

Conceptual Process for Dimethyl Carbonate Synthesis

The synthesis of dimethyl carbonate (DMC) by oxidative carbonylation of methanol is typically carried out in one of two ways. ENIChem uses a liquid phase system with the reaction conducted in a slurry reactor, containing copper chloride "catalyst" suspended in liquid methanol. Carbon monoxide and methanol are fed into the reactor bottom and oxygen added at a carefully controlled rate along the reactor to avoid explosion. CuCl functions as a red-ox agent with the oxidation and reduction proceeding simultaneously in the same reactor. CuCl is removed from the product stream outside of the reactor. Dow Chemical has developed a vapor phase process based on supported copper catalyst with activated carbon used as the support. In either case, the reaction is highly exothermic (76 kcal/mole DMC) and the coproduction of water reduces the reaction rate. The amount of water in the reactor and the rate of water removal are critical limits on the rate of DMC production.

A new type of reactor concept is proposed which will address many of the deficiencies of the previous two that we have described. The concept is prompted by earlier work in the late 1960s by Monsanto¹ on continuous propylene hydroformylation in a gas-sparged reactor. The basic idea is to suspend the catalyst in a high boiling solvent such as dioctylphthalate and then feed an excess of gas so that the reaction products are stripped from the reactor leaving the catalyst inside suspended in the solvent. This eliminates the problem of external separation of the catalyst from the reaction products and also deals with the reaction exothermicity by conducting the reaction in a well mixed reactor with some of the reaction heat used to vaporize the products such as DMC. Outside of the reactor, a chiller is installed on the gas product stream to function as a partial condenser so that the condensable materials (DMC, methanol, and dimethyl ether) are removed with the unreacted CO and nitrogen recycled back to the reactor inlet. Additionally the coproduced water will be rapidly removed in the stripping gas so that the CuCl reagent will function at high efficiency. The Monsanto studies used propylene with an excess of hydrogen and carbon monoxide with a soluble rhodium catalyst and the system performed very well. We believe this concept can be translated to the oxidative carbonylation of methanol and result in many of the same benefits.

Not only does the gas-sparged reactor lead to improved performance in the laboratory, but it will also scale quite nicely to commercial production and consists of a relatively simple design with no elaborate reactor internals or catalyst disengagement sections. A particularly nice aspect of this reactor concept is that fresh catalyst can be added and spent catalyst withdrawn while the reactor is operating eliminating the need for reactor shutdown to change catalyst. This addition-withdrawal scheme is, of course, similar to the idea used in coal liquefaction for the H-Coal ebullated reactor and many of those details have already been worked out on loading and discharge ports.

Since the idea needs to first proceed through a process feasibility stage, we would like to move rapidly into that phase without spending large amounts of money and special design. We propose to use air as the oxygen source, rather than molecular oxygen, since it is easier to handle and less hazardous. It will be mixed with carbon monoxide and sparged into the bottom of a tubular reactor with dimethyl ether and methanol fed separately with metering pumps. A small sintered metal frit will be positioned in the bottom of the reactor to disperse the gas and agitate the reactor contents. We expect the mixing in the reactor to simulate a single continuous stirred tank reactor (CSTR). This will distribute the reaction heat so that there are no "hot spots" leading to CO oxidation to carbon dioxide or unexpected catalyst deactivation.

The proposed experimental plan is:

- * □construct the reactor (~ 300 cc) from simple stainless steel heavy wall pipe fitted with unions.

- * □attach feed system to reactor consisting of gas metering of CO and air, with a metering pump used to feed a blend of DME and methanol.

- * □install product recovery system using high pressure double ended vessel as the partial condenser chilled with a mixture of dry ice and acetone. Back pressure regulator can be used to maintain reactor at 10-15 atm and vent the unreacted nitrogen and CO through it.

- * □instrument the reactor with temperature controls and high limit temperature alarms to automatically shut the unit down in case of temperature runaway. To prevent overpressure, the reactor will be fitted both with preset relief valves and rupture discs handle spontaneous pressure excursions.

- * □establish product sampling and analysis system with online GC analysis of reactor off gas.

Amoco plans to conduct this program in cooperation with Mega-Carbon Company, a small business in St. Charles, IL.

They have several members that are highly experienced in catalyst and reactor testing and have run many systems similar to what we are proposing. The experiments will be conducted at their facilities since they have experimental space available which lends itself nicely to this rapid construction and test schedule.

A simple process flow diagram is attached and illustrates the basic idea of this new reactor concept. We think that the probability of this concept is relatively high and would be very interested in moving forward to test its feasibility.

References

1.Hershman, A., K.K. Robinson, J.H. Craddock, and J.F. Roth, " Continuous Propylene Hydroformylation in a Gas Sparged Reactor", I&EC Product Research and Development, Vol. 8, December 1969

