Improving Methanol Plant Performance with Process Gas Chromatographs

Process gas chromatographs have been used since the 1950s to provide real-time compositional data to process control systems. Today, there are tens of thousands of process gas chromatographs in use throughout the process industry making the gas chromatograph the analytical workhorse for on-line compositional measurements. One example of how process gas chromatographs are used for improving process operations can be found in the methanol plant in a refinery.

While the production of methanol has been common for many years, it surged in popularity in the early 1990s when the U.S. Environmental Protection Agency issued the Clean Air Act. This Act mandated the use of oxygenates in gasoline, usually methyl test butyl ether or MTBE for cleaner burning. This placed a huge demand for methanol since it was the building block chemical to make MTBE. Since then, the demand for methanol has leveled off with the movement away from methyl test butyl ether or for cleaner burning as an oxygenate, but there is still the need for methanol in the manufacture of other chemicals such as formaldehyde (used in the manufacture of formica countertops, resin glues, fungicides, etc.) and acetic acid (used in the manufacture of nail polish remover, aspirin, synthetic rubber, etc.).

The Methanol Plant

The manufacture of methanol entails a number of chemical reactions that convert a hydrocarbon stream into a hydrogen-rich stream that is in turn reacted with the carbon oxides to form the methanol (CH₃OH). The hydrocarbon feed stream is almost always a natural gas stream although some feed streams of naphtha or other heavy oils are also used.

The feed stream is first run through a desulfurization reactor to remove sulfur and other compounds that would damage the catalyst of the other reactors (see Figure 1). Steam is then added to this treated stream before it enters two reformer reactors that convert the hydrocarbons and water (steam) into hydrogen and carbon monoxide. This can be seen in the following chemical reaction:

\[ CH_4 + H_2O \rightarrow 3H_2 + CO \]

Some of the CO will react with the water to form more H₂:

\[ CO + H_2O \rightarrow CO_2 + H_2 \]
Refining

Two reformers are used since only 30–40% of the hydrocarbons are reformed in the first reactor. Oxygen is added to the second reformer to help in the formation of CO and CO₂. The gases exiting the reformers are primarily H₂, CO, CO₂, and any unreacted hydrocarbons (C1) in addition to the O₂.

The stream is next compressed to over 1000 psi and then enters the synthesis reactor where the conversion is made to methanol by the following reaction:

\[
\begin{align*}
2H_2 + CO & \rightarrow CH_3OH \\
3H_2 + CO_2 & \rightarrow CH_3OH + H_2O
\end{align*}
\]

The effluent from the synthesis reactor is cooled to condense and remove the alcohol products. The unreacted gases are returned to the compressor for reprocessing. There is also a small purge gas stream taken from this recycling process to control the build-up of inert gases that accumulate in the process. The purge gas is often used as a fuel gas to heat burners and furnaces in the plant.

The crude methanol product leaving the bottom of the separator is sent to a distillation tower to strip out the acetone (and lighter) components. The stream then enters a second column that separates the methanol product from the other heavier compounds such as ethanol that are formed in the synthesis reactor. The heavier compounds might be further separated if the recovery of the ethanol is desired.

Improving Unit Performance with Process Gas Chromatographs

There are a number of key measurements that are often performed in a methanol plant. The first process gas chromatograph (AX #1 in Figure 1) measures the effluent of the reformers to monitor the levels of unreacted methane which helps the control system keep the reformers at the optimum conversion severity.

To minimize the losses of methanol in the acetone stream, a second gas chromatograph (AX #2 in Figure 1) monitors the acetone tower overhead stream to measure the level of methanol present.

The final two measurements (AX #3 and #4 in Figure 1) monitor the overhead and bottom streams of the methanol tower. The overhead stream is monitored for impurities in the methanol product; typically ethanol. The bottom stream is monitored to minimize loss of methanol in the heavier stream. A summary of these applications can be seen in Figure 2.

The Emerson Solution

Emerson has a long history of providing process gas chromatographs for the methanol industry. Emerson’s process gas chromatographs have set the standard for online process measurement by supplying analyzers that are both robust and capable of handling the analytical requirements.

### Table 1 - Summary of Process Gas Chromatograph Applications in a Typical Methanol Plant

<table>
<thead>
<tr>
<th>Analyzer #</th>
<th>Stream</th>
<th>Components Measured</th>
<th>Measurement Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reformer effluent</td>
<td>C1</td>
<td>Monitor for unconverted C1</td>
</tr>
<tr>
<td>2</td>
<td>Acetone tower overhead</td>
<td>MeOH</td>
<td>Minimize losses of methanol in acetone tower overhead</td>
</tr>
<tr>
<td>3</td>
<td>Methanol tower overhead</td>
<td>EtOH</td>
<td>Minimize impurities in methanol product stream</td>
</tr>
<tr>
<td>4</td>
<td>Methanol tower overhead</td>
<td>MeOH</td>
<td>Minimized losses of methanol in methanol tower bottom stream</td>
</tr>
</tbody>
</table>

©2012 Emerson Process Management. All rights reserved.

The Emerson logo is a trademark and service mark of Emerson Electric Co. Rosemount Analytical is a mark of one of the Emerson Process Management family of companies. All other marks are the property of their respective owners.

The contents of this publication are presented for information purposes only, and while effort has been made to ensure their accuracy, they are not to be construed as warranties or guarantees, express or implied, regarding the products or services described herein or their use or applicability. All sales are governed by our terms and conditions, which are available on request. We reserve the right to modify or improve the designs or specifications of our products at any time without notice.