

# IMPROVED DIMETHYL CARBONATE SYNTHESIS AND PROCESS DESIGN VIA OXIDATIVE CARBONYLATION OF DIMETHYL ETHER METHANOL MIXTURES.

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## INTRODUCTION

Enichem has commercialized a continuous solution/slurry-phase process for preparation of dimethyl carbonate (DMC) via the copper (II)-catalyzed oxidative carbonylation of methanol.<sup>(1)</sup> As of 1993 the capacity of this plant is 22 million pounds/year with worldwide demand approximately half of this amount. Recently in Japan Ube industries has completed construction of a semicommercial plant with a capacity of 11-22 million pounds per year.

DMC has strong growth potential as a phosgene replacement in some applications and as a high-oxygen high-octane fuel additive. As a phosgene replacement, there is a strong environmental incentive to use DMC since it would replace a very toxic compound with a relatively nontoxic one and eliminate environmental concerns resulting from hydrogen chloride production and recycle.

DMC also has strong potential to replace part of the growing worldwide MTBE market, which is expected to reach 66 billion pounds/year by the end of the century. As a gasoline blending agent, DMC has an oxygen content of 53% and a blending octane value of 105 (R+M/2), and these high values dictate a somewhat higher overall value for DMC in comparison to MTBE.

The key to entering this market and the phosgene replacement market lies in the development of an efficient low-cost DMC process based on inexpensive starting materials. Its current cost of \$1.40/lb (non-contract) is prohibitively expensive. There are inherent problems in the Enichem process which limit per-pass methanol conversion to about 20% as the result of coproduction of water. This coproduction also results in catalyst degradation/deactivation and hardware corrosion. Production rates of 0.1 LHSV are reported for this system. Similar problems also exist in gas-phase processes such as that developed by Dow Chemical which utilize a copper (II) catalyst supported on carbon. Catalyst modifications have reportedly solved some of the deactivation problems but methanol conversion is still limited to about 25%.

## BACKGROUND AND OBJECTIVES

Liquid and gas-phase processes for synthesis of DMC via Cu(II)-catalyzed oxidative carbonylation of methanol (MeOH) offer limited reactor performance as the result of the effects of water formed as a coproduct.<sup>(2)</sup> Reactor water inhibits the catalytic reaction and limits reactant conversion to 30-40%. In halide-containing fixed bed catalyst systems water leaches halide away from the catalyst resulting in long-term deactivation and excessive corrosion of metallic reactor and downstream hardware components. A major goal of this project is to limit water formation and improve gas-phase reactor performance by incorporation of dimethyl ether (DME) as a dehydrated methanol equivalent into the reactor feedstream. DME is less expensive to produce than MeOH on a methanol-equivalent basis and its oxidative carbonylation to DMC would not produce water as a coproduct.

## RESULTS AND DISCUSSION

A catalyst consisting of CuCl<sub>2</sub>/C (Darco-active carbon), known to be active for the oxidative carbonylation of methanol/CO to DMC was found to be inactive for oxidative carbonylation of DME. At all conditions tested, low levels of CO<sub>2</sub> was the only product detected. A catalyst consisting of CuCl<sub>2</sub>/AMSAC (an acidic molecular sieve) was also inactive and produced significantly more CO<sub>2</sub>, suggesting that the sieve-supported Cu(II) species was more of a deep oxidation catalyst than the C-supported material. In the presence of a small amount of water

added to promote initial hydrolysis of DME to methanol, the sieve-based catalyst generated a significant amount of MeOH in addition to the CO<sub>2</sub> but no DMC product. A third catalyst, consisting of an admixture of CuCl<sub>2</sub>/C and AMSAC was tested with DME/water feed. In this case methanol was formed but with no DMC production. Very little CO<sub>2</sub> was formed with this catalyst so returning the Cu(II) to the carbon support eliminated the deep oxidation activity.

Productive results were obtained with the admixture catalyst and with a DME/MeOH cofeed consisting of DME/MeOH/CO/O<sub>2</sub> (1/1.1/7.2/1.2 mole ratio). Throughout a 1100-minute test, carried out at 126°C, conversion of DME was steady at 30-33%. Methanol conversion was negative, at -20% to -30%, thus indicating net production of methanol via hydrolysis of DME. Two principle products, DMC and dimethoxymethane (DMM), were formed, each in about 50% selectivity, and methyl formate and methyl chloride were observed in trace quantities. The net conversion of the total methoxy functionality (CH<sub>3</sub>O) in the feed to take into account the negative conversion (or production) of methanol has been calculated. This value ranged from 10-16% over the course of the study. To our knowledge this finding represents the first known net conversion of DME to DMC in an oxidative carbonylation reaction.

The high production of DMM in this study was not anticipated. The formation of this compound, the dimethyl acetal of formaldehyde, suggests that some of the methanol has undergone conversion to formaldehyde and subsequently reacted with methanol to form the acetal. Acidic molecular sieves are well known catalysts for acetal formation, and this reaction would be heavily favored in a low-water reaction environment.

At a more optimum level of CuCl<sub>2</sub> (7.6% Cu) and with a new bimodal carbon support, a developmental material obtained from the Mega Carbon Company, significantly higher conversions were obtained with higher selectivities to the desired DMC product. Results are shown in Figure 1. Throughout the course of a 900-minute study, net conversion of CH<sub>3</sub>O was maintained at 42-53%. At a typical sample point methanol conversion was 39% and DME conversion was 48%. Selectivity to DMC was 73-81% and selectivity to DMM was 17-25%. These results suggest significantly higher yields than those reported for the commercial liquid-phase process or those obtained in gas-phase studies which utilize only methanol as the oxidative carbonylation substrate.

## CONCLUSIONS ON CATALYSIS STUDIES

A traditional catalyst for the oxidative carbonylation of methanol and CO to DMC admixed with a mildly acidic molecular sieve catalyst allows for the oxidative carbonylation of DME/methanol mixtures to DMC. The results of this study clearly indicate the potential for obtaining high net methoxy conversions via the application of in situ dehydration with DME.

## CONCEPTUAL DMC PROCESS TAILORED FOR GASOLINE BLENDING

Based on the initial laboratory data obtained under this DOE-sponsored research and previous Amoco-sponsored work on DMC recovery from a product mixture containing methanol plus water, we have initiated an economic evaluation for the production of DMC as a gasoline oxygenate. In this paper we have briefly summarized some of our initial work on the process integration of syngas production (from natural gas) and DMC synthesis steps, including cost savings ideas on DMC recovery and blending as a gasoline oxygenate. While the initial cost studies will be based on using natural gas as the feedstock, the data can be revised in future to include syngas generation via coal and biomass gasification.

### Background on DMC Separation

Separation is a critical aspect of DMC production and is one of the more expensive steps. In a conventional DMC synthesis process via oxidative carbonylation of methanol (e.g., ENiChem technology), DMC is produced at low concentrations (20-40%) and its recovery involves a separation of the ternary system of methanol/DMC and water. This system comprises at least two binary azeotropes which makes the DMC recovery quite challenging:

Component	Normal Boiling Temperature, (°C)
Methanol	65
DMC	90
Water	100
70% Methanol + 30% DMC	62.7
89% DMC + 11% Water	7.5

Based on the patent literature, there are numerous claims on various separation techniques, including extractive distillation, liquid-liquid extraction, evaporation and selective absorption.<sup>(1)</sup>

In the past, Amoco had evaluated various engineering options for recovering DMC from a mixture of methanol/DMC and water. In related R&D work, Amoco had obtained three patents on novel liquid/liquid extraction methods using various hydrocarbon solvents.<sup>(3-5)</sup> In one of these methods, specifically tailored for the use of DMC as a gasoline additive, specific gasoline blendstocks are used to extract DMC from the ternary mixture of DMC, methanol and water. Additional water is used to prevent co-extraction of methanol. In this scheme, distillation of a DMC azeotrope is completely avoided, and a gasoline blendstock with reasonably high oxygen concentration can be produced. The use of gasoline blending components as the extraction solvent eliminates any need for separation and recovery of the extraction solvent. A conceptual flowscheme of the proposed idea is shown in Figure 2.

Various laboratory studies have indicated that with suitable gasoline-range blendstocks, the DMC recovery can approach 90-95% level with (a) very low levels of water (<0.01 wt%) and methanol (<0.5 wt%) in the DMC-rich extract and (b) low levels of DMC (<0.4%) and the extraction solvent (<0.1 wt%).

#### Conceptual Process Flowscheme

As shown in Figure 2, the key process steps in the production of DMC based on the use of a methanol/DME mixture are: syngas generation from natural gas and oxygen (from air liquefaction), methanol plus DME synthesis from syngas, DMC synthesis from methanol, DME, carbon monoxide and oxygen, carbon dioxide and hydrogen recovery from unreacted gases in the methanol/DME synthesis step and DMC extraction from methanol/DMC/water mixture. For this specific study, DMC is extracted with a refinery hydrocarbon stream (e.g., a reformat stream) that can be blended directly with gasoline.

One key consideration for the overall process scheme is that if the hydrogen from the syngas production step is to be used as fuel only, we need to select a suitable syngas generation process that will minimize hydrogen/carbon monoxide ratio (e.g., a partial oxidation process rather than a steam reformer). Regarding methanol/DME synthesis, various publications from Haldor Topsoe and Air Products have indicated that suitable catalysts can be developed to tailor to specific methanol/DME product ratio. In general, the co-production of DME and methanol is favored (namely, needs lower reactor severity) over the production of methanol alone. We are currently evaluating various options for the recovery of unconverted DME, carbon dioxide and hydrogen, and integration of various processing steps to minimize overall capital and operating costs.

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Figure 1

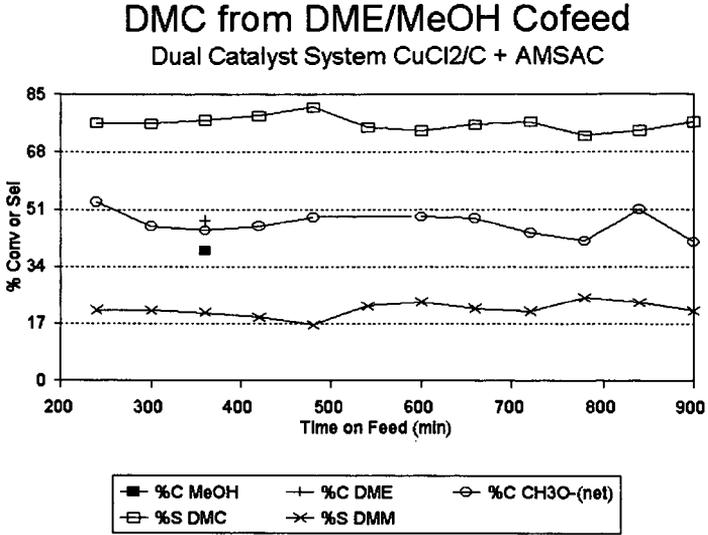


Figure 2

### Conceptual Amoco DMC Synthesis Process

