Nexant’s ChemSystems Process Evaluation/Research Planning program has published a report, Phenol/Acetone/Cumene (05/06-4). To view the table of contents or order this report, please click on the link: http://www.chemsystems.com/reports/index.cfm?catID=2

CONVENTIONAL TECHNOLOGY – PHENOL/ACETONE VIA CUMENE OXIDATION

Modern phenol technology involves oxidation of cumene with air at high efficiency to produce cumene hydroperoxide (CHP). CHP is then concentrated and cleaved to phenol and acetone in the presence of an acid catalyst. The catalyst is removed, and the cleavage mixture is fractionated to give phenol and co-product acetone.

\[
\text{Catalyst + } \text{CH}_2\text{=CHCH}_3 + \text{O}_2 \xrightarrow{\text{O}} \text{CH}_3\text{CCH}_3 + \text{OH} + \text{CH}_3\text{CCH}_3
\]

Approximately 0.6 pounds of acetone is produced for each pound of phenol, so that marketing of quantities of acetone is central to the economics of phenol production.

In recent years, the equipment count has been reduced significantly when compared to earlier designs. A high efficiency oxidation system has been developed which improves yield by lowering the formation of byproducts. An advanced cleavage system produces improved selectivity of phenol from CHP. Distillation columns have been eliminated, with simplified heavy ends recovery resulting from reaction efficiency improvements. High efficiency internals have been adopted in contacting columns.

Yields in the individual steps have been improved to very high levels:

- Oxidation: 95%
- Cleavage: 99.3%
- Cumene Recovery: ~100%

Overall process yield now stands at 97.7 percent, closing in on the best theoretically attainable performance.
New improvements to the overall design include a high efficiency energy integration system and a number of environmental control systems, such as an integrated vent scrubbing system, catalytic incineration of oxidation off-gas, and efficient removal of phenol from exhaust gas streams.

**MINIMIZATION OR ELIMINATION OF ACETONE CO-PRODUCT**

Despite the significant ongoing improvement of the cumene hydroperoxide route to phenol and acetone, there remains the difficulty of finding a ready and profitable market for the quantity of acetone produced. This problem is exacerbated by a higher growth rate for phenol demand compared to the growth rate for acetone demand. Essentially all current acetone production is as a co-product with phenol. Production from propylene via dehydration of intermediate isopropanol is very limited and generally uneconomic. The acetone oversupply problem will be further worsened by the continuing trend towards increasing size of phenol plants towards 300,000 metric ton per year capacity or even greater. This situation is spurring development of co-product free routes to phenol.

**Mitsui Acetone Recycle Process**

Mitsui has developed a process to recycle the acetone back to the cumene process. The acetone produced is hydrogenated to produce isopropyl alcohol, which is then dehydrated to produce crude propylene. The crude propylene stream is then further purified and recycled to the cumene process.

\[
\text{Acetone} + \text{H}_2 \xrightarrow{\text{Catalyst}} (\text{CH}_3)_2\text{CHOH} + 17 \text{ Kcal/mol (Exothermic)}
\]

\[
(\text{CH}_3)_2\text{CHOH} \xrightarrow{\text{Catalyst}} \text{C}_3\text{H}_6 + \text{H}_2\text{O} - 12 \text{ Kcal/mol (Endothermic)}
\]

**Solutia Direct Benzene Oxidation with N\textsubscript{2}O**

Solutia Corp. (formerly Monsanto) in conjunction with the Boreskov Institute of Catalysis (BIC), has developed a new benzene oxidation route to phenol production using nitrous oxide as the oxidizing agent, in the presence of a zeolite catalyst. Solutia has an economic advantage for the use of this technology (AlphaOx™), with virtually free nitrous oxide available as a waste product from their adipic acid process. Adipic acid production at Solutia’s Pensacola, FL facility is over 600 million pounds per year which equates to almost 200 million pounds of nitrous oxide. The chemistry is such that a relatively small phenol plant requires a world-scale adipic acid plant for its nitrous oxide supply. The chemistry of such an integrated approach is shown below.
The economic viability of this phenol process for other producers not in the adipic acid manufacturing business depends on the ability to produce or purchase nitrous oxide at a favorable price.

**Shell MEK Co-Product Process**

To overcome the problem of excess acetone co-product from phenol processes, Shell Chemical has announced their intention to commercialize a new phenol process in Asia that will reduce acetone production. This approach is believed to involve co-oxidation of cumene and sec-butylbenzene to give phenol, with acetone and MEK as co-products. Sec-butylbenzene (SBB) can be made via alkylation of benzene with n-butenes. The chemistry of this route is shown below (simplified in that the co-oxidation of cumene to CHP is omitted).
Other Co-Product Free Routes

Additional phenol processes that are devoid of major co-products are also covered in the report in varying degrees of detail:

- From toluene via 2-stage oxidation (benzoic acid intermediate)
- From benzene via hydrogenation, oxidation/hydration, and dehydrogenation
- From benzene via oxidation with hydrogen peroxide
- From benzene via reaction with oxygen/hydrogen mixture
- From benzene via acetoxylation to phenyl acetate, followed by hydrolysis

A further process covered is the so-called “waste-less phenol process” being promoted by ILLA.

ECONOMIC COMPARISON OF PROCESSES

Cost of production assessments of the following processes are provided in the report (the basis for these analyses are the USGC, 300 thousand metric tons per year capacity, and 2nd quarter, 2006):

- Conventional cumene oxidation process
- Mitsui acetone recycle process
- Solutia nitrous oxide-based benzene oxidation process (N₂O at zero value and at on-purpose production cost)
- Shell MEK/Acetone co-product process

The results highlight that neither the acetone recycle process nor oxidation with on-purpose nitrous oxide manufactured from ammonia appears competitive with the conventional phenol process with acetone credited at market price.

In the special situation enjoyed by adipic acid producers, access to essentially free (some gas cleanup costs) nitrous oxide as an effluent from adipic acid production provides phenol economics that appear to be attractive versus the conventional case.

The Shell Phenol/MEK/Acetone process appears to be a very interesting and competitive technology that will allow the effects of the ups and downs of the acetone and MEK markets to be optimized, thus minimizing phenol production costs. The Shell process has the potential to change the acetone/MEK ratio, within reasonable limits, allowing co-product revenue to be maximized.

COMMERCIAL ANALYSIS

The various end-uses for phenol are:

- Phenolic-based resins, with a broad range of end-uses including circuit boards and wood chip boards, insulation binders, molding compounds
- Bisphenol A for conversion into polycarbonate and epoxy resins. Polycarbonate is used to make compact discs
- Caprolactam for conversion into nylon 6 for fibers and engineering plastics
- Intermediate for adipic acid, aniline, and 2,6-xylenol
- Plasticizers
- Alkyl phenols and other specialty chemicals
- Water treating (slimicide)
- Disinfectant and anesthetic in medicinal preparations
- Acetyl salicylic acid (aspirin)

Figure 1 and Figure 2 show the phenol value chain and phenol downstream integration, respectively.

The majority of acetone is produced as a co-product of phenol production from cumene. Small volumes are produced from molasses fermentation and acetic acid production. The only on-purpose acetone production is from dehydrogenation of isopropyl alcohol.

Acetone has numerous uses:

- Methyl methacrylate (via acetone cyanohydrin)
- Bisphenol A
- Solvent, either directly or as intermediate for MIBK/MIBC for specialty coating applications
- Chloroform intermediate
- 6 -

- Pharmaceutical/antioxidant intermediate

**Figure 2** Level of Downstream Phenol Integration

Detailed supply, demand, and trade data are given for the United States, Western Europe, and Asia Pacific, with forecasts to 2010.

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