

PERP Program

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Chem Systems' Process Evaluation/Research Planning program has published a new report, ***Developments in Dimethyl Carbonate Production Technologies (99/00S6)***.

Dimethyl carbonate (DMC) has increased in production volume as its uses have evolved from specialty applications to larger-scale use as an intermediate in phosgene-free polycarbonate processes. DMC has also been mentioned as a possible gasoline blending component due to its very high oxygen content, good blending octane, freedom from phase separation, low toxicity, and rapid biodegradability. These qualities may be more attractive with the current debate over the suitability of continued use of MTBE as a gasoline oxygenate due to potential ground water contamination.

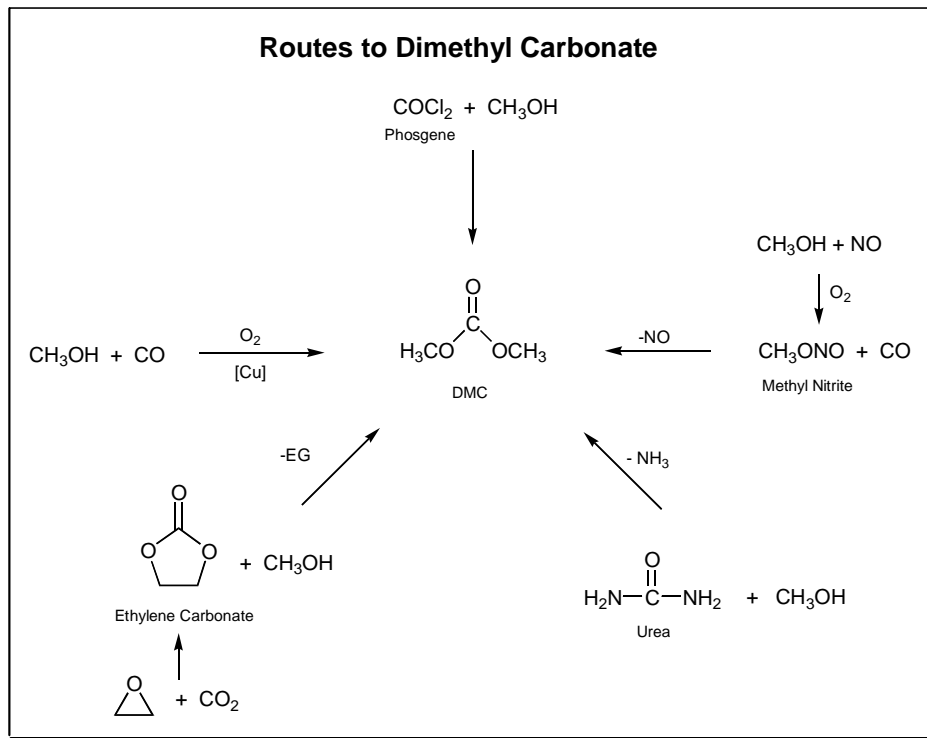
The classic route to DMC involves the use of phosgene. This route is disadvantaged by the safety problem of handling highly toxic phosgene and the environmental problem of disposing of sodium chloride. While existing plants based on the phosgene route continue to operate, it is doubtful that many new plants of significant capacity will use this process in the future.

Three routes to DMC are given primary attention in this report: oxidative carbonylation using copper chloride 'catalyst' (actually a redox agent), transesterification between ethylene carbonate and methanol, and urea methanolysis. A variation of the oxidative carbonylation route using nitric oxide as catalyst/redox agent is also discussed.

Oxidative carbonylation of methanol is a nonphosgene route to DMC that is practiced commercially by EniChem, a major DMC producer. The process utilizes a copper chloride catalyst system. In the first step, copper is oxidized from the cuprous to the cupric state with the formation of cupric methoxychloride intermediate. In the second step, the intermediate is reduced by carbon monoxide to give DMC and restore the cuprous chloride.

In recent patent activity, EniChem has patented a loop reactor design, while Bayer and Ube have disclosed specialized separation schemes. The Ube scheme uses dimethyl oxalate (DMO) as an extractive distillation agent.

Ube has commercialized an oxidative carbonylation route that employs the use of nitric oxide as the redox agent. This route involves the formation of methyl nitrite from methanol, nitric oxide, and oxygen. Methyl nitrite is subsequently reacted with carbon monoxide to give dimethyl carbonate and releases nitric oxide for recycle. This approach eliminates the handling of solids/slurries as in the EniChem process.



Dimethyl carbonate is also formed by the transesterification reaction between ethylene carbonate and methanol, giving ethylene glycol as a coproduct. The DMC reactor is assumed to be a boiling pot, operating at 150°C, surmounted by a trayed or packed section from the top of which DMC is distilled as the methanol/DMC azeotrope. As a consequence of the continual removal of product DMC from the tower overhead, it is assumed that conversion of ethylene carbonate is 90 mol percent. Extractive distillation with water and a second column to remove water from DMC provides a pure product. Additional columns separate ethylene carbonate and methanol for recycle, as well as coproduct ethylene glycol.

The tin-catalyzed reaction of methanol with urea to give dimethyl carbonate is a well-known synthesis; however, yields are typically low because intermediate methyl carbonate is prone to decompose to isocyanic acid or isocyanuric acid. Catalytic Distillation Technologies has developed technology using high-boiling organic electron donor solvents, such as triethylene glycol dimethyl ether (triglyme), in conjunction with tin-based catalysts, and continuous distillation of product dimethyl carbonate as it is made. This allows high yields of dimethyl carbonate to be realized. A patent example showed that, at 350°F, urea/methanol conversion of 98.3 percent could be achieved. Selectivity of urea/methanol to dimethyl carbonate was 98.2 percent.