Conversion of CO_2 to Value-Added Specialty Chemicals

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ABSTRACT

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 (1980) to 23.8 million GWh (2014), the annual CO_2 emission increased from 5.5 to 13.3 billion tonnes [1]. Today the continued global demand for energy-intensive products, such as ammonia, cement, solvents, coatings and plastics, is also expanding with the growing population and improved standards of living in emerging markets. The challenges associated with CO_2 capture, transport, and storage have been well documented, and other proposed non-sequestration economic solutions are envisioned as a series of "***wedges***" for CO_2 abatement. E3Tec has developed an integrated process for conversion of captured CO_2 to alkyl carbonate. The techno-economic merits are analyzed for an integrated process of CO_2 capture and conversion to alkyl carbonate.

Keywords: CO_2 utilization, alkyl carbonates, value-added specialty chemicals, integrated capture conversion process

1 INTRODUCTION

In 2015 the major oil and gas companies outlined economic solutions to reduce CO_2 emissions; one of which is CO_2 conversion to products [2]**.** Considering the magnitude of the issue, concerted efforts will be required to stabilize and then reduce CO_2 levels in the atmosphere. The challenges associated with CO_2 capture, transport, and storage have been well documented [3,4].

Enhanced oil recovery (EOR) remains the large-scale commercial use for CO_2. However, few major industrial CO_2 sources are located close to these EOR sites. Additional economic solutions include CO_2 conversion to products [2]**.** Conversion of CO_2 to value-added products includes the following four categories.

1) Fuels: Conversion to methanol and syngas by catalytic reforming with natural gas.
2) Bio-Fixation: Microalgae and bioconversion of CO_2 and hydrogen to butanol.
3) Solid Products: Graphene, inorganic carbonates and concrete.
4) Chemicals: Methanol, ethylene oxide, acetic acid and ***alkyl carbonates***.

The techno-economic merit criteria employed are:

1) Technical viability of the process and down-stream processing required for commercial use of products;
2) C-footprint of the product and process for net consumption of CO_2 or offsetting CO_2 emission from the commercial processes;
3) Competitive product margin for offsetting costs associated with CO_2 capture;
4) Market potentials of the product(s); and
5) Service life of the product and end products at the end of service life.

Based on these criteria, the E3Tec team pursued the development of a heat integrated reactive distillation (HIRD) process for conversion of captured CO_2 to alkyl carbonates. This joint research effort with Michigan State University (MSU) initially received a grant from Emission Reduction Alberta. Currently, it is being advanced under a DOE SBIR Phase II project.

2 CO_2 TO ALKYL CARBONATES

Methanol and ethylene oxide are secondary feedstocks for co-production of the high-value products dimethyl carbonate (DMC) and mono-ethylene glycol (MEG). The early phase of the project development was presented at the 2017 TechConnect [5] and further development with the focus on integration of the DMC process with CO_2 sources is presented in this paper.

The supply chain of DMC and MEG is well established as presented in Fig. 1. Therefore, alternate CO_2-based processes need to effectively integrate within the prevailing supply chain leading to consumer products. The present supply chain is based on use of natural gas (NG) or syngas by coal gasification syngas as feedstock. Both commercial 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 process competitiveness of the process. DMC is an ideal chemical for conversion of captured CO_2 to value-added specialty chemicals. E3Tec has performed global market analysis based on reports [6, 7], in-house market data and advisory support from a business planning company.

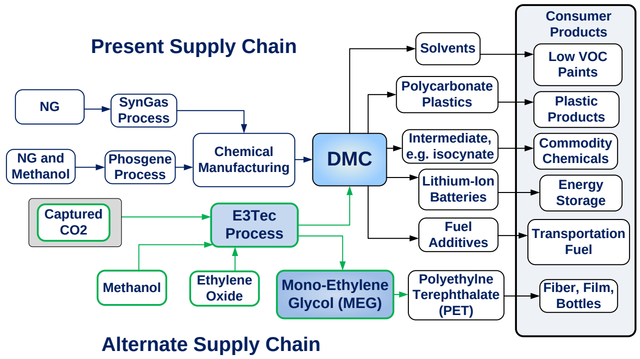

Figure 1: DMC Supply Chain

3 PROCESS DESCRIPTION

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

Ethylene Oxide + CO_2 $\rightarrow$ Ethylene Carbonate (EC)

EC + Methanol $\leftrightarrow$ DMC + MEG

An alternate process using ammonia as a reaction carrier has also been developed.

Ammonia + CO_2 $\rightarrow$ Urea

Urea + Methanol $\leftrightarrow$ DMC + Ammonia (recycled)

The first reaction in both processes is practiced commercially; however, the second is a reversible catalytic reaction requiring a 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 and pervaporation (PerVap) membrane, as shown in Fig. 2. 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 [8].

Table 1 presents a summary of process parameters for a 51.6 kTA (thousand tonnes/year) plant. 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 product recovery column to 88 wt% before being recycled to the side reactors and pre-reactor. PerVap membranes are integrated with the process for recovering methanol and for breaking the azeotrope. Integration of the PerVap membrane further improves the energy efficiency and hence reduces the C-footprint. DMC is purified to 99.99 wt% in the product recovery column. The MEG is co-produced with high selectivity in the stoichiometric balance and recovered as a side stream product at 98.9 wt% purity. Commercially, ethylene oxide is reacted with water to produce mixed (mono, di and tri) ethylene glycols that requires multi-effect evaporators for recovery of high-purity MEG. MEG is a major commodity chemical and its separation of MEG from mixed glycols is energy-intensive. Therefore, this energy-efficient process with premium purity of DMC and high selectivity of MEG has significant advantages.

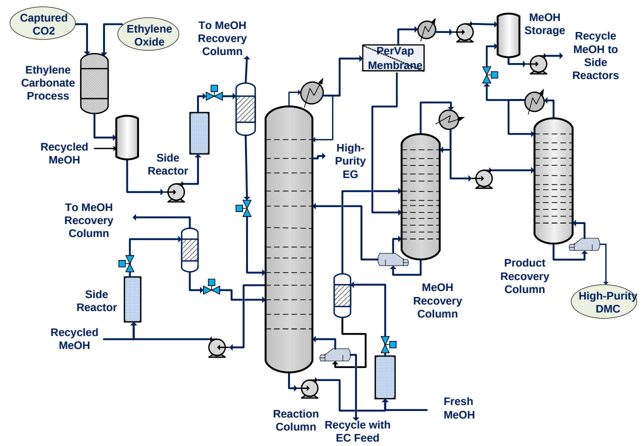

Figure 2: DMC Process Flow Diagram

Feed, kg/hr		Products, kg/hr	
CO_2	3,246	DMC, 99.99%	6,550
Methanol	4,710	MEG, 98.9%	4,539
Ethylne oxide	3,249	Purge	116

Table 1: Process Paramters of 51.6 kTA DMC Plant

4 INTEGRATION WITH CO_2 CAPTURE PROCESS

E3Tec is pursuing integration of the DMC process with CO_2 sources in collaboration with the Illinois Sustainability Technology Center (ISTC). Fig. 3 presents a schematic of the DMC process integrated with the CO_2 capture unit. The key design features of an integrated process are: a) CO_2 is not compressed to high pressures or liquified for transportation for sequestration; b) heat integration, including CHP (combined heat and power), improving the overall C-footprint of an integrated process; c) modular design allowing cost-effective integration with CO_2 Sources.

Post treatment of captured CO_2 depends on the source. The presence of sulfur compounds adversely affects the catalyst and oxygen is not acceptable in the ethylene carbonate process. The presence of moisture could be managed with a dehydration unit. Based on the published data of emerging new CO_2 capture processes, captured CO_2 can be directly used in the integrated process.

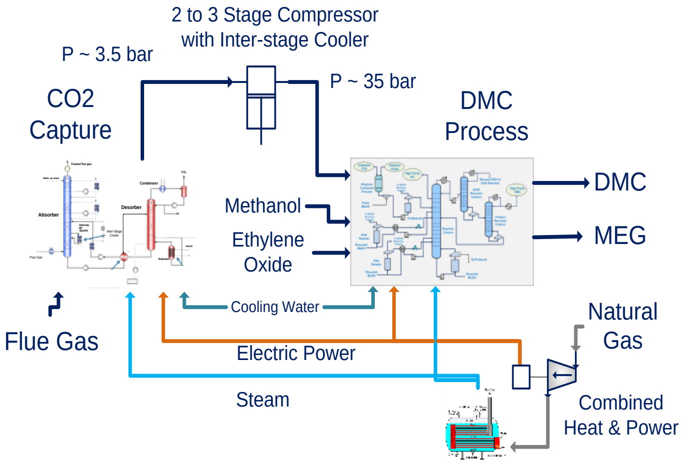

Figure 3: Schematic of an Integrated Process

The thermal and electric power required for the integrated process are provided by the CHP system. This design approach minimizes the adverse impact on the CO_2 source, e.g. utilization of low pressure steam from and the utility plant.

5 INTEGRATION WITH METHANOL PRODUCTION

E3Tec has also evaluated integrating the DMC process with methanol production. Conventional methanol plants based on natural gas (NG) have a C-footprint of about 0.54 kg/kg methanol. However, methanol synthesis processes using captured CO_2 and natural gas are being developed with lower C-footprint. If hydrogen can be generated using renewable energy, the C-footprint will be substantially lower [9]. With the availability of high-purity CO_2 from such new-generation methanol plants, the DMC process can be integrated with CO_2-based methanol plants, the DMC process shows a special advantage for integration. The overall economic benefits are favorable, while at the same time having a lower C-footprint.

6 TECHNO-ECONOMIC ANALYSIS

6.1 Carbon-footprint (C-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 ASPENPlus® process analysis within the Inside Battery Limit (ISBL) 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, cooling water and byproducts. A summary of C-footprint analysis is presented in Table 2. The results show clearly that the CO_2-based DMC process has potential to offset the CO_2 emission.

CO_2 Consumption or Emission, kg CO_2 / kg DMC	E3Tec Process	Commercial Process
Consumption	0.51	0.0
Emission		
Without feedstock C-footprint	0.54	1.60
With commercial methanol	1.08	2.14
With ethylene oxide	1.44	NA
Credit for co-product MEG	0.34	NA
Net Emission kg CO_2/kg DMC	0.59	2.14

Table 2: C-footprint Analysis

6.2 Competitive Production Costs

Under a subcontract to E3Tec, Jacobs Consultancy estimated capital costs (CAPEX), operating costs (OPEX) and database for estimating raw material costs. The ISBL costs are based on the design parameters derived from the ASPENPlus® simulation for a plant capacity of 51 kTA. A *ProForma* based economic analysis is then performed to evaluate the competitiveness of the process compared to syngas-based commercial production. The cost estimates of a syngas-based commercial process are made with the available design and cost information. Table 3 presents a summary of cost estimates. The resulting selling price of the E3Tec process is lower than the commercial process. The resulting Net Present Value (NPV) and Internal Rate of Return (IRR) of the E3Tec process are $151 million and 18%, respectively. Thus, the initial cost analysis clearly demonstrates the competitiveness of the CO_2-based DMC.

	E3Tec	Commercial
CAPEX, $ million	$156	$221
Total Variable, $/tonne DMC	$613	$441
Total Fixed, $/tonne DMC	$199	$259
Production Cost, $/tonne DMC	$812	$700
Capital Charge, $/tonne DMC	$798	$1,127
Selling Price, $/tonne DMC	$1,610	$1,827

Table 3. Sumarry of Cost Estimates

6.3 Integrated Process for Offsetting CO_2 Capture Costs

A case study was performed to evaluate what fraction of CO_2 emission from a coal utility plant needs to be utilized in the DMC/MEG process to offset the costs associated with capturing and potentially sequestering the CO_2 emissions. The basis is the 15 MWe Abott plant at the University of Illinois, Urbana-Champaign with 300 tonnes/day CO_2 emissions. The purpose of this analysis was to determine what fraction of CO_2 needs be converted to DMC with adequate product margin that would offset the costs associated with CO_2 capture and sequestration of the remaining fraction of CO_2. Table 3 presents a summary of the cost analysis that shows favorable product margin to offset the CO_2 capture and sequestration costs with minimum impact on the cost of electricity (COE).

Baseline Case	**15 MW Coal Plant**	
Power Generation	15	MWe
CO_2 Emission	300	T/Day
CO2 Capture & Sequestration Costs		
CO_2 Capture Costs @ $56.2/T CO2*	$16,860	$/Day
Sequestration Costs @ $44.8/T CO2*	$10,080	
COE Impact (assuming 90% availability)	$83	$/MWh
DMC/MEG Production		
Fraction of CO_2 Consumed in DMC	25%	
DMC Production	150	Tonnes/Day
Product Margin Required for Offsetting CO_2 Costs		
CO_2 Capture / Sequestration Costs	$66 / $40	$/Tonne DMC
Combined	**$106**	
Selling Price of 99.99 % Purity DMC	$1,827	
Production Costs of DMC	$1,610	
Product Margin	**$217**	

* Ref: Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity Revision 3, DOE/NETL-2015/1723,July 2015.

Table 3: Cost Analysis of an Integrated Process

7 CONCLUSIONS AND PATH FORWARD

CO_2 conversion to DMC is a "***win-win***" solution for both the CO_2 capture market and those with an expanding demand for DMC. A *ProForma* based economic analysis showed that the conversion of CO_2 to DMC has high potential to be competitive against commercial syngas-based DMC processes with their high C-footprint.

The E3Tec team focused on the following criteria in this project:

a) identifying specialty chemicals that can be produced from CO_2 with favorable economics;
b) replacing domestic phosgene-based polycarbonate manufacture with a non-phosgene process;
c) developing HIRD process equipped with side reactors as a potentially transformative technology of ***Process Intensification*** for manufacturing specialty chemicals with lower CAPEX and higher energy efficiency;
d) producing DMC and higher alkyl carbonates for use as an electrolyte for lithium-ion batteries, as an industrial solvent, in addition to meeting the growing demand for polycarbonates; and
e) placing the US in the lead for manufacturing CO_2-based DMC, thereby reducing imports.

The E3Tec team successfully developed the HIRD process equipped with side reactors for conversion of captured CO_2 to DMC with co-production of MEG. The basic conclusion from the completed ERA project and on-going DOE SBIR project is that this approach is ideally suited for conversion of CO_2 to alkyl carbonates. The ASPEN Plus® process model, validated with pilot-scale tests, is developed to accelerate the process development and technology demonstration while minimizing the scale-up uncertainties.

The project team acknowledges that not a single group of chemical products would be able to make a major impact on CO_2 abatement, either by direct consumption and/or offsetting CO_2 emission for the end product. However, CO_2 utilization plants from distributed CO_2 source sites will make a significant dent into the overall CO_2 abatement target.

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