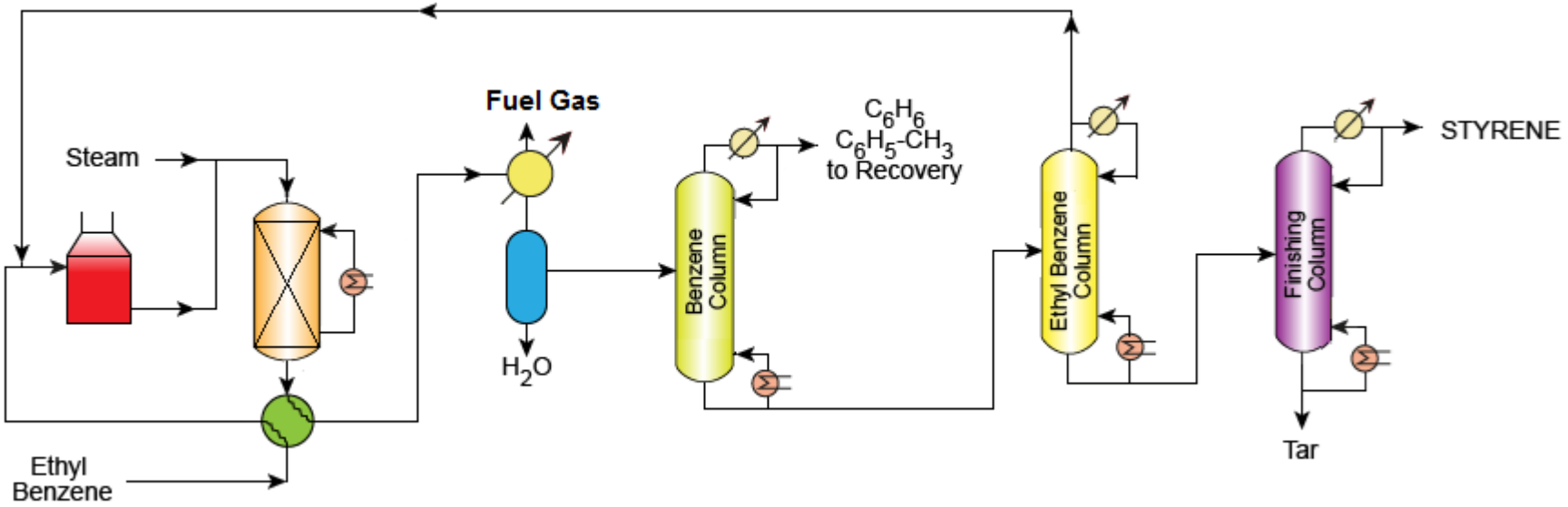
- The reaction system produces extremely low levels of impurities boiling in the range of EB, resulting in EB product purities in excess of 99.97 wt%.

- ExxonMobil's proprietary guard bed catalyst removes traces of nitrogen containing compounds which would otherwise poison the process catalysts, minimizing the frequency of catalyst regeneration.

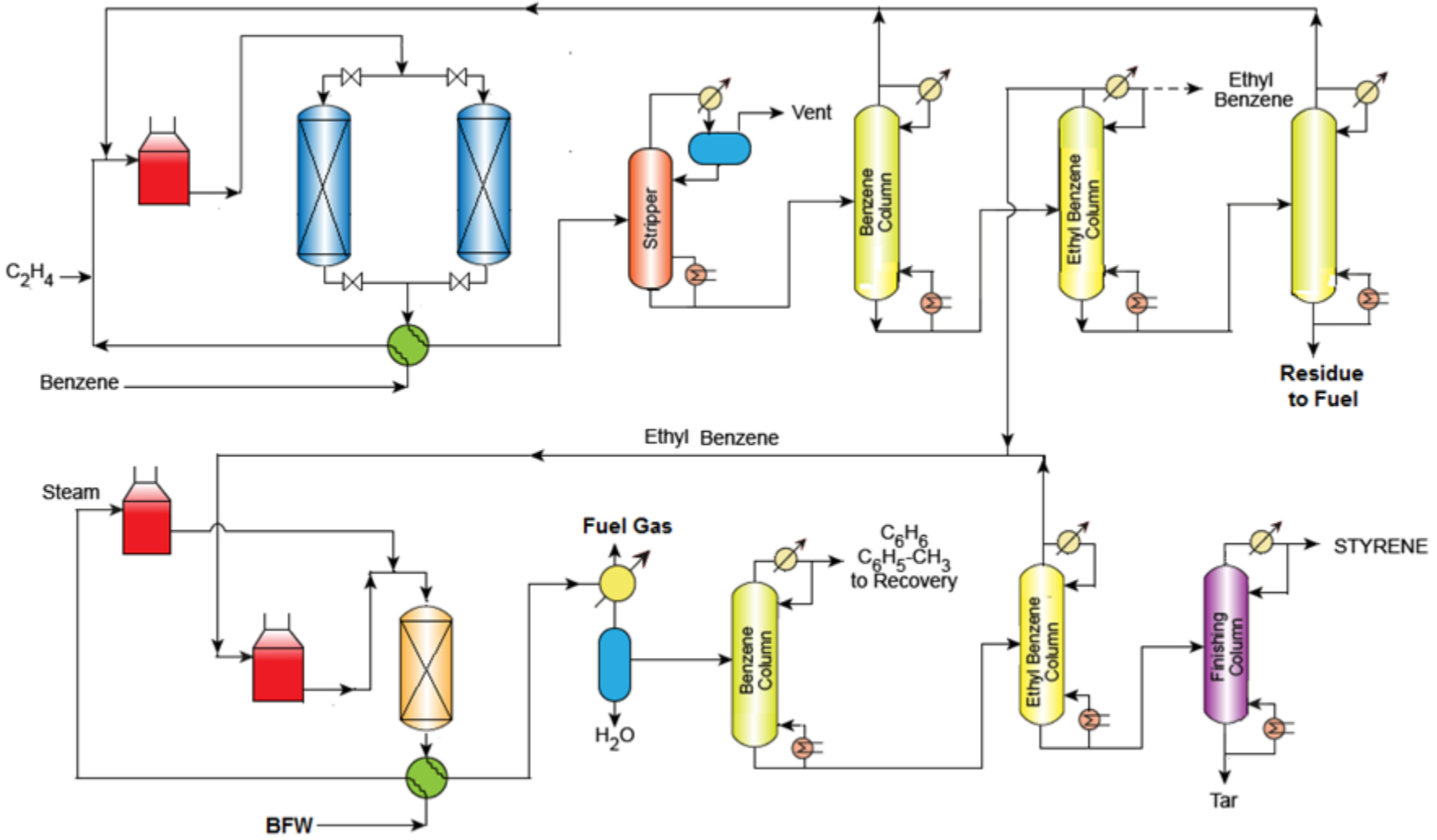


Catalyst: Fe_2O_3 or ZnO mixed with 0.5-1% Cr_2O_3

All these catalysts are mixed with a small amount of potassium carbonate which facilitates the removal of carbon deposited on the catalyst surface, thereby prolonging its activity.

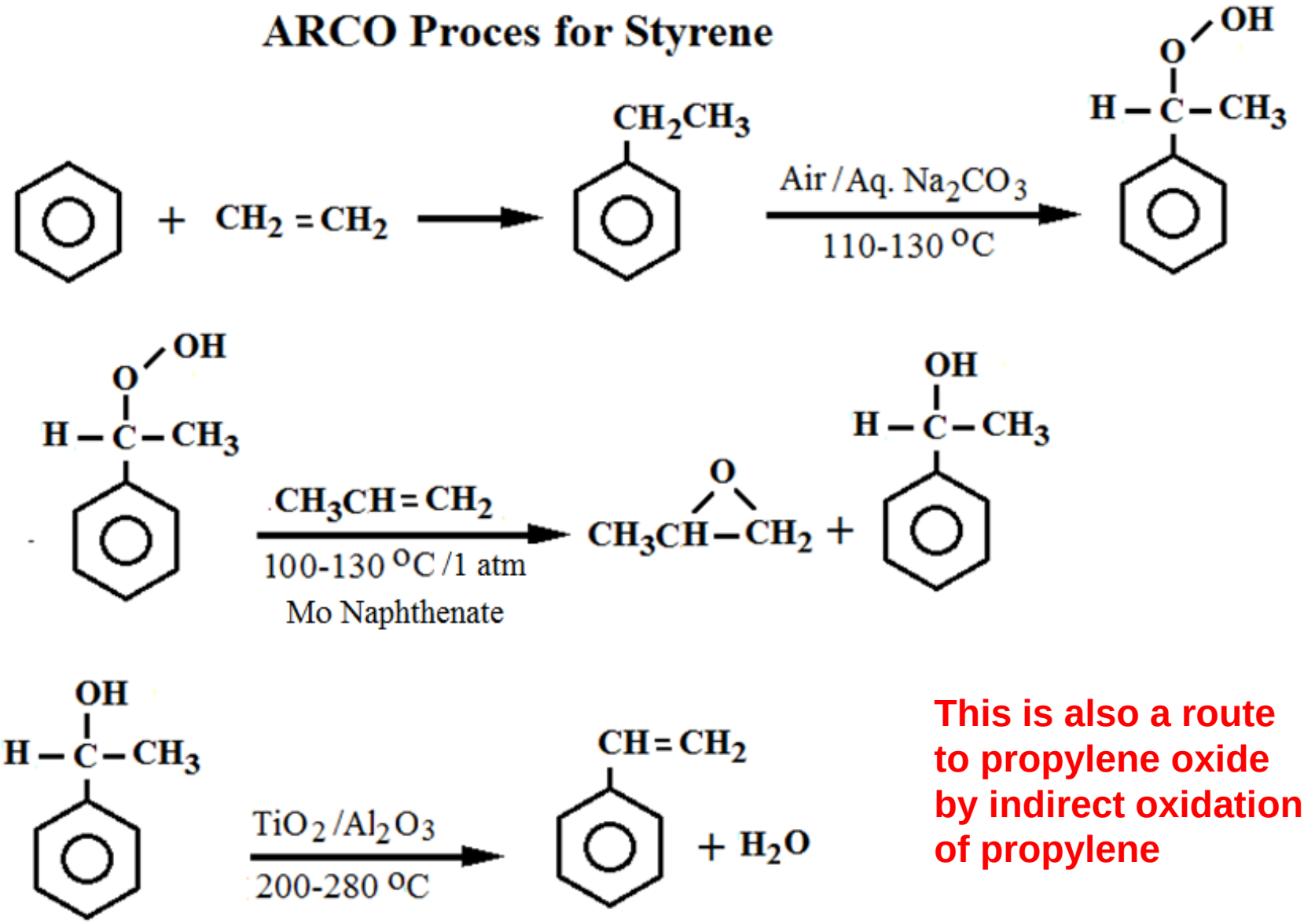


Production of Styrene from Ethyl Benzene



Production of Styrene from Benzene

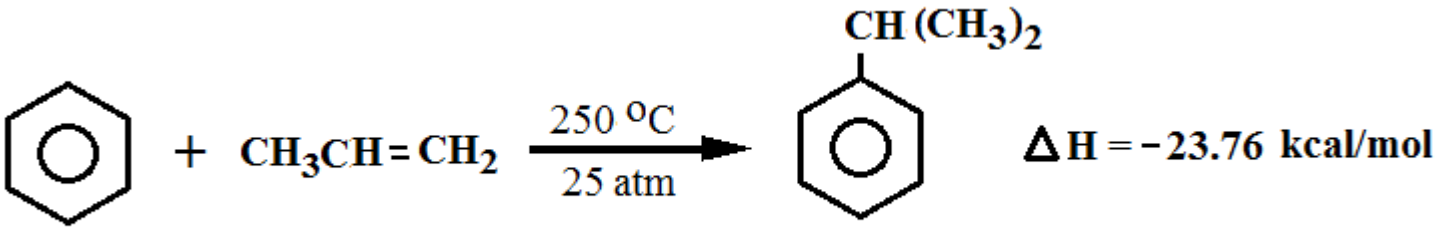
ARCO Proces for Styrene



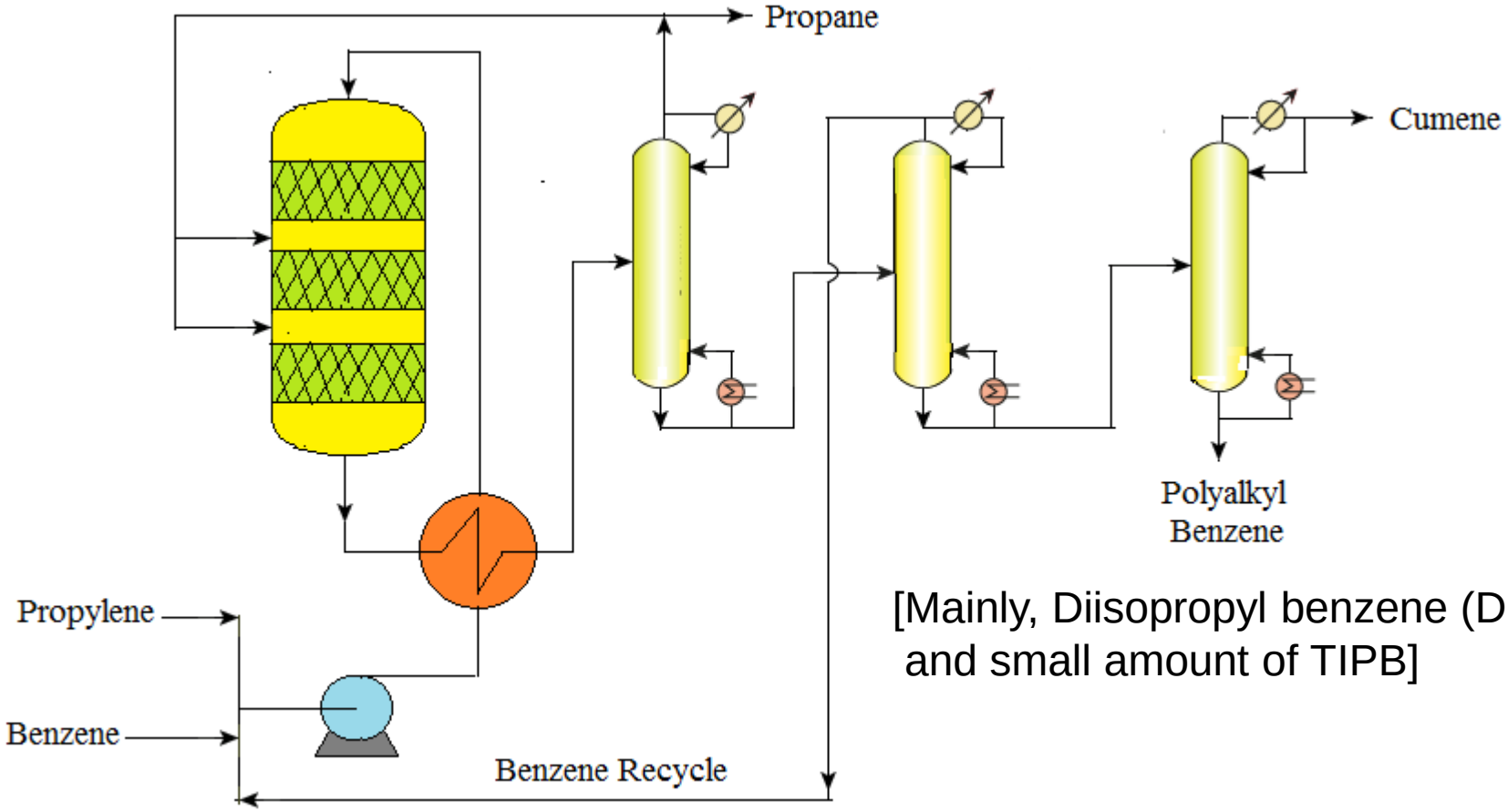
This is also a route to propylene oxide by indirect oxidation of propylene

ARCO had been established in 1966 as the "Atlantic Richfield Company", an independent oil and gas company formed after the merger of Atlantic Petroleum and the Richfield Oil Corporation.

Production of Cumene
and
Phenol



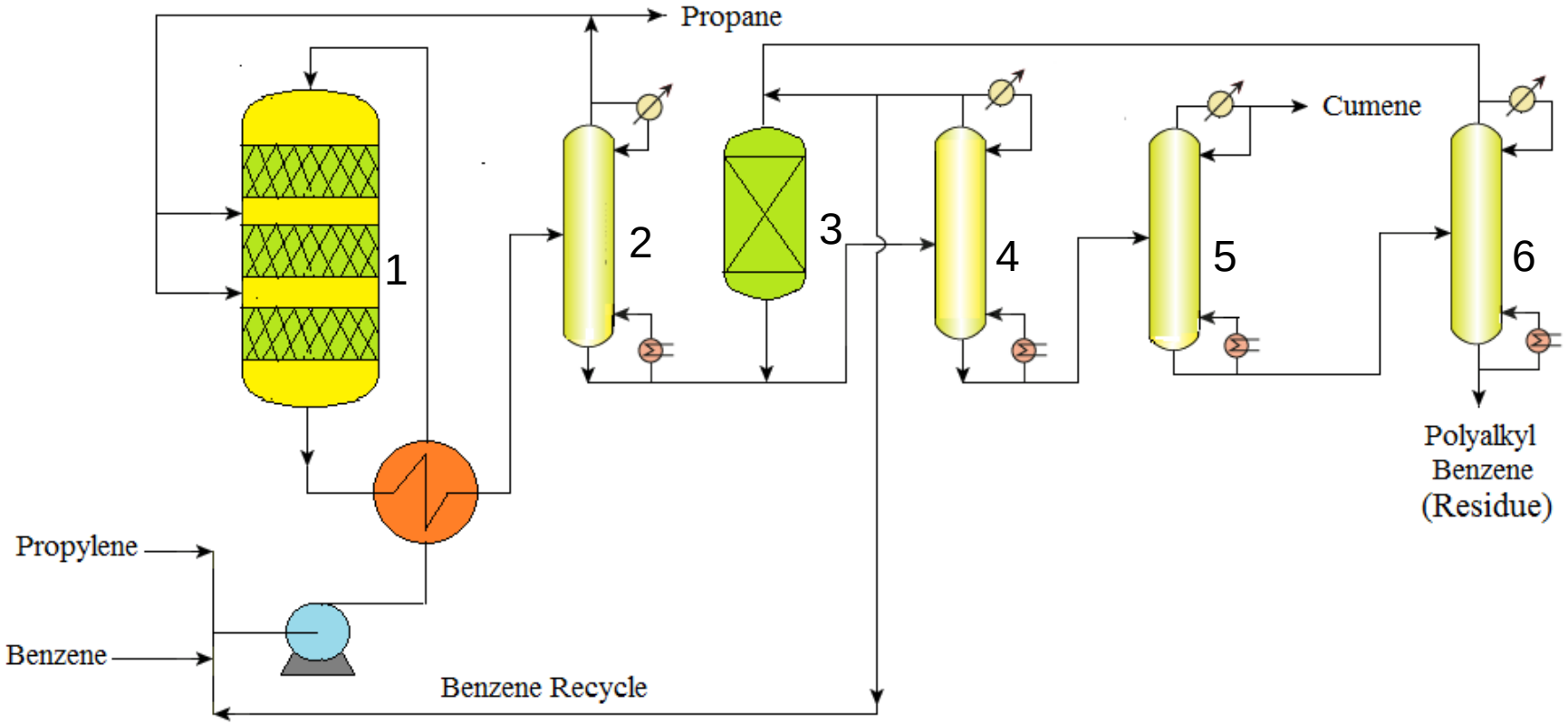
Catalyst: Solid phosphoric acid (Phosphoric acid on Kieselguhr)



[Mainly, Diisopropyl benzene (DIPB) and small amount of TIPB]

Production of Cumene by Propylation of Benzene

Catalyst: QZ-2001



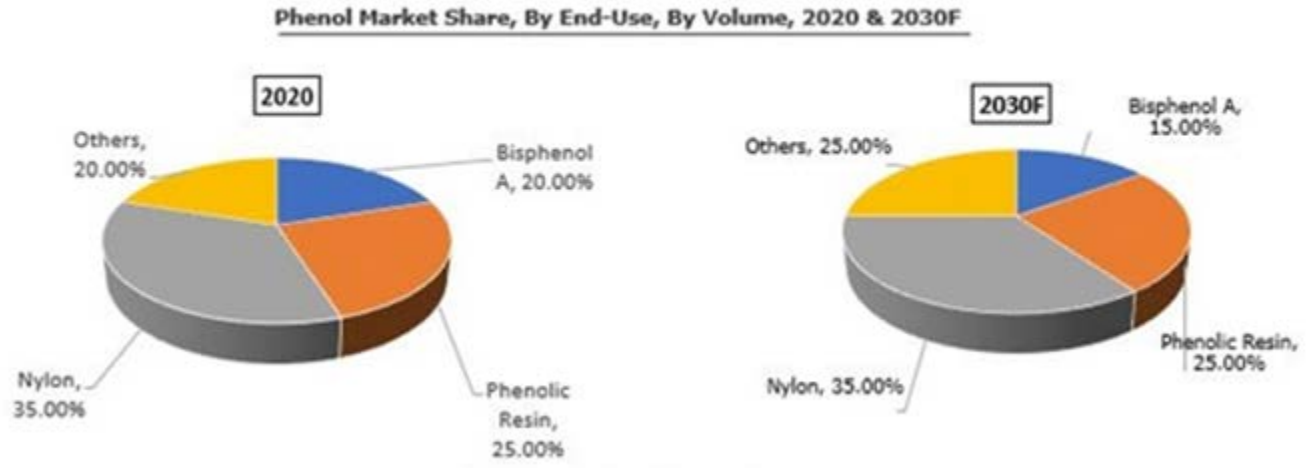
1: Alkylation Reactor, 2: Depropanizer, 3: Transalkylation Reactor,
4: Benzene Column, 5: Cumene Column, 6: DIPB Column

UOP's Q-Max Process for Cumene

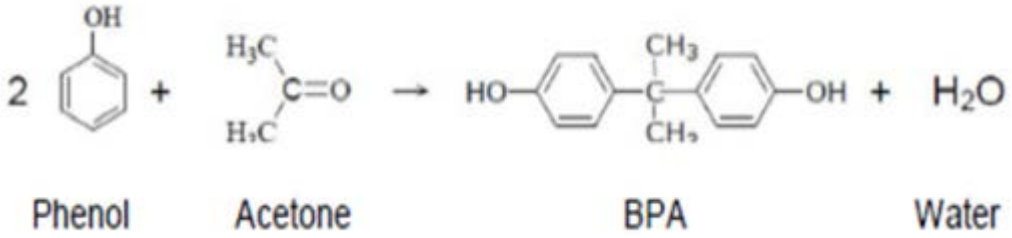
In fiscal year 2021, the production volume of phenol across India was around 61 thousand metric tons.

The demand for Phenol in India reached 311.00 thousand tonnes in FY2021 and is anticipated to grow at around CAGR 5.20% to reach 490.80 thousand tonnes by FY2030.

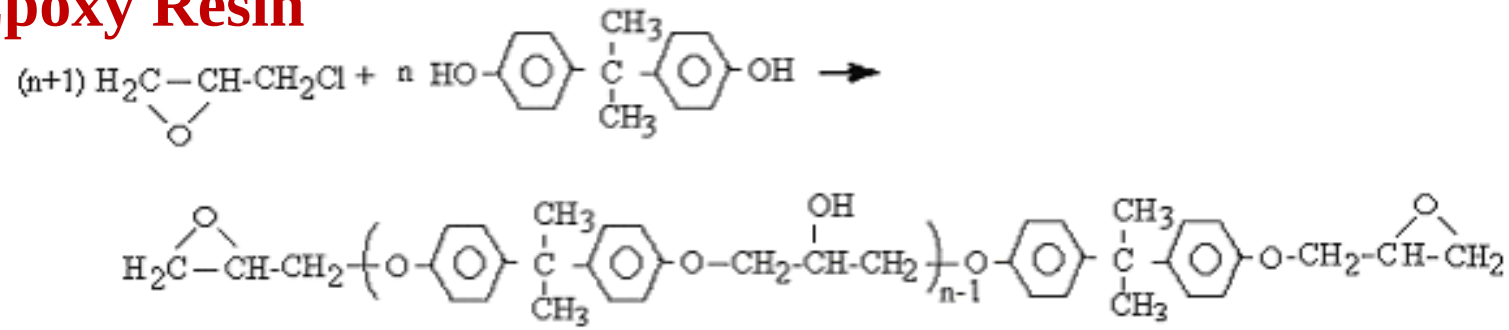
Globally Phenol is consumed majorly in BPA production. Major applications for BPA come from polycarbonate and epoxy resins. Polycarbonates are widely used in electronics, automotive, optical, etc. industries whereas epoxy resins are widely used in the paint & coating industry. Phenol is also used in producing Phenolic / Formaldehyde resin, which is further used in furniture, laminates, etc.



Bisphenol A (BPA)

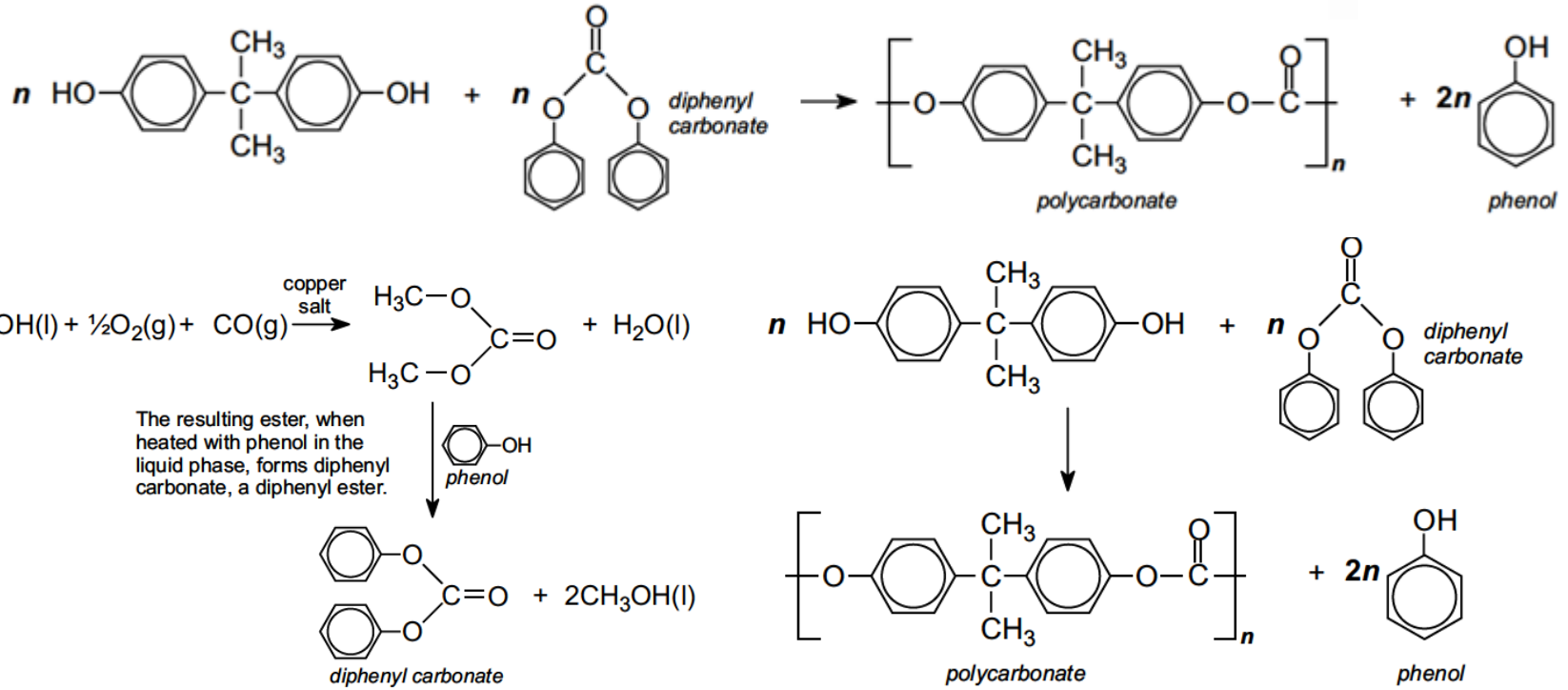


Epoxy Resin



Epoxy resins are oligomers resulting from the condensation of bisphenol A and epichlorohydrin. When cross-linked, they are hard, chemically resistant, and dimensionally stable, and have excellent electrical properties. Their largest use is for protective coatings of metal containers, appliances and ships, as well as for general maintenance where resistance to severe corrosion is required. They are used in the computer industry for "potting" electrical components. The second largest use is in fibre-reinforced composites for circuit boards, aerospace components, and sporting equipment. Other uses include adhesives, sealants, patching and flooring compounds, and castings.

Polycarbonate Resin

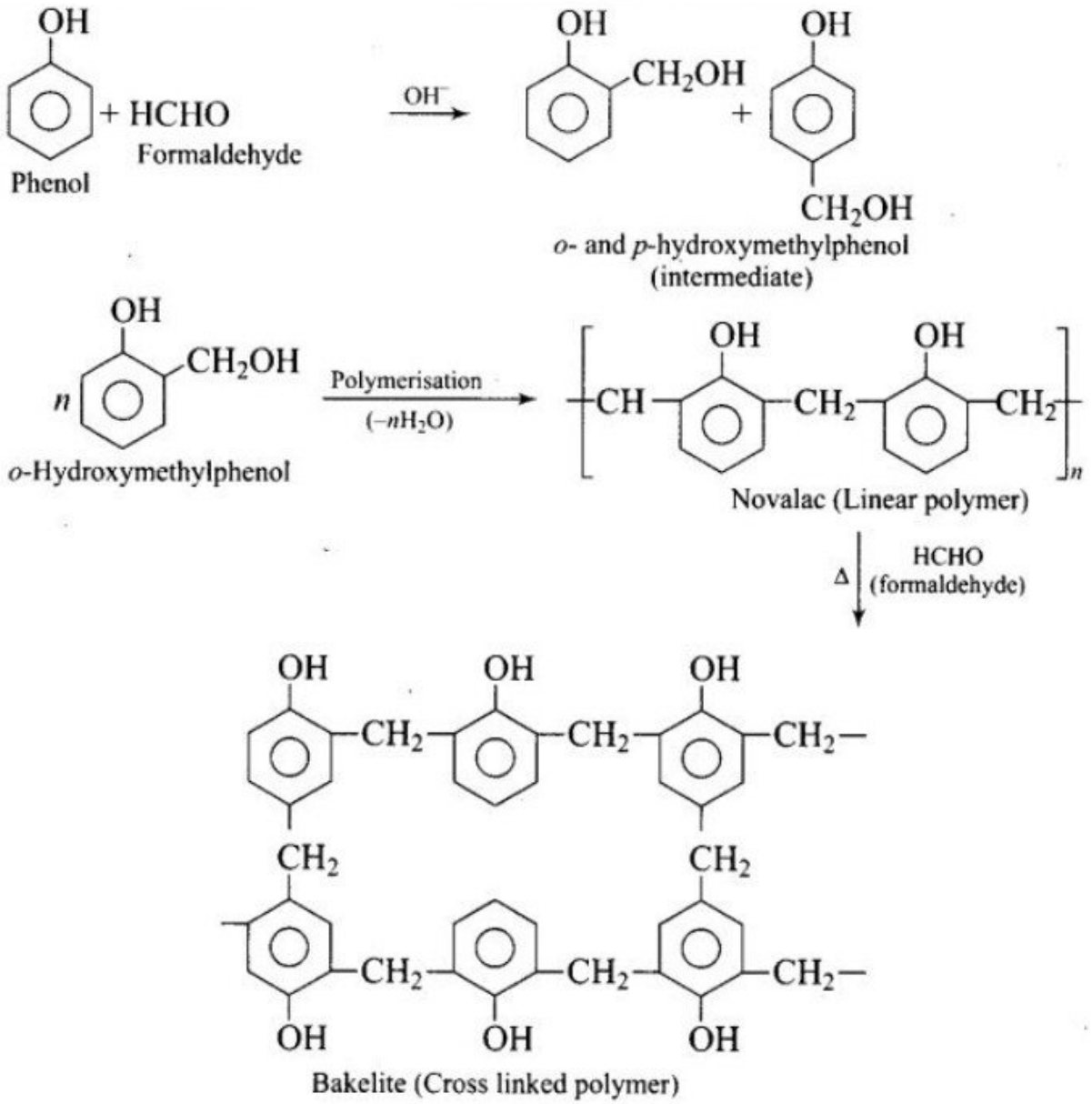


The largest application of polycarbonates is in the electrical and electronics sector for compact disks, business machine enclosures, connectors and plugs, telephones and electrical distribution devices.

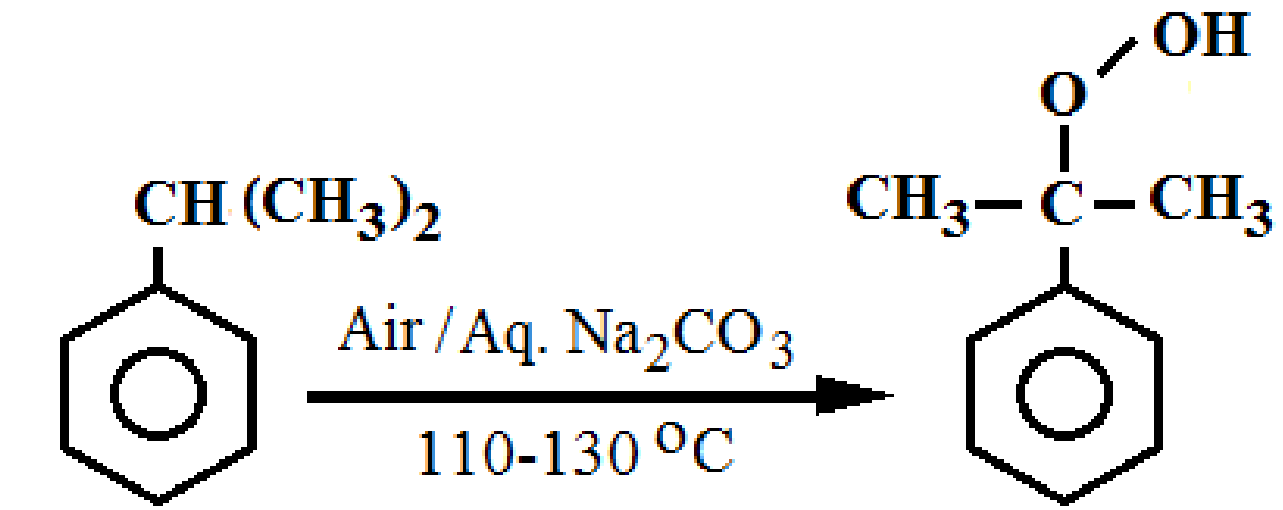
The second largest application is for window glazing and related applications such as binoculars, where a virtually unbreakable molding with exceptional optical properties is required.

Polycarbonates are also blended with poly(ethylene terephthalate) or poly(butylenes terephthalate) to make impact resistant polymer alloys useful, for example, for automobile bumpers and even for side panels.

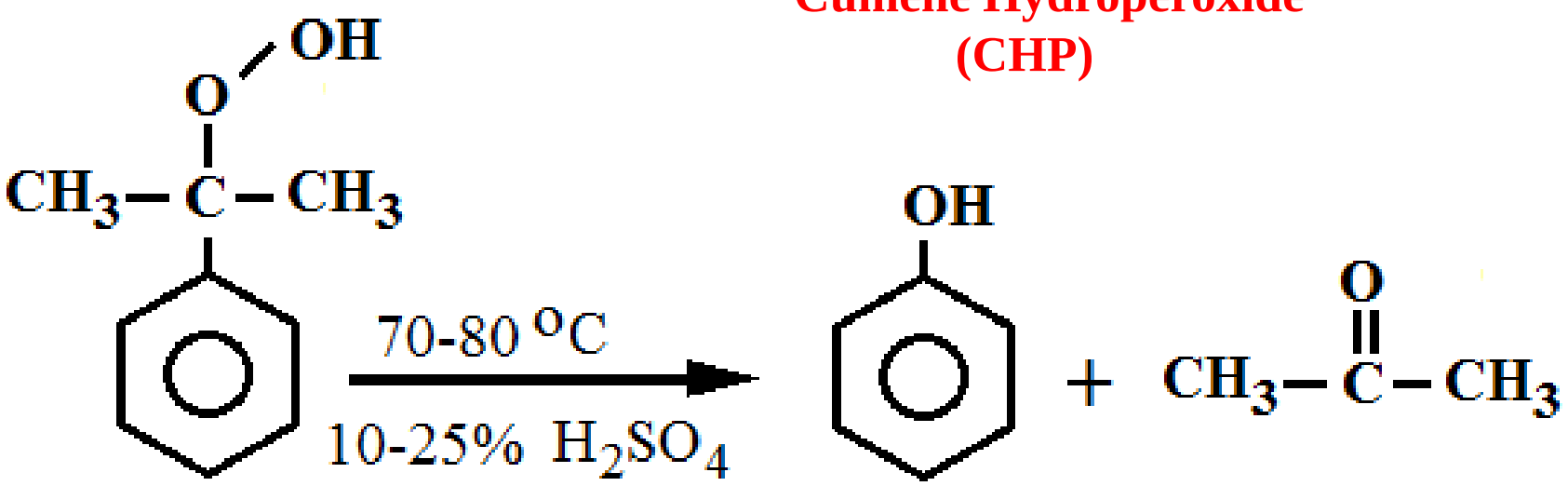
Phenol-Formaldehyde Resins

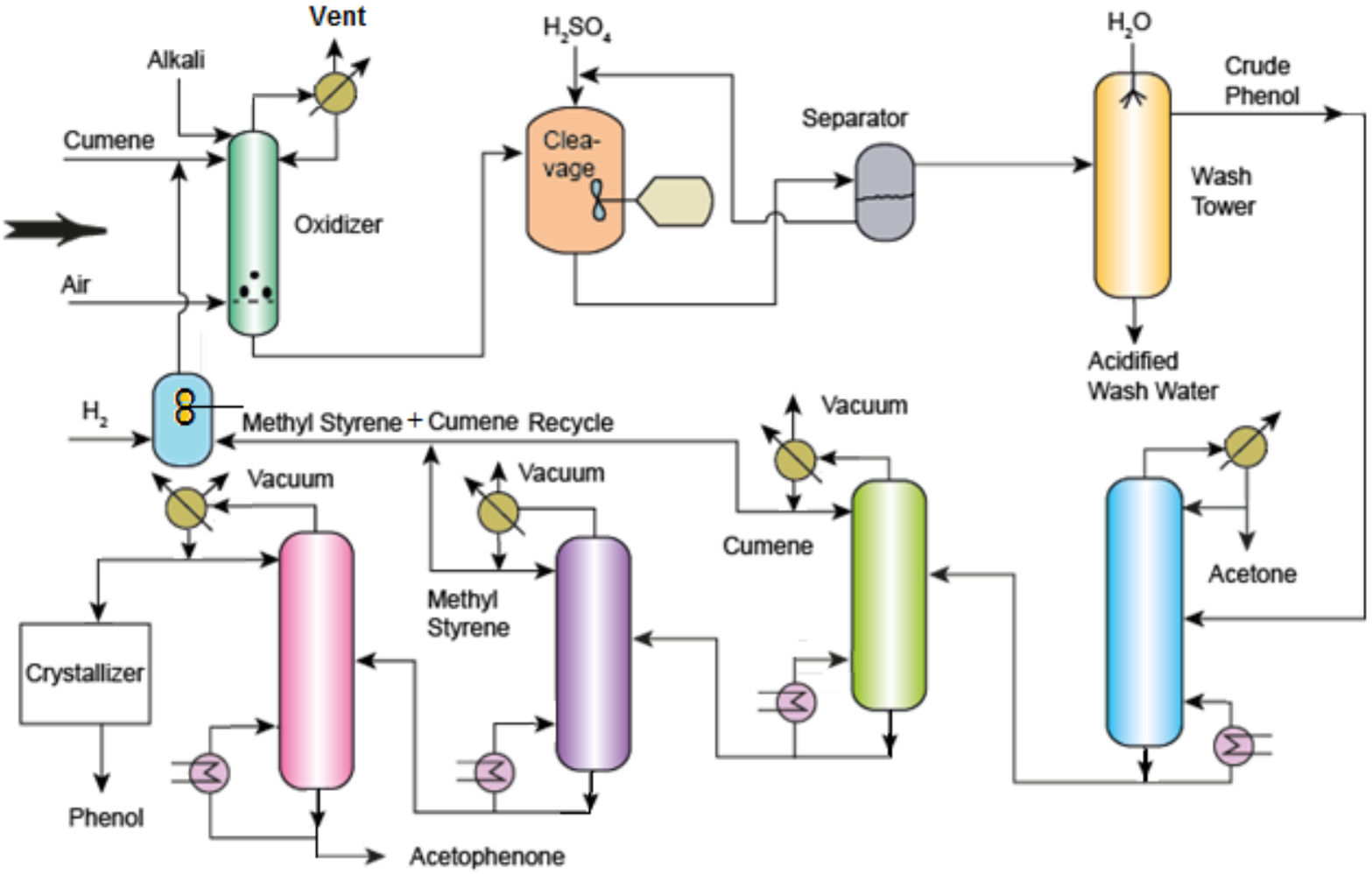


Synthesis of Phenol from Cumene



Cumene Hydroperoxide (CHP)

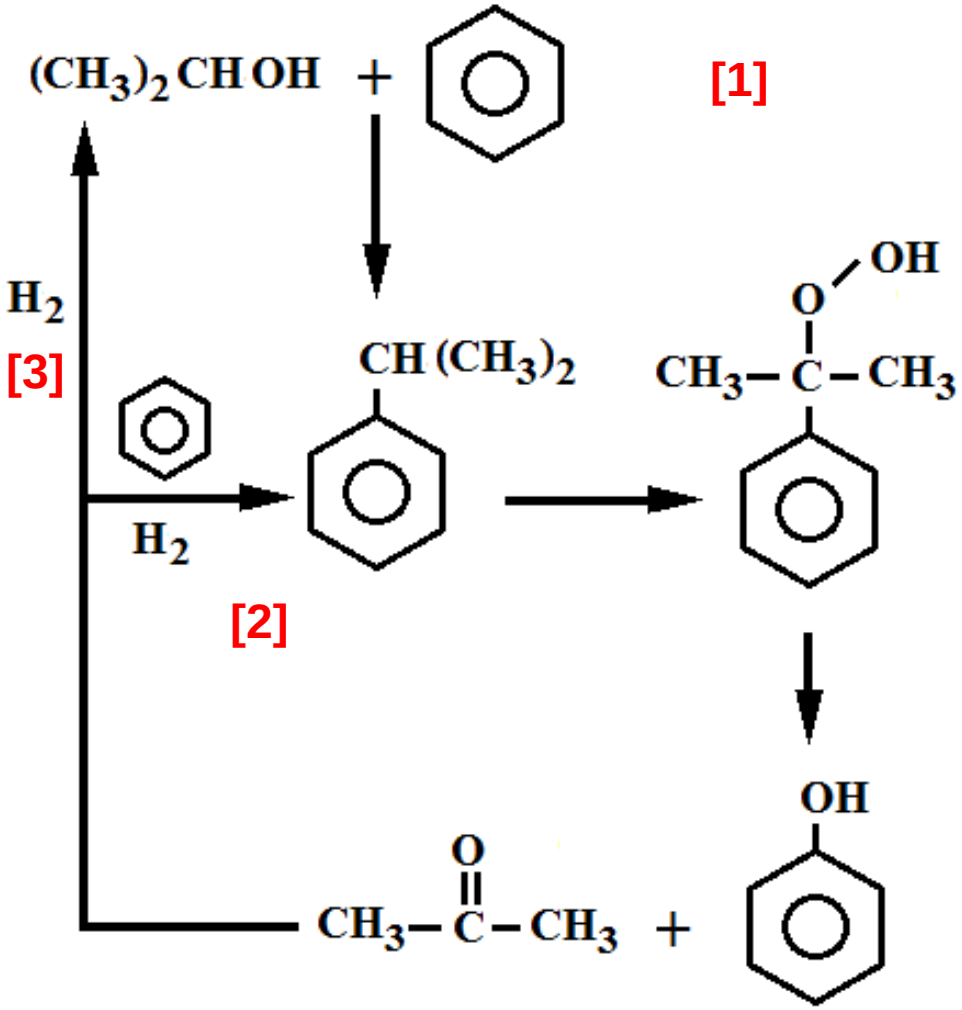




Boiling points: Cumene, **152 °C**; Alpha-methyl styrene, **166 °C**; Phenol, **181.7 °C**; Acetophenone, **202 °C**

Production of Phenol from Cumene

Cumene synthesis using by-product Acetone



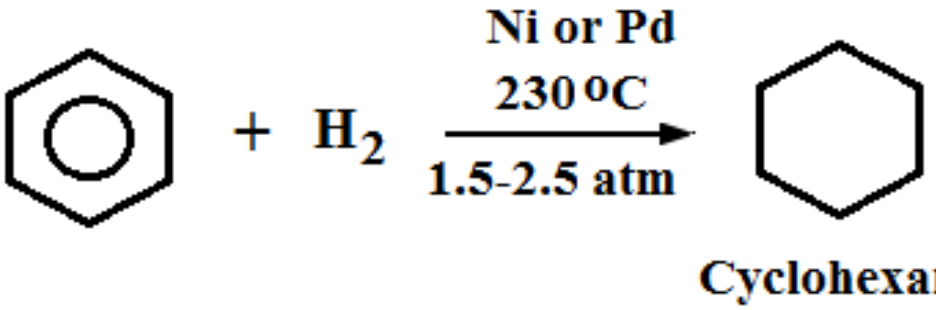
1. Sreedevi *et al.*; *Ind. Engg. Chem. Res.* **2001**, *40(14)*, 3133-3138.

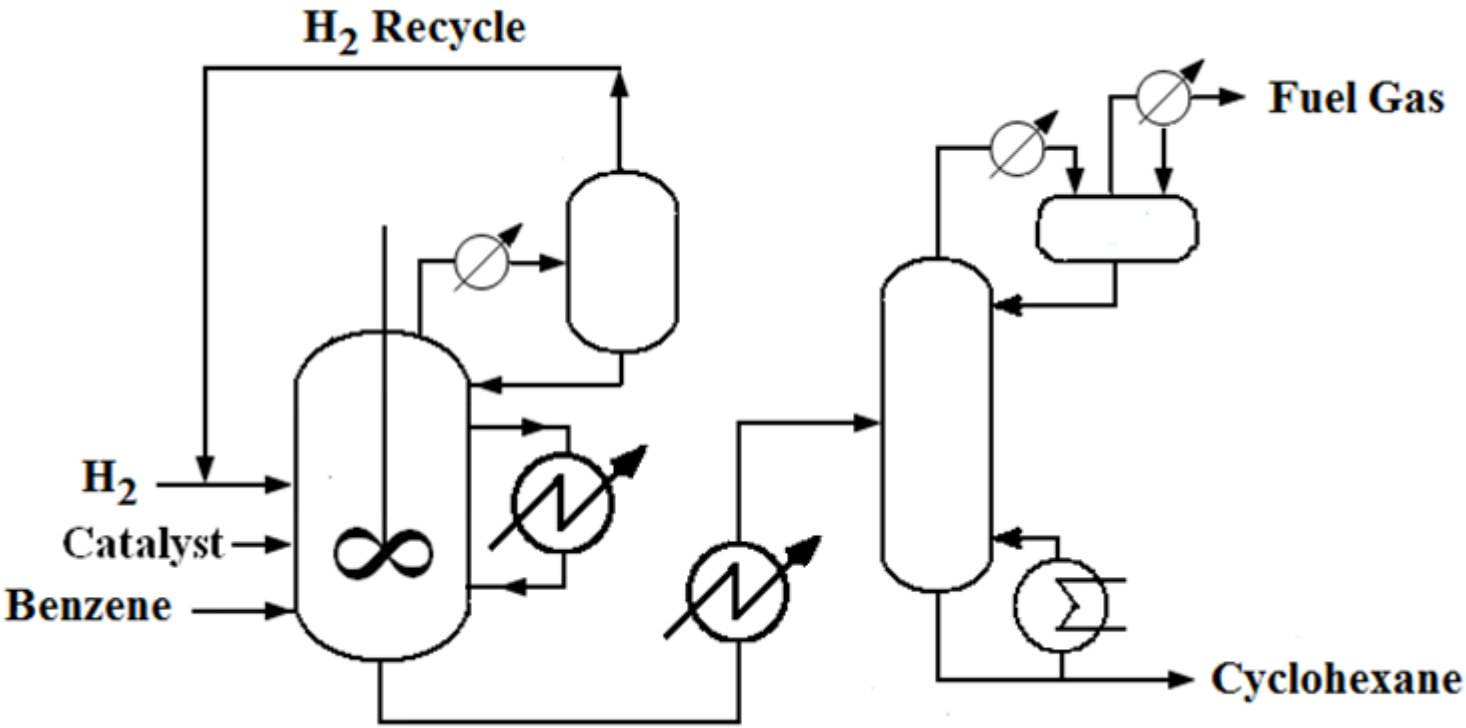
2. Barman *et al.*; *Ind. Engg. Chem. Res.* **2006**, *45(10)*, 3481-3487.

3. Basu, S. and **Pradhan, N. C.**; *Catal. Today*, **2019**, *348*, 118-126.

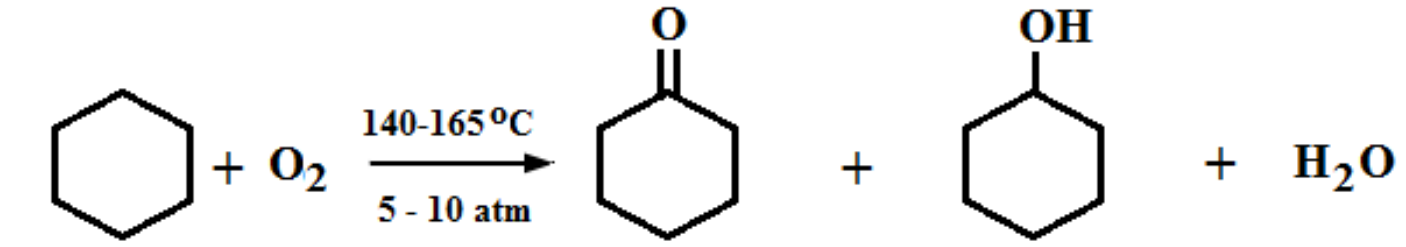
Production of Adipic Acid and Caprolactam

Cyclohexane from Benzene



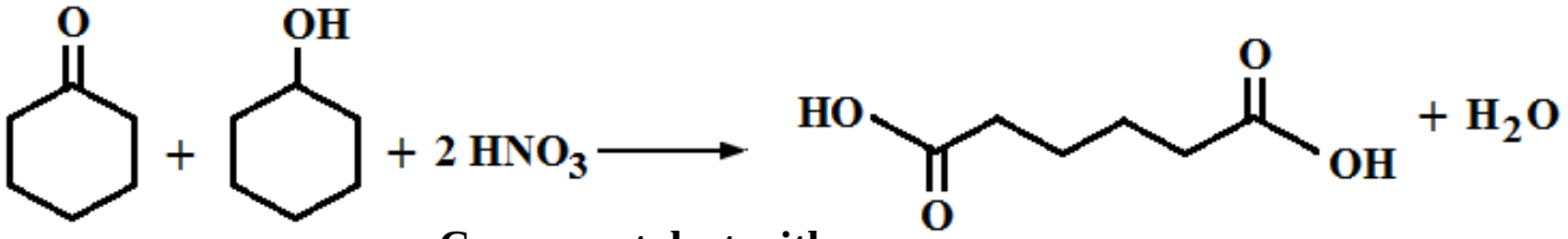


Adipic Acid from Cyclohexane



Cyclohexane | Cyclohexanone (K) Cyclohexanol (A) KA Oil

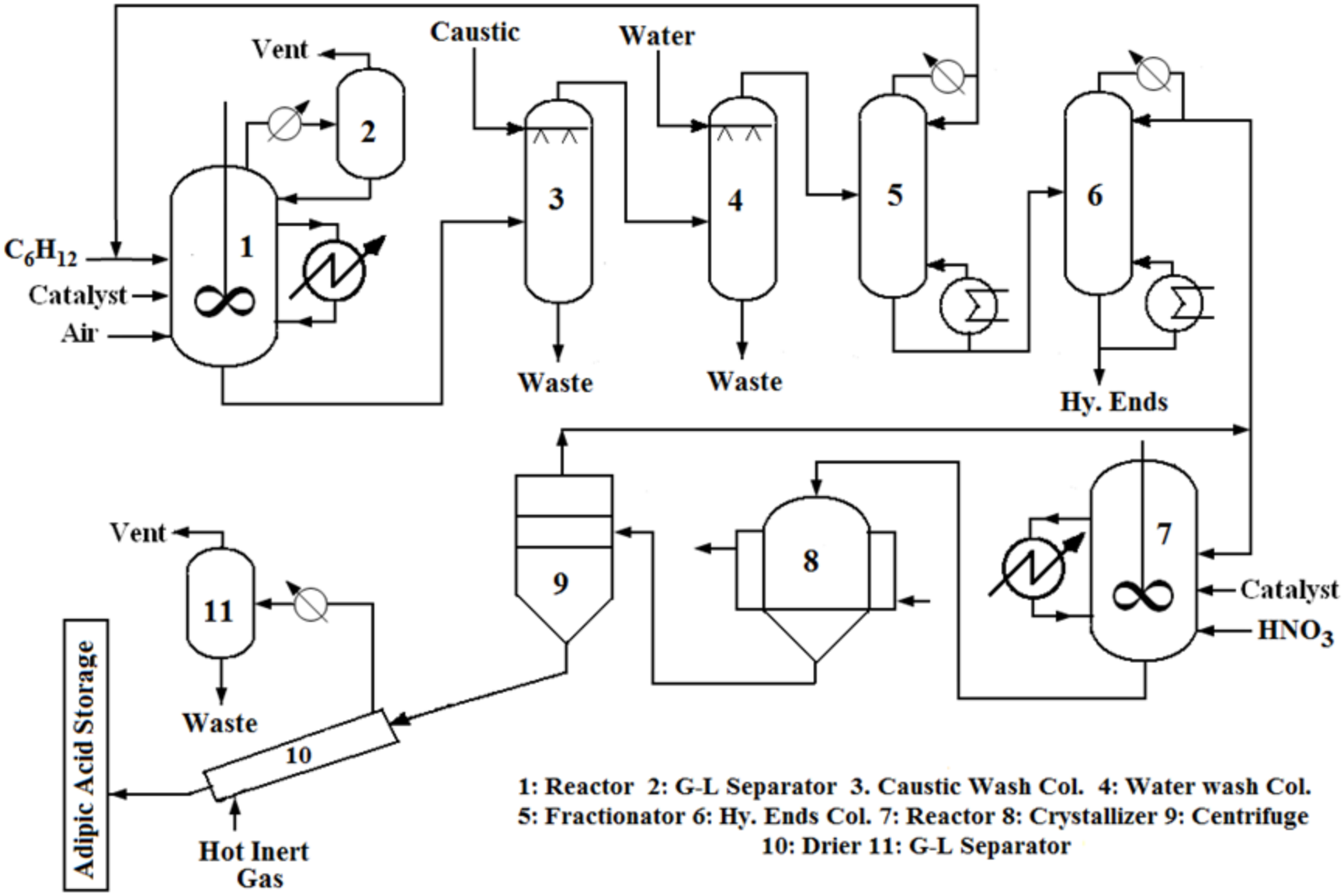
Catalyst: Cobalt salt (Cobalt naphthenate or octanoate)



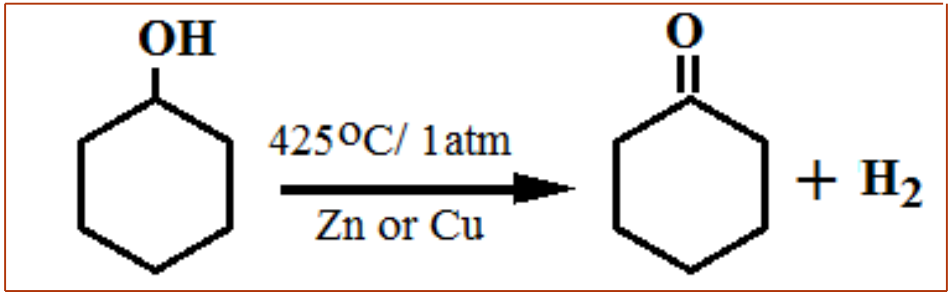
KA Oil

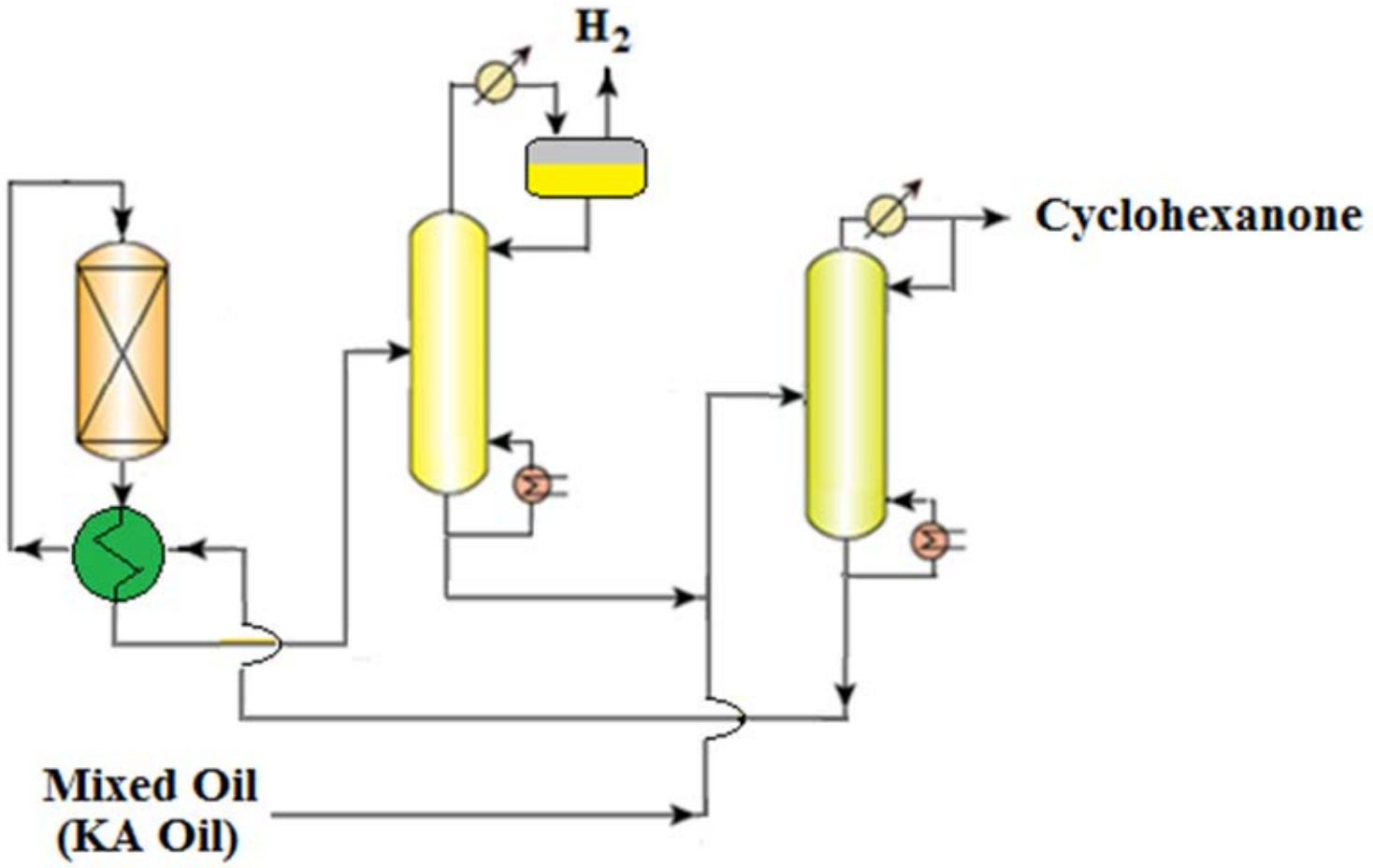
Copper catalyst with ammonium vanadate

Adipic Acid

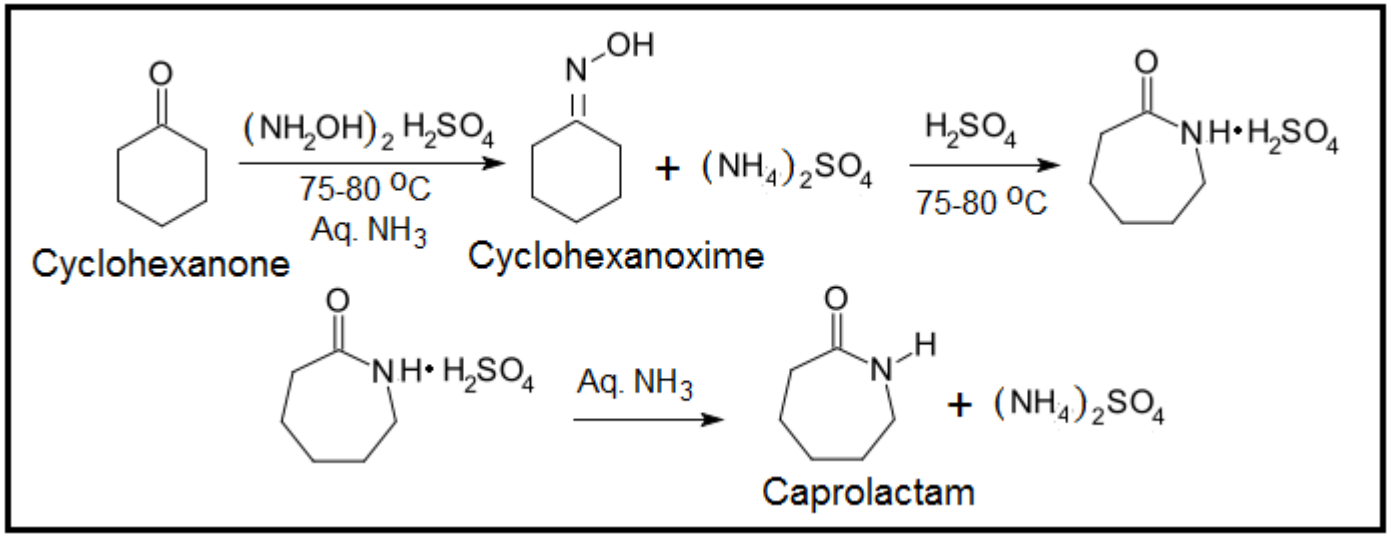


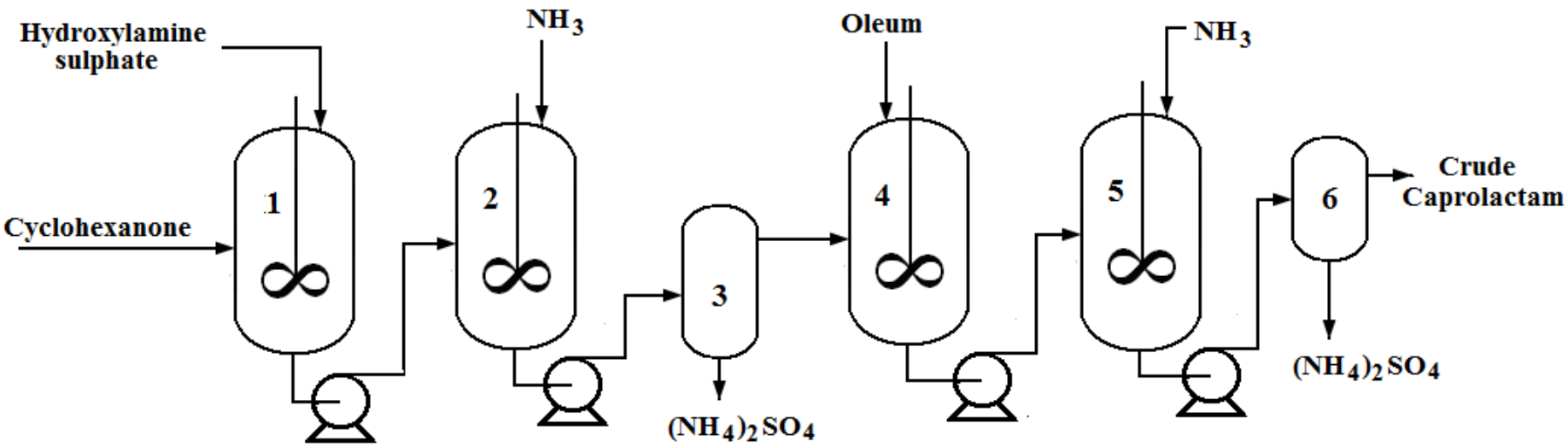
Production of Adipic Acid from Cyclohexane





Production of Cyclohexanone from Cyclohexanol





1: Oximation Recator; 2 & 5 Neutralizer; 3 & 6: Settler
4: Reactor for Beckmann Rearrangement

Caprolactam from Cyclohexanone

Production of Nitrobenzene and Aniline

Nitrobenzene Market size was valued at US$ 10.34 Bn. in 2021 and the total Nitrobenzene revenue is expected to grow at 5.8% from 2022 to 2027, reaching nearly US$ 14.5 Bn.

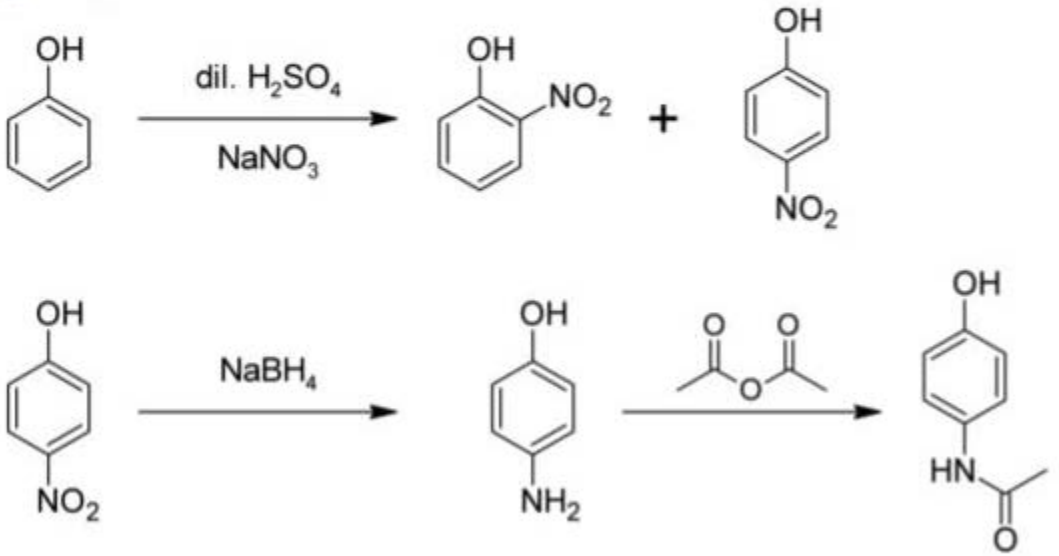
Aniline manufacturing makes up the bulk of nitrobenzene applications, accounting for more than 95% of the total.

The aniline-derived methylene diphenyl di-isocyanate (MDI) serves as a primary predecessor for polymers utilized in a variety of end-user sectors, notably architecture, automobile, and many others. Additionally, polyurethane foams made from MDI, which are primarily applied in different structural insulation applications, are one of the most crucial characteristics in architecture, both in their ductile and brittle forms.

Aside from aniline, the substance is also used as an insecticide ingredient.

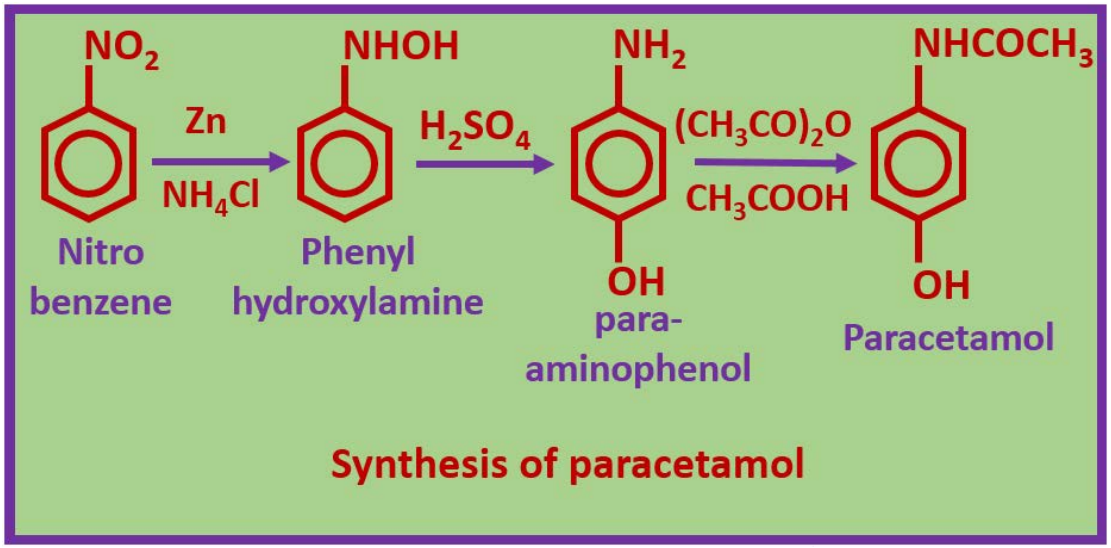
Nitrobenzene is used in the pharma industry to make paracetamol, the most widely used drug on the planet. Because paracetamol is mostly produced in India and China, APAC is the pharma industry's biggest user of aniline and hence nitrobenzene.

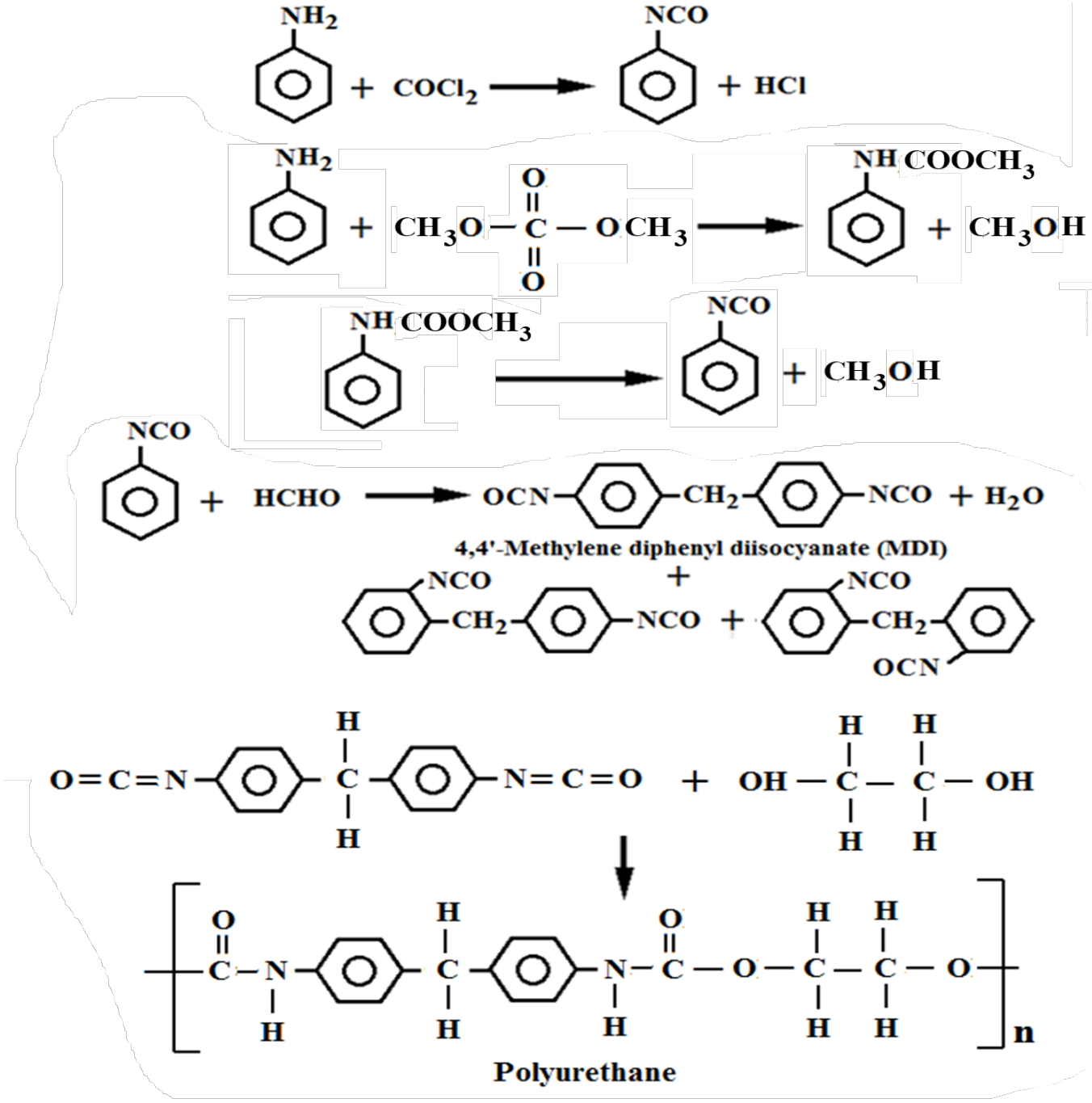
Synthesis of Paracetamol

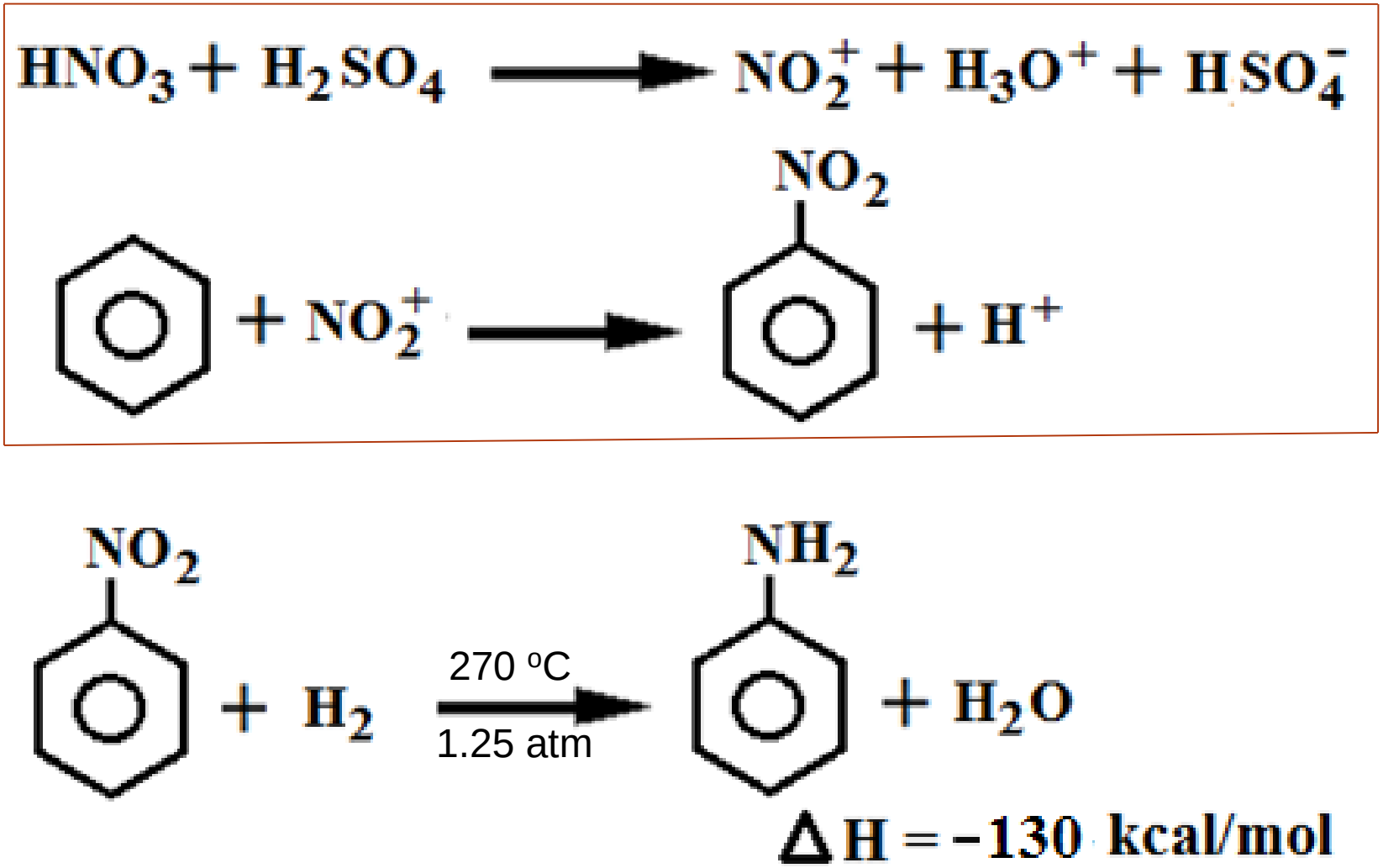


Paracetamol

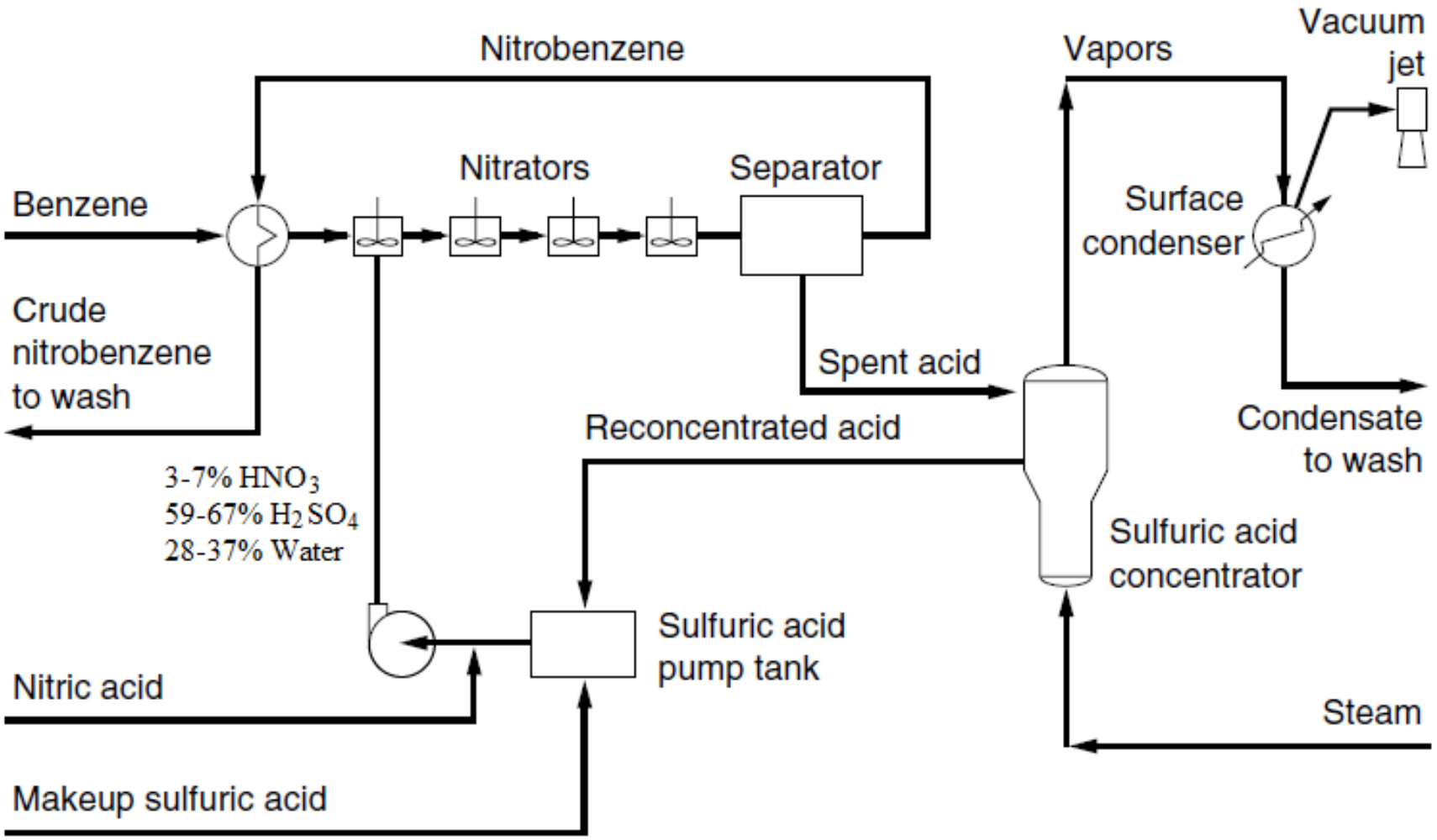
(Acetaminophen)



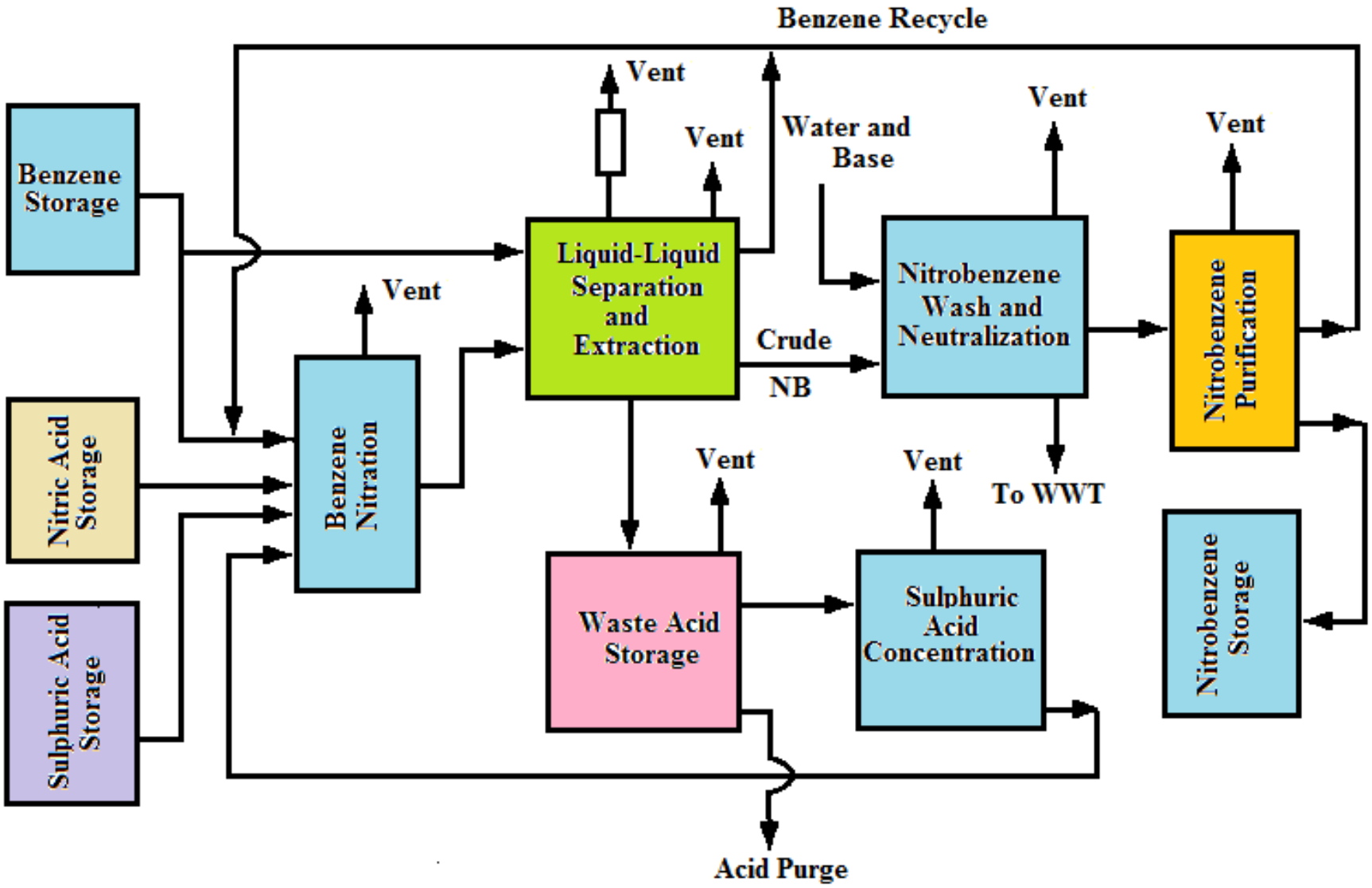

NH2
+ COCl2
NCO
+ HCl
NH2
+ CH3O – C – OCH3
O
O
NH COOCH3
+ CH3OH
NH COOCH3
NCO
+ CH3OH
NCO
+ HCHO
OCN – CH2 – NCO + H2O
4,4'-Methylene diphenyl diisocyanate (MDI)
+
NCO
CH2
NCO
+
NCO
CH2
OCN
O=C=N – C – N=C=O
H
H
+
OH – C – C – OH
H H
H H
O
C – N
H
H
C
H
H
O
N – C – O – C – C – O
H
H
H H
H H
n
Polyurethane



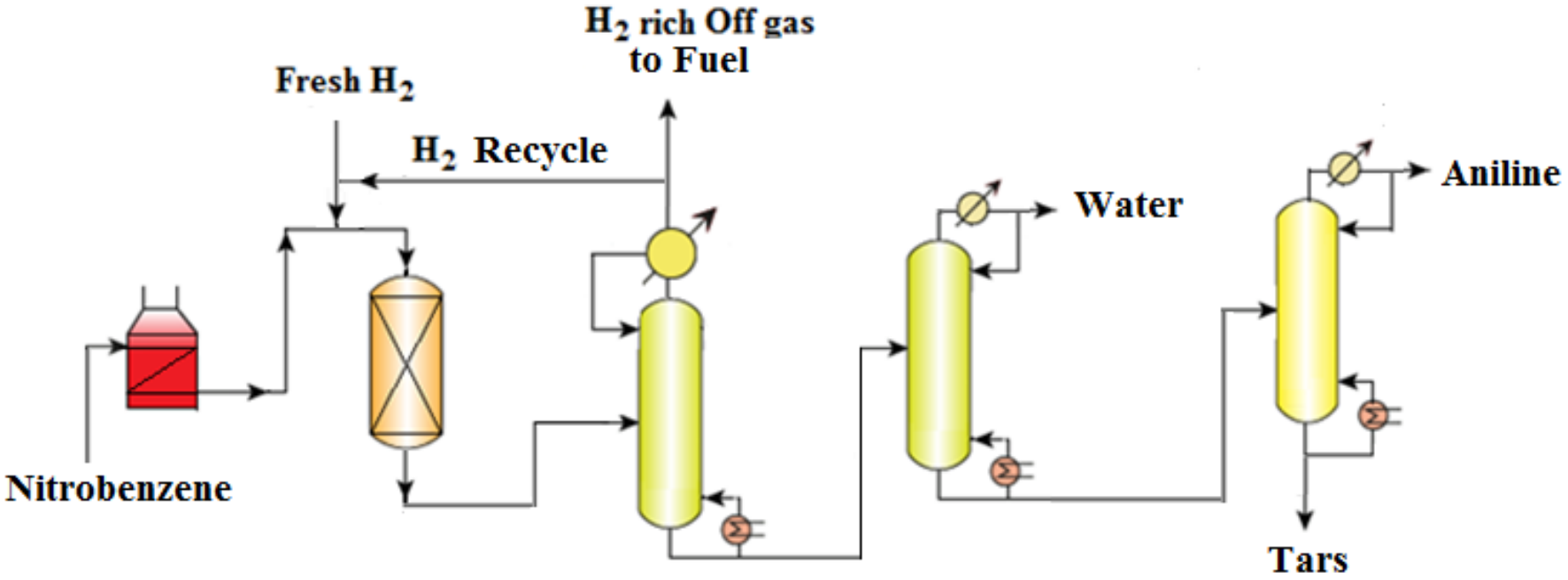
Catalyst: Cu or Pd on activated carbon or Alumina in combination with other metals (Pb, V, P and Cr) as modifiers/promoters



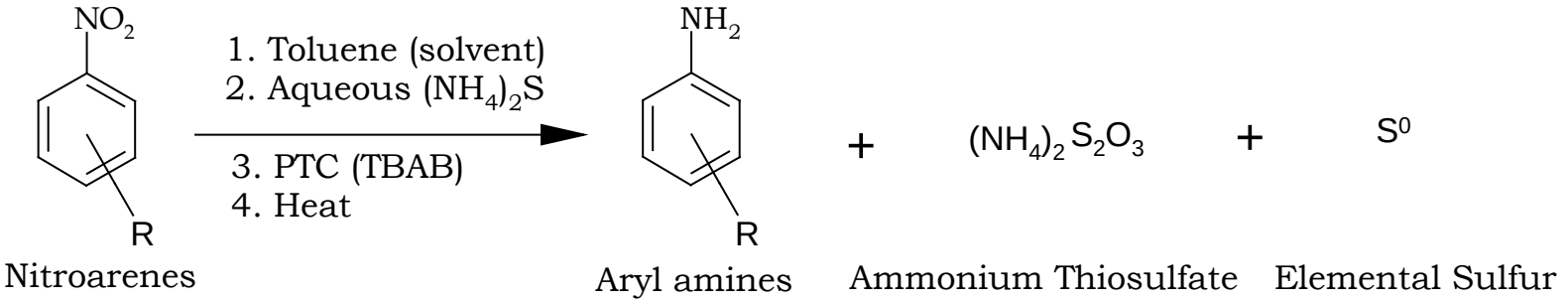
Flowsheet for the Production of Nitrobenzene



Block Diagram of Nitrobenzene Production



Production of Aniline from Nitrobenzene



Nitroarenes | Aryl amines | Ammonium Thiosulfate | Elemental Sulfur

where, R=CH_3 (Nitrotoluenes) or Cl (Chloronitrobenzenes)

Stoichiometry

- **Dauben (1973):**

$$4ArNO_2 + 6S^{2-} + 7H_2O \rightarrow 4ArNH_2 + 3S_2O_3^{2-} + 6HO^- \quad (1)$$

- **Gilman (1941); Lucas and Scudder (1928); Meindl et al. (1984):**

$$ArNO_2 + 3HS^- + H_2O \rightarrow ArNH_2 + 3S + 3HO^- \quad (2)$$

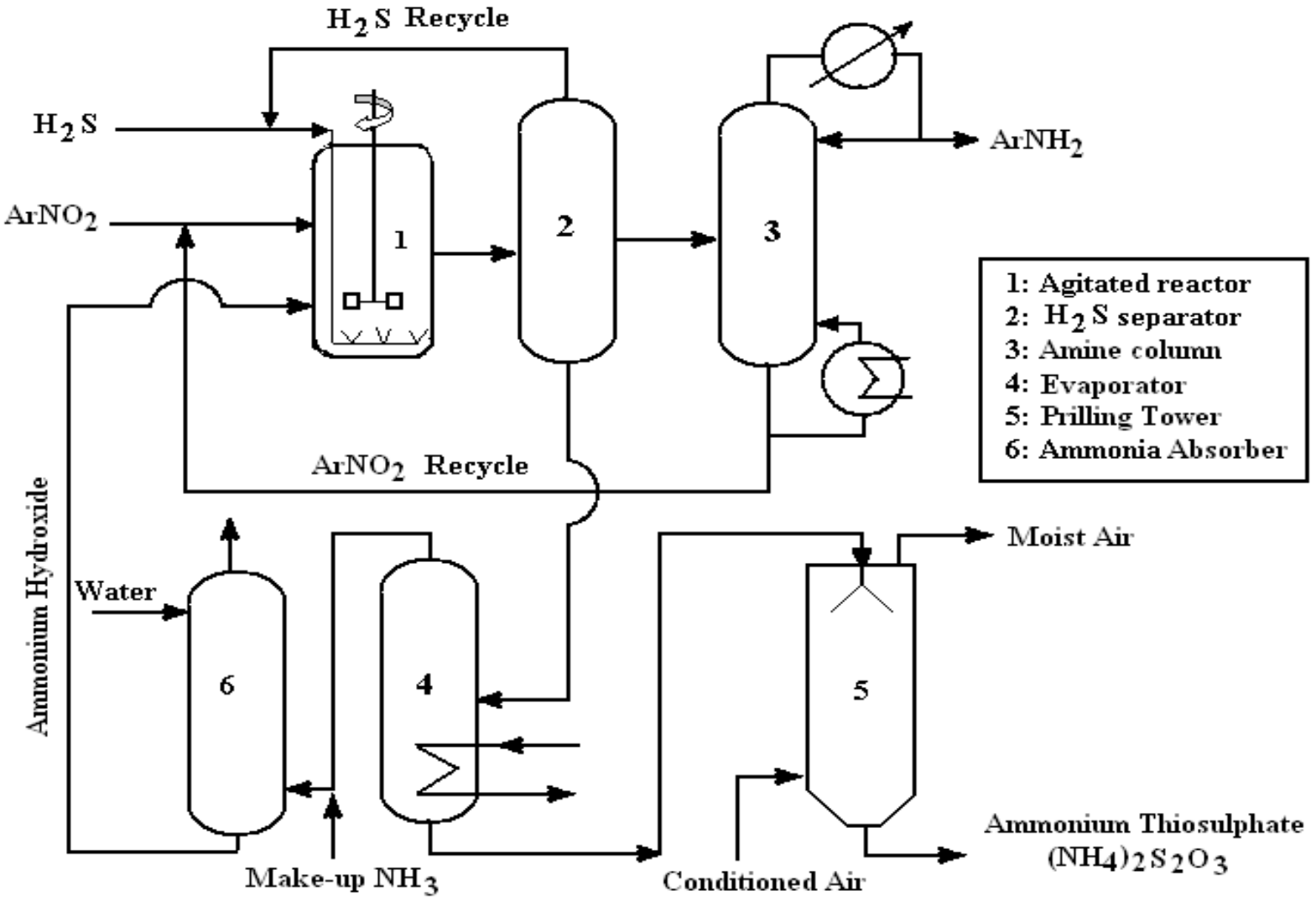
- **Hojo et al. (1960); Bhave and Sharma (1981):**

$$ArNO_2 + S_2^{2-} + H_2O \rightarrow ArNH_2 + S_2O_3^{2-} \quad (3)$$

Maity *et al., Appl. Catal. A: General*, **2006**, *30 (2)*, 251-258.

Maity *et al., Appl. Catal. B: Environmental* **2008**, *77(3-4)*, 418-426.

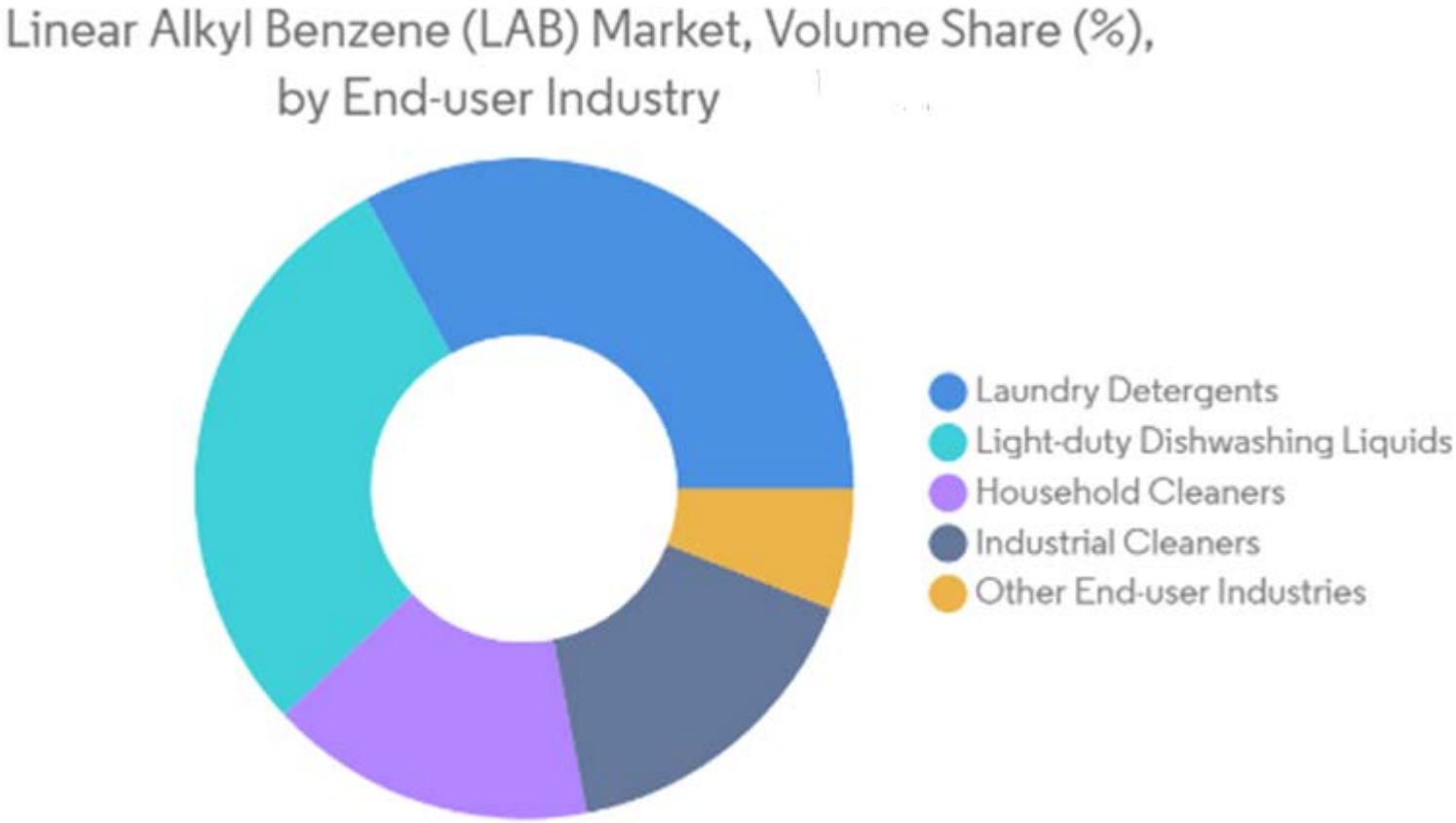
Jeeru *et al., Indian Chem. Engr.* **2016**, *58(3)*, 279-296.



Process Flow Diagram for the Production of Aromatic Amines by Absorption of H_2S in Aqueous NH_3 Solution and Simultaneous Reaction with Aromatic Nitro-compounds

Production of
Linear Alkyl Benzene
(LAB)

The Linear Alkyl Benzene Market size is estimated at 3.41 Million tons in 2024, and is expected to reach 3.98 Million tons by 2029, growing at a CAGR of 3.14% during the forecast period (2024-2029).

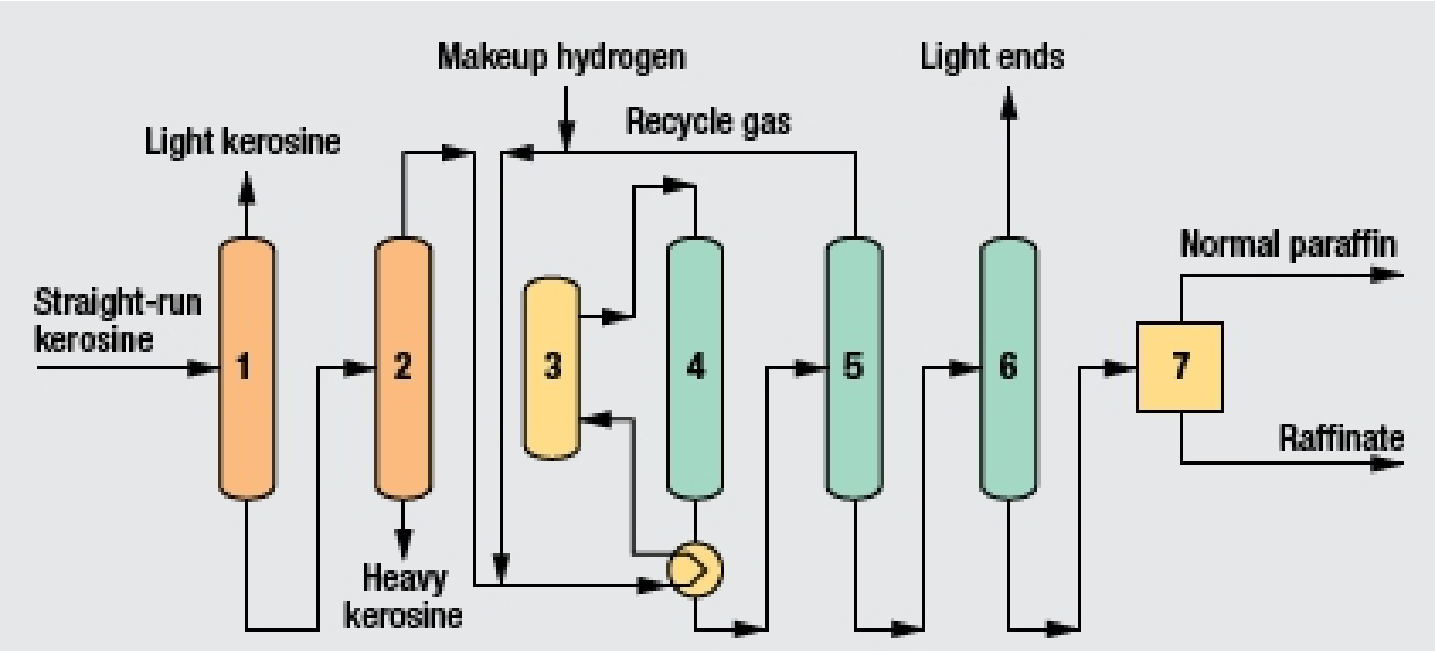


A Review in Linear Alkylbenzene (LAB) Production Processes in the Petrochemical Industry. Aref Shokria and Safoora Karimia, Russian Journal of Applied Chemistry, 2021, Vol. 94, No. 11, pp. 1546–1559.

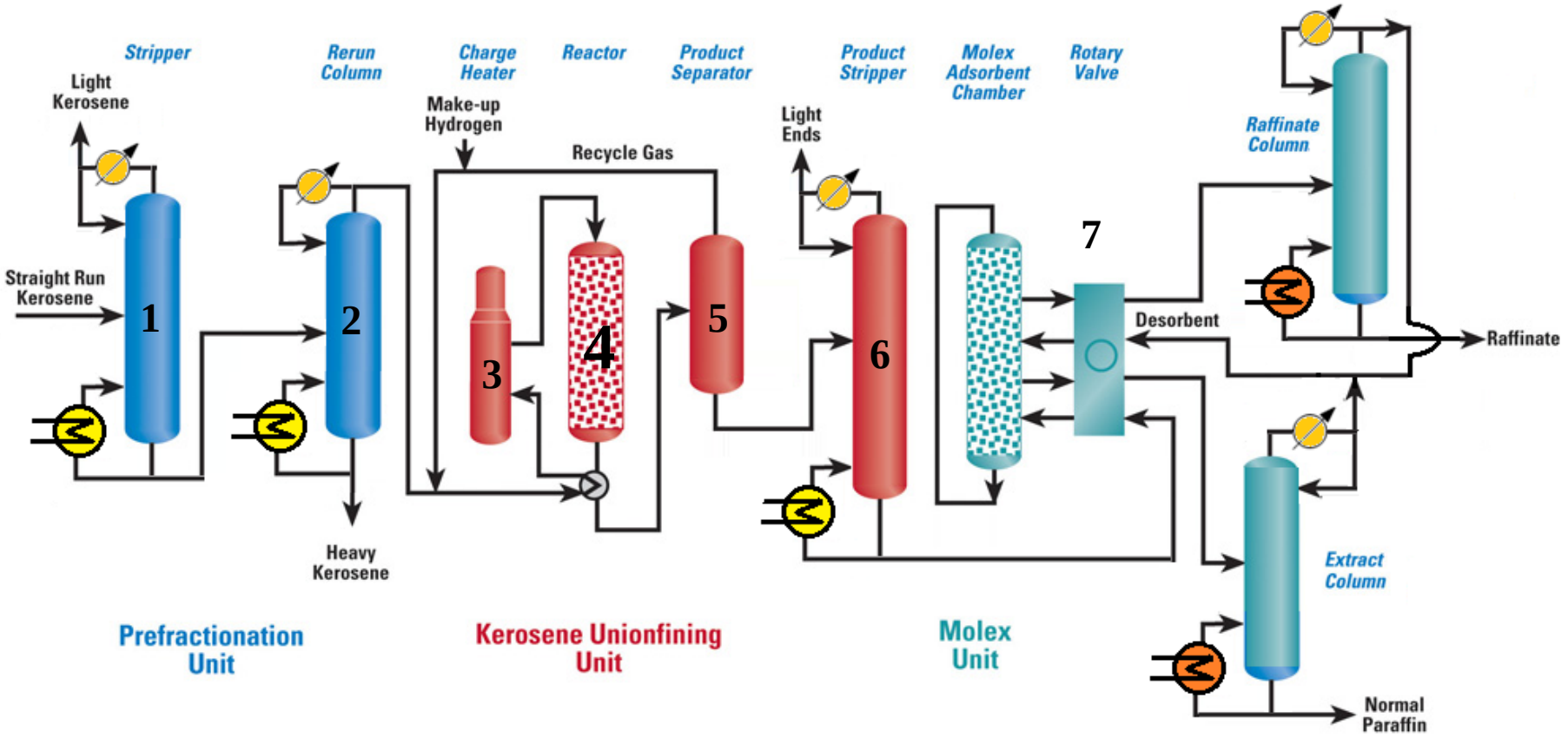
n-Praffin from Straight-run Kerosene

Straight-run kerosine is fed to a Stripper (1) and a Rerun column (2) to remove light and heavy materials. The remaining heart-cut kerosine is heated in a charge Heater (3) and then treated in a Unionfining reactor (4) to remove impurities. The reactor effluent is sent to a product Separator (5) to separate gas for recycle, and then the liquid is sent to a product Stripper (6) to remove light ends. The bottoms stream from the product stripper is sent to a Molex unit (7) to recover normal paraffins.

Feedstock is typically straight-run kerosine with 18 – 50% normal paraffin content. Product purity is typically greater than 99 wt%.



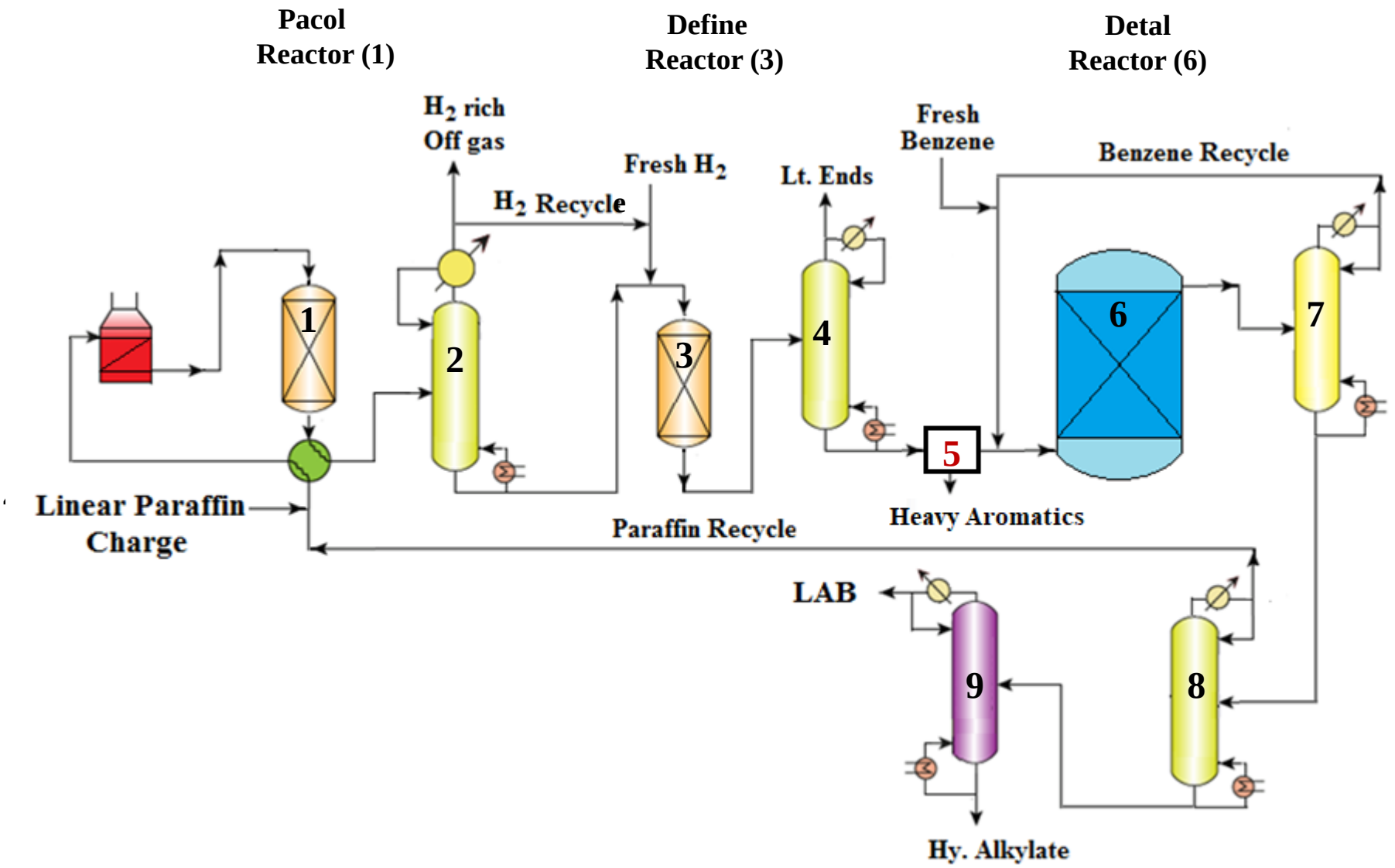
Flowsheet of Molex Unit



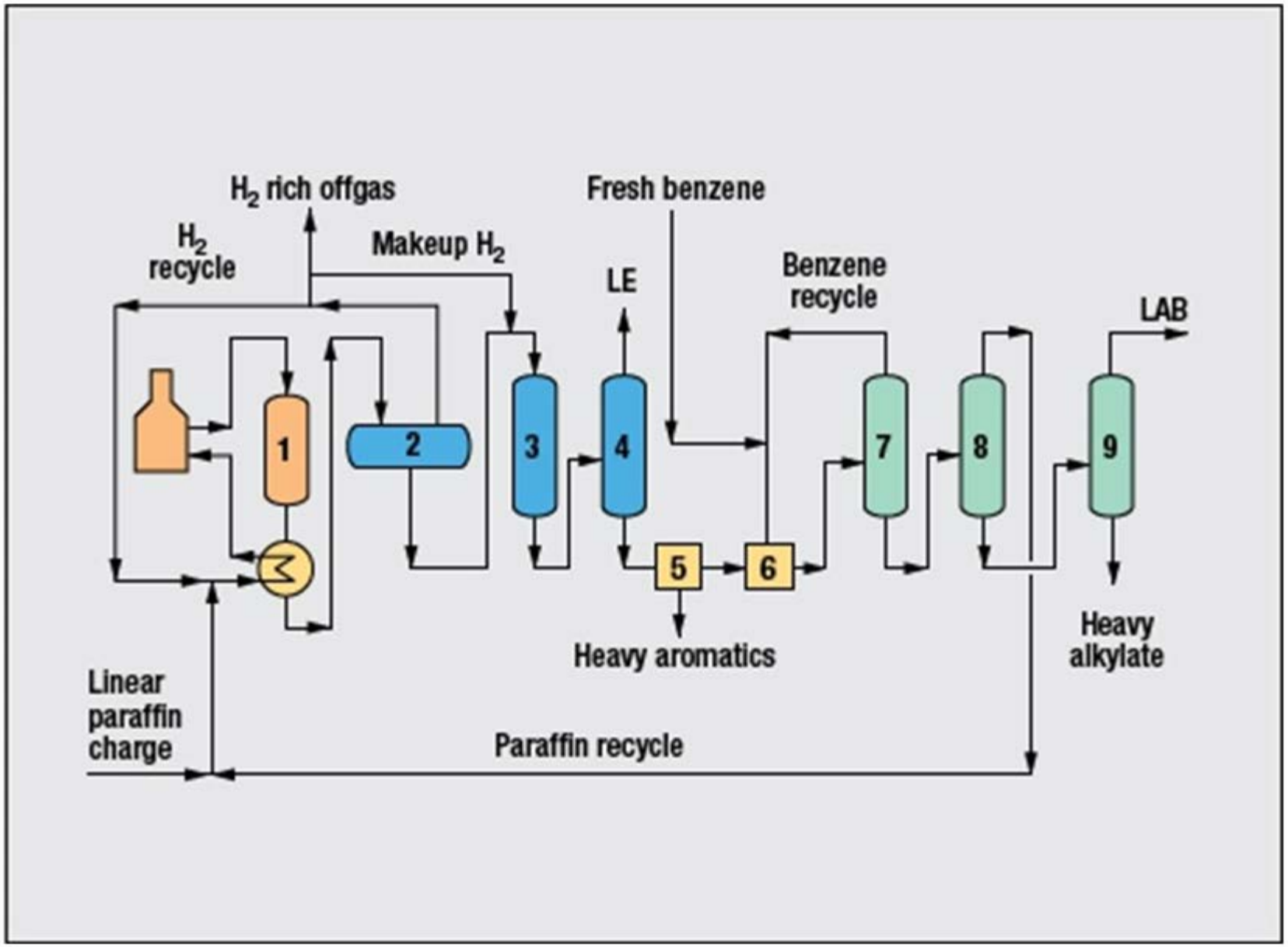
Flowsheet of Molex Complex

Linear paraffins are fed to a Pacol reactor (1) to dehydrogenate the feed into corresponding linear olefins. Reactor effluent is separated into gas and liquid phases in a Separator (2). Diolefins in the separator liquid are selectively converted to mono-olefins in a DeFine reactor (3). Light ends are removed in a Stripper (4) and the resulting olefin-paraffin mixture is sent to a PEP (Powdered Expanded Perlite) adsorber (5) where heavy aromatics are removed prior to being sent to a Detal reactor (6) where the olefins are alkylated with benzene. The reactor effluent is sent to a fractionators (7, 8) for separation and recycle of unreacted benzene to the Detal reactor, and separation and recycle of unreacted paraffins to the Pacol reactor. A rerun column (9) separates the LAB product from the heavy alkylate bottoms stream.

Feedstock is typically C_{10} to C_{13} normal paraffins of 98+% purity. LAB product has a typical Bromine Index of less than 10. Based on 100 weight parts of LAB, 81 parts of linear paraffins and 34 parts of benzene are charged to a UOP LAB plant.



Production of Linear Alkyl Benzene (LAB)


H_2 rich offgas
H_2 recycle
Makeup H_2
Fresh benzene
LE
Benzene recycle
LAB
1
2
3
4
5
6
7
8
9
Heavy aromatics
Heavy alkylate
Linear paraffin charge
Paraffin recycle

Thank you!