Butyl acetate replaces toluene to remove phenol from water

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Plastics Engineering Co. manufactures phenol formaldehyde resins and molding compounds at a plant in Sheboygan, WI. Process water from the plant, containing 7% phenol and 1% methanol, requires treatment prior to discharge to the sewer. Toluene was used as a solvent in a countercurrent liquid-liquid extraction column. A vacuum distillation of the extract separated the phenol and toluene. The raffinate (1% methanol, 98% water and 1% toluene) was stripped to recover the toluene and remove methanol from the bottoms prior to discharge. Methanol was not recovered. Disposal costs for the waste methanol (with about 10% toluene as an azeotrope) were high.

"Toluene is relatively insoluble in water [500ppm solubility] and relatively safe to handle. It worked reasonably well for extracting phenol," says Wayne Kleine, chemical project engineer at Plastics Engineering Co. "However, toluene left a lot of phenolic resins in the water stream." He explains, "We were having trouble with fouling problems downstream of the extraction column in the pumps, piping and the reboiler on the distillation columns and on the trays of the toluene recovery column."

When the plant came on line in 1985, toluene was readily available and used worldwide. At that time, it was not regulated. A few years later, the EPA regulations were changed to limit toluene in wastewater to 27ppb. Two plans were investigated:

1) Adding a column for steam-stripping the toluene from the wastewater.
2) Changing solvents.

Kleine says, "We thought changing solvents was a better long-term solution. With steam stripping, we would have to run all of the wastewater through the column, monitor the column discharge for toluene and reprocess the water if something were out of compliance."

Plastics Engineering Co. specified plant operating parameters, product purity requirements and discharge limitations. Consulting engineers were hired to conduct a liquid-liquid equilibrium-data literature search and to provide process design and project engineering services.

Based on activity coefficients, selectivity and solubilities, the engineers selected n-butyl acetate as the best candidate for a solvent. There was a potential problem, however, because acetates, in the presence of acids or bases, hydrolyze to their primary alcohol and acetic acid.
The engineers ran tests to determine the amount of butyl alcohol that would result from using butyl acetate as the solvent. Fortunately, the quantity generated by these tests was small.

Additional laboratory tests were performed to verify the solvent-to-feed ratio for extraction. Pilot plant tests, run at an off-site laboratory, were successful, and Plastics Engineering Co. decided that butyl acetate would be an acceptable solvent to use.

Kleine says, "Although we knew of no one else using butyl acetate as a solvent for extracting phenol, other solvents like isopropyl ether and MIBK [methyl-isobutyl ketone] were rejected because of toxicity. Butyl acetate, although a flammable liquid, presents a lower fire hazard because of its lower vapor pressure. It also has a very low toxicity rating."

**Simulation Fine-Tunes the Design**

The consulting engineers simulated the proposed process design on a desktop computer. The butyl acetate/phenol distillation column was simulated to process the stream leaving the top of the extraction column (the extract). Phenol, the bottoms product, was recycled to the resin plant. Butyl acetate (distillate) was recovered and returned to the extraction column. The only significant equipment change necessary was the relocation of the feed point.

Aqueous raffinate from the bottom of the extraction column was processed in the existing stripper column. All the volatile organics were stripped, resulting in a much cleaner wastewater discharge.
Ternary liquid-liquid equilibrium (LLE) data for butyl acetate-phenol-water is shown plotted on a triangular diagram in terms of weight percent. The slope of the tie lines reveal that the distribution coefficient is very favorable for extraction of phenol with butyl acetate. The distribution coefficient is about 22 (wt fraction of phenol in the organic divided by the wt fraction of phenol in the water phase). In comparison, the distribution coefficient in the dilute range for the toluene system is about 2. Butyl acetate is a much more efficient solvent for phenol than toluene. (Courtesy of Schlowsky Engineers, Inc.)

to the sanitary sewer. The overhead of the stripper column contained two phases: a ternary water phase refluxed to the top of the tower, and a small butyl acetate phase recycled to the extraction column. A new overhead decanter was needed to separate the distillate phases.

The part of the raffinate distillate phase that was not refluxed—a mixture of 35% methanol, 2% butyl acetate and 63% water—was fed to a new steam distillation column to recover 99.5% methanol. The butyl acetate, steam-distilled from the tower bottoms, remained in the tower because its boiling point is higher than the methanol's. The simulation showed that a vapor side-draw (at the feed tray) was necessary to remove butyl acetate from the column. The column bottoms was recycled back to the raffinate stripper column.

Simulation of the existing extraction column as five mixer/setter stages confirmed the ability of the existing roating disk extraction column to remove phenol from the process-water stream using butyl acetate as a solvent. (The model was conservative because the extraction column is capable of providing eight or nine theoretical stages.) The butyl acetate (solvent) phase flowed up through the tower to remove phenol from the wastewater phase, which was fed to the top of the column.

**Equipment Modifications**

The feed point on the butyl acetate/phenol distillation column was relocated. A new overhead decanter was added to the existing raffinate-stripper column to separate the distillate phases. Also, ancillary equipment and a new distillation column were added to the existing wastewater treatment system to purify the methanol.
PD-Plus® provides steady-state simulation of flow-sheets for refinery, petrochemical and chemical processes. It is an easy-to-use, low-cost alternative to process simulation. The program includes operations for columns, flash drums, mixers, splitters, component separators, heat exchangers, reactors, compressors, expanders, decanters, controllers and in-line Fortran “calculators.” PD-Plus requires an IBM® PC-compatible computer with 500K bytes of RAM, a math coprocessor and about 2.5 megabytes of hard disk space. A limited-capacity version is available for $50 for evaluation purposes or for those with simple modeling needs. The Fortran source language for subsystems or the entire simulator is also available for adapting to custom applications.

The new 6"-diameter methanol purification column employs high-efficiency, structured packing. The optimum location of the side-draw on this column, at the feed tray, was convenient because it is difficult to take a side draw in the middle of a packed bed.

System Performance Enhanced
The new process design with butyl acetate as the solvent has eliminated the use of toluene in the plant. Phenol in the waste water has been reduced from about 500ppm (with toluene as the solvent) to about 1ppm. Methanol (combined with 10% toluene as an azeotrope), which required costly disposal by incineration, is now recovered at 99.5% purity, reused in production, and sold. In addition, the capacity of the treatment facility has been increased by 50% while using essentially the same utilities.