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Dimethyl Carbonate

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Abstract

Dimethyl carbonate (DMC) is an important industrial chemical. It is used as an intermediate for making polycarbonate, which consumes roughly 50% of its production. Other notable areas of its use include solvents, pesticides, and pharmaceuticals. It is also used as a chemical reagent, particularly for methylation and methoxycarbonylation reactions. It is nontoxic to humans and does not negatively impact the environment, and is also quickly biodegradable, which makes it especially suitable for use as a chemical.

DMC is considered and recommended by some environment and industry experts as a viable choice for use as an oxygenate in transportation fuels, primarily due to its favorable properties needed for fuels—it has about three times more oxygen than methyl tertiary butyl ether (MTBE), and its other plus points as a fuel additive include low vapor pressure, low toxicity, higher boiling point, nonhygroscopic nature, complete miscibility with fuels, and its overall attractive emissions characteristics as a fuel component. If DMC's use as a fuel oxygenate is accepted officially, that would open an enormous market for it. In addition to being environmentally friendly, DMC can also be prepared from natural gas (methanol and CO) and oxygen (air). Hence, unlike MTBE or other solvents, it is not a petroleum derivative. Thus, DMC can potentially also reduce dependence on imported oil.

Traditional synthesis of DMC required toxic and hazardous phosgene as a base material. This disadvantage of the source material prompted researchers to investigate alternate routes for DMC manufacturing that would lower the impact of DMC use on human health and the environment without seriously affecting the economics of production.

This report, therefore, presents technoeconomic assessments of three such nonphosgene-based technologies for DMC production listed below, and the process economics only for the fourth technology listed below:

- Versalis/CB&I's liquid-phase direct methanol oxycarbonylation technology
- Ube's gas-phase indirect methanol oxycarbonylation technology
- Two-step urea-methanol transesterification technology (not commercialized yet)
- Asahi's ethylene carbonate-methanol transesterification technology (only process economics)

The urea-based technology is in the development and refining stage. Different researchers and developers are trying to improve the overall yield of DMC in the process. This technology is now owned by CB&I, which has currently stopped further work on it.

Versalis/CB&I's methyl oxycarbonylation technology is based on a single-step, liquid-phase, cuprous chloride–catalyzed process, which was originally developed by Polymeri/EniChem. Versalis was created as a subsidiary or rename for Polymeri/EniChem. CB&I is the partner in licensing and engineering of contracts. Our evaluation of the technology is based on a single-train plant, producing about 25,000 metric tons per annum (MTPA) of DMC. The chemistry of the process is simple, but small amounts of corrosive by-products are generated that necessitate the use of glass-lined material for certain equipment. The overall

yield of DMC, according to IHS estimates, is 91.9% (based on methanol). Versalis/CB&I primarily produces DMC for the merchandise market.

Ube's methanol oxycarbonylation technology is based on a two-step (or indirect), gas-phase, palladium–copper chloride–catalyzed process. This process has a somewhat more complex chemistry. In the first-phase, methyl nitrite (MN) is carbonyl-ated producing DMC and nitric oxide (NO) in a fixed-bed reactor. In the second step, NO reacts noncatalytically with oxygen and methanol, producing MN and water. This MN is recycled into the first step. Hence, basically only CO, O_2, and methanol are consumed in the process. Overall yield of DMC is equivalent to 92.5% (based on methanol). Ube's process, according to IHS estimates, is somewhat costlier than Versalis/CB&I's process in terms of capital cost. However, the production cost of DMC for the two processes is pretty close, mainly due to the fact that the Ube process produces dimethyl oxalate also as a by-product, which improves the economy of the process. Ube produces DMC primarily to sell it in the merchandise market.

Our third technology analysis is for DMC production by a urea transesterification process using methanol. Since this process is not commercialized yet, a generic-type analysis is presented, based on the data given in the patents of Catalytic Distillation Technologies (CDTECH). The conversion of urea-methanol to DMC is carried out in two steps—first, the urea is converted to methyl carbamate (MC) by reacting with methanol at relatively low temperatures (e.g., 100°C in the presence of a catalyst, or 150°C without catalyst); then, the carbamate is further reacted with methanol at 180–190°C in the presence of a catalyst, producing DMC.

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