PERP Program
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Chem Systems' Process Evaluation/Research Planning program has published a new report, ***Formaldehyde (00/01-8)***.

Currently, the only production technologies for formaldehyde of commercial significance are based on the partial oxidation and dehydrogenation of methanol using a silver catalyst, or partial oxidation of methanol using a metal oxide-based catalyst.

Because formaldehyde is highly water soluble, it is usually marketed as a liquid solution, typically at 37 weight percent formaldehyde solution, combined with water and up to 16 percent methanol. However, higher concentrations are sold and are required for the production of some derivative products such as polyacetal resins. The market trend is to sell solutions at higher concentrations to reduce shipping costs. Stabilizers are usually required when shipping higher concentrations of formaldehyde solutions.

The silver catalyst process employs two main reactions to convert methanol to formaldehyde, dehydrogenation and partial oxidation:

(1) $CH_3OH \rightleftharpoons HCHO + H_2$ $\Delta H = +20{,}400$ kcal/kmol

(2) $CH_3OH + \frac{1}{2}O_2 \longrightarrow HCHO + H_2O$ $\Delta H = -37{,}400$ kcal/kmol

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An excess of methanol is used in this process. In addition, there are several side reactions leading to byproducts, which include carbon dioxide, carbon monoxide, methyl formate, and formic acid. Hydrogen from the dehydrogenation reaction can form water by reaction with oxygen.

There are two variations of the silver catalyst process:

- Incomplete conversion plus separation and recycle of unreacted methanol
- Complete conversion

The basis of the metal oxide catalyst process is the vapor-phase oxidation of methanol with excess oxygen at temperatures of 250-400°C.

Metal oxides in the catalyst are typically molybdenum and iron at a molar ratio of 1.5 to 2.0 (Mo:Fe). Small amounts of oxides of vanadium, cobalt, phosphorus, chromium and copper may also be included. The Fe/Mo oxide catalyst is relatively insensitive to impurities such as iron carbonyls in the methanol feedstock.

Further reactions can occur to some extent, depending on temperature. These include the continued oxidation of formaldehyde to formic acid and carbon monoxide, and dehydration of methanol to dimethyl ether.

A significant variation on this process is the absorption of the formaldehyde into a urea solution to make urea-formaldehyde precondensate. This can be used for the production of urea-formaldehyde resins, the largest single use of formaldehyde.

About two-thirds of the absorber offgas is recycled. Licensors claim methanol conversion per pass of 92-94 percent, versus 86-87 percent for the silver catalyst process with recycle. Therefore, no distillation column is required to recover and recycle methanol in the product stream. However, overall capital cost versus a silver catalyst process is higher due to the higher volume of air required. Maximum methanol content ranges from between 0.5 and 1.0 percent for 37 weight percent product to 1.5 percent for 50 weight percent product. The formaldehyde solution typically contains 0.02-0.04 percent formic acid.