

CCEMC EOI # K130091

Final Report: May 2016

Project ID EOI # K130091

Final Report Public Release

**Production of Dimethyl Carbonate (DMC) from
Captured CO₂ and Methanol**

By

E3Tec Service, LLC

1 Denali Court

South Barrington, Illinois 60010-1061

USA

Principal Investigator

Dr. Chandrakant B. Panchal

E3Tec Service, LLC

Project Advisor

Dr. Duke DuPlessis

Alberta Innovates

Calgary, Alberta

Canada

Completion Date: June 2016

May 2016

Table of Contents

1	EXECUTIVE SUMMARY	5
2	PROJECT DESCRIPTION.....	8
2.1	Introduction and Background	8
2.2	Technology Description	9
2.2.1	Urea-Based DMC Process	9
2.2.2	Ethylene Oxide Based DMC Process	9
2.3	Project Goals	11
2.4	Work Scope Overview	11
3	OUTCOMES AND LEARNING	13
3.1	Literature Survey	13
3.2	Technology Development	15
3.3	Experimental Procedures and Methodology	16
3.3.1	Kinetic Tests	16
3.3.2	PerVap Performance Tests.....	18
3.3.3	Validation Tests with Prototype Test Units	19
3.4	Modeling Details	21
3.4.1	Kinetic Model	21
3.4.2	ASPEN Plus® Process Models.....	22
3.4.3	Integration of DMC Process	23
3.5	Results and Discussion	26
3.5.1	Kinetic Parameters	26
3.5.2	PerVap Performance	27
3.5.3	Prototype Test Results	28
3.5.4	Process Analysis	28
3.5.5	Design of Pilot Plant	30
3.6	Project Outcome	33
3.7	Lessons Learned	34
4	GREENHOUSE GAS AND NON-GHG IMPACTS	35
4.1	Impact of CO ₂ Conversion to DMC on GHG Emission	35
4.2	C-Footprint Analysis.....	35
4.3	C-Footprint of Raw Materials	38
4.4	CO ₂ Emission Abatement	40
4.5	Challenges and Opportunities	42
5	OVERALL CONCLUSION	42
6	SCIENTIFIC ACHIEVEMENTS	43
7	PROGRAMMATIC ACHIEVEMENTS.....	44
8	NEXT STEPS	46
8.1	Technology Innovation	46
8.2	Commercialization Plan	46
9	COMMUNICATIONS PLAN	47

List of Figures

Figure 3-1: Supply chain of Dimethyl Carbonate (DMC).....	14
Figure 3-2: Global DMC demands 2015	14
Figure 3-3: Schematic diagram of scaling the catalytic process from lab to commercial plants..	16
Figure 3-4: Schematic diagram and pictorial view of the DKTU.....	17
Figure 3-5: Flow schematic of the PerVap test unit.	19
Figure 3-6: Pictorial view of the PerVap test unit.	19
Figure 3-7: Process diagram of the prototype test unit for the urea based process.	20
Figure 3-8: Process diagram of the prototype test unit for the ethylene oxide based process.....	21
Figure 8-1: E3Tec commercialization plan.....	47

List of Tables

Table 3-1: Characterization of CO ₂ from three sources.....	24
Table 3-2: Design parameters of a commercial scale process unit.	30
Table 3-3: Process parameter of the pilot plant for the urea-based process.	32
Table 3-4: Process parameters of the pilot plant for the ethylene oxide-based process.	33
Table 4-1: C-Footprint of the urea-based process.....	37
Table 4-2: C-Footprint of the ethylene oxide-based process.	38
Table 4-3: C-Footprint of the SynGas-based Versalis process.	38
Table 4-4: Alberta's CO ₂ abatement potentials by four major applications of DMC.	41

1 EXECUTIVE SUMMARY

In the past two centuries, fossil fuels – coal, petroleum and natural gas – have played a key role in establishing the modern world. They have allowed for affordable electricity, the development of high-speed long-distance transportation, the supply of potable water, and the production of ammonia fertilizers with direct impact on food production. Between 1980 and 2012 the global demand for electricity increased from 8.3 to 22.7 million GWh, and the resulting annual CO₂ emissions increased from 5.5 to 13.3 trillion tonnes. ***The impact of rising CO₂ levels on the climate is now taken seriously as demonstrated by the COP21 meeting in Paris (December 2015). The accord from COP21 is expected to stimulate global action to reduce CO₂ emissions, as well as to find economic ways to convert CO₂ to products. Recent announcements by major oil and gas companies show that industry is ready for serious engagement on this issue.*** Considering the magnitude of the issue, every effort to stabilize and then reduce CO₂ levels in the atmosphere will be required. The challenges associated with CO₂ capture and storage (CCS) have been well documented. Since few of the major industrial and utility CO₂ sources are located close to CO₂ storage sites, additional and substantial transportation and injection costs will be incurred. ***Converting captured CO₂ to value-added products such as DiMethyl Carbonate (DMC) via the proposed process would eliminate CO₂ transportation and storage costs from distributed CO₂ sources. It encourages facilities to convert CO₂ into a revenue stream that would benefit Alberta.***

E3Tec's project focuses on the CCEMC mission of reducing Alberta CO₂ emissions by using CO₂ as a feedstock to manufacture DMC, an ideal chemical for CO₂ conversion because of its expanding applications in current and emerging markets. DMC presently is used for manufacturing polycarbonates – replacing a more hazardous phosgene-based route, it is used as a low VOC solvent, and as an electrolyte solvent in lithium-ion batteries. It is being evaluated as an oxygenated fuel additive for diesel. DMC is also used to produce isocyanates, a family of chemicals with high industrial use as an intermediate for manufacture of polyurethane and synthetic materials.

The governing objective of this Grand Challenge project was to develop a process for converting captured CO₂ to the value-added product di-methyl carbonate (DMC). There is a growing global demand and emerging new applications for DMC. The E3Tec team understands that no one technology alone can meet Alberta's 2008 Climate Change Strategy; however, by converting captured CO₂ to DMC, E3Tec's technology would be part of the portfolio for making significant contributions to the overall goal within the desired time frame. The E3Tec Team, in partnership with Michigan State University (MSU), has developed an innovative energy-efficient process; combining heat-integrated reactive distillation (HIRD) with side reactors equipped with either PerVaporation (PerVap) membranes or side reboilers for separation of byproduct and excess reactants. With a low Carbon-Footprint, the CO₂-based DMC has potentials for significant abatement of CO₂ in Alberta.

The major scientific achievements were: a) development of ASPEN Plus® design methodology of two CO₂-based DMC processes; b) establishment of CO₂ abatement potentials; c) competitive edge of the CO₂-based DMC process to conventional SynGas-based DMC process; d) development of the databases of kinetic parameters and performance parameters using prototype test units for validating the ASPEN Plus® design model; and e) pilot plant design for demonstrating the technology in Alberta.

The four DMC market opportunities that would result in significant CO₂ abatement are: a) polycarbonates; b) environmentally friendly solvents; c) lithium-ion batteries; and d) a potential fuel additive to diesel. All together these markets constitute the potential for greater than 9 million tonnes/year of CO₂ abatement with 25% market share of the global demands as shown in table below. Alberta would become a major manufacturing center of CO₂-based DMC for exporting to the US, Asia, and Europe.

Application	2016 Global Demands kTA	Growth kTA	25% Market Penetration	DMC in Product	CO2 Abatement Potentials, kTA	
					Growth	25% Market
Polycarbonate	6,430	444	1,608	1.0	129	466
Solvents (Replacing Ketones)	1,430	29	358	1.0	23	286
Fuel Additives (Diesel)	1,580,000	31,600	395,000	0.076	700	8,752
Lithium-Ion Battery	\$25 billion/yr	Electrolyte market \$5.23 billion/yr			227	

In addition to technical accomplishments, there were significant programmatic achievements. E3Tec has secured strong IP positions through patent protection in “Method for Producing Concentrated Dimethyl Carbonate Composition and Co-Products,” US # 14/445,992 (Patent Issued) and “Differential Kinetic Test Unit (DKTU),” US Patent 9,222,924 (December 2015). The ASPEN Plus® design methodology provides the basic foundation for rapidly scaling laboratory data and pilot plant performance parameters to commercial plants. E3Tec received US SBIR Phase I grant for developing an alternate process to convert of CO₂ to DMC using ethylene oxide as feedstock. This process produces mono-ethylene glycol (MEG) as coproduct and this should improve the process techno-economic viability. E3Tec team members visited Enerkem and Alberta Innovates Technology Futures in July 2014 to explore collaboration and evaluate sites for demonstration of the technology in Round 2. Collaboration with Enerkem will focus on methanol produced from municipal waste as feedstock for the DMC process and potentially an integrated DMC-Methanol process. The integrated process is expected to significantly improve the overall C-Footprint by eliminating liquefaction or pressuring for transportation of CO₂. E3Tec is exploring potential collaboration with Illinois Sustainability Technology Center (ISTC), Champaign, Illinois for developing an integration process of CO₂ capture and conversion.

The major conclusions from Round 1 projects in three categories are as follow.

CO₂ Abatement Target

1. DMC is an ideal value-added specialty chemical with expanding global market for conversion of CO₂ to value-added product.
2. Both the urea-based and ethylene oxide-based processes showed potentials for significant CO₂ abatement in Alberta.
3. Methanol produced using the conventional SynGas process has a high C-Footprint. Therefore, biomass or renewable energy based methanol must be pursued.
4. Integration of CO₂ capture and conversion with the process showed high potential for significant CO₂ abatement from coal utility plants in Alberta.
5. Integration of the DMC process with SynGas methanol manufacturing has potentials for significant CO₂ abatement; therefore, it should be pursued with the Methanex plant in Alberta.
6. An integrated DMC-MEG process has favorable techno-economic merits; therefore, it should be pursued with ethylene plants in Alberta.

Process Development

7. The ASPEN Plus® process model, along with component models, developed in this project are shown to be very valuable design tools for evaluating and configuring the process to meet the desired goal of CO₂ abatement with favorable economics.

8. Heat Integrated Reactive Distillation (HIRD) equipped with side reactors and PerVap membranes is ideally suited for the complex process chemistry of conversion of CO₂ to alkyl carbonates.
9. Catalyst ZnO forms organometallic complex with urea in the urea-based process. The ZnO-complex is sparingly soluble in reacting media, which required E3Tec to modify the original process configuration based on totally heterogeneous catalyst. In Round 2, an alternate design for the side reactors will be developed to maximize DMC yield and high rates of conversion.
10. Commercial Amberlyst® catalyst performed well for conversion of ethylene carbonate to DMC in the ethylene oxide-based process. The process can be readily scaled to a fully integrated pilot plant demonstration.
11. Performance parameters of the ceramic tubular PerVap membranes provided a basis for integrating them into the process to improve product yield. This permits the trade-off analysis of energy efficiency vs. capital cost of PerVap and process equipment.
12. ASPEN Plus® process modeling was effectively validated with prototype tests. The next step is to validate the process model with an integrated pilot-plant.

Technology Transfer

13. CO₂-based DMC process is getting encouraging responses from industry and research organizations.
14. Technology transfer plans developed in this project show a well-defined roadmap for commercially implementing CO₂-based DMC production in Alberta using this process.
15. CO₂-based DMC process shows favorable techno-economic merits in comparison to the conventional SynGas based DMC process that is being considered for replacing current commercial phosgene-based polycarbonate processes.
16. Demonstration of an integrated DMC process and reliable economic analysis are key to commercialization of the DMC process in Alberta.

During Round 1 of the CCEMC project, E3Tec's team advanced the DMC process development from Technology Readiness Level (TRL) 3 of *Critical Function or Proof of Concept Established* to TRL 5 of *Laboratory Testing of Integrated/Semi-Integrated System*. In Round 2, E3Tec expects to advance it to TRL-7 of *Integrated Pilot System Demonstrated*. The ASPEN Plus® process model provided the basic foundation for rapidly scaling laboratory data and pilot plant performance parameters to commercial plants.

2 PROJECT DESCRIPTION

2.1 Introduction and Background

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. It has allowed affordable electricity, the development of a global transportation network, the supply of potable water, and manufacture of chemicals such as ammonia with a direct impact on food production. When the global demand for electricity increased from 8.3 million GWh in 1980 to 22.7 million GWh in 2012,¹ 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, continues to expand 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 (December 2015) which is stimulating global action to reduce CO₂ emissions. In response the major oil and gas companies have outlined economic solutions; one of which is CO₂ conversion to products.***² Considering the magnitude of the issue, all 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. The Global CCS Institute recently published a cost analysis for CO₂ capture, transport, and storage in the European Union.³ This report looked at transport costs via pipeline or ship and included costs associated with single and multiple sources and sinks. The report highlighted the challenges and costs of coordinating the development of a CO₂ transportation infrastructure. Since few of the major industrial and utility CO₂ sources are located close to CO₂ storage sites, additional and substantial transportation and injection costs will be incurred. Delivering the CO₂ to the fence at pipeline pressure (130 bar) raises the energy cost to 1.16 kW/kg CO₂⁴ and this differential cost for liquefaction and pumping (0.35 kW/kg CO₂) will increase the energy consumption. The costs of pipeline transport followed by further pressurization to move the CO₂ into pore cavities 1-2 km deep are additional energy costs. Recognizing this, chemical conversion of CO₂ at an on-site merchant facility producing a marketable product should be a high priority for providing an economically important alternate path. CO₂ sources such as hydrogen plants that employ amines, or raw natural gas processing facilities appear to be the most economical sources for CO₂. Two recent projects support this. In November 2015 Shell's Quest carbon capture and storage (CCS) project near Fort Saskatchewan, Alberta, Canada started-up and will capture approximately 1 MMtpy of CO₂ from the hydrogen plant at the Scotford Upgrader for underground sequestration. In December 2015, the Sturgeon Bitumen Refinery in Alberta started up, again with CO₂ capture from the hydrogen plant.

A recent AIChE/DOE sponsored Carbon Management Technology Conference (CMTC) meeting (Sugar Land, TX, November 2015) focused on techno-economic barriers of carbon capture and sequestration (CCS). Other than the CCEMC Grand Challenge program, there is limited activity on CO₂ utilization. E3Tec was able to make effective comments on expanding the scope of the DOE's Carbon Management plan to include CO₂ utilization in the overall portfolio. Other attendees also voiced similar opinions on CO₂ utilization. The outcome from this conference was that there would be increased focus on CO₂ utilization.

¹ *As appetite for electricity soars, the world turning to coal*, Washington Post News Report, (October 16, 2015).

² *Oil and gas CEOs jointly declare action on climate change*, PennEnergy e-news report, (October 19, 2015).

³ "The Cost of CO₂ Capture, Transport, and Storage," Zero Emissions Platform, Global CCS Institute, (July 2011).

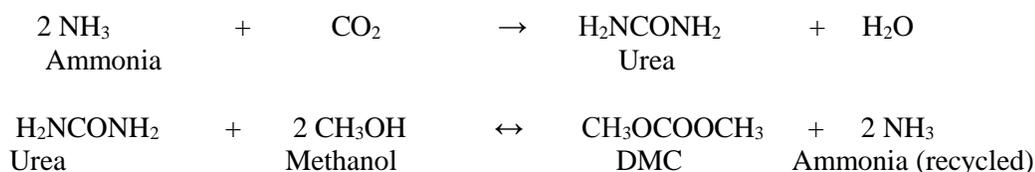
⁴ Doctor, R.D. , *Future of CCS Adoption at Existing PC Plants Economic Comparison of CO₂ Capture and Sequestration from Amines and Oxyfuels*, Argonne Report, ANL/ESD/12-9 (Dec. 29, 2011).

2.2 Technology Description

The E3Tec Team, in partnership with Michigan State University (MSU), has developed an innovative energy-efficient process built upon heat-integrated reactive distillation (HIRD). The HIRD with side reactors is equipped with either PerVaporation (PerVap) membranes or side reboilers for separation of byproduct and excess reactant. This highly integrated process converts captured CO₂ to alkyl carbonate, specifically Di-Methyl Carbonate (DMC). Originally, E3Tec proposed urea-based process for conversion of CO₂ to DMC. However, after completing US DOE SBIR Phase I project of conversion of CO₂ to DMC using ethylene oxide as co-feedstock with mono ethylene glycol (MEG) and evaluating its techno-economic merits, E3Tec decided to consider both processes for the CCEMC project.

2.2.1 Urea-Based DMC Process

The urea-based process is based on the following chemical pathway.



The process consists of two steps: A) reacting CO₂ with ammonia to form urea; and B) further reaction of urea with methanol for DMC synthesis that releases ammonia for recycle back to the urea process. As such, ammonia acts as a chemical reaction carrier. Step A is a well-established commercial process for manufacturing urea fertilizer; therefore, it was not included in the Round 1 scope of work.

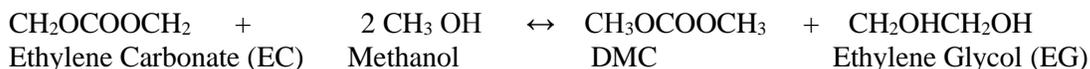
The commercial process consists of a reaction column to which two or more side reactors are connected, two fractionation columns for product recovery, and one fractionation column for separating ammonia released in the process for recycle. It was discovered in Round 1 that zinc forms an organometallic Zn-complex and it is partially soluble in the reacting media. Therefore, the reaction product from each side reactor is fed to the reaction column and the product is separated while unreacted urea, intermediate products, and Zn-complex catalyst are collected at the bottom of the column and recirculated with recovered methanol. In Round 2, tests will be performed with side reactors packed with ZnO to maintain an optimum level of active Zn-complex in the system. The product stream is fed to the separation system consisting of fractionation columns and a PerVap membrane. Ammonia released in the process is recycled to react with fresh CO₂ forming urea. Methanol recovered from the fractionation and PerVap membrane also is recycled. A process stream consisting of unreacted intermediate methyl carbamate (MC) is recycled to the reactor feed with recycled methanol. Based on the preliminary ASPEN Plus™ process analysis, DMC purity and yield would be greater than 99.9% and greater than 78%, respectively. The yield is affected by formation of byproduct n-methyl methyl carbamate (NMMC), which has product value, and decomposition of DMC in the presence of the Zn-complex catalyst.

2.2.2 Ethylene Oxide Based DMC Process

As reported previously, E3Tec received a DOE/SBIR Phase I grant in 2015 for the development of the DMC process using ethylene oxide as co-feedstock with co-production of mono-ethylene glycol (MEG). The Phase I project was completed in November 2015 and E3Tec was awarded a Phase II grant. The overall scope of this SBIR Phase I project was very similar to the early part of the CCEMC project; therefore, the two projects were carried out in parallel in order to leverage the effort. As a result, the CCEMC project has benefitted from the expanded scope and both the originally proposed urea-based

DMC process and the ethylene-oxide-based DMC process will be considered in Round 2 to improve the techno-economic viability of commercial DMC plants in Alberta.

Like the urea-based process, this process consists of two steps: A) reacting CO₂ with ethylene oxide to form ethylene carbonate; and B) further reaction of ethylene carbonate with methanol for synthesis of DMC and MEG. Step A is a well-established commercial process for manufacturing ethylene carbonate; therefore, it is not included in the present scope of work.



The process consists of three distillation columns, four side reactors and one PerVap membrane unit. Ethylene oxide readily reacts with CO₂ to form ethylene carbonate (EC) releasing heat that can be used in the downstream process. Ethylene carbonate 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 are integrated with the process for recovering methanol and also for breaking the azeotrope. Integration of the PerVap membrane improves the energy efficiency and hence reduces the C-Footprint in addition to reducing the size of methanol recovery column.

Considering the high costs of PerVap membranes, a trade-off analysis will be performed to optimize the design based on CAPEX and energy efficiency. DMC is purified to 99.99 wt% in the product recovery column. The remaining pre-reacted effluent is fed to the reaction column where ethylene glycol and unreacted EC are separated. The ethylene glycol is removed as a side stream product at 99.5 wt% purity. 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.*

An initial analysis shows that the ethylene-oxide-based DMC process will have the following techno-economic benefits to Alberta in addition to CO₂ utilization:

1. The DMC process selectively produces MEG, which is a major high-value commodity chemical for synthesis of end-user products; such as fiber, film and bottles.
2. The overall C-Footprint of the DMC plant with MEG co-production is quite favorable when compared against separate production of DMC and MEG by commercial processes.
3. Alberta is leading producer of ethylene and its derived products, including ethylene oxide and ethylene glycol. Indeed, market analysis shows that Alberta has a favorable excess capacity. The DMC process can be readily integrated with such petrochemical plants.
4. The test data show that the commercial catalysts are very effective and produce no side products – an advantage which further improves the C-Footprint.
5. Economic merits of co-production of DMC and MEG show high product margin at the present prices.

2.3 Project Goals

The governing objective of this Grand Challenge proposal was to develop the HIRD process for production of DMC and establish the techno-economic viability of CO₂ sequestration based on life-cycle analysis (LCA) represented by Carbon-Footprint (C-Footprint) analysis.

Specific objectives were:

- a) to validate the CO₂ sequestration potential for the proposed DMC process;
- b) to experimentally determine kinetic parameters and evaluate catalyst effectiveness, under prototype process conditions thus assuring rapid commercial scale-up;
- c) to develop design tools for the rapid commercial scale-up from lab/pilot scale operation;
- d) to perform ASPEN Plus® process analysis to establish an optimum process configuration of HIRD with side reactors and PerVap membranes; and
- e) to perform a technology merit analysis for CO₂ sequestration in Alberta.

The expected outcomes of this phase of the project were:

- a) establishment of the CO₂ emission reduction potential for captured CO₂ conversion to high-value DMC on the basis of C-Footprint analysis;
- b) experimental validation of the DMC manufacturing process using a pilot-scale test unit;
- c) generation of a validated ASPEN Plus® process model for applying pilot-scale data to commercial plant design;
- d) conceptual design for integrating the proposed process with concentrated CO₂ sources in Alberta; and
- e) commercialization strategy with the focus on installing the first pre-commercial plant in Alberta within 5 years after completing Round 2.

2.4 Work Scope Overview

The project work plan consisted of nine major tasks plus project management and reporting. Each task was carefully structured and interlinked with other tasks for a comprehensive approach towards developing a process for captured CO₂ conversion to DMC. Each task was led by one of the team members, while others provide the technical support. This approach utilized capabilities of team members in an effective manner, while maintaining the focus on the primary goal.

Year 1

Task 1: Life Cycle Analysis (LCA) of CO₂ Sequestration (E3Tech Lead)

Purpose: To establish CO₂ sequestration potential of the proposed DMC process and compare with commercial DMC processes

- Task 1.1 Develop concept-level LCA model and apply to the proposed process to determine net CO₂ sequestration
- Task 1.2 Compare CO₂ sequestration potential with commercial Ube and Versalis DMC processes
- Task 1.3 Perform DMC market analysis to establish CO₂ sequestration potential
- Task 1.4 Perform techno-economic merit analysis and commercialization potential and identify technical and economic barriers

Task 2: Integration of DMC Process with Concentrated Industrial CO₂ Sources (E3Tec Lead with GTI Technical Support)

Purpose: To identify potential concentrated industrial sources of CO₂ in Alberta that can be cost-effectively integrated with the proposed DMC process plant

- Task 2.1 Develop technology merit criteria for selection of industrial CO₂ sources
- Task 2.2 Categorize industry sectors of concentrated CO₂ sources in Alberta
- Task 2.3 Apply merit criteria for ranking industry sectors in Alberta
- Task 2.4 Select the most promising industry sector for integrating with the DMC process

Task 3: Experimental Determination of Kinetic Parameters (MSU Lead with E3Tec Technical Support)

Purpose: To determine kinetic parameters under prototype conditions necessary for rapid, reliable scale-up

- Task 3.1 Design and Install DKTU for prototype dynamic kinetic tests
- Task 3.2 Perform batch kinetic tests for a range of DMC process conditions
- Task 3.3 Determine catalyst effectiveness, deactivation and in-situ activation
- Task 3.4 Develop Fortran-based kinetic model for incorporating into ASPEN Plus® process simulation model

Task 4: PerVap Performance Tests (GTI Lead with E3Tec Technical Support)

Purpose: To determine PerVap membrane performance and design criteria for integrating with distillation column

- Task 4.1 Set up PerVap membrane separation test rig
- Task 4.2 Perform PerVap tests to determine separation efficiency of DMC and MeOH
- Task 4.2 Evaluate the effects of process parameters on separation efficiency and selectivity
- Task 4.4 Develop Fortran-based performance model for incorporating into ASPEN Plus® process simulation model
- Task 4.5 Design criteria for integrating PerVap with distillation column

Task 5: ASPENPlus Process Analysis (E3Tec Lead)

Purpose: To develop an optimized configuration of heat-integrated reactive distillation (HIRD) using side reactor and PerVap for production of dimethyl carbonate

- Task 5.1 Integrate validated Fortran-based kinetic and PerVap performance models into ASPEN Plus® analysis
- Task 5.2 Perform process analysis of HIRD using side reactors and PerVap and evaluate design options to maximize energy-efficiency
- Task 5.3 Perform conceptual design of a commercial unit for supporting LCA in Task 1
- Task 5.4 Perform planning-level economic analysis to establish value-added DMC products to offset CO₂ capturing costs

Year 2

Task 6: Validation Tests with Pilot Plant (MSU Lead with GTI Technical Support for PerVap)

Purpose: To develop experimental database using pilot-scale test unit for validating the process design model

- Task 6.1 Integrate Side Reactors, PerVap, and heat integration with MSU's pilot scale test facility
- Task 6.2 Performance tests at baseline design conditions
- Task 6.3 Performance tests to evaluate sensitivity of process parameters
- Task 6.4 Validation of the ASPEN Plus® process simulation model

Task 7: Design Methodology for Scaling Pilot-Scale to Commercial Plants (E3Tec Lead with MSU & GTI Technical Support)

Purpose: To develop a frame-work of design methodology for scaling the laboratory pilot-scale test data to design commercial plants and perform RMR to evaluate techno-economic risks

- Task 7.1 Design methodology consisting of integrated ASPEN Plus® process model
- Task 7.2 Scale-up criteria for side reactors, divide-wall column, and PerVap membrane
- Task 7.3 Risk Management Register (RMR) analysis of scaling pilot plant to commercial plants
- Task 7.4 Develop and document design methodology

Task 8: Design of Pilot Plant (E3Tec Lead with Technical Support from MSU & GTI)

Purpose: To design pilot plant for field testing at in Alberta in the next phase

- Task 8.1 Systems design and process flow diagram (PFD)
- Task 8.2 Conceptual integration of the DMC process with a plant in Alberta
- Task 8.3 Equipment list and preliminary cost estimates
- Task 8.4 Planning-level total installed costs (TICs) and cost of product

Task 9: Industry Workshop (E3Tec-MSU-GTI)

Purpose: To present the techno-economic merits of the DMC process to the industry for conversion of captured CO₂ to value-added products of expanding demands

- Task 9.1 Development of roadmap for commercialization of the DMC process
- Task 9.2 Preparation of *Pro Forma* of the DMC process for long-term economic viability
- Task 9.3 Organization of the industry workshop
- Task 9.4 Analysis and documentation of the industry feedback

Task 10: Project Management and Reporting (E3Tec)

Necessary changes were made for some of the tasks based on the technical progress and budgetary constraints imposed by the currency exchange rates between the US and Canada.

The Major Milestones and Schedule were as Follows:

Milestone 1:	Execution of Grant Agreement	April 2014
Milestone 2:	CO ₂ sequestration potentials of the DMC process	December 2014
Milestone 3:	Experimental database for validating the process model	June 2015
Milestone 4:	Interim Milestone – LCA based on ASPEN Plus®	June 2015
Milestone 5:	Database of pilot plant tests	February 2016
Milestone 6:	Validated design methodology for scaling pilot-scale tests to commercial units	May 2016
Milestone 7:	Design of pilot plant for field tests in Alberta	February 2016
Milestone 8:	Industry workshop	June 2016

3 OUTCOMES AND LEARNING

3.1 Literature Survey

The literature survey focused on three key aspects of evaluating the present status of conversion of CO₂ to value-added products: a) identifying an ideal chemical product with expanding global market and with emerging application for a substantial and sustainable impact on CO₂ emission; and b) present commercial processes for manufacturing the selected value-added chemical product.

DMC has a well-defined value chain leading to consumer products as presented in Figure 3-1. Therefore, the focus has been to develop an energy efficient process for captured CO₂ conversion with favorable economics. Furthermore, the commercial phosgene-based process is being phased out and replaced by the SynGas based process with high C-Footprint. Figure 3-1 indicates that the CO₂-based

DMC process would effectively fit within the existing supply chain, thereby increasing its chances for acceptance by an industrial partner. The supply chain presented in Figure 3-1 focuses on feedstocks for DMC synthesis and its derivative chemicals. Both commercial processes use natural gas (NG) as a feedstock. The use of oxygen makes these processes inherently more dangerous. Both processes are energy intensive and require handling of corrosive chemicals in certain parts of the process. Polycarbonate resins are widely used to manufacture plastic products including bottles, eye-glasses, etc. Dow Chemicals and others market solvents to pigment and coating industries. There are large numbers of manufacturers of lithium-ion batteries, e.g. Sanyo Corporation. For hybrid autos the leading manufacturers of lithium-ion batteries are Tesla – soon to be the world’s largest battery maker, A123Systems – US-based, but now under Chinese control, Axion, Envia and Panasonic.

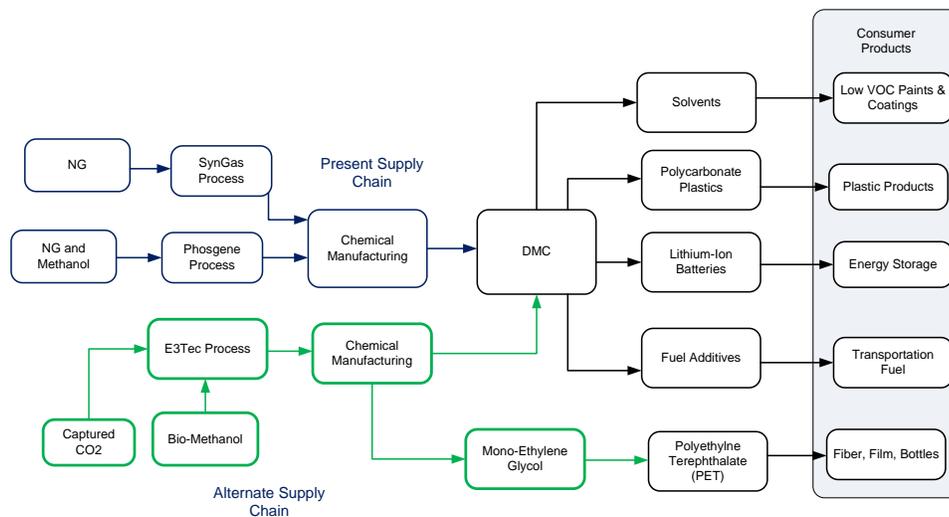


Figure 3-1: Supply chain of Dimethyl Carbonate (DMC)

The bulk of DMC production is occurring in China and South Korea. Key players in the DMC market include Versalis S.p.a., Bayer Material Science, SABIC IP (previously GE Plastics), PPG Industries, Ube Industries, LTD, SNPE, Inc., Danicel Polymer Ltd, DOW-DuPont and BASF.

Currently, most DMC is produced in Europe and Asia by either the Versalis (previously Enichem) or Ube processes. Market share⁵ by region is depicted in Figure 3-2. **The processes in Asia use coal-derived SynGas as feedstock with high C-Footprint.** The Versalis Synthesis employs CuCl as a catalyst for a sub-ambient temperature oxycarbonylation of methanol.⁶ The Ube process manufactures DMC by reacting nitric oxide (NO) with oxygen, carbon monoxide, and methanol over a palladium-supported catalyst. Copper chloride is required as a co-catalyst for this process to prevent the reduction of palladium. Bayer purchased EniChem's Polycarbonate business in 1995 and presumably purchased the rights to use their non-phosgene route, shown below. SABIC IP is reported to use the EniChem process in their polycarbonate

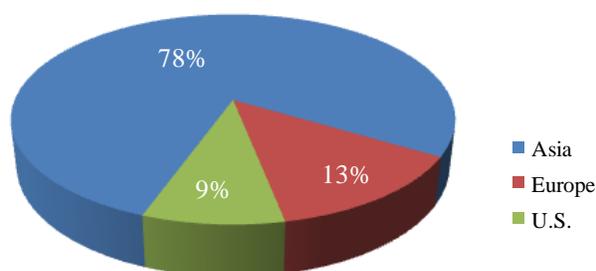


Figure 3-2: Global DMC demands 2015

⁵ 2015 Market Research Report on Global DMC Industry, QYResearch DMC Research Center, (Sep 2015).

⁶ Tundo, P. (2001) *New developments in dimethyl carbonate chemistry*, J. Pure Appl. Chem., Vol. 73, No. 7, pp. 1117–1124

plant in Spain. Dow is also a major player with a Polycarbonate facility in Freeport, Texas. Various medium size manufacturers in China⁷ produce DMC primarily for export as solvent and small-scale applications. ***Carbon monoxide used to manufacture DMC is produced by gasification of coal and/or petroleum coke with a high C-Footprint.***

Phosgene-based process:

natural gas + steam	→	carbon monoxide + hydrogen
carbon monoxide + chlorine	→	phosgene
methanol + phosgene	→	DMC + hydrochloric acid

SynGas-based process:

natural gas + steam	→	carbon monoxide + hydrogen
methanol + carbon monoxide + oxygen	→	DMC + water

In summary, a ***Window of Opportunity*** exists to replace the current phosgene-based processes with a commercialized CO₂-based DMC process. This process, once commercial, will also have a smaller overall C-Footprint than the current non-phosgene SynGas-based DMC process.

3.2 Technology Development

The technology development goal for CO₂ conversion to value-added DMC was to advance the Technology Readiness Level (TRL) from concept level to pilot plant demonstration. E3Tec is pursuing a Heat Integrated Reactive Distillation (HIRD) process for conversion of captured CO₂ to DMC using two separate chemical pathways. The 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. E3Tec, jointly with Michigan State University (MSU), has developed the HIRD process equipped with side reactors and pervaporation (PerVap) membranes in pursuit of process intensification and high-levels of energy efficiency. The Team contends that either technology will have a ***disruptive impact*** on global DMC production, leading to a ***transformative shift*** from net CO₂ generation to net CO₂ utilization. E3Tec's prototype Differential Kinetic Test Unit (DKTU) covered by US Patent 9,222,924 B1 (December, 2015), ASPEN Plus[®] process models, pilot-scale tests at MSU and ASPEN Plus[®] cost analysis all provide a strong design basis for scaling the process using the E3Tec's design methodology illustrated in Figure 3-3.

The process of CO₂ conversion to DMC has been advanced to TRL 5: ***Laboratory Testing of an Integrated/Semi-Integrated System: System component and/or process validation in relevant environment.*** In the Round 2 project, it will be further advanced to TRL 7: ***Integrated Pilot System Demonstration: System/process prototype demonstration in an operational environment*** meeting some criteria of TRL 8: ***System Incorporated in Commercial Design.*** E3Tec team has applied these TRL guidelines and the industrial "***Stage-Gate***" decision-making process at each development stage to a number of previous projects. This will ensure that the commercialization path will remain as short as possible and is an important technology edge over other Grand Challenge projects for CO₂ conversion to value-added products.

⁷ 2015 Market Research Report on Global Dimethyl Carbonate (DMC) Industry – Table of Contents.

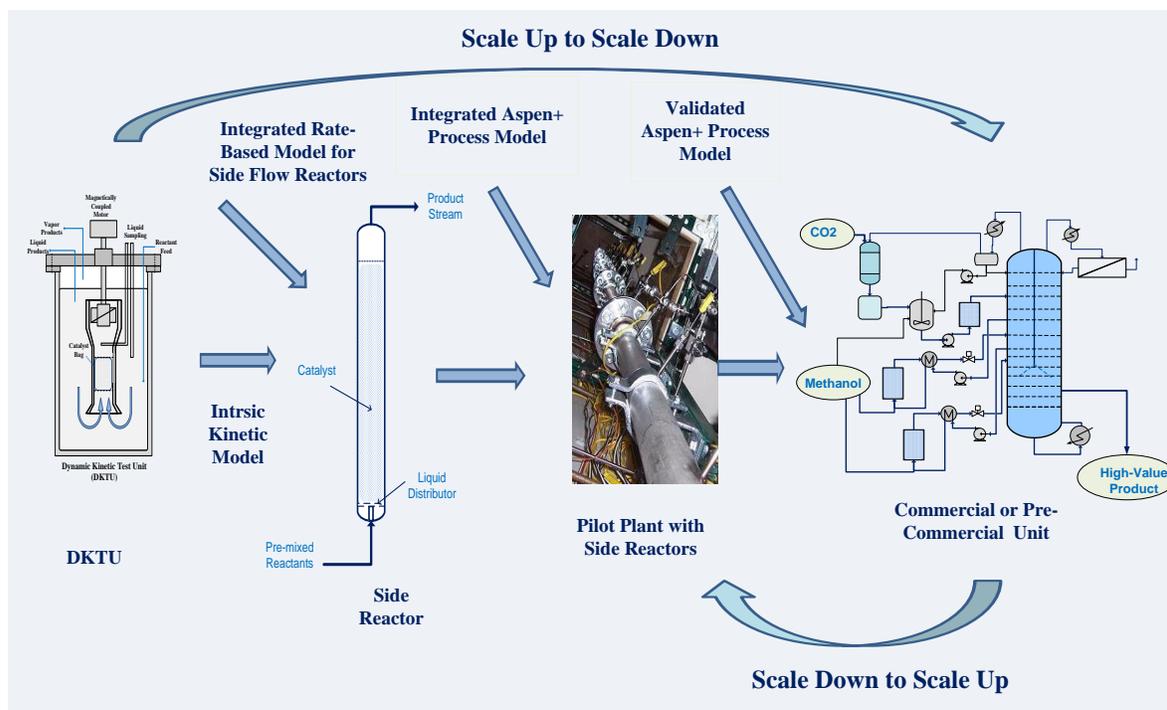


Figure 3-3: Schematic diagram of scaling the catalytic process from lab to commercial plants.

3.3 Experimental Procedures and Methodology

Two major project tasks fall under this category - Task 3 of Experimental Determination of Kinetic Parameters and performance of PerVaporization (PerVap) membranes and Task 6 of Validation Tests with Pilot Plant. A discuss of each of these is contained in their respective section below.

3.3.1 Kinetic Tests

E3Tec designed a Differential Kinetic Test Unit (DKTU) as shown in Figure 3-4 which presents the schematic diagram and pictorial view of the DKTU. The DKTU was fabricated by PDC Machines, located in Warminster, Pennsylvania. The fabrication cost of this DKTU was originally estimated to be CAN\$35,000, with 50% cost share by E3Tec (i.e. CAN\$17,500 CCEMC fund). However, the actual fabrication cost was US\$50,000, which required additional E3Tec cost share. E3Tec contends that the DKTU has unique design features, including careful control of the liquid shear velocity, and E3Tec plans to make this unit their benchmark for obtaining kinetic parameters under prototype conditions for catalytic flow reactors. A patent based on background intellectual property has been issued for the DKTU.⁸

⁸ C. B. Panchal, "Differential Kinetic Test Unit," US Patent 9,222,924 B1, December 29, 2015.

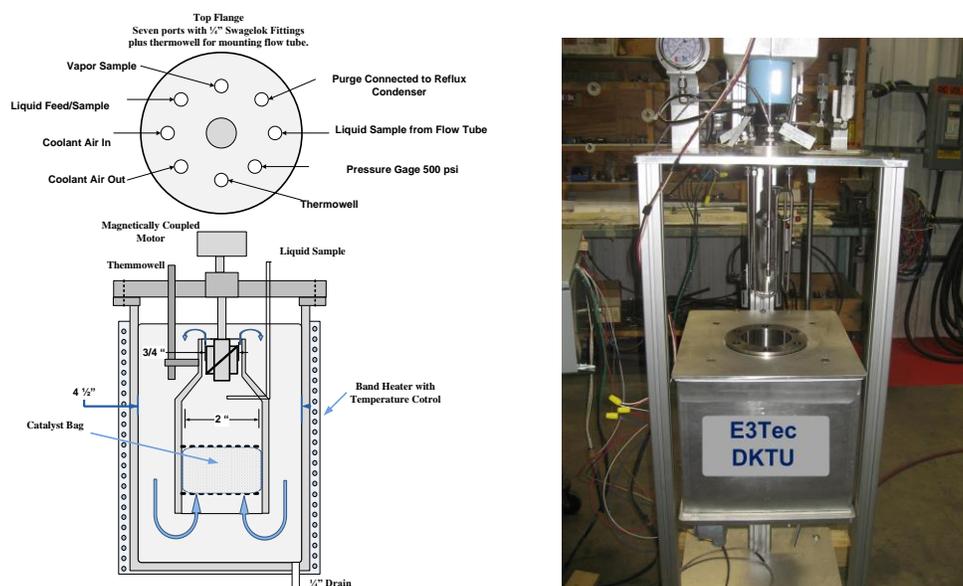


Figure 3-4: Schematic diagram and pictorial view of the DKTU.

The first reaction of urea with methanol to form methyl carbamate (MC) is relatively fast and does not require catalyst. Therefore, the focus of kinetic studies was on the second reaction of MC with methanol to form DMC, which is slow and reversible. Furthermore, other irreversible reactions are possible during this reaction step that form byproducts which will affect the overall process C-Footprint. This task focused on evaluating catalysts reported in the literature based upon Zn, La, Pb, Ca, Mg, Zr, and Sn.⁹ ZnO was found to be the most selective catalyst in converting MC to DMC.

Several catalysts based on ZnO have been prepared for the kinetic studies; the procedures followed below are generally taken from those reported in the literature.

ZnO/Al₂O₃: Initially, ZnO supported on γ -Al₂O₃ was prepared by depositing Zn(NO₃)₂ onto the alumina by incipient wetness followed by drying and calcining in air at 500°C.

Zn/Urea complex: Zinc oxide was mixed with urea in a round-bottomed flask (with a condenser) and heated to 150°C. At this temperature, the contents became a milky liquid. The solution was mixed for 40 minutes at 150°C. Upon cooling, the solution became a solid.

ZnFe₂O₄: An aqueous solution of Zn(NO₃)₂ and Fe(NO₃)₃ was added drop-wise to an aqueous solution of (NH₄)₂CO₃. An ammonia solution was used to maintain the solution pH= 8. The solution was then aged overnight and the precipitate washed, dried, and calcined in air at 500°C. Procedures were followed from Wang et al.⁸.

Over 30 batch-scale tests were conducted using this array of catalysts to replicate the results reported in the literature and identify the strengths and weaknesses of each. As a result of the extensive work developing and studying these heterogeneous catalysts based upon ZnO, it was determined that the best catalyst from the list above was ZnO by itself. Unfortunately, during the studies with ZnO alone, it was determined that the catalyst was sparingly soluble in the reaction medium. Hence, process modifications would be required to handle a homogeneous rather than a heterogeneous catalyst. With the efforts

⁹ Wang et al. *Catalysis Communications* 11 (2010) 430-433

required to modify the process, the E3Tec team has effectively expanded its process technology to include both types of catalyst.

Reactive distillation using side reactors provides a reliable design approach that enables the control of the DMC residence time over the catalyst so that degradation and undesired byproduct formation may be minimized. This can be accomplished by operating the side reactors at temperatures and pressures differing from the column temperatures and pressures, which are governed by separation. Better control over DMC-catalyst contact times can also be achieved by isolating the catalyst to the side reactors and using the distillation column solely for purification. ASPEN Plus® process analysis comparing conventional reactive distillation with E3Tec's integrated side reactor technology was performed so that the best competitive alternative may be developed. E3Tec's original process was based on heterogeneous catalyst in side reactors with DMC/Ammonia product and excess methanol separated after each side reactor. In light of these experimental results, the process was modified to recirculate the homogenous, sparingly soluble "ZnO-Urea Complex Catalyst" to the side reactors while maintaining optimum residence time in each side reactor to minimize undesired byproduct formation. These byproducts are further decreased by removing DMC from the remaining reactants in either the distillation or pervaporation units.

As a final step in this task a batch kinetic study was conducted on the effect of the ZnO catalyst loading and temperature on the reaction between urea and methanol. Six experiments at temperatures covering 80-120°C and 0.3-1.2 wt% Zn were conducted. Parameters from the detailed kinetic rate expression were determined from regression of this data using ASPEN Plus®. This expression was then used to refine the ASPEN Plus® process analysis for the pilot-plant and commercial plant.

3.3.2 PerVap Performance Tests

Gas Technology Institute (GTI) was the lead for this Task 4. GTI procured the equipment, and constructed the PerVap test rig. Subsequently, GTI completed 13 PerVap tests using DMC/methanol azeotropic mixtures. The performance data from these tests were converted to an EXCEL model¹⁰ and are now incorporated into the ASPEN Plus® process design model. Figures 3-5 and 3-6 present the schematic diagram and pictorial view, respectively. Two types of membranes were tested for their separation efficiency when fed both a liquid and a vapor DMC/methanol azeotropic mixture. The mass flux of the methanol permeate was measured as kg/s per m² of membrane area (DMC remains with the retentate):

- Ceramic tubular membranes are more expensive; however, they can be operated at high temperature, yielding high mass flux.
- Polymeric hollow-fiber membranes are cheaper and exhibit relatively high flux at low temperatures, but often with lower separation efficiency and possible compatibility problems.

The initial tests employing the polymeric hollow fiber membrane found that the hollow fiber assembly was not compatible with DMC and methanol. Therefore, further tests were conducted using the ceramic membrane obtained from Pervatech™.

¹⁰ Lovasz A., P. Mizsey, Z. Fonyo; "Methodology for parameter estimation of modelling of pervaporation in flow-sheeting environment," Chem.Eng.J. 133 (2007) 219-227.

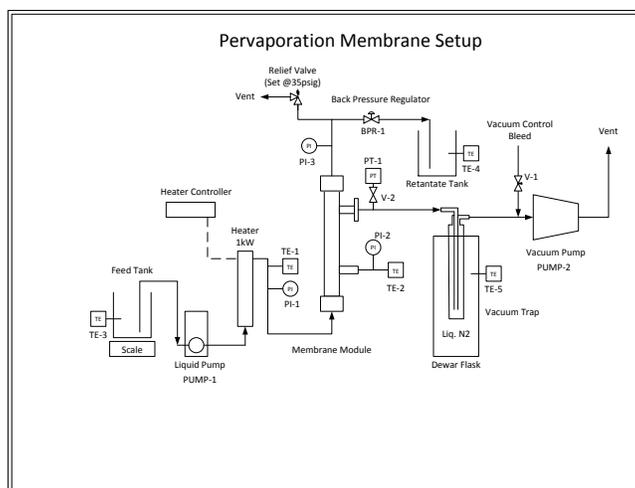


Figure 3-5: Flow schematic of the PerVap test unit.



Figure 3-6: Pictorial view of the PerVap test unit.

3.3.3 Validation Tests with Prototype Test Units

Urea-Based DMC Process

The scope of this task was to validate the batch kinetic tests performed in Task 3 using a test unit that is a prototype of full-scale pilot plant representing the commercial plant. Subsequently, the test data are used for validating the ASPEN Plus® process model. It should be noted that the overall process consists of two steps. In the first step, captured CO₂ reacts with recycled ammonia to form urea. This reaction step is fast as it is in commercial urea production; therefore, the project focused on the catalytic reaction of urea with methanol for DMC synthesis. An extensive series of batch kinetic tests in Task 3 were performed to verify reported results in the literature. From these tests the following conclusions were derived:

1. Zinc oxide (ZnO) forms complex with urea which acts as catalyst; ZnO by itself has limited catalytic activity. Furthermore, the Zn-complex catalyst is found to be partially soluble in the reaction mixture.

2. Fixing ZnO on aluminum oxide - alumina (Al_2O_3) to make it a heterogeneous catalyst showed limited activity.
3. An intermediate product, methyl carbamate (MC) is first formed by replacing one of the two amine (ammonia) groups by a methyl oxide group. MC then further reacts with methanol to form DMC by replacing the second amine (ammonia) group.
4. In the batch kinetic tests the DMC formed reacts and is decomposed in the presence of the Zn-complex catalyst and through further reaction with MC to form a side product N-methyl methyl carbamate (NMMC).
5. As suspected, the batch kinetics showed considerable inconsistency with the literature data that was used to develop the original urea-based process. However, the present database of extensive kinetic tests provides a reliable basis for the improved commercial DMC process.

The batch kinetics, as described above, presented some challenges to the process concept that was designed for a heterogeneous catalyst. Redesign to include the homogeneous catalyst and address the issues relating to the undesired reactions led to the incorporation of a side reactor recirculation flow loop. There are two basic requirements for this approach: a) effective use of homogeneous Zn-complex catalyst; and b) efficient separation of DMC as it is formed to minimize side reaction(s) and possible decomposition that would reduce DMC yield adversely affecting the C-Footprint.

The ASPEN Plus® process analysis showed that the proposed initial design employing reactive distillation using side reactors with heterogeneous catalysts can be equally effective using this recirculation flow loop with a homogeneous catalyst. Therefore, a prototype test unit was designed as shown in Figure 3-7. The recirculation flow loop represents one of the side reactors of the pilot plant and full process, as discussed in next section on pilot plant design. The catalyst reaction mixture is recirculated through the side reactor and DMC, methanol, and a limited amount of MC are separated from the reactor product stream by vaporization. The reactant rich mixture along with homogeneous catalyst is then recirculated and a fresh feed of urea, MC and methanol is mixed with the recirculating reactant flow and fed to the side reactor. Samples were taken at proper intervals during the test period. The primary focus was to determine the effects of temperature and feed composition on the relative rates of conversion and selectivity of DMC in the product stream. The predicted overall conversion of MC and urea was reasonable for a single side reactor and recirculation loop. Furthermore, by separating DMC from the recirculating flow stream, further reactions are reduced yielding high selectivity of DMC in the product stream. The batch kinetic tests showed low selectivity in the closed environment of a batch reactor.

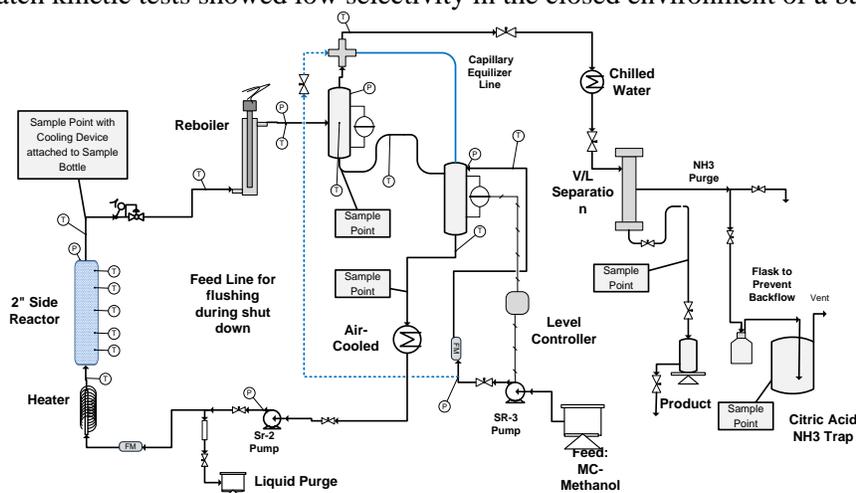


Figure 3-7: Process diagram of the prototype test unit for the urea based process.

Ethylene Oxide-Based DMC Process

The ethylene-oxide based DMC process uses commercially available heterogeneous catalysts. Extensive batch kinetic tests were performed under DOE SBIR Phase I project, and the kinetic parameters from these tests were used to design the test matrix for CCEMC experiments with a smaller-scale prototype test unit. This leveraging effort was beneficial to the CCEMC project. The test results and analysis are carefully documented to avoid conflicts between the two projects, while taking advantages of both projects.

The prototype tests were performed using a stand-alone side reactor, as shown in Figure 3-8. The reaction between CO₂ and ethylene-oxide is known and commercially practiced for synthesizing ethylene carbonate (EC). Handling of ethylene oxide requires additional safety precautions; therefore, tests were performed using EC. Initial tests were performed using a larger side reactor, 5 cm diameter and 91 cm height. Subsequent tests were performed using a smaller side reactor to evaluate the scale up methodologies and to baseline the smaller unit for future experiments with this system in Round 2. The smaller side reactor was 1 cm diameter and 8 cm height. The two series of tests with different sizes validated the ASPEN Plus® process scale method.

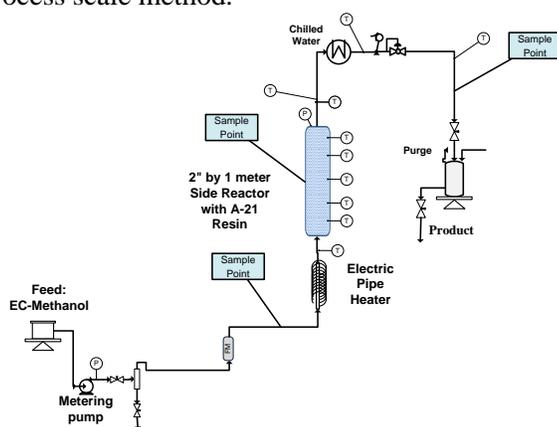


Figure 3-8: Process diagram of the prototype test unit for the ethylene oxide based process.

3.4 Modeling Details

3.4.1 Kinetic Model

Kinetic Models (urea-based process): A power-law based kinetic model was developed for the conversion reactions of MC and DMC and linked into the ASPEN Plus® model. These kinetics models permitted E3Tec to use ASPEN Plus® to optimize the process configuration for the commercial plant based upon CAPEX/OPEX. The model assumes that the reactions are: 1) first order with respect to each reactant concentration; and 2) proportional to the reactor catalyst loading (W_{cat} in units of gm Zn/gm reaction solution). The ZnO-Urea Complex catalyst used in these studies contains 42 wt% Zn as measured by ICP analysis; the theoretical Zn loading in the ZnO-Urea Complex catalyst is 35 wt%, indicating that our Zn-Urea Complex contains some partially complexed zinc.

The general rate equation for the batch reactor is:

$$-dC_i/dt = -r_i = k \cdot W_{cat} \cdot C_i$$

Concentration of the reacting species “i” can be represented as $C_i = C_{i,o} (1-x_i)$, where x_i is fractional conversion of the reacting species as determined by GC analysis in real time during the test. The above

rate equation can be separated and integrated over the reaction time at the reaction temperature to give the following expression:

$$-\ln[(1-x_i)/(1-x_{i,0})] = k \cdot W_{\text{cat}} \cdot t$$

Where reaction constant $k(T) = k_{0,i} \exp(E_a/(RT))$ and

$k_{0,i}$ = pre-exponent reaction constant for reacting species i

$E_{a,i}$ = Energy of activation, J/kmol

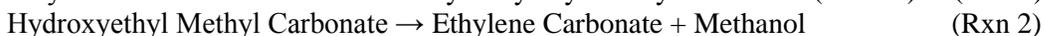
R = Gas constant, J/kmol K

T = Reaction temperature, K

Here $x_{i,0}$ is the conversion of the reacting species at the point in time (defined as $t=0$) that the reaction mixture reaches the specified reaction temperature. It was observed that both the forward and reverse reaction took place while the reactor was heating up to the reaction temperature. This approach was employed to obtain the kinetic parameters for both the desired and undesired reactions.

Kinetic Models (ethylene oxide-based process): An approach similar to the one described above for the urea-based process was undertaken for the ethylene-oxide-based process during the SBIR Phase I project. Small-scale batch kinetic studies were conducted and a simplified power-law model incorporating catalyst loading was developed. This model was then employed to generate a test matrix for large-scale pilot studies conducted with a stand-alone packed-bed reactor. The Amberlyst A-21 catalyst showed the most promise for the reaction of EC and methanol to form DMC. A few other catalysts were screened during the study, but the kinetic models were all developed on data collected using the A-21 catalyst.

As expected, the data collected from the stand-alone packed-bed reactor showed improvement in catalyst performance over those obtained during the batch kinetic studies. Because of the density differences between catalyst and solution, it is believed that contact between the two in the batch reactors was not representative of that occurring within the packed-bed reactor. So, the packed-bed reactor data then were regressed using the plug-flow reactor model in ASPEN Plus®. The rate constants were determined by numerical integration of all species balances along the length of the packed-bed reactor shown in Figure 3. The packed catalyst bed porosity was assumed to be 0.485 based upon our previous experience with other Amberlyst catalysts and the catalyst particle density was assumed to be 1.2 g/cc. For each of the packed-bed experiments, a total of four rate constants were fit simultaneously for the reactions:



The rate constant values obtained for each reaction were then fit to an Arrhenius relation to determine the temperature effect. The ASPEN Plus® model with these expressions for the reaction rate constants were then used to generate a test matrix of conditions for the smaller-scale packed-bed reactor.

3.4.2 ASPEN Plus® Process Models

E3Tec has developed a portfolio of ASPEN Plus® process models for an integrated system of distillation, a series of side reactors, PerVap membranes and/or other separation units. The process models are based on E3Tec's design methodology that effectively scales the laboratory kinetic parameters for side reactors to the full process with a high-degree of certainty. The ASPEN Plus® models for both DMC processes are validated using kinetic data and PerVap performance parameters. The process

analysis for the urea-based process is based on a commercial-scale plant with 51 kTA DMC production capacities. The ethylene-oxide based process analysis is based upon a commercial-scale plant of similar DMC production capacities. The purpose of the ASPEN Plus® process analysis is to develop a rigorous description of an energy and capital efficient commercial-scale DMC process based upon the best information currently available. This effort, while initially time-consuming, helps focus the process development efforts on improving the quality of the information that would most affect the process description. As the quality of the information (e.g. kinetic parameters, PerVap performance parameters, etc.) is improved, the process analysis revises the rigorous commercial process description - identifying a new set of information whose quality would most affect it. The rigorous process model currently contains the kinetic parameters from lab-scale studies that are subsequently validated with performance parameters from prototype pilot-scale tests.

The process analysis plays a significant role in the pilot-scale validation through generation of the test matrix to be conducted at this scale. A separate rigorous test unit process model is constructed and a comprehensive sensitivity study is conducted. The objective of this study is to identify the operating regions that are most affected by those parameters whose quality has been improved through the lab-scale studies. By integrating rigorous process descriptions into the development process, E3Tec's methodologies are able to rapidly commercialize a chemical process; allowing those developing the process to move to larger scale demonstrations with confidence.

3.4.3 Integration of DMC Process

E3Tec is pursuing integrating the DMC process with the following industry sectors.

- a. Utility and process industry with CO₂ sources.
- b. Methanol manufacturing plants; conventional SynGas as well as biomass or renewable energy based methanol plants.
- c. Ethylene chain manufacturing plants; ethylene oxide and ethylene glycol.

An integrated process of CO₂ capture and conversion to DMC is expected to have significant techno-economic merits over separate CO₂ capture and conversion processes. Heat integration between the two processes is expected to have a lower C-Footprint, specifically because CO₂ does not have to be liquefied or compressed for transportation. E3Tec is pursuing collaboration with Illinois Sustainability Technology Center (ISTC) for an integrated plant. Methanol is the primary feedstock in addition to captured CO₂; therefore, it is logical to integrate the DMC process with the methanol plants. The conventional SynGas process has high C-Footprint; however, the integrated process will utilize CO₂ from the SMR process used for producing hydrogen needed in the methanol process. So, integrating the CO₂ source and methanol as feedstock, will have significantly lower C-Footprint than separate processes. E3Tec intends to pursue such an integrated process with the Methanex plant in Alberta. Alberta has a major producer of ethylene and its derivatives.¹¹ The production capacity of ethylene and ethylene glycol are about 4,000 and 800 thousand tonnes/year. Apparently, there is excess capacity of ethylene oxide, which can be utilized for ethylene oxide based DMC process.

Integrating with CO₂ Sources: The proposed process can be integrated with the following three primary CO₂ sources: 1) Gas Turbine Combined Cycle (GTCC) – industry and utility scale; 2) Steam Methane Reforming (SMR) for production of hydrogen; and 3) coal utility plants with installed CO₂ capture system. Table 2 presents a summary of CO₂ recovery from these three sources. These three sources of CO₂ are relevant to Alberta. Presently, about 60% of Alberta's power generation is coal-based.

¹¹ Canadian Energy Research Institute, CERI Report "Examining the Expansion Potentials of Petrochemical in Canada, Study no 153, August (2015).

However, Alberta would very likely follow a similar path to the US and convert many of these to GTCC in the foreseeable future.

GTCC Flue Gas Amine Absorber-Stripper for CO₂ Capture: Gas Turbine Combined Cycle (GTCC) is expected to be a major source of power generation new capacity additions at the utility as well as the industrial level. In parallel, some industry sectors use Co-Gen provided they can optimally balance power and steam demands. Conditioned flue gas with low levels of Oxygen, NO_x and SO_x (<15 ppmv) is sent to an absorber tower where it is contacted with “lean” amine feed consisting of an aqueous solution of alkanolamines, which react with CO₂ to form the bicarbonate (HCO₃⁻) or carbamate ions (RNHCO₂⁻). One system using amines for flue-gas CO₂ recovery that has been demonstrated on a commercial-scale is Fluor’s Econamine® process.

SMR Amine Absorber-Stripper for CO₂ Capture: The SMR process is primarily used for hydrogen and syngas (H₂ + CO) production. Alberta industries include methanol plants, oil-sand processing plants, and refineries. A typical SMR amine process produces high-purity CO₂ (99.8%) at a rate of 8.32 kg/ kg of H₂. CO₂ generation from thermal energy required for the SMR process is 1.96 kg/kg H₂. In Steam Methane Reforming of hydrocarbon feeds, natural gas is converted to high purity hydrogen and for the bulk of existing capacity, a CO₂ side product through the overall reaction: CH₄ + 2H₂O → CO₂ + 3H₂. Amines can be used for recovering this CO₂; however, in this case the recovery tower does not have to handle even traces of oxygen. Only moisture and traces of inert gases are present in the CO₂ product.

CO₂ Capture from coal utility plant: There have been pilot tests of many flue gas CO₂ capture systems. However, one of the few systems to be demonstrated at a commercial scale is Fluor Econamine®. Amine recovery of CO₂ from either flue gas has an energy cost around 0.81 kW/kg CO₂ and it could be expected that the proprietary mix of amines used by Fluor should be better than this.¹² There is a disadvantage for flue gas capture in that the presence of oxygen degrades the costly amines, hence recovery of flue gas will be at a disadvantage compared to recovery from an oxygen-free process stream such as those from hydrogen plants. The new generation of CO₂ capture technology is expected to deliver 90 percent CO₂ capture at 99% purity and take other emissions such as SO_x and NO_x to near-zero levels, as indicate din Table 3-1.

Table 3-1: Characterization of CO₂ from three sources.

Source	Flue-Gas Amine	SMR-Amine	Captured CO ₂ from Coal Plants
Product	Electricity	Hydrogen	Electricity
Temperature	Ambient	Ambient	Ambient
Pressure	2.6 bar	14 bar	Atmospheric
H ₂ O	1.8 %		Trace
N ₂	0.6%		None
O ₂	None	None	Trace
CO ₂	97.6%	99.8%	99.5%

Integration with Methanol Plants: E3Tec is actively pursuing integration of the DMC plant with three types of methanol production plants in Alberta: a) conventional SynGas based plant by Methanex; b) municipal waste to methanol plant by Enerkem; and c) methanol as by-product from the forest products, pulp & paper industry (e.g. ALPAC).

¹² Doctor, R.D. , *Future of CCS Adoption at Existing PC Plants Economic Comparison of CO₂ Capture and Sequestration from Amines and Oxyfuels*, Argonne Report, ANL/ESD/12-9 (Dec. 29, 2011).

For the Kraft pulp process, the amount of methanol produced at the digester is about 10 kg per tonne of pulp. In Alberta, Dishawa-Marubeni International has a plant at Peace River with name-plate production capacity of 400 kTA (thousand tonnes/yr). So, the methanol produced as by-product for this plant is on the order of 4 kTA. This corresponds to the feed methanol requirements of a 5.6 kTA DMC production case using the E3Tec process technology. Since methanol is produced as a by-product of the pulp process derived from forest products, the resulting CO₂ consumption would be 3.64 kTA as per the C-Footprint analysis.

Energkem Alberta Biofuels LP, Edmonton (AB) expects to produce about 38 million liters of methanol per year from municipal waste, which corresponds to 30 kTA. Again CO₂ equivalent emission (including methane release avoidance from landfill) from the municipal waste to methanol process is relatively small, if not negative (net consumption). Therefore, the resulting CO₂ consumption would be 27.3 kTA, if the DMC plant is integrated with the Energkem or an equivalent plant producing methanol from organic municipal waste. With an aggressive technology development and business strategy, this production is achievable by 2020. As per Alberta's 2008 Climate Change Strategy, the target CO₂ reduction is 50 megatonnes/yr (MTA) total with about 9.25 MTA from greening energy production wedge, which includes renewable energy and CO₂ consumption as feedstock. The DMC process or one of the other similar processes alone will not meet this target; however, it can be part of the portfolio to meet the long term goal. Alternatively, with the DMC production using bio-based methanol established, industry in Alberta will be encouraged to expand the production of DMC using methanol from the Methanex facility in Medicine Hat, Alberta which operates a 600 kTA plant and markets methanol throughout North America. E3Tec's target is to achieve 1,000 kTA DMC production using this new technology in Alberta by 2030 with a resulting CO₂ consumption of 0.29 MTA.

Integration with Ethylene Plants: E3Tec will also pursue DMC production using ethylene oxide (EtO) as feedstock based on E3Tec's US/DOE SBIR Phase I project. This process can be integrated with an ethylene oxide/ethylene glycol plant located in Alberta. Shell Chemicals has 450 kTA ethylene glycol plant using Shell's process OMEGA (Only Mono-Ethylene Glycol Advantage) in Scotfield, Alberta. E3Tec's ethylene oxide to DMC process produces mono-ethylene glycol selectively, E3Tec will pursue a partnership with Shell Chemicals for future expansion of mono-ethylene glycol in Alberta to meet the expanding global demand.

The next strategic question to focus on is what incentives would be necessary for industry and investors to locate DMC plants in Alberta. Note that this question also applies to other technologies for converting CO₂ to high-value products. In the case for DMC, the strategic points to be considered are: a) the DMC global market is expanding, creating an economic opportunity for a competitive technology; b) Alberta is strategically positioned and currently transports chemicals to both Asian and US markets; c) the US could be a major market for more than 1,000 kTA DMC by replacing phosgene based polycarbonate production; d) the Ethylene Oxide (EtO) to DMC process alternative will also benefit from Mono-Ethylene Glycol (MEG) market growth and interest from the petroleum industry in supporting DMC as a fuel additive; e) there is a positive image for a company consuming CO₂ to make high-value products; f) DMC can be more easily transported than other CO₂ derived products (e.g. inorganic carbonates); g) either of the E3Tec process alternatives can be commercialized in a short period of time; h) linking the DMC process with methanol production from Pulp & Paper industry located in Alberta and other parts of Canada as well as to Energkem's municipal organic waste to methanol plant results in an overall process with a very low C-Footprint; and i) DMC production will attract high-tech, end-user industries to Alberta such as manufacturers of Lithium-ion batteries and polycarbonates.

In summary, the value of E3Tec's DMC process technology is that it can be readily integrated with plants having sources of captured CO₂ and with plants having feed sources of methanol. E3Tec is also

developing a process with US/DOE SBIR Phase I grant for conversion of captured CO₂ to alkyl carbonate (in this case DMC) using ethylene oxide as feed stock and co-producing mono-ethylene glycol. This process can be integrated with a petro-chemical plant having both sources of captured CO₂ and ethylene oxide. This ethylene-oxide based DMC process will be included in the next phase of the CCEMC project. In Round 2, E3Tec will interact with the relevant industries to establish techno-economic merits of locating DMC production plants in Alberta based on the emerging global demands for DMC.

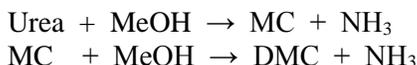
3.5 Results and Discussion

3.5.1 Kinetic Parameters

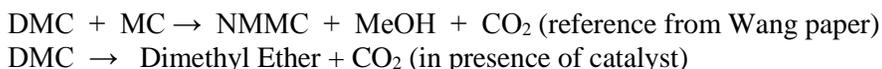
Urea-Based Chemistry: As mentioned previously, ZnO forms an organometallic complex with urea that is sparingly soluble in methanol. Further experiments showed that ZnO in its free form or supported on γ -alumina (Al₂O₃) has limited activity for conversion of MC to DMC. Rather, the ZnO-urea complex formed in-situ during reaction acts as the active catalyst. Further kinetic tests have been conducted using the ZnO-urea complex, and an initial set of kinetic parameters was obtained.

Experiments have been carried out to characterize the kinetics of methyl carbamate conversion to dimethyl carbonate. The focus of these initial experiments has been on the conversion rate of methyl carbamate (MC), and on the decomposition rate of dimethyl carbonate (DMC). These experiments were conducted at temperatures of 130-170°C using 0.25 – 2.0 wt% of zinc in reaction solution in the form of “Zn-Urea Complex.” Molar ratios of 10:1 and 20:1 MeOH:MC and a ratio of 28:1 MeOH:DMC were used in initial experiments.

The primary desired reactions are:



Decomposition and/or further reaction of DMC has been characterized as well. It is postulated that these reactions occur via one or more of the reaction pathways listed below. The first of these pathways includes the formation of N-methyl methyl carbamate (NMMC) in the presence of “ZnO-Urea Complex” catalyst.



Without the catalyst there was no degradation of DMC, even when exposed to high temperatures of 190°C for several hours. Since there was a question as to whether NMMC was formed via methylation by DMC or methanol, experiments were run with MC and methanol in the presence of the catalyst. These studies provide evidence that NMMC is only formed in measurable quantities after some MC is converted to DMC.

Approximately 60 batch experiments were conducted in order to determine the kinetic parameters for all four reactions listed previously. The reaction rate model for this system is:

$$\begin{aligned} \frac{d[\text{MC}]}{dt} &= -k_1[\text{MC}][\text{MeOH}] + k_2[\text{Urea}][\text{MeOH}] - k_4[\text{DMC}][\text{MC}] \\ \frac{d[\text{Urea}]}{dt} &= -k_2[\text{Urea}][\text{MeOH}] \end{aligned}$$

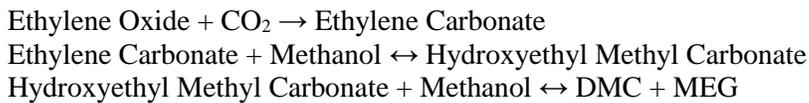
$$\frac{d[DMC]}{dt} = k_1[MC][MeOH] - k_3[DMC] - k_4[DMC][MC]$$

$$\frac{d[NMMC]}{dt} = k_4[DMC][MC]$$

The effects of temperature and catalyst loading on the reaction rate parameters (i.e. k_1 through k_4) were determined through regression of each individual experiment.

Ethylene Oxide-Based Chemistry

The reactions to produce DMC via the ethylene oxide pathway are as follows:



The initial lab-scale batch kinetic work was performed under DOE/SBIR Phase I. In order to maintain the confidentiality of the two projects the details of the kinetic parameters are not presented in this report. However, the kinetic parameters are used in the ASPEN Plus® process, which is used for both processes. The work covering the pilot-scale work was supported by both this project and DOE/SBIR Phase I and so only results of the pilot-scale work are included here.

Since the first reaction to produce ethylene carbonate is commercially practiced, and special safety procedures are required for handling ethylene oxide, the kinetics of this reaction were not studied. Production of DMC from ethylene carbonate involves two reversible reactions. The first reaction step to produce Hydroxyethyl Methyl Carbonate (HEMC) is rapid and quickly equilibrates. The second reaction step to produce DMC and MEG is slow. Ion Exchange Resins Amberlyst A-21 and A-26 were used to catalyze these reactions during the initial screening studies. The A-21 resin was used for the pilot-scale work.

$$\frac{d[EC]}{dt} = -k_1[EC][MeOH] + k_2[HEMC]$$

$$\frac{d[HEMC]}{dt} = -k_2[HEMC] + k_1[EC][MeOH] - k_3[HEMC][MeOH] + k_4[DMC][EG]$$

$$\frac{d[DMC]}{dt} = \frac{d[EG]}{dt} = k_3[HEMC][MeOH] - k_4[DMC][EG]$$

3.5.2 PerVap Performance

Two series of tests were performed. In the first series of tests the feed was maintained in the liquid phase by operating the membrane at pressures above the bubble point of the azeotrope. The first two tests were performed at 95°C and 30 psig pressure, while the remaining tests were performed at 105°C and 40 psig. The permeate side vacuum was maintained at 20 mbar. The permeate flux was 6.1 kg/hr m² at 95°C and varied between 7.1 and 8.2 kg/hr m² at 105°C, respectively. In a second series of tests the DMC/methanol mixture was fed in the vapor phase to simulate the condition of the overhead stream from the distillation column. By feeding the mixture in the vapor phase the HIRD process would not require condensing the overhead stream. The temperature was maintained between 95°C and 105°C for all tests,

except the last two Tests 12 and 13 for which temperature was maintained between 133°C and 139°C to determine the effects of temperature with vapor feed. There were no significant effects of temperature on flux or selectivity for vapor feed. In two tests, methanol was maintained at a higher concentration that reduced the flux; however, selectivity increased. For other tests, the permeate flux and selectivity were lower compared to liquid feed. A trade-off analysis will be performed on the commercial-scale process to determine whether it is better to condense the overhead to provide liquid feed to PerVap or maintain the overhead stream in vapor phase. In summary, the PerVap tests were completed as planned and the performance data are incorporated in the ASPEN Plus® process model.

3.5.3 Prototype Test Results

Urea-Based Process

As a consequence of the leak in the prototype test unit, there was insufficient time remaining in the project to complete more than three test conditions. However, while the test unit were not sufficiently long for the compositions in the recirculation loop to reach steady state, the dynamic response of the membranes and an inferred steady-state permitted partial validation of the kinetic model, and the ASPEN Plus® simulation model was applied based on quasi-steady state conditions. The compositions at the inlet and outlet of the reactor were collected. From the model comparisons, the ASPEN Plus® model predicts the product species distribution within measurement uncertainties. The quality and quantity of test parameter measurements were deemed adequate for validating the ASPEN Plus® process model. Additional pilot-plant conditions operated at steady-state with model predictions around the entire system and its individual components will be performed in Round 2.

Ethylene Oxide-Based Process

Performance tests were conducted using two separate side reactors for validating the scaling up design methodology; 1) 5-cm by 91-cm and 2) 1-cm by 8-cm. The tests on the larger pilot-scale reactor were regressed using ASPEN Plus® to determine the kinetic parameter values (k_1 through k_4) for the reaction model. These values were then used in an ASPEN Plus® model of the small-scale flow reactor to validate the model. EC conversions observed for the range of temperatures and flowrates on the small flow reactor are predicted well by the model, specifically at reaction temperatures of 70°C and 80°C including the effects of flow rates. These results give us the confidence that the model will accurately predict performance of the reactors on the commercial scale.

3.5.4 Process Analysis

Process analysis remains the project *cornerstone* and consists of the following elements:

- a. Process configuration of HIRD integrated with side reactors, PerVap membrane and auxiliary equipment.
- b. Exploring the ASPEN Plus® process simulation to determine an optimum process configuration
- c. Energy analysis to evaluate potential heat integration without significant equipment costs, specifically heat exchangers and associated pumps.
- d. Pilot-plant design, including equipment specifications.
- e. Validation of the process model based on kinetic test data and performance parameters from prototype test units.

The results from the process analysis are discussed in various sections. Therefore, an overview of the ASPEN Plus® process analysis is described here as it is applied to commercial scale process units.

ASPEN Plus® flow diagrams shown in this section are for the purpose of understanding the details incorporated in the process model.

Urea-Based Process Unit

The Urea-based commercial plant process parameters are presented in Table 3-2, along with those for the alternate ethylene oxide-based process. PerVap membrane performance was evaluated for the separation of methanol from the DMC/methanol azeotrope. A trade-off analysis was performed with and without the use of PerVap. The process analysis showed that ammonia released from urea can act as an entrainer to break the DMC/methanol azeotropic mixture in the urea-based DMC process. As a result, PerVap may not be required. The two processes with and without PerVap have comparable energy efficiency; however, the process without PerVap would require a high-degree of heat integration to achieve the energy efficiency of the process with PerVap already demonstrated. This trade-off analysis will be continued in Round 2 with the focus on the added CAPEX costs of heat exchangers for heat integration with and without PerVap. Furthermore, the critical issues of process operation will be evaluated to assure that the process will operate optimally with minimum side reactions that would reduce the product yield and adversely affect the C-Footprint.

Ethylene Oxide-Based Process Unit

The ethylene oxide-based process involves two products, which required careful process configuration for low capital and high-energy efficiency. Various process configurations were evaluated based on ASPEN Plus® process simulations. Design parameters are presented in Table 3-2 along with those for the urea-based process. Compared to the urea process, where ammonia can act an entrainer, PerVap improves the energy efficiency as well as reduces the size of the methanol recovery distillation column.

Design parameters presented in Table 3-2 provide a summary of the overall mass and energy balances. Both processes were designed to produce ~50 kTA DMC with corresponding consumption of CO₂, methanol and ethylene oxide. The urea-based process requires makeup for ammonia lost to byproducts and/or purging. It produces process water that can be recycled by removing traces of urea. The ethylene oxide-based process produces 0.706 kg MEG / kg of DMC, and forms no side products. The process analysis as well as the prototype tests validated the production rates. Presently, the 441 kg/hr is purged for balancing the ASPEN Plus® process analysis. It consists of MEG, EC and intermediate product, which can be recycled in the process. As a consequence of problems encountered operating the prototype test unit for the urea-based process, the urea process analysis is based on the literature kinetic parameters, which do not fully account for byproducts. Obtaining reliable, independent kinetic parameters from the prototype test unit will permit us to validate the ASPEN Plus® design. This will have high priority in Round 2 since it is critical to making the final process selection for demonstration in Alberta. The urea-based process operates at higher temperatures and pressures, which allows for effective heat recovery as compared to the ethylene oxide-based process.

SynGas-Based Versalis Process

An ASPEN Plus® process model was also developed for the leading commercial process being marketed by Versalis/ENI/ABB Lumus. The ASPEN Plus® model for this commercial process was developed and validated based on public data and the company's marketing material. The calculated energy consumption was used to estimate the commercial process C-Footprint.

Table 3-2: Design parameters of a commercial scale process unit.

	Urea Based Process	Ethylene Oxide Based Process
Production Capacity, KTA (Thousand tonnes/year)	51	49
Feed Rates, kg/hr		
Captured CO ₂	3,145	3,246
Methanol	4,608	4,547
Makeup Ammonia	7	
Product Streams		
DMC, kg/hr	6,406	6,213
Mono Ethylene Glycol		4,388
Process Water, kg/hr	1,287	Not Produced
Byproduct, kg/hr	66	441
Process Conditions		
Reaction Column, Reboiler Temperature, C	190	183
Reflux Temperature, C	81	48
Pressure, bar	4.0	0.5
Side Reactors, Temperature C	170	80
Pressure, bar	27.6	10.3
Utilities		
Cooling water, L/min	Not Used	Not Used
Cooling air, m ³ /s	103	305
Energy Consumption		
Thermal from Natural Gas, MW	4.4	13.1
Electricity, kW	663	456

3.5.5 Design of Pilot Plant

Considering the favorable techno-economic merits of using ethylene oxide feedstock with CO₂ and methanol for DMC and MEG coproduction, E3Tec has decided to evaluate both processes in depth. This task developed demonstration plant preliminary designs for *both* process technologies so that we could down select the best system to be installed and operated in Alberta. Since it is difficult to perform accurate energy balances for this scale plant, these designs focused on delivering high purity DMC with acceptable yields. This should result in favorable C-Footprints. For both processes, conversion of captured CO₂ to DMC has been validated with batch kinetic and prototype tests and then linked to the respective ASPEN Plus® process models. In order to demonstrate the technology, an integrated system consisting of a distillation column with side reactors and PerVap membrane is required. Refinements to each design will continue, representing a major Round 2 task.

Design and operating experiences from MSU's integrated distillation column and multiple side reactors has provided the basis for designing the plant in Alberta. MSU's test unit was configured and successfully operated for E3Tec's DOE/SBIR project entitled "Process Intensification by Integrated Reaction and Distillation for Synthesis of Bio-Renewable Organic Acid Esters." The key design features of the test unit are:

- a. The 10-m HIRD column comprised of 1-meter sections loaded with structure packing;
- b. Partition devices for side-draw of liquid to side reactors and product return to the column;
- c. An effective way to connect side reactors;
- d. Integrated level-controllers and variable frequency pumps for controlling side draw liquid levels;
- e. The top section of the column is equipped with an internal reflux condenser; and
- f. The pilot HIRD is equipped with instruments and sampling points for monitoring concentration profiles in the column and other strategic locations along the side reactors.

The pilot plant for demonstrating the technology in Alberta will be based on the MSU test unit, which has about 2-meter by 3-meter footprint and 15-meter height.

Pilot Plant of the Urea-Based DMC Process

The pilot plant configuration consisting of 4 distillation columns and a PerVap unit. The feed is urea and methanol. Columns will be equipped with internal reflux condensers and with electrically heated internal or coupled reboilers. Approximate diameters of reaction, methanol recovery, DMC recovery and ammonia separation columns are 100 mm, 70 mm, 75 mm and 27 mm, respectively with column heights between 7-m and 15-m. The process parameters are presented in Table 3-3. If necessary to meet the allocated budget in Round 2, the number of columns could be reduced to two. If only two columns are possible, then the reaction ammonia columns would be operated and products would be collected. Some of these products would then be subsequently fed to the two columns operated as if they were the methanol recovery and product columns. Under these circumstances, more thought would have to go into the design so that each column could serve a dual purpose to replicate the commercial unit. Ammonia, which is recycled in the full process, is generated in the pilot plant at a rate shown in Table 3-9 and would be absorbed in mild acid solution.

The feed consists of 24 wt% urea dissolved in methanol and the flow rate is 0.9 kg/hr (15 gm/min). The molar ratio in the fresh feed stream is 6:1 (methanol to urea), which is greater than the stoichiometric ratio of 2:1. This higher ratio will be soluble at ambient conditions avoiding the additional costs of heat tracing lines in the demonstration plant. In the commercial process, excess methanol in the feed will be recovered and recycled so the overall feed ratio will be closer to the stoichiometric ratio. The commercial scale target purities of DMC and yield are >99.9 wt% and > 78 wt%, respectively. Achieving this level of purity and yield will demonstrate the merits of this technology for conversion of captured CO₂. In general, it is difficult to accurately close the energy balance for a pilot plant; therefore, the focus of the pilot plant will be to demonstrate conversion of CO₂ to high-purity DMC with high yield for a favorable C-Footprint. The pilot plant designed in this task is expected to meet this objective.

Table 3-3: Process parameter of the pilot plant for the urea-based process.

Process Parameters	
Feed rate	0.9 kg/hr (15 gm/min)
Feed composition – urea	24 wt%
Molar ratio - methanol to urea	6:1
Product streams	
Flow rate DMC	0.25 kg/hr
DMC purity	99.99 %
DMC yield based on urea feed	77.0 %
Ammonia, if urea process is not integrated	0.13 kg/hr (2.2 gm/min)
Side reactors, temperature and pressure	165 °C, 21 atm
Reaction column	
Pressure	0.8 atm
Reflux / Bottom temperature	58 °C / 70 °C
Methanol recovery column	
Pressure	2 atm
Reflux / Bottom temperature	82.6 °C / 83 °C
Product recovery column	
Pressure	10 atm
Reflux / Bottom temperature	137 °C / 183 °C
Ammonia separation column	
Pressure	21 atm
Reflux / Bottom temperature	46 °C / 169 °C

Pilot Plant of Ethylene Oxide-Based DMC Process

The pilot plant consists of three distillation columns, three side reactors and one PerVap membrane unit. It will require up to 10 metering pumps and about 6 heat exchangers for condensing and heating/cooling purposes. Columns will be equipped with internal reflux condensers and at least one column with an electrically heated internal or coupled reboiler. The pilot plant is based on using 2-in schedule 40 pipes with internal diameter of 52.6 mm (2.07 inch). Approximate column heights of the reaction, methanol recovery and product recovery columns are 11-m, 16-m, and 6-m, respectively. Further process analysis will be performed to reduce the column heights without sacrificing product purity. The process parameters are presented in Table 3-4.

The feed rate of 0.8 kg/hr (13.3 gm/min) is typical for a column of 52.6 mm diameter. The molar ratio in the feed stream is 2.5:1 (methanol to ethylene carbonate), which is slightly greater than the stoichiometric ratio of 2:1. The excess methanol in the feed as well as additional methanol fed to side reactors is recovered and recycled. The target purities of DMC and MEG are >99 wt% and 95 wt%, respectively. Achieving this level of purity without side products will demonstrate the merits of this technology for conversion of captured CO₂ to co-production of DMC and MEG; two high-value commodity chemical products.

Table 3-4: Process parameters of the pilot plant for the ethylene oxide-based process.

Process Parameters	
Feed rate	0.8 kg/hr
Feed composition – ethylene carbonate	52.4 wt%
Molar ratio – methanol to ethylene carbonate	2.5:1.0
Product streams	
Flow rate DMC/MEG	0.41 / 0.27 kg/hr
DMC purity	99.99 wt %
MEG purity	95 wt %
Side reactors, temperature and pressure	70 °C and 0.5 bar
Reaction column	
Pressure	0.5 bar
Reflux / bottom temperatures	51 °C / 175 °C
Methanol recovery column	
Pressure	8.1 bar
Reflux / bottom temperatures	129 °C / 199 °C
Product recovery column	
Pressure	2.0 bar
Reflux / bottom temperatures	114 °C / 218 °C

3.6 Project Outcome

This project successfully completed all the tasks outlined in the proposal. Approximately 100 batch kinetic tests were conducted to achieve the following outcomes: 1) successful identification of a promising catalyst for DMC production from urea; 2) developing the reaction rate expressions describing the reactions for production of both the desired products and byproducts; 3) incorporation of these rate expressions and kinetic parameters into ASPEN Plus® so that refinements to the commercial plant design can be made. Further validation of the kinetic model was attempted with design and operation of a pilot-scale side-reactor recirculation unit. While the incident on the pilot-scale unit prevented a complete validation of the urea-to-DMC kinetic model, there are sufficiently close comparisons between the model and experiment to expect that validation on the larger-scale will result in only minor model refinements. While these refinements are anticipated to be minor, we plan to complete the pilot-scale work on the recirculation unit as a leading task in Round 2 to provide further assurance to ourselves and our partners.

The E3Tec team has also validated the kinetic model for the ethylene oxide-based process. While this was not an original project task, the E3Tec team's efforts during the CCEMC Round 1 project period has been focused solely on identifying the best processes for utilizing CO₂ in order to help Alberta meet its CO₂ abatement goals. The preliminary efforts for the ethylene-oxide pathway were funded by the U.S. Department of Energy (DOE) and show great promise. In Round 2, E3Tec intends to evaluate both processes and select the best for the demonstration plant to be built and operated in Alberta.

Design of the demonstration plant for both processes has been completed during this project. Further refinements will continue during Round 2 with the assistance of Jacobs Consultancy and others. A major focus of this project was the refinement of the C-Footprint for the urea-based process. After obtaining feedback from experts in this area, E3Tec has developed a standard methodology for determining the C-Footprint that segregates the C-Footprint into major areas (e.g. utilities, raw materials,

etc.) which can be easily identified for further improvements. This standard methodology has been applied to manufacturing DMC using 1) the urea-based process; 2) the ethylene-oxide-based process; and 3) the conventional SynGas-based process.

Detailed ASPEN Plus® process analysis supports nearly all the project outcomes. Models of the urea and ethylene-oxide commercial pilot-scale processes have been continually refined as new information is collected on the lab- and pilot-scales. After using the ASPEN Plus® models to regress data from the lab-scale kinetic experiments and pilot-scale tests the parameters obtained have been incorporated into the commercial-scale process models for the CO₂-based DMC production. These in turn have been compared against a rigorous model of the current commercial process for manufacturing DMC from SynGas. All three of these commercial-scale models serve as the basis for the C-Footprint analysis. ASPEN Plus® also has been employed to generate the test matrices for the pilot-scale work so as to maximize the quality of information with the minimal number of experiments.

As a result of the funding from the CCEMC, the E3Tec team has developed a path forward plan for both the processes based on the DMC markets the final product would serve. The team is encouraged by what has been achieved during Round 1 and believes the potential for converting CO₂ to DMC and other alkyl carbonates has been demonstrated. Additional work remains primarily in the demonstration of an integrated process and this will be the primary focus of Round 2.

3.7 Lessons Learned

The efforts of this project confirm the value of converting CO₂ to DMC and other alkyl carbonates. Additional market research has identified an expanding market for DMC in addition to the four applications of DMC. There now are potential uses of DMC in isocyanates – another chemical pathway where non-phosgene DMC production could replace phosgene. These efforts have allowed the E3Tec team to identify the key players in the DMC market and open communications with them.

The rigorous C-Footprint analysis of both the urea and ethylene oxide processes identified the sensitivity of the overall process' C-Footprint to the C-Footprint of the raw materials; particularly methanol. E3Tec is seeking ways to minimize the C-Footprint impact from methanol and this has led the E3Tec team to open communications with two bio-based methanol manufacturers in Alberta (Enerkem and ALPAC) as well as Alberta's primary commercial methanol manufacturer (Methanex). As a result, the team has identified a possible synergistic opportunity where an integrated DMC-Methanol process, conventional or bio-based, might have a lower C-Footprint than the two processes without integration. Similar opportunities are being explored for an integrated DMC-Ethylene Oxide process. We now believe that this integration may naturally lead us to a willing partner for licensing the technology.

Initially, the team was aware of byproduct formation during DMC production from urea and the detailed process models have focused on minimizing them. In contrast, most investigators in the area are focused on creating a heterogeneous catalyst. However, success in developing a heterogeneous catalyst will not address the primary issue affecting the C-Footprint – DMC yield losses caused by byproducts. Rather than join these investigators, the E3Tec team has modified their preliminary process to allow for the homogeneous nature of the catalyst while simultaneously minimizing byproduct formation. Efforts in Round 2 will continue to identify ways of further minimization. Some approaches involve alternate reactor designs and the use of solvents. As always, the E3Tec team's methodology requires the focus be on the commercial-scale with an eye toward what factors most affect it. Consequently, the commercial scale process is expected to change depending upon which of these alternates minimize byproduct formation most effectively.

The funding support from CCEMC on this project has allowed E3Tec to identify additional opportunities for utilizing CO₂ as a raw material for specialty chemicals. As a result of these efforts, we successfully obtained a DOE SBIR/Phase I grant to begin exploring a process for the conversion of CO₂ to DMC and MEG using ethylene oxide. The E3Tec team has been developing both processes in tandem and plans to select the best process technology in Round 2 for demonstration in Alberta.

4 GREENHOUSE GAS AND NON-GHG IMPACTS

4.1 Impact of CO₂ Conversion to DMC on GHG Emission

E3Tec is converting captured CO₂ to DMC using Heat Integrated Reactive Distillation (HIRD) process intensification. DMC is an ideal chemical for CO₂ conversion because of its expanding applications in current and emerging markets. DMC is considered a *Green Chemical* because it is neither toxic nor a skin irritant, is biodegradable¹³ and can be produced from captured CO₂. The current DMC market opportunity is defined by its application in production of polycarbonate, and solvents. DMC trans-esterification with phenol yields diphenyl carbonate, which is an essential starting material for polycarbonate resins by the “non-phosgene” process. DMC also serves as a methoxycarbonylation agent for isocyanates, which are used to manufacture polyurethane foams.⁵ As per the SRI Reports,^{14,15} the global consumption of polycarbonate was 4.9 MMTA in 2007, with a 7% global growth rate between 2007 and 2012. Current global DMC consumption by end use is illustrated in Fig. 3. Nearly half of DMC is used for polycarbonates with remaining half for solvents and other applications. Emerging markets for lithium-ion batteries use alkyl carbonates as the electrolyte solution for lithium ion transport.¹⁶ *DMC and other alkyl carbonates, now produced off-shore using coal-based SynGas, serve as the primary source for battery electrolytes and constitute about 10% of stationary and mobile battery costs in that rapidly growing global market.*

4.2 C-Footprint Analysis

C-Footprint analysis focused on the following three basic questions for CO₂ sequestration and a fourth one that may require strategic business decisions based on near-term and long-term North American and global market opportunities.

1. How much CO₂ is consumed in the process, kg CO₂/kg DMC?
2. How much CO₂ (equivalent) is generated in the DMC process, kg/ CO₂/kg DMC?
3. How much CO₂ (equivalent) is generated in the conventional DMC process?
4. What is the potential for production of DMC in Alberta based on present and future demands for DMC in the global marketplace?

This focus of C-Footprint analysis was to establish the present status and focus on ways the DMC process would meet Alberta’s goal of CO₂ emission reduction. After receiving guidance regarding the format and basis to perform the C-Footprint analysis, a comprehensive Excel worksheet was developed. The ASPEN Plus® process design model served as the basis for evaluating both the C-Footprint and capital costs (CAPEX) for a commercial-scale DMC process. In addition, as the basis for comparison of

¹³ Coker A., Dimethyl Carbonate (abstract), ChemSystems PERP Program, Nexant, 2012.

¹⁴ Polycarbonate, Chemical Research Report, SRI Report 2008.

¹⁵ Polycarbonate Resins, Chemical Research Report, SRI Report 2013.

¹⁶ Shiao, H.-C. et al, (2000) *Low temperature electrolytes for Li-ion PVDF cells*, Journal of Power Sources, Vol. 87, Issues 1–2, (April 2000,) pp.167–173

the E3Tec approach against base-line technology, an ASPEN Plus® process model was applied to the SynGas-based DMC process licensed by Versalis¹⁷ based on the available design data.

The C-Footprint analysis was based on the process block diagrams which clearly defines energy and mass flow within the system and from outside. These process block diagrams were based on the process flow diagrams of commercial scale units. The major process units were represented within the boundary of the block diagrams, which is defined as Inside Battery Limits (IBL). External input of energy and material to the process was presented by blocks outside the boundary; defined as Outside Battery Limit (OBL). The C-Footprint of these external blocks was obtained from literature databases or available sources applicable to Alberta.

The Excel-based C-Footprint analysis consists of the following worksheets:

Worksheet 1 - Summary: This worksheet displays content of the Excel model and results summary.

Worksheet 2 - Process Overview: The DMC process flow diagram is described in this worksheet.

Worksheet 3 - Material & Energy Balance: This worksheet contains the process block diagram, which is based on the process flow diagram presented in Worksheet 2 above. The overall mass and energy balances are presented here, along with their normalized values with respect to DMC production.

Worksheet 4 - Process Analysis: This is the primary worksheet where all mass and energy balances and C-Footprint calculations are performed as per the algorithm described below.

Worksheet 5 – CO₂ Conversion Factor: In this worksheet the C-Footprint of raw materials and CO₂ emission factors for process utilities are compiled from the literature and other databases. Utilities include electricity, process water and natural gas. These database values are compiled specifically for Alberta when available.

Worksheet 6 – C-Footprint: This worksheet presents the overall results answering the first three questions described above.

The calculation algorithm consists of the following steps:

- a. Mass balance for each component in the process flow diagram, including interactions of components, is balanced as per process parameters derived from the ASPEN Plus simulation.
- b. Energy balance for each component is recorded as per the ASPEN Plus simulation. Energy balance consists of: a) thermal energy provided by natural gas; b) electric power servicing process pumps and blowers; and c) cooling provided by air-cooled heat exchangers/condensers.
- c. Heat integration consists of feed/effluent heat exchangers. Heat integration using thermal heat pumps was not performed at this stage. This will be performed in Round 2 with significant improvement of the energy efficiency and hence C-Footprint.
- d. C-Footprint of each component is calculated and examined for consistency with the process analysis.

The C-Footprint results are summarized in Tables 4.1, 4.2 and 4.3 for the urea based, ethylene-oxide based and conventional SynGas based DMC processes, respectively. The results in these tables are presented in the format of responses to the three questions described above. The C-Footprint breakdown provides the details of the raw materials and utilities contributions. In general thermal energy and electric power are the two primary utilities in all three C-Footprints. Methanol is the primary raw material with the largest impact on the C-Footprint. The conventional SynGas process for manufacturing methanol has a relatively high C-Footprint. Therefore, E3Tec has been exploring the use of biomass-based methanol. Further discussion of the results of these efforts can be found in the next section. Because of the

¹⁷ “Dimethyl Carbonate Proprietary Process Technology,” ENI Polimeri Europa Brochure.

substantial effect the methanol source can have on each process' C-Footprint, each C-Footprint was determined using methanol values for both the conventional SynGas and biomass based production. Similarly, C-Footprint of ethylene oxide is not included at this stage of analysis.

The net CO₂ sequestration within the IBL is consistent with the original estimates shown in the proposal. For the urea process, the net consumption of CO₂ would be 0.279 kg/kg DMC production, which is based on biomass or renewable energy based methanol. The carbon merit ratio (consumed/generated) is 2.32. For the ethylene oxide process, it is necessary to normalize the C-Footprint based on a combined process, which would include a conventional mono ethylene glycol (MEG) process. Note that the net CO₂ consumption is 0.093 kg/kg DMC, which is lower than the urea process. However, by accounting for the C-Footprint of MEG, the net CO₂ abatement would be 0.403 (0.093 + 0.31) kg CO₂/kg DMC by replacing conventional MEG production (present and future) in Alberta with an integrated DMC-MEG process.

The conventional SynGas-based Versalis process has high C-Footprint of 1.674 kg CO₂/kg DMC with conventional methanol and 1.182 kg CO₂/kg DMC with biomass-mass based methanol. Note that this is after accounting for the energy value of hydrogen produced in the SynGas process by power generation using fuel cell level efficiency.

In summary, both CO₂-based DMC processes have favorable IBL C-Footprint that is significantly lower than the conventional SynGas-based DMC process. With further development of Heat Integrated Reactive Distillation (HIRD) in Round 2, E3Tec team strongly believes that the energy efficiency and hence C-Footprint will be further improved.

Table 4-1: C-Footprint of the urea-based process.

Summary of Carbon-Footprint					
Question # 1: How much CO ₂ is consumed in the process, kg CO ₂ /kg DMC produced?					
Answer: From the "Material & Energy Balance" Worksheet data			0.491	kg CO ₂ /kg DMC	
Question #2: How much CO ₂ (equivalent) is generated in the process, kg CO ₂ /kg DMC produced?					
Answer: From the calculations below			0.672	Using commercial SynGas MeOH process	
			0.212	Using biomass-based or renewable energy MeOH	
And, the Net CO ₂ consumed (generated) in the process, kg CO ₂ /kg DMC produced					
			(0.181)	Using commercial SynGas MeOH process	
			0.279	Using biomass-based or renewable energy MeOH	
Component	Unit	Quantity per kg DMC	CO ₂ /unit	CO ₂ /kg DMC	Remark
Methanol	kg	0.72	0.64	0.460	Commercial SynGas based process, e.g. Methanex
Ammonia	kg	0.001	1.67	0.002	
Power	kWh	0.09	0.65	0.061	Applied for Alberta
Natural Gas	kBTU	2.81	0.05	0.149	
Process Water	L	0			No process water consumed
Cooling Water	L	0			Air cooling, so no cooling water
Inert Gas	m ³	0			No inert gas
Byproduct Processing	kg	0.010			Not accounted for
Process Water	kg	0.20	0	0	Assumed to be reused with minimum treatment
Total				0.672	
Question #3: How much CO ₂ (equivalent) is generated in the conventional DMC process, kg CO ₂ /kg DMC produced?					
Answer: Based on E3Tec C-Footprint Analysis			1.674	SynGas based Versali Process	
			1.214	Using biomass-based or renewable energy MeOH	

Table 4-2: C-Footprint of the ethylene oxide-based process.

Summary of Carbon-Footprint					
Question # 1: How much CO ₂ is consumed in the process, kg CO ₂ /kg DMC produced?					
Answer: From the "Material & Energy Balance" Worksheet data		0.522	kg CO ₂ /kg DMC		
Question #2: How much CO ₂ (equivalent) is generated in the process, kg CO ₂ /kg DMC produced?					
Answer: From the calculations below		0.764	Using commercial SynGas MeOH process		
		0.429	Using biomass-based or renewable energy MeOH		
And, the Net CO ₂ consumed (generated) in the process					
		(0.241)	Using commercial SynGas MeOH process		
		0.093	Using biomass-based or renewable energy MeOH		
Component	Unit	Quantity per kg DMC	CO ₂ /unit	CO ₂ /kg DMC	Remark
Methanol	kg	0.52	0.64	0.335	Commercial SynGas based process, e.g. Methanex
Ethylene Oxide	kg	0.732	0.00	0.000	Needs further evaluation - not considered
Power	kWh	0.07	0.65	0.048	Applied for Alberta
Natural Gas	kBTU	7.19	0.05	0.381	
Process Water	L	0			No process water consumed
Cooling Water	L	0			Air cooling, so no cooling water
Inert Gas	m ³	0			No inert gas
Byproduct Processing	kg	0.071			Not accounted for
Waste Water	kg	0.00	0	0	
Total				0.764	
Question #3: How much CO ₂ (equivalent) is generated in the conventional DMC process, kg CO ₂ /kg DMC produced?					
Answer: Based on E3Tec's C-Footprint Analysis		1.674	SynGas based Versalis Process		
C-Footprint of mono-EG Based on DOE Chemical Bandwidth Study		0.311	Hydration of ethylene oxide followed by separation		
Total - Combined DMC and mono-EG Production		1.985			

Table 4-3: C-Footprint of the SynGas-based Versalis process.

Summary of Carbon-Footprint					
Question # 1: How much CO ₂ is consumed in the process, kg CO ₂ /kg DMC produced?					
Answer: From the "Material & Energy Balance" Worksheet data		0.000	kg CO ₂ /kg DMC		
Question #2: How much CO ₂ (equivalent) is generated in the process, kg CO ₂ /kg DMC produced?					
Answer: From the calculations below		1.674	Using commercial SynGas MeOH process		
		1.182	Using biomass-based or renewable energy MeOH		
And, the Net CO ₂ consumed (generated) in the process, kg CO ₂ /kg DMC produced					
		(1.674)	kg CO ₂ /kg DMC		
Component	Unit	Quantity per kg DMC	CO ₂ /unit	CO ₂ /kg DMC	Remark
Methanol	kg	0.77	0.64	0.492	Commercial SynGas based process, e.g. Methanex
Power	kWh	0.05	0.65	0.029	Applied for Alberta
Natural Gas	kBTU	21.72	0.05	1.152	
Process Water	L	0			
Cooling Water	L	0			Air cooled heat exchangers
Inert Gas	m ³	0			No inert gas
Byproduct Processing	kg	0.133			Not accounted for
Hydrogen	kg				
Process Water as Byproduct	kg	0.26	0	0	Assumed to be reused with minimum treatment
Total				1.674	

4.3 C-Footprint of Raw Materials

The urea and ethylene oxide based processes have potential for CO₂ abatement based on IBL analysis. When C-Footprint of methanol and ethylene oxide manufactured by conventional means are included, then it would be difficult to justify CO₂ abatement. Therefore, E3Tec is actively pursuing alternate sources and proper ways to account for raw materials as outlined below.

- a. Alternate sources of methanol from biomass, such as Enerkem's technology.
- b. Methanol produced as byproduct in the pulping process.
- c. Offsite manufacturing of raw material; outside Alberta.
- d. Benchmarking current manufacturing of raw materials in Alberta.

Methanol: The C-Footprint for the manufacture of methanol, a raw material for the DMC process, using commercial processes based on SynGas is relatively high. With improved energy efficiency the C-Footprint of methanol plants is about 0.54 kg CO₂/kg methanol; however, it is 0.64 kg CO₂/kg methanol for the Methanex plant in Alberta, which was used in the C-Footprint analysis. Therefore, alternate methanol manufacturing processes with low C-Footprint must be evaluated and the C-Footprint analysis tools developed will easily allow that task. The process of converting organic municipal waste to methanol is of particular interest; consequently, E3Tec visited the Enerkem site and discussed use of methanol. E3Tec also visited ALPAC and discussed the use of methanol produced as byproduct in the pulping process. Methanol purity is a factor in qualifying methanol for the DMC process. Also, the two projects funded by the CCEMC Grand Challenge for manufacturing methanol using renewable energy will be evaluated in Round 2.

Alberta's Methanex plant with a capacity of 470 kTA was started in 2011. As indicated above, it has higher C-Footprint than energy efficient methanol plants outside of Canada. Investigators are actively pursuing converting CO₂ to methanol using new catalysts.¹⁸ Such a methanol process may or may not be competitive to a SynGas-based methanol plant. However, regardless of the methanol process, an integrated methanol-DMC plant would have a favorable C-Footprint and economic merits. E3Tec intends to collaborate with organizations pursuing CO₂-based methanol production plants. E3Tec has initiated conversations with Methanex and has invited them to the industrial workshop.

Ethylene Oxide: Ethylene oxide is produced by catalytic oxidation of ethylene. Alberta is one of the major producers of ethylene at about 4 million tonnes/year, followed by ethylene oxide and ethylene glycol.¹⁹ Alberta has production capacity for 1,395 kTA of ethylene glycols, of which 1,045 kTA are specifically for MEG.¹⁶ The opportunity for further expansion using the proposed technology comes from the current overcapacity in Alberta for Ethylene Oxide Production. Therefore, an integrated process of ethylene oxide and DMC would have CO₂ abatement potentials greater than 0.4 kg CO₂/kg DMC production with high product margin. E3Tec intends to actively pursue an integrated plant with one of the producers of MEG and/or ethylene oxide.

Captured CO₂: Energy consumption of CO₂ capture depends on source and technology. Amine recovery of CO₂ from flue gas has an energy cost around 0.81 kW/kg CO₂ and it could be expected that the proprietary mix of amines used by Fluor should be better than this.²⁰ This represents 0.07 kg CO₂ generated/kg CO₂ captured. There is a disadvantage for flue gas capture of CO₂ because even trace levels of oxygen degrades the costly amines. In addition to this high economic cost, there is an increase in the process C-Footprint. Hence, recovery from flue gas will be at a disadvantage compared to CO₂ recovery from an oxygen-free process streams from hydrogen plants. The new generation of CO₂ capture technology is expected to deliver 90 percent CO₂ capture at 99%+ purity with lower C-Footprint than the conventional Amine process. Delivering the CO₂ to the fence at pipeline pressure (130 bar) raises the

¹⁸ Mar Pérez-Fortes et al., "Methanol synthesis using captured CO₂ as raw material: Techno-economic and environmental assessment," *Applied Energy*, 161, 718-732 (2016).

¹⁹ Canadian Energy Research Institute, CERI Report "Examining the Expansion Potentials of Petrochemical in Canada, Study no 153, August (2015).

²⁰ Doctor, R.D., *Future of CCS Adoption at Existing PC Plants Economic Comparison of CO₂ Capture and Sequestration from Amines and Oxyfuels*, Argonne Report, ANL/ESD/12-9 (Dec. 29, 2011).

energy consumption to 1.16 kW/kg CO₂,²¹ and this differential cost for liquefaction and pumping (0.35 kW/kg CO₂) further increase the C-Footprint of CO₂ capture and delivery. Therefore, an integrated IBL CO₂ capture and conversion process should be developed, specifically for distributed CO₂ sources. This is the primary focus on the E3Tec approach.

4.4 CO₂ Emission Abatement

DMC is a valuable organic solvent, a practical oxygenated diesel-fuel additive,²² and a feedstock in the production of other alkyl and aryl carbonates.²³ DMC's market share in solvents (the current US solvent market of 5 MTA) is expected to expand significantly in US and Europe. ***Growing environmental concerns and regulatory pressure will drive demand for green solvents that are derived from renewable raw material and from captured CO₂.*** DMC is not corrosive and will not produce environmentally damaging or health related by-products. DMC has perhaps lowest maximum incremental reactivity (MIR) of any liquid solvent in commercial use as reported by Dr. William Carter in work funded by Exxon-Mobil Chemicals.²⁴ *This ultra-low MIR, gives DMC a very favorable ozone reduction potential, allowing for fast approval even by cautious states such as California. Due to its VOC exempt classification, DMC has grown in popularity and more applications are expected. DMC may replace methyl-ethyl ketone (MEK), tertiary-butyl acetate, and parachloro-benzotrifluoride. DOW's PARALOID B66 DMC ultra low-VOC acrylic coating containing DMC as the solvent is an ideal example of this market trend.*

While the US market is about 20% of the global market, the global DMC market is driven by the growing polycarbonate demands outside the US, particularly in China. The US market share could significantly change with new applications of DMC in lithium-ion batteries, as a fuel additive, or as a low VOC solvent. ***The E3Tec Technology provides a great opportunity for Alberta to become the major DMC producer from captured CO₂ to meet the step-change in market demand.*** Table 4.1 provides a summary of DMC market potential and corresponding CO₂ abatement. The DMC market for lithium-ion batteries depends on maintaining and expanding production. DMC as fuel additive depends on three key factors: a) regulatory approval of DMC use; b) validated benefits, such as reduced diesel pollution; c) economics.

In order to make significant contribution to CCEMC's goal of CO₂ sequestration, it is essential to meet the two following market and business criteria: a) global market for DMC and derived alkyl carbonates; and b) locating DMC production plants in Alberta.

In addition to the current primary DMC market for use in polycarbonate manufacturing, DMC is a critical chemical employed in emerging applications in sustainable energy technologies and as specialty chemical as discussed below.

Polycarbonates: Dimethyl carbonate currently is consumed in the manufacture of polycarbonates via the well-established and rapidly expanding non-phosgene melt process. The U.S. and global

²¹ Doctor, R.D. , *Future of CCS Adoption at Existing PC Plants Economic Comparison of CO₂ Capture and Sequestration from Amines and Oxyfuels*, Argonne Report, ANL/ESD/12-9 (Dec. 29, 2011).

²² Zhang, G.D. et al, *Effects of dimethyl carbonate fuel additive on diesel engine performances*, Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering (July 1, 2005), 219: pp. 897-903

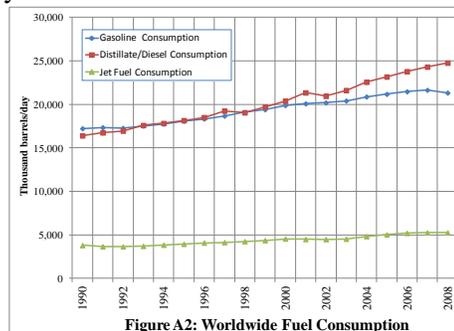
²³ ExxonMobil Chemicals US Patent 6,407,279 (June 18, 2002).

²⁴ William P.L. Carter, D. Luo, and I.L. Malkina, Investigation of the Atmospheric Ozone Formation Potential of Selected Carbonates, Report to ExxonMobil Chemical Company (November 17, 2000). <http://www.cert.ucr.edu/~carter/pubs/carbonat.pdf>

production of polycarbonate are about 0.9 and 4.7 million tonnes per year, respectively and growing at a global rate of 7.0%.²⁵

Battery Electrolytes: DMC and other alkyl carbonates are leading candidates for electrolyte solvents used in lithium-ion batteries. This is because their high polarity enables them to dissolve lithium salts. This emerging market could become a major source of demand for DMC over the next five years.

Oxygenated Additives for Gasoline and Diesel: Considerable ongoing effort is focused on using DMC as a diesel additive.^{26,27} DMC is not corrosive and does not produce environmentally damaging byproducts upon combustion. Diesel is a particularly promising market. Recent combustion tests have indicated that a 4% DMC/96% diesel formulation reduced total hydrocarbons, CO, and particulate matter in the exhaust by 50%. Fuel additives would represent a large market for DMC and, as seen in the adjacent figure,²⁸ worldwide diesel consumption exceeds gasoline. Every 1% of diesel fuel displaced by DMC worldwide (140 billion gallon diesel fuel consumed annually) would require 4.2 million tonnes/yr DMC and would result in a fossil CO₂ abatement of 13 million metric tonnes/yr. The basic guideline for diesel additive is 4% with potential CO₂ abatement of 52 million tonnes/yr.



Solvents: DMC could have a large role in displacing petroleum-based, non VOC-exempt organic solvents. This emerging market is driven by policy and would represent the largest displacement market that could be filled by DMC. For example, in North America alone, solvent demand for paints and coatings is 3 million tonnes/yr.

Altogether, these markets constitute the potential for greater than 9 MTA of CO₂ abatement with 25% market share of the global demands. Table 4.1 presents the breakdown of CO₂ abatement for different end-usages of DMC. Alberta could become a major manufacturing center of DMC from CO₂ with export to the US, Asia, and Europe.

Table 4-4: Alberta's CO₂ abatement potentials by four major applications of DMC.

Application	2016 Global Demands kTA	Growth kTA	25% Market Penetration	DMC in Product	CO ₂ Abatement Potentials, kTA	
					Growth	25% Market
Polycarbonate	6,430	444	1,608	1.0	129	466
Solvents (Replacing Ketones)	1,430	29	358	1.0	23	286
Fuel Additives (Diesel)	1,580,000	31,600	395,000	0.076	700	8,752
Lithium-ion Battery	\$25 billion/yr	Electrolyte market \$5.23 billion/yr			227	

²⁵ Polycarbonate Resins, Chemical Economics Handbook, SRI Consulting (2013)

²⁶ Rounce, P., A. Tsolakis, P. Leung, and A.P.E. York, "A Comparison of Diesel and Biodiesel Emissions Using Dimethyl Carbonate as an Oxygenated Additive" Energy & Fuels, 24, pp. 4812-4819 (2010)

²⁷ Zhang, Liu, Xia, and Zhang, "Effects of dimethyl carbonate fuel additives on diesel engine performance," Proc of Inst of Mech Eng, Part D: J of Automobile Eng (July 2005)

²⁸ http://oilindependents.org/wp-content/uploads/2012/01/EIA-World-Consumption-of-Selected-Petroleum-Products_1-11-12.xls

4.5 Challenges and Opportunities

The major challenges of qualifying the DMC process for CO₂ abatement in Alberta to meet the CCEMC goal are as follows:

- a. Alberta does not have conventional DMC production that can be replaced with CO₂-based DMC.
- b. Methanol manufactured using conventional processes has a high C-Footprint which would inhibit CO₂ abatement using the DMC process, unless alternate sources of methanol is used or an integrated process of DMC-Methanol is developed.
- c. There is no immediate use of DMC in Alberta; therefore, the production would be based on export of DMC to the US, Europe and Asia. This will require an infrastructure for exporting DMC.
- d. In order to achieve industrial support and acceptance of the process, it is essential to demonstrate the process viability with clearly defined techno-economic merits. This is the primary focus of Round 2.
- e. The overall CO₂ abatement is limited by the global DMC demand, specifically using DMC as a fuel additive in diesel.

All of the techno-economic challenges identified above can be overcome. There are strong opportunities for commercialization of the DMC process in Alberta in the near term. The major opportunities are as follows:

- a. CO₂ abatement with favorable economics, that would allow near-term implementation.
- b. E3Tec has advanced the technology from TRL 3 to TRL 5, and has the potential of advancing the process to TRL 7 in Round 2. This is close to commercialization.
- c. Improved energy efficiency in methanol production from an integrated DMC-Methanol process.
- d. Integrated process of Co-production of DMC and MEG having a low combined C-Footprint with favorable economics.
- e. Integrated process of CO₂ capture and conversion having a lower combined C-Footprint, specifically for distributed CO₂ sources.

5 OVERALL CONCLUSION

The major conclusions from Round 1 projects in three categories are as follow.

CO₂ Abatement Target

1. DMC is an ideal value-added specialty chemical with expanding global market for conversion of CO₂ to value-added product.
2. Both the urea-based and ethylene oxide-based processes showed potentials for significant CO₂ abatement in Alberta.
3. Methanol produced using the conventional SynGas process has a high C-Footprint. Therefore, biomass or renewable energy based methanol must be pursued.
4. Integration of CO₂ capture and conversion with the process showed high potential for significant CO₂ abatement from coal utility plants in Alberta.
5. Integration of the DMC process with SynGas methanol manufacturing has potentials for significant CO₂ abatement; therefore, it should be pursued with the Methanex plant in Alberta.
6. An integrated DMC-MEG process has favorable techno-economic merits; therefore, it should be pursued with ethylene plants in Alberta.

Process Development

7. The ASPEN Plus® process model, along with component models, developed in this project are shown to be very valuable design tools for evaluating and configuring the process to meet the desired goal of CO₂ abatement with favorable economics.
8. Heat Integrated Reactive Distillation (HIRD) equipped with side reactors and PerVap membranes is ideally suited for the complex process chemistry of conversion of CO₂ to alkyl carbonates.
9. Catalyst ZnO forms organometallic complex with urea in the urea-based process. The ZnO-complex is sparingly soluble in reacting media, which required E3Tec to modify the original process configuration based on totally heterogeneous catalyst. In Round 2, an alternate design for the side reactors will be developed to maximize DMC yield and high rates of conversion.
10. Commercial Amberlyst® catalyst performed well for conversion of ethylene carbonate to DMC in the ethylene oxide-based process. The process can be readily scaled to a fully integrated pilot plant demonstration.
11. Performance parameters of the ceramic tubular PerVap membranes provided a basis for integrating them into the process to improve product yield. This permits the trade-off analysis of energy efficiency vs. capital cost of PerVap and process equipment.
12. ASPEN Plus® process modeling was effectively validated with prototype tests. The next step is to validate the process model with an integrated pilot-plant.

Technology Transfer

13. CO₂-based DMC process is getting encouraging responses from industry and research organizations.
14. Technology transfer plans developed in this project show a well-defined roadmap for commercially implementing CO₂-based DMC production in Alberta using this process.
15. CO₂-based DMC process shows favorable techno-economic merits in comparison to the conventional SynGas based DMC process that is being considered for replacing current commercial phosgene-based polycarbonate processes.
16. Demonstration of an integrated DMC process and reliable economic analysis are key to commercialization of the DMC process in Alberta.

During Round 1 of the CCEMC project, E3Tec's team advanced the DMC process development from Technology Readiness Level (TRL) 3 of *Critical Function or Proof of Concept Established* to TRL 5 of *Laboratory Testing of Integrated/Semi-Integrated System*. In Round 2, E3Tec expects to advance it to TRL-7 of *Integrated Pilot System Demonstrated*. The ASPEN Plus® process model provided the basic foundation for rapidly scaling laboratory data and pilot plant performance parameters to commercial plants.

6 SCIENTIFIC ACHIEVEMENTS

During Round 2 of the CCEMC project, E3Tec team has advanced the DMC process development from Technology Readiness Level (TRL) 3 of *Critical Function or Proof of Concept Established* to TRL 5 of *Laboratory Testing of Integrated/Semi-Integrated System*. E3Tec expects to advance it to TRL 7 of *Integrated Pilot System Demonstrated* in Round 2. E3Tec has secured strong IP position with a patent "Method for Producing Concentrated Dimethyl Carbonate Composition and Co-Products," US # 14/445,992 (Patent Pending) and "Differential Kinetic Test Unit (DKTU)," US Patent 9,222,924 (December 2015). The patented DKTU obtains kinetic parameters of complex multi-step reactions under prototype flow reactor conditions. This allows scaling of the laboratory data to pilot plant with a high-level of certainty. The ASPEN Plus® design methodology provides the basic foundation for scaling laboratory data and pilot plant performance parameters to commercial plants. E3Tec's commercialization

strategy *focuses primarily on licensing or strategic alliance with one or more industrial partners*. Industry interactions in Round 1 were productive and should lead to a formal working relationship in Round 2.

The specific scientific achievements in this CCEMC Grand Challenge Round 1 project were:

- a. Development of two HIRD processes for CO₂ conversion to alkyl carbonates.
- b. Establishment of CO₂ abatement potentials for the urea-based and ethylene oxide-based processes.
- c. Validation that the CO₂-based DMC processes have a significantly lower C-Footprint than conventional SynGas-based DMC process.
- d. Establishment of the techno-economic merits of the DMC process as compared to the conventional SynGas Versalis process.
- e. Development of the kinetic and performance parameters database using prototype test units.
- f. Characterization of catalyst for both processes.
- g. Development of ASPEN Plus® based scale-up design methodology for scaling laboratory performance parameters to commercial plants for rapid implementation of commercial CO₂-based DMC process in Alberta.

These scientific achievements are expected to have significant impacts on manufacturing DMC to meet the expanding global demands. The CO₂-based DMC would serve as a benchmark for other conversion technologies contributing to achieving Alberta's CO₂ abatement target.

7 PROGRAMMATIC ACHIEVEMENTS

E3Tec has built a strong technical team for successful development of the CO₂-based DMC process. Successful technology transfer by the E3Tec Team to industry depends on E3Tec's capabilities to: a) present the techno-economic merits to the industry, b) to leverage CCEMC Grant with equity, debt, other R&D support (such as US DOE SBIR); and c) well-defined business plan for licensing the technology. E3Tec Team is confident of these capabilities and enthusiastic of developing and commercializing CO₂-based DMC process.

The major programmatic achievements relevant to E3Tec's CCEMC project are as follows.

Intellectual Property (IPs): E3Tec filed the following two patents with the US Patent & Trade Office (USPTO). Previously provisional patent applications (PPA) were filed before the CCEMC proposal was submitted.

- a. Method of Producing High-Concentration Alkyl Carbonates using CO₂ as Feedstock, US Patent Application # 14/445,992, July 2014.
- b. Differential Kinetic Test Unit, US Patent Application # 14/319,086, June 2014.

E3Tec's Alberta Visit (August 2014): Two members of the E3Tec team visited Alberta for a discussion with Prof. Emeritus Karl Chuang of the University of Alberta. He is a member of the E3Tec team on the CCEMC project. E3Tec visited Enkern to discuss integrating the DMC process with its methanol process. Enkern has developed a proprietary process to manufacture methanol using municipal waste. We agreed to continue low-level communication as the project progresses with the intent of more serious interaction as the E3Tec approach shows technical promise. E3Tec also visited Alberta Innovates Technology Futures for a discussion with Allan Chambers and other associates for potential collaboration in the next phase of CCEMC project. They showed

strong interest in E3Tec's DMC process and are willing to consider using their pilot plant test facility to demonstrate the process in Alberta during the next phase of the project.

CO₂ Capture Technology Meeting (June 23/27, 2015): E3Tec participated in this DOE/NETL sponsored meeting with a poster presentation featuring the CCEMC work. The NETL sponsored meeting focused on CO₂ capture from coal utility plants using different technologies including membranes and different forms of sorbents. E3Tec's poster presentation was one of the few technologies developing energy-efficient process of converting captured CO₂ to value-added product with potentials of net consumption of CO₂. The E3Tec CCEMC approach could replace SynGas-based commercial DMC processes with significant impact that would reduce CO₂ emissions.

Jacobs Consultancy: Jacobs Consultancy, a division of Jacobs Engineering, contacted E3Tec for possible participation in the project. E3Tec visited Jacobs Consultancy office in Chicago and presented the overall scope of both CCEMC and DOE SBIR projects with a common goal of developing technology for captured CO₂ conversion to value-added products. Jacobs Consultancy tentatively agreed to participate in Round 2 project. Most likely they will coordinate the work from their offices in Chicago, Illinois and Calgary, Alberta.

Illinois Sustainable Technology Center (ISTC): E3Tec staff met with Dr. Kevin O'Brien and his associates at the AIChE CMTC meeting in Sugar Land, TX (Nov. 2015). ISTC is actively pursuing demonstration of new energy-efficient CO₂ capture technologies with low CAPEX. E3Tec and ISTC mutually agreed to communicate for potential collaboration with the focus on an integrated process of CO₂ capture and conversion to DMC and other alkyl carbonates.

Intellectual Property (IPs): Status of E3Tec's patents

- a. Method of Producing High-Concentration Alkyl Carbonates using CO₂ as Feedstock, US Patent Application # 14/445,992, July 2014. Received comments from the USPTO Examiner and E3Tec responded in March 2016.
- b. Differential Kinetic Test Unit (DKTU): Patent issued, US 9,222,924 B1, December 29, 2015.

US DOE SBIR Phase I Project: E3Tec completed DOE SBIR Phase I project entitled "Conversion of CO₂ to Alkyl Carbonates using Ethylene Oxide as Feedstock," and E3Tec has applied for Phase II grant.

E3Tec's Alberta Visit (September 2015): Two members of the E3Tec team visited Alberta for a discussion with Alberta-Pacific Forest Product Inc. (ALPAC). Dr. Karl Chuang (E3Tec's consultant), Emeritus Professor at the University of Alberta, also joined the meeting with ALPAC. The purpose of the meeting was to evaluate possibility of using biobased methanol produced as byproduct in the pulping process. Commercial SynGas based commercial methanol processes have high C-Footprint which adversely impact the C-Footprint of the DMC process. Biobased methanol from the pulping process would have relatively low C-Footprint. However, methanol produced from the pulping process contains significant amount of sulfur compounds. ALPAC and E3Tec agreed to collaborate on methanol purification outside the CCEMC project. E3Tec staff also talked to Enerkem during this visit to discuss integrating the DMC process with its methanol process. Enerkem has developed a proprietary process to manufacture methanol using municipal waste. In a previous visit, E3Tec staff visited Enerkem plant.

AIChE Carbon Management Technology Conference (CMTC) Meeting (November, 2015): E3Tec participated in this CMTC meeting at Sugar Land, Texas and made presentation on, "Techno-Economic Merit Analysis of Conversion of Captured CO₂ to Value-Added Products."

AICHe/DOE sponsored meeting focused on techno-economic barriers of carbon capture and sequestration (CCS). Currently DOE does not have a program focusing on CO₂ utilization. E3Tec was able to make effective comments advocating expanding the scope of the DOE's Carbon Management plan to include CO₂ utilization in the overall portfolio. Other attendees also voiced similar opinions on CO₂ utilization. Furthermore, E3Tec commented and asked question after panel presentation by Richard Adamson of CMC Research Institute about collaboration between DOE/Fossil Energy Office and CCEMC on jointly developing CO₂ utilization technologies. Apparently there is low-level unofficial communications between the two organizations.

8 NEXT STEPS

8.1 Technology Innovation

In CCEMC Round 1, and the DOE SBIR Phase I project, E3Tec advanced the technology one step closer to commercialization. During this time, key technical challenges encountered and the innovations in response were:

- a. The high C-Footprint of methanol. This needs to be addressed by alternate sources of methanol including biomass and/or renewable based methanol. Alberta has two potential sources and programmatic research that may yield further innovation.
- b. It was discovered that ZnO forms a complex with urea in the urea-based DMC process. The ZnO complex is sparingly soluble in the reactant mixture. The process configuration had to be revised from the proposed configuration. It was demonstrated that the homogenous catalysis approach is workable and appears to be economically attractive.
- c. DKTU studies using our proprietary test unit were performed at MSU to develop process kinetics for the primary reactions and the side-product reactions using the homogenous catalyst.
- d. Side reactors with a homogenous catalyst can be effectively integrated with HIRD.
- e. The PerVap membranes were tested at GTI and then MSU. PerVap effectively broke the azeotrope and prevented back-reaction of the product.

This list highlights innovations that surmounted technical barriers. It is essential to mitigate the impacts of these technical challenges to achieve the overall project goal of commercializing the CO₂-based DMC process in Alberta for abatement of CO₂ emissions.

8.2 Commercialization Plan

E3Tec's commercialization strategy *focuses primarily on licensing or strategic alliance with one or more industrial partners* as presented in Figure 8-1. In this case, the E3Tec Team will retain the IP and in turn grant licenses to outside parties on a royalty basis. During CCEMC Round 2, E3Tec will continue to evaluate both options for commercial approaches: licensing or strategic alliance. The decision process as to which approach to pursue is presented in Figure 8-1. This CCEMC project, along with other on-going projects, will provide stimulus financing for E3Tec to become a center of excellence supporting the Alberta process industry in energy intensification.

Details of the commercialization plan are presented in the report Technology Transfer Plan, submitted separately. The plan focuses on the following key elements:

- a. Demonstrating the competitive edge and CO₂ abatement potentials of the CO₂-based DMC process.
- b. Integration of the DMC process with CO₂ sources and/or with methanol or ethylene oxide production plants in Alberta.
- c. Infrastructure required for a large-scale production of DMC in Alberta for exporting to the market places in North America, Europe, and Asia.
- d. Technology milestones consist of: a) demonstration plant in Alberta during Round 2; b) commissioning revenue generating 20 kTA pre-commercial plant in 2021; and c) three commercial-scale 50 kTA DMC plants by 2024.
- e. E3Tec prepared necessary financial plan for developing the technology to commercialization level, followed by deployment of commercial plants.

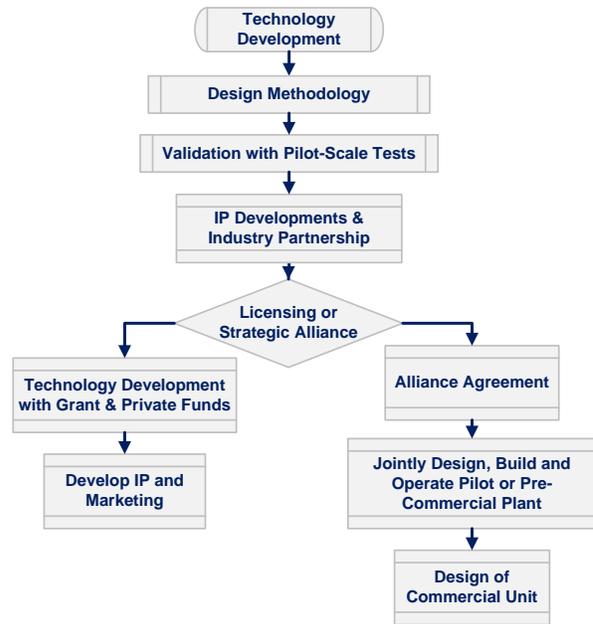


Figure 8-1: E3Tec commercialization plan.

E3Tec evaluated the challenges and opportunities of developing and deploying a new technology; and E3Tec is confident that the techno-economic merits of the CO₂-based DMC process will be favorably received by the industry. The commercialization plan is adequately structured for licensing the CO₂-based process.

The path forward for the commercialization strategy consists of: a) active interactions with relevant industrial organizations in North America, with the focus on Alberta; b) direct discussion with Methanex, Enerkem and ALPAC for integrating the DMC plant with methanol process; c) direct discussion with ethylene producers in Alberta for an integrated process of ethylene oxide-based DMC process; c) pursuing collaboration with research institutes such as ISTC in Illinois and others in Alberta; and d) active participation in CO₂ abatement workshops, conferences, and meeting in the USA and Canada. E3Tec received SBIR Phase II Grant, which will provide leveraging support to the Round 2. E3Tec plans to investment organizations on the basis of competitive technology edge of the CO₂-based DMC process. However, E3Tec being a small business with limited resources, Round 2 Grant is an essential next step for E3Tec to successfully commercialize the CO₂-based DMC process in Alberta.

9 COMMUNICATIONS PLAN

The primary customers of the CO₂ conversion to DMC process are chemical manufacturers and engineering companies. Therefore, the communication plan focuses on disseminating the technology merits in an effective manner to these companies with clearly defined path forward and advancing the TRL to commercialization. E3Tec's marketing media consists of web-site, project brochures, and direct communications with potential collaborators, partners or licensors. Coupled with this will be a record of technical presentations at professional and sponsored meetings and conferences and publications in trade journals. The availability of this material will provide prospective customers with a more substantive insight into the technical merits of the proposed route to DMC.

E3Tec team has a broad base of industrial contacts and the team has worked and negotiated collaborative projects directly with some of the largest petroleum and chemical companies. As a small business entity, making a business case to a large corporation is always a major challenge. However, E3Tec team members have pursued licensing of their intellectual property (IP) to such corporations in the past and are confident they can negotiate agreements that will add value to both parties. Interaction with research and academic organizations is also an effective means of reaching potential customers. The most effective method of making initial contacts with customers is through networking with individuals who are key to the decision-making process at their company. E3Tec is focusing on the chemical production and engineering companies in Alberta. Furthermore, E3Tec is communicating with manufacturers of methanol and ethylene oxide for an integrated process. Several relevant companies are invited to the Webinar-based workshop in June 2016 that will highlight our process for DMC and possibly, DMC with MEG. Personal contacts with businesses that support chemical manufacturing in Alberta have been initiated to make this presentation one of interest to these companies and each has received its formal invite.

E3Tec team maintains regular visibility at professional meetings, such as AIChE in the US and E3Tec intends to attend Canadian Chemical Engineering Conferences in the future for increasing visibility to Canadian organizations. Professional meetings and conferences, specifically AIChE Spring meetings, provide significant opportunities to interact with industry. E3Tec attended and presented conversion of CO₂ to value-added alkyl carbonates at: a) DOE/NETL Workshop on CO₂ capture technologies at Pittsburg, PA in 2015; and b) AIChE/DOE sponsored carbon management technology conference, Sugar Land, TX in 2015. With increased recognition of CO₂ capture and conversion at professional and sponsored meetings and workshops, E3Tec will expand its participation.

E3Tec's team routinely visits potential industry partners and licensors to explore ways to collaborate and for feedback on our project. During the Round 1 project E3Tec visited Alberta Innovates Technology Future to explore the possibility of hosting pilot plant demonstration in Round 2. E3Tec also visited Enerkem and Alberta Pacific (ALPAC) Forest Industries Inc. to evaluate the use of biomass-based methanol as feedstock in the DMC process. Recently, E3Tec visited Jacobs Consultancy in Chicago to explore possibility of its participation in Round 2 project from their office in Calgary, Alberta. E3Tec is planning to collaborate with Illinois Sustainability Technology Center (ISTC), Champaign, Illinois. ISTC is actively pursuing new technology for CO₂ capture in a joint collaboration with Linde using new solvent from BASF. The collaboration will focus on an integrated process of CO₂ capture and conversion to DMC, which is expected to have techno-economic merits over separate processes of capture and conversion.

In summary, E3Tec has taken effective steps of communicating the techno-economic merits of the CO₂-based DMC process with industry and research institutes. It provides a strong base for advancing the technology closer to the commercialization stage in Round 2.