

COMMERCIAL-SCALE DEMONSTRATION OF A LIQUID-PHASE METHANOL PROCESS

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ABSTRACT

The Eastman Chemical Company operates a coal gasification complex in Kingsport, Tennessee. The primary output of this plant is carbonylation-derived acetic anhydride. The required methyl acetate is made from methanol and acetic acid. Methanol is currently produced from syngas by a gas-phase process, which must receive stoichiometric quantities of carbon monoxide and hydrogen to avoid overheating the catalyst. Control of this CO/H₂ ratio is accomplished with a shift reactor. A liquid-phase methanol process (LPMEOH™) has been developed by Air Products. Efficient heat removal permits the direct use of syngas without the need for the shift reactor. An Air Products/Eastman joint venture, with partial funding from the Department of Energy under the Clean Coal Technology Program, has been formed to build a demonstration-scale liquid-phase methanol plant. This talk will focus on the unique features of this plant and how it will be integrated into the existing facilities.

INTRODUCTION

Eastman Chemical Company has practiced the carbonylation of methyl acetate to acetic anhydride for many years.^{1,2} In an array of integrated plants, coal is gasified and the resulting synthesis gas purified to a high degree. This gas, which consists chiefly of carbon monoxide and hydrogen, is used to feed the chemical plants. Methanol is produced in one plant by the Lurgi low-pressure gas-phase process. The methanol is combined with returned acetic acid to produce methyl acetate. Acetic anhydride is produced by the reaction of this methyl acetate with carbon monoxide.

The syngas needed for these plants is produced by two high-pressure gasifiers. High-sulfur coal is ground and fed to these gasifiers as a water slurry with pure oxygen. The hot gas is scrubbed with water to reduce the temperature and remove ash. A portion of the crude syngas is routed to a water-gas shift reactor to enrich the stream in hydrogen so that the stoichiometry required for methanol synthesis can be attained. Hydrogen sulfide is then scrubbed from the gas streams and converted to elemental sulfur. After final purification in a cryogenic "cold box" the syngas is pure enough to serve as feed to the methanol and acetic anhydride processes. Key changes to the gas stream as a result of these manipulations are illustrated in Figure 1.

DISCUSSION

In a methanol plant, the reaction between carbon monoxide, carbon dioxide, and hydrogen is exothermic and, because of the fixed bed reactor design, heat control and removal is of prime concern. If too much carbon dioxide or carbon monoxide is present, the reactor can overheat and damage the catalyst. Catalyst sensitivity to overheating is a chief reason that a more forgiving reaction system has been sought for syngas-based methanol production.

For a given catalyst, a liquid-phase reactor is preferable for numerous reasons. The basic characteristics of a liquid-phase reactor allow it to be cooled internally. This is a significant advantage for removing the rather large net heat of reaction encountered during methanol synthesis. By removing this heat with an internal heat exchanger, steam can be co-generated and employed for various process uses. In the liquid-phase reactor, an inert oil is used to slurry the methanol catalyst and to carry away the heat of reaction. Because of the efficient heat removal offered by the oil component, isothermal operation is possible, and per pass conversion is not as limited in comparison to a gas-phase reactor. While the latter reactor must rely upon dilution with recycle gas to control the reaction and carry away the heat, the inert oil in the liquid-phase reactor serves as a heat sink, thereby protecting the active sites of the catalyst from overheating. Added benefits resulting from this configuration are that the H₂/CO/CO₂ stoichiometry need not be controlled as closely (CO-rich mixtures are permissible) and carbon dioxide can be present in high concentrations. The net result of this last feature is that the expense and added complexity of a shift reactor can be eliminated because, in most cases, syngas can be used directly.

The liquid-phase methanol process (LPMEOH™)³, developed by Air Products and Chemicals, Incorporated, offers a sound way to take advantage of the benefits of internal heat removal. As shown in Figure 2, this process allows purified but otherwise unaltered synthesis gas to be fed directly to the reactor. The copper/zinc oxide-based methanol catalyst is suspended in an inert oil, which serves as the heat transfer medium. Internal heat exchangers remove the heat generated by the highly exothermic reaction and provide process steam for appropriate uses. The gross effluent is separated from the oil in a cyclone separator and then cooled to condense traces of oil. The vapor

is then chilled to remove the methanol, and the off-gas is warmed and compressed for recycle or sent to downstream uses.

An Air Products/Eastman joint venture, with partial funding from the Department of Energy under the Clean Coal Technology Program, has been formed to build a demonstration-scale version of liquid-phase methanol plant. The gasification complex in Kingsport, Tennessee provides an ideal source of synthesis gas to test this plant. In addition to providing methanol for the carbonylation process, the demonstration unit will be tested under a large variety of operating conditions. This is possible because smooth operation of the integrated plants will not be completely dependent on the output of the liquid-phase methanol plant. It will therefore be possible to ramp the output up and down, co-produce dimethyl ether (DME), and produce fuel-grade methanol for testing in on- and off-site applications, such as power plant boilers, buses, and vans.

To illustrate how the new methanol process will affect the overall configuration of the coal gas facility, two schematic diagrams of the entire complex are provided below. The conventional, gas-phase methanol process is included in the first schematic (Figure 3), while changes resulting from incorporation of the liquid-phase process are summarized in Figure 4.

A brief description of the overall operation of this complex is offered: Coal is systematically unloaded from rail cars and continuously fed to grinding mills by a highly automated Coal Handling system. In the Coal Slurry section, coal is mixed with water during the grinding process to provide a mobile slurry that can be pumped to the gasifiers. Oxygen is provided by an Air Products separation plant. Use of pure oxygen allows the gasifiers to operate at over 1000°C, which eliminates the coproduction of environmentally undesirable byproducts. Within the Gasification Plant the coal slurry and oxygen combine in Texaco-designed gasifiers in a sustained reaction to produce a CO-rich product. The high-temperature exhaust is then quenched with water to cool the gas and remove ash particles. The crude gas is then passed through a water-gas shift reactor to increase the hydrogen content. Before exiting the gasification plant, the product gas is cooled by water-fed heat exchangers that produce low-pressure process steam for use elsewhere in the complex. Within the Gas Purification section hydrogen sulfide and carbon dioxide are removed by the Linde AG-developed Rectisol process. This is accomplished by selectively absorbing the gases in cold methanol. The hydrogen sulfide/carbon dioxide stream is sent to the Sulfur Recovery plant where a Claus unit, coupled with a Shell off-gas treating unit, converts it to elemental sulfur. This sulfur is clean enough to be sold as a pure byproduct. The final off-gas consists mainly of carbon dioxide, which is converted to the solid form for various commercial uses. As the syngas exits the purification section, a portion of it is passed to CO-Hydrogen Separation, essentially a cryogenic "cold box" (also developed by Linde) which permits separation of carbon monoxide and hydrogen by low-temperature distillation. The hydrogen from this unit is combined with CO/H₂ from the Gas Purification section to serve as feed for the Methanol Plant. The methanol product is fed to an Eastman-developed Methyl Acetate Plant, which uses a novel reactor-distillation column⁴ to continuously convert methanol and acetic acid to methyl acetate in essential one piece of equipment. Carbon monoxide from the cryogenic unit, along with methyl acetate, is sent to the Acetic Anhydride Plant, also developed by Eastman, where carbonylation produces acetic anhydride. If methanol is also fed to this plant, a portion of the acetic anhydride is converted to acetic acid and methyl acetate.

Although the changes appear minor from the level of detail provided in this diagram, many process details are simplified when the CO/CO₂/H₂ mix is not critical:

- * Need for shift reactor eliminated
- * Low sensitivity to flow variations
- * Higher per-pass conversion requires less off-gas recycle
- * Less waste CO₂ because more can be utilized in methanol production
- * Less complex and expensive catalyst replacement requirements

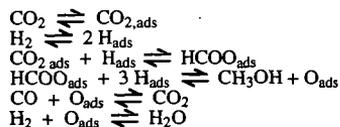
A shift reactor is normally needed to increase the hydrogen/CO ratio of raw synthesis gas so that enough hydrogen is available to satisfy the required stoichiometry for conversion to methanol. If the methanol reactor could operate properly with syngas that is lean in hydrogen, this processing equipment could be eliminated. Moreover, processes downstream of the methanol plant that need CO containing little or no hydrogen, such as that required by the methyl acetate carbonylation process, would also benefit because the methanol plant serves to reduce the hydrogen content from the off-gas so that further processing is either not needed or requires smaller separation equipment. Because of the large heat sink provided by the internal heat exchanger of the LPMEOHTM process, excess CO/CO₂ does not damage the catalyst by inadvertent overheating.

Another way to damage the catalyst in a gas-phase reactor is by transient variations in the syngas flow rate. Here, excess reactant feed rates rather than stoichiometry are the concern. The result of

this condition is similar, however, in that the increased evolution of heat without an accompanying way to remove it can overheat the pellets.

Having an effective way to remove heat also permits the reactors to be operated at higher conversion rates. This benefits the space-time yield of the reactor and significantly reduces the off-gas recycle rate. It also serves to deplete the off-gas of hydrogen, which, as described above, is beneficial to downstream processes needing CO that is low in hydrogen content.

It is well known that the presence of CO₂ is essential to optimal operation of copper/zinc oxide-based methanol reactors. It is critical for conditioning and preventing damage to the catalyst.⁵ Isotopic labeling studies have shown⁶ that essentially all methanol is produced from the reaction of CO₂ with hydrogen. An internal water-gas shift reaction between the resulting water with CO generates more CO₂ for methanol production. The proposed mechanism is provided below for convenience:



Again, because of the heat management capabilities of the LPMEOH™ process, the amount of carbon dioxide normally present in raw syngas can be used without concern for overheating the catalyst. This results in a much more efficient use of carbon in the syngas. Indeed, a substantial amount of waste carbon dioxide is generated by the water-gas shift reactor needed for gas balance in the gas-phase methanol process.⁷

One final benefit of the LPMEOH™ process is that catalyst replacement is less complex and can be done on an on-going basis. Even though the catalyst in a gas-phase methanol reactor can typically operate for about two years before replacement is needed, the actual mechanics of replacement are a challenge. The catalyst itself is difficult to handle in the large quantities involved, and the reactor must be shut down, isolated and opened up to carry out the task. This can result in significant downtime resulting in inconvenience at the least to lost product sales as a major negative consequence. In the case of the liquid-phase process, the catalyst can be intermittently replaced as needed in substantially smaller amounts. Some of the benefits described above have also been discussed in a recent review.⁷

CONCLUSION

The construction and successful operation of the LPMEOH™ plant will be a landmark in development of synthesis gas technology. Given the importance of methanol not only as a chemical feedstock but as a fuel, demonstration of this technology on a commercial scale could have far-reaching importance. We at Eastman are pleased to be a part of this effort.

ACKNOWLEDGMENTS

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Figure 1.

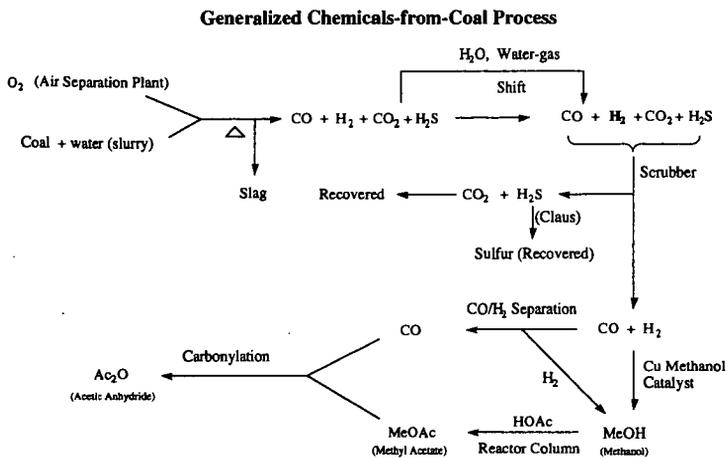


Figure 2. Air Products LPMEOH™ Process.

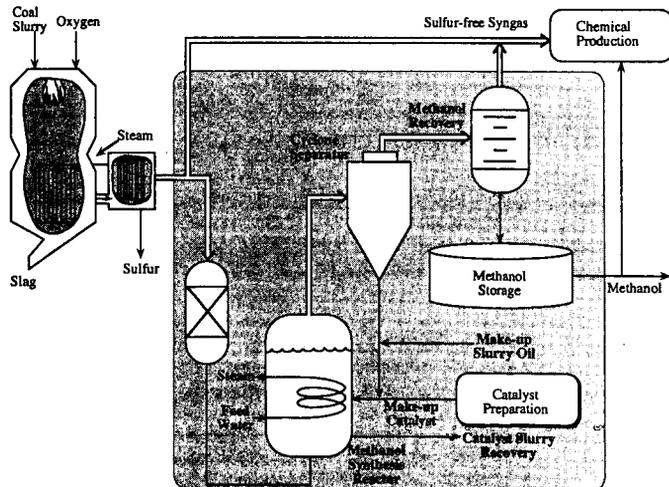


Figure 3: Configuration of Coal-Gasification/Acetic Anhydride Plant with Gas-Phase Methanol

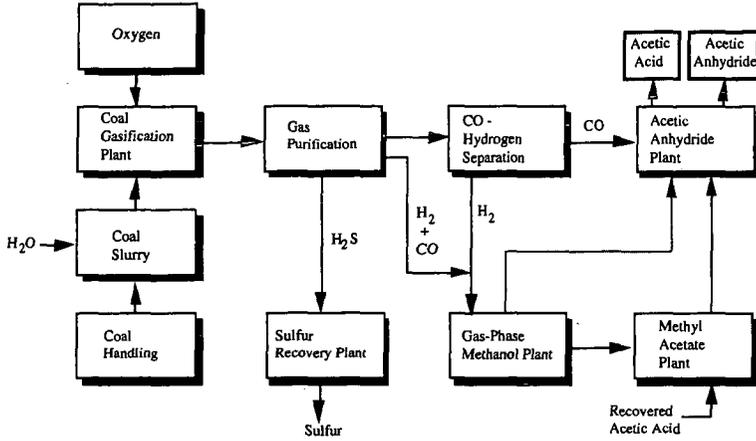


Figure 4: Configuration of Coal-Gasification/Acetic Anhydride Plant with Liquid-Phase Methanol

