Phenol, Acetone, Cumene

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INTRODUCTION
The focus of this report is phenol. The main use of cumene is as a feedstock for phenol production. Acetone is co-produced in the process.

Cumene based routes to phenol are responsible for virtually all global production of phenol. Key elements of the phenol value chain are summarized below.

Cumene (isopropylbenzene, 2-phenylpropane) is a colorless liquid, with an aromatic (sweet) smell, practically insoluble in water. It is flammable.

Phenol is a transparent crystalline solid, soluble in methanol, alcohol, and cold water. It has an aromatic (sweet) smell. It is classified as a poisonous material.

Acetone is a colorless liquid which is miscible in ether, alcohol, and water. This flammable and volatile liquid, with a “fragrant mint-like” smell, is also known as 2-propanone.

COMMERCIAL TECHNOLOGY
Cumene
Nearly all commercial production of cumene is via catalytic alkylation of benzene using propylene.

The reaction between propylene and benzene occurs according to a Friedel-Crafts mechanism. Various acid catalysts such as aluminum chloride (AlCl₃), solid phosphoric acid (SPA) and acidic zeolites have been employed in commercial operations.

New plants normally utilize the more efficient zeolite catalysts, while some older plants may still be employing AlCl₃ or SPA. The desired reaction of benzene with propylene to cumene (bold arrow below) is illustrated in Figure 2.
There is an equilibrium that exists between diisopropylbenzene (DIPB), triisopropylbenzene (TIPB), benzene and cumene, as illustrated in Figure 3. This equilibrium can be shifted in favor of cumene production (so called transalkylation reaction) in the presence of strong acid catalysts.

The PERP report discusses the process technologies offered by:

- Badger Licensing
The commercial cumene to phenol process involves two primary chemical steps, namely oxidation of cumene to cumene hydroperoxide (CHP) and acid catalyzed CHP cleavage to phenol and acetone. However, there are many side reactions which occur and byproducts formed. The process chemistry is discussed in detail in Section 4 of the report.

The phenol manufacturing plant consists of several process units, including:

1. Oxidation of Cumene to CHP
2. CHP Concentration (Cumene Stripping)
3. Cleavage (Decomposition of CHP to products)
4. Neutralization
5. Off-gas Treatment
6. Phenol and Acetone Purification and Recovery
7. Alpha-Methylstyrene (AMS) Hydrogenation to Cumene and/or AMS Recovery

The oxidation, cleavage, and product purification processing units are the most important in terms of process economics and process safety. Phenol process technology is discussed in detail in Sections 5 of the report.

Nearly all commercial production of phenol is via the commercial technology providers/licensors who market both the phenol and acetone products:

- ILLA International – discussed in Section 6.1 of the PERP report
- KBR – discussed in Section 6.2 of the PERP report
- Versalis (formerly Polimeri Europa) / Lummus - – discussed in Section 6.4 of the PERP report
- Sunoco / UOP - – discussed in Section 6.5 of the PERP report

While one commercial producer (Mitsui Chemical) recycles the co-produced acetone back into the process to produce more phenol, and thereby markets only the phenol product - discussed in Section 6.3 of the report.

ALTERNATIVE AND DEVELOPING TECHNOLOGIES

Research in the area of alternative routes to phenol is largely driven by the fact that the market demand for acetone does not quite match the market demand for phenol (approximately four versus five percent annual growth rate, respectively, is estimated over the next 5 to 10 years).

The most well documented research relates to:
• Use of secondary butylbenzene (SBB) in place of cumene

Research on the SBB to phenol process started over twenty years ago. In principle, the process is analogous to that for cumene to phenol, except that oxidation of SBB followed by subsequent cleavage, yields methyl ethyl ketone (MEK) as a co-product (instead of acetone), along with the desired phenol product. MEK has a higher commercial value than acetone so this is an incentive. However, the commercial market demand for MEK is much, much lower than for acetone. Another difference between the cumene to phenol and this SBB to phenol process is that acetopheneone is the major byproduct in the SBB based route as opposed to DMBA. DMBA can be converted to AMS, which has value and in addition AMS can be converted back to cumene for recycle. Acetophenone has no significant ready market. Patents awarded to Shell teach that production of phenol is more efficient with a feed mixture of SBB and cumene. However, when a mixture of cumene and SBB is used, acetone is produced in addition to MEK

This process technology is discussed in detail in Sections 7.2 and 7.3 of the PERP report.

• Use of nitrous oxide as an oxidant in direct benzene to phenol process (BTOP)

Solutia (formerly Monsanto), in conjunction with the Boreskov Institute of Catalysis (BIC), developed a benzene oxidation route to phenol. Dating back nearly 20 years, the Boreskov Institute of Catalysis (BIC) in Novosibirsk, Russia, made the initial discoveries that led to the catalytic system employed in the Solutia process.

Nitrous oxide (N₂O) is used as oxidizing agent and the reaction is carried out in the presence of a zeolite catalyst. Solutia has an economic advantage for the use of this technology called AlphaOx™ due to availability of virtually free nitrous oxide as a waste product from its adipic acid process.

In principle, the chemistry of the process is summarized below:

\[
\text{C}_6\text{H}_5 + \text{N}_2\text{O}\xrightarrow{\text{[Catalyst]}} \text{OH} + \text{N}_2
\]

This process technology is discussed in detail in Section 7.4 of the PERP report.

**PROCESS ECONOMICS**

Process economics have been developed for the following:

• Cumene cost of production via propylene alkylation of benzene (China, N.W. Europe, and USGC location bases)

• Phenol cost of production via conventional cumene oxidation and CHP cleavage, with acetone co-produced and valued at market price - China, N.W. Europe, and USGC location bases

• Phenol cost of production via Mitsui propylene alkylation of benzene to cumene, followed by oxidation and CHP cleavage, with acetone co-product recycled back to
propylene (via hydrogenation to isopropanol and subsequent dehydration to propylene) – Japan and USGC location bases

- *sec*-Butylbenzene (SBB) cost of production via alkylation of benzene with butenes – speculative USGC location basis
- Phenol cost of production via SBB/cumene oxidation and hydroperoxide cleavage, with acetone and methyl ethyl ketone (MEK) co-products valued at market prices - speculative USGC location basis
- Nitrous oxide cost of production via oxidation of ammonia with enriched air – speculative USGC basis
- Phenol cost of production via benzene oxidation with on-purpose nitrous oxide - speculative USGC location basis
- Phenol cost of production via benzene oxidation with waste nitrous oxide (at no cost) - speculative USGC location basis

Variation of the phenol cost of production based on average yearly prices of all major feedstocks and byproducts for the previous five years. A sensitivity analysis has been carried out to analyze the variation of phenol cost of production with variation in plant scale for the speculative SBB/cumene and nitrous oxide based processes.

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**

Following a collapse in demand, and oversupply in 2008, the phenol market recovered sharply, and was very tight over 2010. Major capacity additions will come onstream during 2013 to 2014. Growth is focused in Asia Pacific, while mature markets like North America and Western Europe are effectively static due to slow consumption growth and restricted feedstock availability.

About 98 percent of the world’s phenol production employs the cumene-based co-product acetone technology. However, the growth in the phenol market has outpaced acetone due to the strong growth of BPA. BPA requires two equivalents of phenol for every one equivalent of acetone. This market imbalance has often caused the market to be long in acetone while tight in phenol.

- Phenol and cumene global supply, demand, and trade data are given and discussed.

Discrete regional supply, demand and trade data are also given and discussed for the United States, Western Europe and Asia Pacific

A listing of plant capacities in each of the regions listed above is given, denoting owning company, plant location, and annual tonnage produced.
Acetone regional supply, demand and trade data are also given and discussed for the United States, Western Europe and Asia Pacific.

A listing of plant capacities in each of the regions listed above is given, denoting owning company, plant location, and annual tonnage produced.