

Utilization of Captured CO₂ for Conversion to Alkyl Carbonates

C. B. Panchal, John C. Prindle, Rachel Sturtz and Richard D. Doctor
E3Tec Service, LLC, Hoffman Estates, IL 60192 USA

ABSTRACT

E3Tec is pursuing DOE SBIR project aimed at utilization of captured CO₂ from utility and industrial plants for manufacturing of dimethyl carbonate (DMC) with selective co-production of mono-ethylene glycol (MEG). DMC is a high-value specialty chemical with major applications in manufacturing polycarbonate, as low VOC solvent, in lithium-ion batteries and as an intermediate in manufacturing of polyurethane. DMC is also useful as diesel fuel additive to reduce emission. If adopted this use alone would expand the DMC market tremendously requiring new plants. MEG is a major commodity chemical used in polyethylene terephthalate (PET) with end-use in making films, fibers and bottles. The project team acknowledges that not a single chemical product would be able to make a major impact on CO₂ abatement, either by direct consumption and/or off-setting CO₂ emission for the end product. However, CO₂ utilization plants from distributed CO₂ source sites will make a significant dent into the overall CO₂ abatement target. In order to make a major impact of CO₂ utilization for chemical production on large scale, commodity chemicals such as methanol and urea will have to be pursued. However, it would be very hard to compete in commodity chemicals, especially with low natural gas prices. Specialty chemicals, such as DMC and MEG, with favorable product margin will provide the basis for early commercialization. Furthermore, methanol is feedstock for DMC, so once the DMC technology is demonstrated, an integrated process of CO₂ capture, methanol and DMC can be developed. In essence, DMC is an ideal chemical for utilization of CO₂.

Keywords: carbon dioxide capture, alkyl carbonates, reactive distillation, mono-ethylene glycol

1 INTRODUCTION

In the past two centuries, fossil fuel supplied by coal, petroleum and natural gas has played a key role in establishing the modern world economy. When the global demand for electricity increased from 8.3 million GWh in 1980 to 23.8 million GWh in 2014 [1], the resulting annual CO₂ emission increased from 5.5 to 13.3 trillion tonnes. Today the global demand for energy-intensive products, such as ammonia and plastics, is also expanding with the growing population and improved standards of living in emerging markets. The impact of rising CO₂ levels on climate change is now taken seriously as demonstrated by the COP21 meeting in Paris which has stimulated global action to reduce CO₂ emission. The recent announcement

at this meeting by the major oil and gas companies outlines economic solutions; one of which is CO₂ conversion to products [2]. Considering the magnitude of the issue, all of these efforts will be required to stabilize and then reduce CO₂ levels in the atmosphere. The challenges associated with CO₂ capture, transport, and storage have been well documented [3]. The Global CCS Institute recently published a cost analysis for CO₂ capture, transport, and storage in the European Union [4]. The report highlighted the challenges and costs of building a CO₂ transportation infrastructure.

There are very limited uses for captured CO₂ and the largest commercial use is enhanced oil recovery (EOR) which currently has over 126 projects globally; some as high as a 2 MMtonne/yr capacity. The Global Carbon Capture and Sequestration (CCS) Institute provides a list of current and future storage sites while highlighting the challenges and costs of developing a CO₂ transportation infrastructure. Few major industrial CO₂ generation sources (e.g. refineries, petrochemical production, ammonia/urea manufacturing facilities, fossil power generation plants etc.) are located close to these storage sites. Consequently, a variety of products and different technology pathways for converting captured CO₂ to value-added products are being actively pursued.

E3Tec, jointly with Michigan State University (MSU) is pursuing the development of a process for conversion of CO₂ captured from utility and industrial sources to value-added industrial chemicals. In this process, methanol and ethylene oxide are secondary feedstocks for co-production of the high-value products DMC and MEG from CO₂. The basic sources of captured CO₂ are: a) coal-utility plants; b) gas-turbine combined cycle (GTCC); c) hydrogen production using steam-methane reforming; d) and Natural Gas (NG) combustion as a heat source. Initially E3Tec received grant from Emission Reduction Alberta (ERA, previously CCEMC). Now, E3Tec is advancing the process development under DOE's SBIR Phase II project.

The supply chain presented in Figure 1 focuses on feedstocks for synthesis of DMC and its derivative chemicals. Both commercial processes use natural gas (NG) as feedstock. The use of oxygen makes these processes inherently more dangerous. Both processes are energy intensive and require handling of difficult chemicals, such as phosgene. DMC is an intermediate carbonate for manufacturing other alkyl carbonates for major end-use applications. MEG is a major commodity chemical that improves the overall economic

competitiveness of the process. In essence, DMC is an ideal chemical for conversion of captured CO₂ to value-added specialty chemicals. E3Tec has performed global market analysis based on reports [5], in-house market data and advisory support from a business planning company.

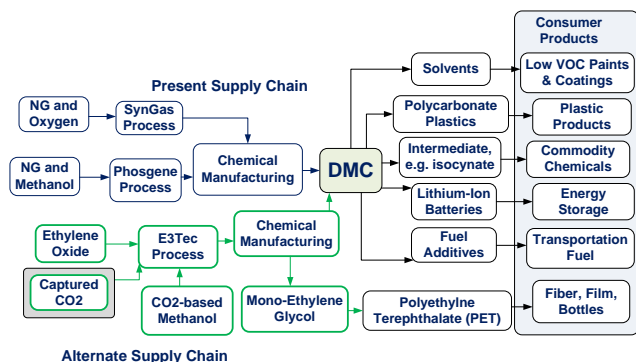


Figure 1: DMC Supply Chain

2 PROCESS DESCRIPTION

The E3Tec synthesis process is based on the following chemical pathway using methanol and ethylene oxide as feedstock.

Ethylene Oxide + CO₂ → Ethylene Carbonate (EC)

EC + Methanol ↔ DMC + MEG

E3Tec is also developing an alternate process based on the following chemical pathway.

Ammonia + CO₂ → Urea

Urea + Methanol ↔ DMC + Ammonia (recycled)

The first reaction in both processes is practiced commercially; however, the second is a reversible catalytic reaction requiring process configuration with effective separation of DMC as it is formed. Conventional reactive distillation (RD) with catalyst mounted in some form inside the distillation column has limitations and cannot be applied to the DMC process. To overcome these limitations of conventional RD, the E3Tec team has developed a process of Heat Integrated Reactive Distillation (HIRD) equipped with side reactors, with the possible use of pervaporation (PerVap) membrane. The patented HIRD process with side reactors is ideally suited for complex chemical reactions such as DMC synthesis, whose reaction rate is slow, reversible, and equilibrium controlled [6]. Kinetic parameters obtained using an E3Tec prototype test unit [7] and/or stand-alone plug-flow reactor (PFR) are linked to the ASPEN Plus® process model to provide an optimal for CO₂ conversion to DMC with a low C-Footprint.

Figure 2 presents a simplified process flow diagram of the process. EC is pre-reacted with excess methanol in a packed-bed reactor. Most of the methanol and DMC are removed from the effluent and sent to product recovery columns. Because there is a methanol/DMC azeotrope, the methanol is only purified in the methanol recovery column to 88 wt% before being recycled to the side reactors and pre-reactor. PerVap membranes can be integrated with the process for recovering methanol and for breaking the azeotrope. Integration of the PerVap membrane will further improve the energy efficiency and hence reduce the C-Footprint. Considering the high costs of PerVap membranes, a trade-off analysis is performed to optimize the design based on capital costs (CAPEX) and energy efficiency and thereby C-Footprint. DMC is purified to 99.99 wt% in the product recovery column. The remaining pre-reacted effluent is fed to the reaction column where MEG and unreacted EC are separated. The MEG is removed as a side stream product at 99.5 wt% purity. Plug-flow reactor tests showed that MEG is co-produced with high selectivity in the stoichiometric balance with ethylene oxide. Commercially, ethylene oxide is reacted with water to produce mixed (mono, di and tri) ethylene glycols. MEG is a major commodity chemical and its separation from mixed glycols is energy-intensive. Therefore, this energy-efficient process with high selectivity of MEG has significant advantages.

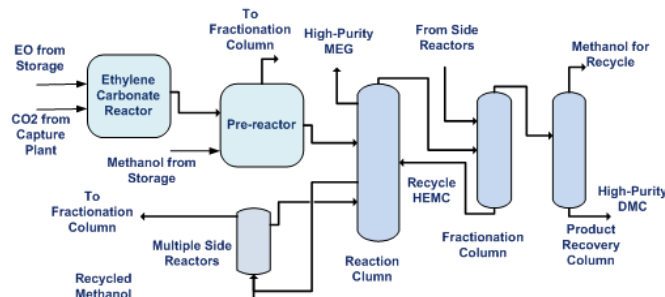


Figure 2: DMC Process Flow Diagram

3 INTEGRATION WITH CO₂ CAPTURE PROCESS

In collaboration with Illinois Sustainability Technology Center (ISTC), E3Tec is pursuing integration of the DMC process with CO₂ capture unit. Emerging new CO₂ capture processes would be thermally integrated for small to medium capacity CO₂ sources. The thermal integration would reduce the overall C-Footprint of the integrated process and the high product margin would offset the cost of CO₂ capture. The techno-economic merits of an integrated process will be assessed in the second year of the on-going DOE SBIR project.

Figure 3 presents a schematic of an integrated CO₂ capture DMC conversion process. The key design features

of an integrated process are: a) CO₂ does not have to be compressed to high pressures or liquified for transportation; b) heat integration improves the overall C-Footprint; c) modular design allows for a balanced approach of CO₂ sequestration and utilization.

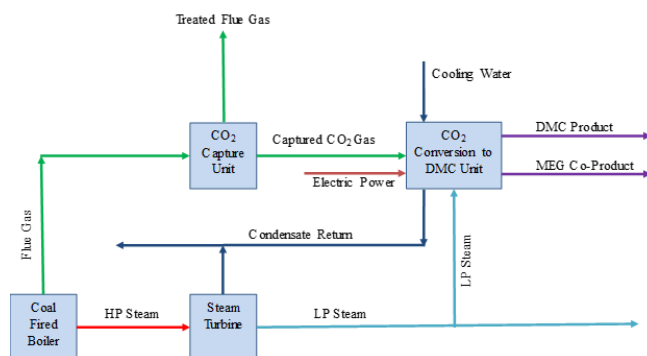


Figure 3: Schematic of an Integrated Process

4 INTEGRATION WITH METHANOL PLANTS

E3Tec is also evaluating integration of the DMC process with methanol production plants. Conventional methanol plants are based on natural gas (NG) with C-Footprint of about 0.54 kg/kg methanol; however, methanol synthesis processes using captured CO₂ and natural gas are being developed [8]. Such plants will still have CO₂ emission, although lower than conventional plants. With the availability of high-purity CO₂ from such new-generation methanol plants, the DMC process can be integrated with CO₂-based methanol plants. The overall economic benefits and C-Footprint of the integrated process would provide significant advantages over separate processes.

E3Tec is planning to evaluate such an integrated process in the second year of the DOE SBIR project. E3Tec also evaluated methanol produced as byproduct from the pulp & paper process. The major limiting factor in biomass based methanol is the presence of sulfur compounds that requires an energy-efficient separation process for reducing the sulfur level accepted in the DMC process due to the presence of catalyst.

5 CARBON-FOOTPRINT ANALYSIS

An Excel-based C-Footprint model was developed to identify and quantify process steps with high and low C-Footprints. The C-Footprint analysis is based on detailed ASPEN Plus™ process analysis within the Inside Battery Limit (ISBL), as shown by the process diagram in Figure 2, and on the literature-based C-Footprint for Outside Battery Limit (OSBL) elements. These include methanol and ethylene oxide feedstocks, electricity, Natural Gas (NG) as fuel, waste water, and byproducts. At this stage, the C-

Footprint associated with CO₂ capture is not included. The integrated system of CO₂ capture and conversion will account for C-Footprint of the CO₂ capture process. The C-Footprint of the E3Tec process is 0.59 kg/kg DMC with co-production of MEG, by taking into account of 0.29 kg CO₂/kg DMC consumed in the process. The C-Footprint of feedstock methanol also contributes to the overall C-Footprint. If biomass based methanol or emerging process of CO₂ based methanol production are used, the process would have net consumption of CO₂. On the other hand, the C-Footprint of the syngas based DMC process, combined with commercial MEG production, is 3.13 kg/kg DMC. If syngas based DMC is produced by gasification of coal, the C-Footprint would be about 50% greater than the value above.

6 PUBLIC BENEFITS

CO₂ conversion to DMC is a “win-win” solution for both the CO₂ capture market and those with an expanding demand for DMC. A preliminary economic analysis showed that the conversion of CO₂ to DMC has high potential to be competitive against conventional syngas based DMC processes with its high C-Footprint. One of the key points emphasized at AIChE’s Carbon Management Technology Conference, Sugar Land, TX 2015 is that it would be of great benefit to develop a modular plant that would convert captured CO₂ at the source, thereby eliminating the storage, transport, and injection costs of CO₂ sequestration from distributed CO₂ sources.

E3Tec directly addresses this crucial need by:

- identifying specialty chemicals that can be produced from CO₂ with favorable economics;
- replacing domestic phosgene-based polycarbonate manufacture with a non-phosgene process with low C-Footprint;
- developing HIRD process equipped with side reactors as a potentially transformative technology for the next generation of intensified manufacturing processes with lower CAPEX and higher energy efficiency;
- producing DMC and higher alkyl carbonates for use as an electrolyte solvent for lithium-ion batteries, as an industrial solvent, as an industrial chemical intermediate, and as a potential fuel additive, in addition to supplying the growing demand for polycarbonates; and
- placing the US in the lead for manufacturing CO₂-based DMC, thereby reducing imports.

7 CONCLUSIONS AND PATH FORWARD

The E3Tec team successfully developed the HIRD process equipped with side reactors for conversion of captured CO₂ to DMC with co-production of MEG. The

basic conclusion from the initial ERA project and on-going DOE SBIR project is that this approach is ideally suited for conversion of CO₂ to DMC as well as other alkyl carbonates. Additionally, incorporating kinetic parameters obtained by MSU into the ASPEN Plus® process model E3Tec has developed a design methodology based on the concept of “scale-down to scale-up”. This design methodology accelerates the process development while minimizing the scale-up uncertainties.

There is a *window of opportunity* for replacing phosgene-based process in the US with CO₂-based DMC production. Phosgen based process is being replaced with syngas based process with high C-Footprint. The E3Tec team is actively pursuing to advance the HIRD process to technology readiness level (TRL) closer to commercialization. In the second year of the SBIR project, the ASPEN Plus® process model will be validated with an integrated pilot-scale test unit at MSU and the techno-economic merits will be analyzed for assessment of the competitiveness of the process. The techno-economic merit analysis will be based on capture CO₂ to alkyl carbonate vs capture CO₂ to sequestration, including CO₂ transportation, either as compressed gas or liquefied CO₂.

The project team acknowledges that not a single chemical product would be able to make a major impact on CO₂ abatement, either by direct consumption and/or offsetting CO₂ emission for the end product. However, CO₂ utilization plants from distributed CO₂ source sites will make a significant dent into the overall CO₂ abatement target.

8 ACKNOWLEDGEMENTS

This project was sponsored by the U.S. Department of Energy's (DOE's) Office of Basic Science through the Small Business Innovative Research (SBIR) Program. These investigations described herein were conducted under DOE Contract No. DE-SC0013233 with E3Tec Service, LLC. The authors also acknowledge the grant from Emission Reduction Alberta (ERA) through Round-1 Grand Challenge.

REFERENCES

- [1] "Key Electricity Trend" *Excerpt from Electricity Information*, International Energy Agency, 2016.
- [2] "Oil and gas CEOs Jointly Declare Action on Climate Change," *PennEnergy e-news Report*, 19 October 2015.
- [3] R. D. Doctor, "Adoption at Existing PC Plants Economic Comparison of CO₂ Capture and Sequestration from Amine and Oxyfuels," Argonne National Laboratory Report, Argonne, 2011.

- [4] "The Cost of CO₂ Capture, Transport and Storage, Zero Emission Platform," Global CCS Institute, 2011.
- [5] "2015 Market Research Report on Global DMC Industry," QYResearch DMC Center, 2011.
- [6] C. B. Panchal and J. C. Prindle, "Method of Producing High-Concentration Alkyl Carbonates using Carbon Dioxide as Feedstock". US Patent 9,518,003 B1, 13 December 2016.
- [7] C. B. Panchal, "Differential Kinetic Test Unit (DKTU)". US Patent 9,222,924 B1, 29 December 2015.
- [8] M. Perez-Forte, J. C. Schoneberger, A. Boulamanti and E. Tzimas, "Methanol Synthesis using Capture CO₂ as Raw Material: Techno-Economic and Environmental Assessment," *Applied Energy*, vol. 161, 2016.