Dimethyl Carbonate

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Report Abstract
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INTRODUCTION

Dimethyl Carbonate (CH$_3$OC(O)OCH$_3$) is a non-toxic, versatile chemical that exhibits a high reactivity. Dimethyl carbonate (DMC) finds use as a solvent in paints, inks, and coatings etc. and electrolyte within lithium ion batteries, and as an intermediate in the synthesis of polymer (i.e., polycarbonate), pharmaceuticals, pesticides, antioxidants, high performance resins etc.

The potential demand for DMC could be much higher. Its main use is as an intermediate in polycarbonate production, which currently accounts for just over half of its consumption. However, there is future potential demand as a possible fuel additive and as an intermediate in the manufacture of isocyanates (which are used to make polyurethane foams). DMC’s possible use as a gasoline blending component has been under consideration for some years, due to its very high oxygen content (53 weight percent), good blending octane, and freedom from phase separation, low toxicity, and rapid biodegradability. Automotive emission tests at Amoco showed that, at the same weight percent oxygen in the fuel, DMC reduced total hydrocarbon, carbon monoxide, and formaldehyde more than did MTBE. The use of dimethyl carbonate as a gasoline blending component in major regions such as North America and China is uncertain. In the United States, while MTBE is largely phased out, ethanol remains the major gasoline blending agent. In China, MTBE still appears to be the gasoline additive of choice. At present, research into DMC as a serious substitute in isocyanate production processes is at the early R&D stages.

Despite the uncertainty with respect to very large scale applications (such as a fuel additive/blending agent), there is significant growth demand for dimethyl carbonate into its various established/semi-established applications such as solvent use (especially as an electrolyte solvent), plastics production intermediate etc.

TECHNOLOGY

The traditional route to dimethyl carbonate involved using phosgene (COCl$_2$). It is a route disadvantaged by the safety issues involved in handling highly toxic phosgene (which is a former war gas and heavily regulated in most countries).

It is normal that phosgene is prepared and utilized on site because it is toxic and hazardous to transport. The entire phosgene production plant is designed for lethal service. The reaction is performed in a tubular heat exchanger packed with activated carbon catalyst. Previously dried and filtered carbon monoxide and chlorine gases enter the tubes. Cooling water passing through the shell side of the exchanger removes the exothermic heat of reaction (1.09 GJ/ton of phosgene). Heat transfer is the limiting factor; therefore, the heat exchange surface is more critical than space velocity in the reactor design. Typical reactor yields of 98 percent based on chlorine are achieved, and carbon monoxide is added at a six percent excess to ensure completed reaction of chlorine. The carbon monoxide feed purity is at least 99 mole percent. Due to slow reaction rates and engineering concerns phosgene was produced by numerous small scale batch reactors. Hence, new technologies that avoided these limitations were developed, prompted by a combination of health and safety concerns and improved quality of products.
Dimethyl carbonate is prepared by the reaction of phosgene with methanol in the presence of concentrated sodium hydroxide (to speed up the reaction). Phosgene is usually consumed in around 10 percent excess of methanol. Excess phosgene is hydrolyzed or decomposed in later reactions. The reaction proceeds via a methyl chloroformate intermediate. The reaction also produces hydrochloric acid (HCl) that subsequently reacts with the sodium hydroxide that is present to yield sodium chloride.

However, because phosgene is highly toxic and requires rigorous standards for its production and handling, coupled with other problems such as environmental issues related to the disposal of the sodium chloride produced, a number of non-phosgene routes have been developed and are in commercial operation. It is extremely unlikely that new plants will use the phosgene based process in the future.

The commercial routes to produce dimethyl carbonate that are currently in operation include:

1. Liquid Phase Oxidative Carbonylation as exemplified by the Versalis/Lummus process (discussed in detail in Section 3 of the report)
2. Vapor Phase Oxidative Carbonylation as exemplified by the Bayer and Ube processes (discussed in detail in Section 4 of the report)
3. Transesterification of a carbonate with methanol, exemplified by the Asahi process using ethylene carbonate and processes operated by several Chinese producers using propylene carbonate (discussed in detail in Section 5 of the report)

In addition, there is a developing process with some promise:

4. Urea methanolysis as exemplified by the processes patented by Catalytic Distillation Technologies (CDT) and the Institute of Coal Chemistry (ICC), Chinese Academy of Sciences (discussed in detail in Section 6 of the report)

A brief overview of alternative technologies under investigation (e.g., utilizing carbon dioxide, and production via electrochemical means), is given in Section 2 of the report.

**PROCESS ECONOMICS**

The report includes detailed cost of production estimates for the following:
- Production of dimethyl carbonate using Liquid Phase Oxidative Carbynylation via cuprous methoxychloride intermediate - Versalis/Lummus technology (China and N.W. Europe location bases)

- Production of dimethyl carbonate using Vapor Phase oxidative carbynylation via methyl nitrite intermediate - Bayer technology (China and N.W. Europe location bases)

- Production of dimethyl carbonate using ethylene carbonate transesterification with methanol process - Asahi technology (China and N.W. Europe location bases)

- Production of dimethyl carbonate using urea methanolysis process - CDT technology (China and N.W. Europe location bases)

Sensitivity analyses to assess the impact of variation in feedstock prices, byproduct prices, and plant scale on VAM cost of production, are included.

The detailed cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities consumed (electrical energy, cooling water, fuel etc.), direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate. Capital costs are broken down according to inside battery limits (ISBL), outside battery limits (OSBL), other project costs, and working capital.

COMMERCIAL MARKET REVIEW

Dimethyl carbonate (DMC) is considered a “green” chemical because it is not toxic, nor a skin irritant, and is biodegradable. It is however, flammable. Depending on the application, different grades of dimethyl carbonate are required. The dimethyl carbonate weight percent ranges from industrial grade (>99.0 weight percent) to pharmaceutical grade (>99.5 weight percent) to battery grade (>99.9 weight percent).

The figure below estimates global consumption of dimethyl carbonate according to end-use.

![Global Dimethyl Carbonate Consumption by End-Use](image)

Solvent use includes the use of dimethyl carbonate as an electrolyte in lithium ion batteries.
The report includes market analysis as follows:

- Global supply, demand and trade data is given and discussed
- A list giving all production plants known to Nexant showing specific plant capacities, owning company, location and annual tonnage produced
- In addition, supply, demand and trade data is given and discussed for China, which is the largest producer and consumer of dimethyl carbonate
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