PERP Program – Formaldehyde and Derivatives
New Report Alert
July 2006

Nexant’s ChemSystems Process Evaluation/Research Planning program has published a new report, *Formaldehyde and Derivatives (04/05S10)*. To view the table of contents or order this report, please click on the link below:


**Technology**

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. No major developments in commercial formaldehyde technology have occurred since the writing of Nexant’s previous ChemSystems PERP Report, 00/01-8, *Formaldehyde*, published in April 2001.

At ambient temperatures, formaldehyde exists in a gaseous state, emitting a familiar sharp odor, irritating the eyes and skin. This gas is relatively stable at temperatures between 80°C and 100°C, but slowly polymerizes at lower temperatures, and is not sold commercially.

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. Therefore, all production comparisons shown in this report are made on a 37 percent basis. 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.

Unreacted methanol in solution helps inhibit formaldehyde polymerization; however, this is highly time and temperature dependent. Other product impurities include formic acid (less than 0.03 percent) and iron compounds (less than 0.5 ppm) in a 37 percent solution.

In the silver catalyst route, vaporized methanol with air and steam is passed over a thin bed of silver-crystal catalyst at about 650°C. Formaldehyde is formed by the dehydrogenation of methanol. The heat required for the endothermic reaction is obtained by burning hydrogen contained in the off-gas produced from the dehydrogenation reaction.

The other route involves the oxidation of methanol over a catalyst of molybdenum and iron oxide (Formox process). A mixture of air and methanol is vaporized and passed into catalyst-packed
reactor tubes. The reaction which takes place at 350ºC is highly exothermic and generates heat to provide steam for turbines and process heating.

Perstorp offers a high pressure version of the Formox process which can be retrofitted to existing plants to boost capacity. The high conversion rate of the Perstorp process eliminates the need for methanol recovery via distillation, and it can produce formaldehyde at concentrations up to 57 percent.

Yields from both processes are around 90 to 92 percent but the oxidation route has a lower reaction temperature and the metal catalyst is cheaper than silver. However, the partial oxidation-dehydrogenation route is still the most prevalent.

Tail gases from the production of formaldehyde may contain carbon monoxide, dimethyl ether, and traces of formaldehyde and methanol. Treatment of the waste stream is an important environmental consideration.

Because of the nature of the process, methanol and air concentrations are strictly controlled to avoid potential explosions. An excess of methanol is used in production to maintain concentration levels above the explosive limits.

A wide range of alternative feedstocks have been considered but not found to be economic. For example, a tiny amount of formaldehyde is produced from the non-catalytic oxidation of propane-butane mixtures. Formaldehyde can be produced from methane but a mixture of products needs to be separated. It is also a byproduct of the oxidation of naphtha to acetic acid.

**Silver Catalyst Process**

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

The equilibrium conversion in the dehydrogenation reaction is highly temperature dependent. The amount of process air controls the temperature by supplying oxygen to the exothermic reactions, including oxidation of hydrogen. The addition of inert materials such as water or nitrogen can also aid conversion by permitting the use of higher methanol concentrations relative to oxygen without entering the explosive region. These techniques permit variations in the process:

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

The usual commercial form of the silver catalyst process involves incomplete conversion of methanol at lower temperatures, which minimizes byproducts, followed by distillation to remove and recycle the methanol. This allows the producer to fine-tune the amount of methanol in the final product.
Formaldehyde product may be produced at concentrations of up to 52-55 percent by adjusting the amount of water added in formaldehyde absorption. Methanol concentrations can be adjusted as required (normally less than 1 percent) by distillation. In some cases, an ion exchange unit is needed to reduce the formic acid concentrations, but most commercial processes claim a figure of 0.06 percent without ion exchange.

The methanol conversion per pass is typically 75-85 percent, and overall process yield of formaldehyde from methanol is 90-92 mol percent.

Impurities, particularly iron, determine the catalyst life. The catalyst bed has a tendency to become matted under conditions of high temperature and throughput. Catalyst life is typically one year, although some licensors claim a catalyst life of up to 20 months; the catalyst may be electrolytically regenerated.

Although steam is generated internally, with most designs there is a net steam import requirement.

At a temperature of around 700°C, methanol conversion is sufficiently high to dispense with the final distillation column. A complete conversion process plant is similar to that described for incomplete conversion in most other respects.

**Metal Oxide Catalyst Process**

The basis of the metal oxide catalyst process is the vapor-phase oxidation of methanol with excess oxygen (from air) 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.

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.

Recycle of inerts permits the use of relatively high methanol concentrations without creating an explosive mixture. Oxygen concentration is kept to approximately 10 percent, whereas methanol is around 6 to 9 percent, both on a molar basis.
The Fe/Mo oxide catalyst is relatively insensitive to impurities such as iron carbonyls in the methanol feedstock. In a typical design, the catalyst is supplied as rings, and a very constant temperature profile is maintained by the use of a number of layers with different catalytic activities. A typical catalyst life is 18 months.

Export steam from the process is around 0.5 pound per pound of product.

Licensors claim methanol conversion per pass of 92-94 percent. Therefore, no distillation column is required to recover and recycle methanol in the product stream.

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. If required, the formic acid concentration can be further reduced in an ion exchanger.

**Economics and Comparison of Processes**

The production costs of 37 percent aqueous formaldehyde solution by the three production processes discussed above are summarized in Figure 1.

The higher capital cost of the metal oxide catalyst plant is compensated for by better process yields from methanol. The silver catalyst process without recycle has the next lowest estimated cost plus return on capital employed (ROCE); however, the product has a higher methanol content than the product resulting from the metal oxide and silver catalyst with recycle processes.

The price of methanol has a dramatic effect on formaldehyde economics, since cost for methanol feedstock represents 80 to 86 percent of cash cost and 67 to 72 percent of cost plus ROCE for the commercial processes studied. Sensitivities show the effect of methanol price over the range 45 to 125 cents per gallon.

Apart from economics, the most important factor in process selection is product quality.

Concentration of the formaldehyde solution is an important consideration for three reasons: downstream derivative requirements, shipping costs, and energy requirements to remove excess water. Polyacetal resins, for example, are direct polymers of formaldehyde, and require as concentrated a solution as possible to achieve polymerization. Resins are usually supplied as a solution of 60 percent solids or more, for which formaldehyde feedstock at more than 50 percent concentration is desirable.
Where concentrated formaldehyde is required, the metal oxide process has the advantage. Conversely, in some cases, such as the highly exothermic production of phenol formaldehyde resins, a more dilute solution is actually desirable.

The silver process with distillation offers a certain amount of flexibility which is appropriate for a plant supplying a complex and varied market. On the other hand, the metal oxide process has an advantage in serving the single largest formaldehyde market in its ability to form urea-formaldehyde precondensate directly in the absorption column.

Existing production capacity is dominated by the silver catalyst process, whereas the majority of new plants being built employ the metal oxide process. This is due to the higher formaldehyde yields on methanol and higher product concentration achieved.

**Downstream Derivatives**

In the body of the report, brief application and process descriptions are given for the following major downstream derivative products:

- Phenol-formaldehyde (PF) resins
- Urea-formaldehyde (UF) resins
Melamine-formaldehyde (MF) resins
Polyacetal resins
1,4-Butanediol
Neopentyl glycol (NPG)
Polyhydric alcohols - pentaerythritol and trimethylolpropane (TMP)

In addition, the production cost for each of the products cited above is estimated, based on transferring formaldehyde at production cost plus return on capital employed.

Environmental Issues

Formaldehyde manufacture and use represent only a partial source of formaldehyde in the environment. Formaldehyde in the atmosphere results primarily from incomplete combustion of hydrocarbons, as well as photochemical oxidation of unconverted hydrocarbons from combustion sources.

Table 1 shows the relative contribution from various sources.

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>(Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motor vehicle and aircraft exhausts</td>
<td>53-63</td>
</tr>
<tr>
<td>Photochemical reactions (largely from hydrocarbons in exhausts)</td>
<td>19-32</td>
</tr>
<tr>
<td>Combustion plants, incinerators</td>
<td>13-15</td>
</tr>
<tr>
<td>Petrochemical refineries</td>
<td>1-2</td>
</tr>
<tr>
<td>Formaldehyde production plants</td>
<td>1</td>
</tr>
</tbody>
</table>

Indoor formaldehyde levels are also of concern. It is known that formaldehyde-based products such as resins and UF foam insulations contribute small amounts of formaldehyde to the air. Some representative products include carpeting, floor and ceiling tiles, pressed wood products, and lined air ducts.

With time, formaldehyde decomposes in both the atmosphere and normal nonsterile water. The initial oxidation product, formic acid, is a component of acid rain. Because of its high solubility there will be efficient transfer into rain and surface water which may be an important sink. Additional quantities are removed by dry deposition or by dissolving in the ocean and other surface waters.
Although discharges to watercourses are strictly limited in most countries, formaldehyde is not subject to the stringent controls that apply to bioaccumulating substances. Specific concerns about formaldehyde are largely focused on the health impact on humans of atmospheric formaldehyde in the workplace or home.

The International Agency for Research on Cancer (IARC), part of the World Health Organization, recently has reclassified formaldehyde from group 2A “probably carcinogenic to humans” to group 1 “carcinogenic to humans”. This move was made based on a finding of “sufficient evidence that formaldehyde causes nasopharyngeal cancer in humans”, affecting the nasal cavity and paranasal sinuses.

As a result of health concerns, most countries in the developed world classify formaldehyde as a toxic compound and require strict handling procedures and labeling of products. Many countries have imposed stringent limits on the concentration of formaldehyde, both in the workplace and home, and have also imposed standards on products such as particle board. The product standards may be expressed as a direct limit on the formaldehyde concentration, or as a maximum emission value for the product.

**Commercial Analysis**

**Applications**

Formaldehyde is a versatile chemical with a wide range of uses. The primary application is the formation of resins such as urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde. Other uses include polyacetal resins, 1,4-butanediol, polyhydric alcohols, and hexamine. These main uses are discussed in moderate detail in the report.

Further uses include slow-release fertilizers based on urea-formaldehyde-containing products and the manufacture of ethylenediaminetetraacetic acid (EDTA) which is used in the synthesis of chelating agents. Other outlets are the manufacture of dyes, tanning agents, dispersants, vitamins, flavoring agents and pharmaceuticals.

**Demand**

The current consumption of formaldehyde stands at around 20 million metric tons per year (37 wt. percent basis), representing the largest use of methanol globally. The substantial costs associated with movement of formaldehyde over larger distances have caused almost all of the formaldehyde plants globally to be integrated with appropriate downstream plants. This has been possible owing to the versatility of formaldehyde end uses. As can be seen in Figure 2, amino resins, which include mainly urea- and melamine-formaldehyde resins, currently constitute slightly more than one-third of the total global formaldehyde consumption. Phenolic resins are the second largest area of consumption.
Figure 2
Breakdown of Global Formaldehyde End Uses
(2005)

The report details the regional formaldehyde end-use breakdown for 2005 by seven categories and for seven regions. Global consumption growth is estimated for nine end use categories through 2015.

Supply

Figure 3 shows the dominance of Western Europe in formaldehyde capacity. The producers in the developed countries tend to have larger capacities distributed over a number of production lines. The producers in developing countries tend to have much smaller production capacities, and the production tends to be opportunistic. When margins are good the plants operate flat out, but when margins are poor, the plants operate only to support the consumption in the downstream plants.

Consistent with the demand growth pattern, Nexant expects that the bulk of new capacity will be established in the countries included in “Rest of the World”, particularly in the Middle East, where the availability of relatively attractively priced methanol is likely to increase substantially in this decade.
Figure 3
Share of Key Regions in Overall Formaldehyde Capacity
(2005)

Supply/Demand Balance

The report presents a global supply/demand balance through 2015. The overall operating rate of the plants globally is expected to increase from the upper 70s in 2005 to the lower 90s by 2015. Fragmentation in the market that has led to poor margins in the past is expected to reduce with the closure of some of the small, relatively uneconomical facilities.

Individual supply/demand balances are also provided for North America, Western Europe, China, Japan, and Rest of the World.