

May 31, 2016

Captured-CO₂ Catalyst for the Production of Ethylene Oxide (C3-PEO)

Final Outcomes Report

Non-Confidential

Prepared for
Climate Change and Emissions Management Corporation (CCEMC)

P.O. Box 3197
Sherwood Park, Alberta
T8H 2T2
Canada

Telephone: (780) 417-1920
E-mail: info@ccemc.ca

CCEMC Project Number K130115
CCEMC Project Advisor: Mark Summers
CCEMC Funds Received: \$467,738

Prepared by
**Paul Mobley, Marty Lail, Jonathan Peters, Nandita Akunuri, and Josh
Hlebak**

RTI International
3040 E. Cornwallis Road
Research Triangle Park, NC 27709

RTI Administrative Point of Contact:
Brian Donovan
Office of Proposal, Project and Procurement Services
Telephone: (919) 316-3424
Fax: (919) 541-6515
E-mail: bdonovan@rti.org

RTI International is a registered trademark and a trade name of Research Triangle Institute.



CONTENTS

<u>Section</u>	<u>Page</u>
Acronyms and Abbreviations	vii
Executive Summary	1
Project Background.....	2
The Proposed Technology	2
The Conventional Process	4
Prior Work	4
Abstraction of Oxygen from CO ₂ by Tin(IV) Oxide Iron(III) Oxide (SnO ₂ Fe ₂ O ₃)–Based Catalysts	4
Development of Catalysts Performing at Lower Temperatures	7
Potential for Application to Ethylene Epoxidation.....	9
Initial Findings	9
Project Objectives	10
Methodology.....	11
Catalyst Preparation.....	11
Wet Deposition Method.....	11
Co-Precipitation Method.....	12
Catalyst Testing	12
Atmospheric Thermogravimetric Analyzer	12
High-Pressure Thermogravimetric Analyzer	13
Automated Microreactor	14
Safety	14
Testing Programs	15
Catalyst Performance Metrics.....	17
Gas Analysis	18
Catalyst Results.....	20
Microreactor Results Summary	23
Catalyst Support Modification.....	23
Catalyst Formula Optimization.....	26
Process Modeling.....	28
Model Architecture	29
Transport Mode.....	29

Cofeed Mode.....	32
Model Assumptions	34
Techno-economic Analysis.....	34
Techno-economic Analysis Architecture.....	34
Model Results	36
Process Sensitivity Analysis	38
Techno-economic Analysis.....	38
GHG LCA.....	41
LCA Results.....	46
GHG Benefit Analysis	47
Techno-economic Analysis and GHG Benefit Analysis for Current Catalyst Performance.....	48
Preliminary Design Package	49
GHG Emissions Reductions Status.....	50
Conclusions.....	50
Scientific Achievements	51
Next Steps	51
References.....	52
Disclaimer.....	54

LIST OF FIGURES

<u>Number</u>	<u>Page</u>
Figure 1. General reaction scheme for CO ₂ utilization approach for ethylene oxidation.	2
Figure 2. Conceptual schematic of the transport reactor process used by C3-PEO.....	3
Figure 3. Removal of oxygen from CO ₂ by using a reduced iron catalyst.	5
Figure 4. Percent weight change of catalyst during thermo-gravimetric analysis (bottom) and the corresponding temperature (top).	6
Figure 5. Labeling of (SnO ₂)(Fe ₂ O ₃)Al ₂ O ₃	7
Figure 6. Oxidation and reduction rates of weight changes for (SnO ₂) _{1.41} (Fe ₂ O ₃) (Al ₂ O ₃) _{1.82} and the improved catalyst.....	8
Figure 7. Technology roadmap for improving the catalytic production of EtO from ethylene and CO ₂	11
Figure 8. The TGA Q500 (TA Instruments) that was used to test catalyst performance.	12
Figure 9. HP-TGA for catalyst performance testing.....	13
Figure 10. The microreactor packed-bed system in a walk-in hood.....	15
Figure 11. The custom ethylene calibration at high concentrations.....	19
Figure 12. Ethylene (white) and EtO (red) overlapping spectra.	20
Figure 13. TGA testing of CO reduction and CO ₂ oxidation of improved catalyst up to 800°C at atmospheric pressure.	21
Figure 14. HP-TGA testing of CO ₂ oxidation on a catalyst at 575°C and up to 19.3 barg (280 psig).	22
Figure 15. TGA testing of CO reduction and CO ₂ oxidation of a catalyst up to 800°C at atmospheric pressure.....	23
Figure 16. Block flow diagram of the transport mode.....	31
Figure 17. Block flow diagram of the cofeed mode.....	33
Figure 18. Comparison of main reaction conversion required to achieve an IRR of 15% for the two cases.	37
Figure 19. Main reaction conversions for the three scenarios.	38
Figure 20. A tornado chart for process sensitivity analysis.	39
Figure 22. A block diagram of the conventional ethylene oxidation process from a GHG perspective.....	43
Figure 23. A block flow diagram of the C3-PEO process, transport mode from a GHG perspective.....	43
Figure 24. A block flow diagram of the C3-PEO process, cofeed mode from a GHG perspective.	44
Figure 25. IRR and GHG variations with different side reaction conversions.	48
Figure 26. Process flow diagram for the C3-PEO pilot system.	50

LIST OF TABLES

<u>Number</u>	<u>Page</u>
Table 1. Comparison of Data from the Literature Regarding Epoxidation Catalysts Used in O ₂ -Based versus CO ₂ -Based Processes	4
Table 2. Comparison of Weight Change due to Reduction by CO and Oxidation by CO ₂ for Conventional Ethylene Oxidation Catalyst (AgO) (Al ₂ O ₃), RTI's Gen 1 CO ₂ Utilization Catalyst (Fe ₂ O ₃)(SnO ₂) (Al ₂ O ₃), and an Early RTI Gen 2 CO ₂ Utilization Catalyst for Epoxidation AgO(Fe ₂ O ₃)(SnO ₂) (Al ₂ O ₃).....	9
Table 3. Design of Experiments Parameters for Testing	17
Table 4. Comparison of a Catalyst on Two Different Supports	25
Table 5. Comparison of Various Compositions of Catalyst	27
Table 6. Summary of Economic Assumptions Considered for the C3-PEO Process.....	34
Table 7. Summary of Product and Raw Material Cost Assumptions	35
Table 8. Capital Costs for the Two Cases.....	36
Table 9. Summary of Process Costs for the Three Scenarios.....	38
Table 11. Results of GHG Benefit Analysis for the Two Cases.....	46
Table 12. IRR and GHG Benefit of Three Top Performing Catalysts	49
Table 13. Cumulative Emissions Reductions from C3-PEO Market Penetration	49

ACRONYMS AND ABBREVIATIONS

^{18}O	heavy oxygen
ANOVA	analysis of variance
BPR	back pressure regulator
C^{18}O_2	produced ^{18}O -labeled CO
C3-PEO	Captured Carbon Dioxide (CO_2) Catalyst for the Production of Ethylene Oxide
CCEMC	Climate Change and Emissions Management Corporation
CO	carbon monoxide
CO_2	carbon dioxide
EBIT	earnings before interest and taxes
EtO	ethylene oxide
Fe_2O_3	iron(III) oxide
FTIR	Fourier transform infrared
GHG	greenhouse gas
H_2	hydrogen gas
H_2O	water
HP-TGA	high-pressure thermogravimetric analyzer
IRR	internal rate of return
LCA	life-cycle analysis
MMBtu	million British thermal units
MS	mass spectrometry
O_2	oxygen
OSHA	Occupational Safety and Health Administration
SNG	substitute natural gas
SnO_2	tin(IV) oxide
$\text{SnO}_2\text{Fe}_2\text{O}_3$	tin(IV) oxide iron(III) oxide
$\text{SnO}_2\text{Fe}_2\text{O}_3\text{Al}_2\text{O}_3$	tin(IV) oxide iron(III) oxide alumina
syngas	synthesis gas
TGA	thermogravimetric analysis
TGA-MS	thermogravimetric analysis–mass spectrometry
WHSV	weight hourly space velocity

EXECUTIVE SUMMARY

The Captured Carbon Dioxide (CO₂) Catalyst for the Production of Ethylene Oxide (C3-PEO), a technology being developed at RTI International, aims at producing ethylene oxide (EtO)—a high-value chemical—while consuming CO₂—a greenhouse gas (GHG). This technology is based on novel catalysts using the following key discoveries:

1. Abstraction of oxygen (O₂) from CO₂ by using the reduced mixed-metal oxide catalysts
2. Transfer of the abstracted O₂ from CO₂ to react with hydrocarbons to form desired products
3. Operation at temperatures that make these catalysts commercially practical to produce EtO.

The catalysts react with CO₂ and remove an oxygen atom to produce carbon monoxide (CO), which is an intermediate for several value-added chemicals (e.g., methanol, acetic acid, vinyl acetate, ethylene vinyl acetate) currently being produced in Alberta, Canada. Prior to this project, the catalysts had been developed for other CO₂ utilization applications such as char gasification and natural gas reforming. During char gasification, the oxygen taken from CO₂ is recombined with char or petcoke to make pure CO from petrochemical feedstock. During natural gas reforming, CO₂ is reformed with methane to create synthesis gas (syngas) with a mole ratio of 1:1 CO:hydrogen (H₂). The task at hand for the first part of this project was to formulate catalysts that can use the oxygen taken from CO₂ for selective oxidation of ethylene to make EtO.

During Round 1, RTI staff improved on its previous catalyst formulations and developed families of catalysts that can remove oxygen from CO₂ and transfer the oxygen to ethylene to make EtO. The catalyst families are based on metal oxide phases, which were found to be similar to iron in terms of reacting with CO₂, but are more selective than iron for ethylene epoxidation. Improvements on the production of EtO have been made by using promoters, probing the catalyst support to identify a correlation with support acidity and observing the impact of surface area on dispersion. Finally, the catalyst was evaluated to obtain catalyst conversion and selectivity data to develop an optimum process design. Towards the end of catalyst development, two impactful trends were identified that improved the catalyst performance with respect to selectivity and conversion. First, it was found that a support with lower surface area and overall lower acidity burned less of the EtO compared to higher surface area supports, which had been used for much of catalyst development. Second, the total amount of EtO produced was improved by increasing a metal oxide content, which resulted in a CO₂ utilization catalyst that shows practically the same activity towards EtO production as one that uses O₂.

EtO has been produced in a fixed-bed catalyst test reactor (between 5% and 8%), and was observed to be produced in the cofeed and transport modes. Bench-scale testing was completed to optimize the process conditions, including varying the space velocity to increase the mole conversions. In addition, the catalyst formulation was modified to increase the active catalyst on the surface of acidic supports. Catalyst improvements were shown to increase the EtO yield to greater than 7%, comparable to the yield from a conventional process using O₂. Experimental data were incorporated into a process model to determine which mode of operation was most economically viable for a complete process. The cofeed mode was found to be the most economical, given the current catalyst performance. A detailed analysis of the potential GHG reductions was completed for the modeled system and was found to reduce greater than 4.3 Mt of CO₂ emissions for each Mt of EtO produced. Finally, a preliminary design package was developed for testing the novel catalyst during a pilot-scale process in Round 2 of the Climate Change and Emissions Management Corporation (CCEMC) Grand Challenge.

PROJECT BACKGROUND

The Proposed Technology

A conventional hydrocarbon feedstock that is of particular interest to Alberta, Canada, is ethylene, which is used to make ethylene oxide (EtO). EtO is an important feedstock for the chemical industry and is used to make many useful products such as polyurethanes, polyols, glycols, nitriles, alcoholamines, and ethers. EtO is manufactured by several closely related industrial processes by major chemical makers worldwide (e.g., DOW Chemical, Japan Catalytic Company, Shell International Chemicals, Sumitomo Chemical, BASF, Scientific Design). EtO is particularly relevant to Alberta, Canada, because it is home to one of the world's largest ethylene production plants. A portion of this ethylene could be converted to valuable EtO by the proposed carbon dioxide (CO₂) utilization process.

The chemical methodology by which EtO is currently produced during a process called epoxidation, which is the partial oxidation of ethylene using oxygen (O₂). A silver-based catalyst is used, and either air or preferably O₂ is the oxidant. Ethylene epoxidation is performed at lower temperatures (220°C to 280°C) compared with other selective oxidation processes and at high pressure (10 to 30 bar).¹

RTI International has developed several catalysts that could be used in the temperature range required for alkene epoxidations. We have tested these catalyst formulations and shown them to be useful for multiple applications such as dry reforming of methane and char gasification using CO₂. We believed that these or similar catalysts can be used to produce EtO by reacting ethylene with CO₂ (rather than with O₂ during current state-of-art processes). The general reaction scheme using the catalyst as a chemical-looping agent is shown in **Figure 1**.

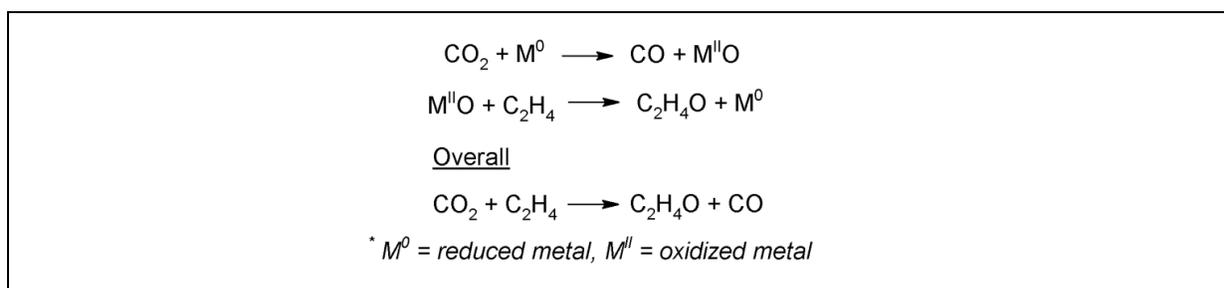


Figure 1. General reaction scheme for CO₂ utilization approach for ethylene oxidation.

When considering the thermal stability of ethylene or EtO, both of these are highly unstable at high temperatures (i.e., greater than 325°C). Our proposed transport reactor process for the Captured CO₂ Catalyst for the Production of Ethylene Oxide (C3-PEO) is a two-step

process detailed in **Figure 2**. During Step 1, an oxygen atom is abstracted from CO_2 , thereby producing carbon monoxide (CO) in the reducing zone of the reactor. During Step 2, this highly reactive oxygen atom reacts with ethylene to produce EtO in the oxidizing zone of the reactor as shown in Figure 2. One reason for this arrangement is the inherent reactivity between CO_2 and EtO, which could lead to the formation of undesirable ethylene carbonate in a cofeed system. There is uncertainty regarding whether this inherent activity is a real concern because this will depend ultimately on the process conditions, specifically on the partial pressure of CO_2 that would be used during a cofeed process. If the partial pressure is low enough, then the ethylene carbonate formation might be avoided. If so, a cofeed system may be advantageous to create a simpler process arrangement, so this possibility was investigated in the project. Another reason for having separate reaction zones is that oxygen abstraction from CO_2 typically requires higher temperature than ethylene oxidation, which is a relatively low temperature process.

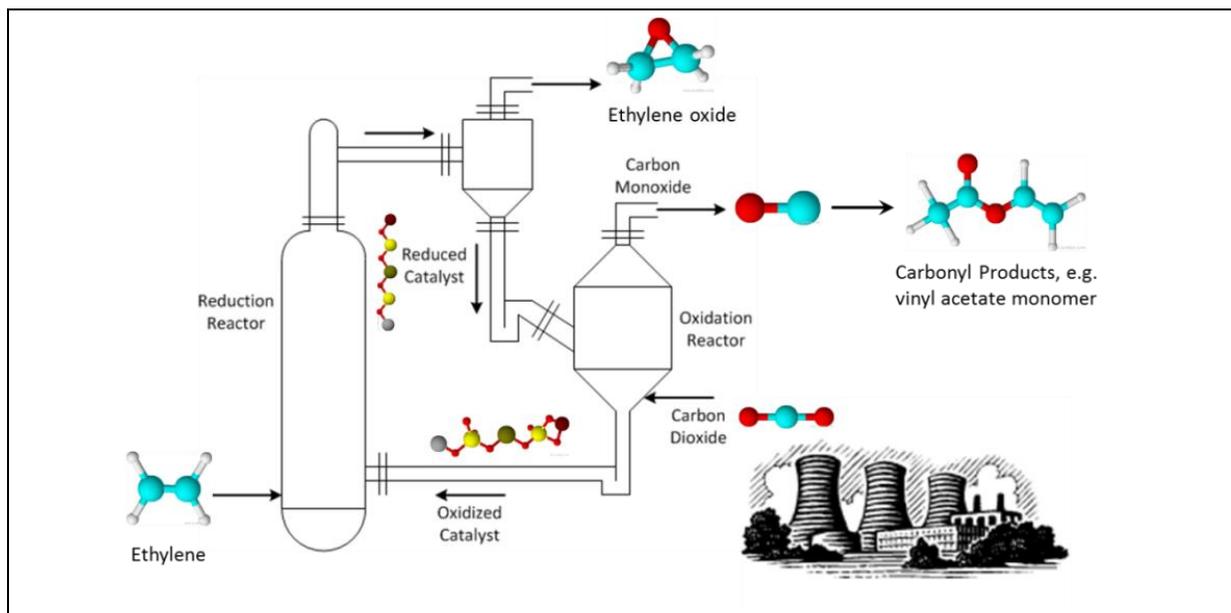


Figure 2. Conceptual schematic of the transport reactor process used by C3-PEO.

The proposed EtO process has a concentrated CO by-product stream, which could be used to manufacture many products. Some of these products include methanol, dimethyl ether, acetic acid, acetic anhydride, vinyl acetate, styrene, terephthalic acid, formic acid, *n*-butanal, 2-methylpropanal, acrylic acids, neopentylacids, propanoic acid, dimethyl formamide, and Fischer-Tropsch hydrocarbons.² Therefore, the two marketable product streams from the proposed process are EtO and CO, which are both valuable intermediates for the established Alberta petrochemical industry.

The Conventional Process

The conventional process for making EtO is performed through epoxidation of ethylene by using air or O₂ separated from air at moderate temperatures (approximately 275°C). Catalysts are primarily silver on α -alumina with common promoters of alkali and chloride salts. Typical single-pass ethylene conversion is approximately 13%, with a 42% selectivity to EtO, and the remainder to the competing side reaction of combustion of either the ethylene feed or produced EtO. **Table 1** presents the data reported in the open literature for epoxidation catalysts used in an O₂-based process compared to RTI's CO₂-based process.^{1,3}

Table 1. Comparison of Data from the Literature Regarding Epoxidation Catalysts Used in O₂-Based versus CO₂-Based Processes

Catalyst	Reaction Temperature (°C)	Ethylene Conversion (%)	EtO Selectivity (%)	EtO Yield (%)
Ag- α -Al ₂ O ₃	275	3.6	77.4	2.8
Ag-SiO ₂	275	4.4	86.4	3.8
Ag-TiO ₂	275	2.5	69.7	1.8
Re-Ag-Al ₂ O ₃	265	13.5	42.0	5.67
RTI-CO ₂	350	25.0	34.0	8.5

Note: Al₂O₃ = alumina; SiO₂ = silica; TiO₂ = titania.

Prior Work

Abstraction of Oxygen from CO₂ by Tin(IV) Oxide Iron(III) Oxide (SnO₂Fe₂O₃)–Based Catalysts

Since 2010, RTI staff have been investigating the processes in which catalysts are used to convert CO₂ into value-added chemicals. The sheer amount of CO₂ that must be consumed to significantly reduce greenhouse gas (GHG) emissions has forced us to focus on the production of fuels and high-volume commodity chemicals. These CO₂ utilization processes must be economically viable to facilitate their implementation. In this arena, we have developed several catalyst formulations that can convert CO₂ and hydrogen (H₂) into substitute natural gas (SNG) in a circulating fluidized-bed reactor with a capital cost that is at least 40% lower than current commercial processes. However, given low natural gas prices in North America because of shale gas plays, many commercial opportunities do not exist for this technology. The second major application of this platform technology, which we have developed through funding from the U.S. Department of Energy, National Energy Technology Laboratory (DE-FE00004329), was to gasify solid carbonaceous feedstocks such as coal, biomass, petcoke, waste, or a suitable mixture thereof, with oxygen abstracted from CO₂. Both of these applications have the potential to easily reduce GHG emissions by at least 1 Mt annually. Our CO₂ utilization technology has focused on

conventional heterogeneous catalysts that are used ubiquitously in gasification and petroleum refining industries. These industries manufacture products that are in high demand and are sustainable for the foreseeable future. As such, the conventional heterogeneous catalysts align well with the thriving hydrocarbon industries throughout the world, in particular those in Alberta, Canada. They can be used in conventional fixed or fluidized-bed reactors.

In the following reverse-Boudouard reaction (Equation 1), the conversion of CO₂ and carbon to CO becomes thermodynamically favored beginning at approximately 700°C, but the conversion is low, below approximately 900°C.



The catalyst increases the rate of reaction at lower temperature. The mixed-metal oxide with tin, iron, and alumina (SnO₂[Fe₂O₃]Al₂O₃) material was shown to increase the rate of the reverse Boudouard reaction by 30 times compared to iron without tin. We performed additional work to show conclusively that the oxygen extracted from CO₂ by the catalyst materials results in the transfer of the extracted oxygen to an external carbon source and that the transfer involves the catalyst's surface and lattice oxygen. We characterized the removal of oxygen from CO₂ (see **Figure 3**). We also studied the reaction by using isotopically labeled C¹⁸O₂, thermogravimetric analysis, and mass spectrometry (MS).

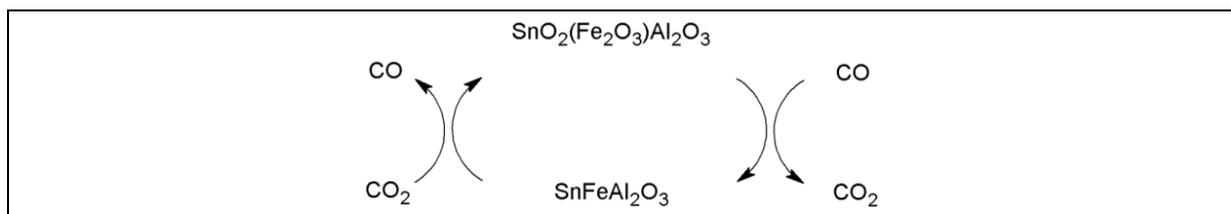


Figure 3. Removal of oxygen from CO₂ by using a reduced iron catalyst.

Tin-oxide phases that are known to have temperature-induced oxygen mobility compose the mixed-metal oxides containing tin.⁴ We performed a series of experiments with a focus on understanding how various phases in the catalyst reduce CO₂. The results yield the conclusions presented in **Figure 4**.

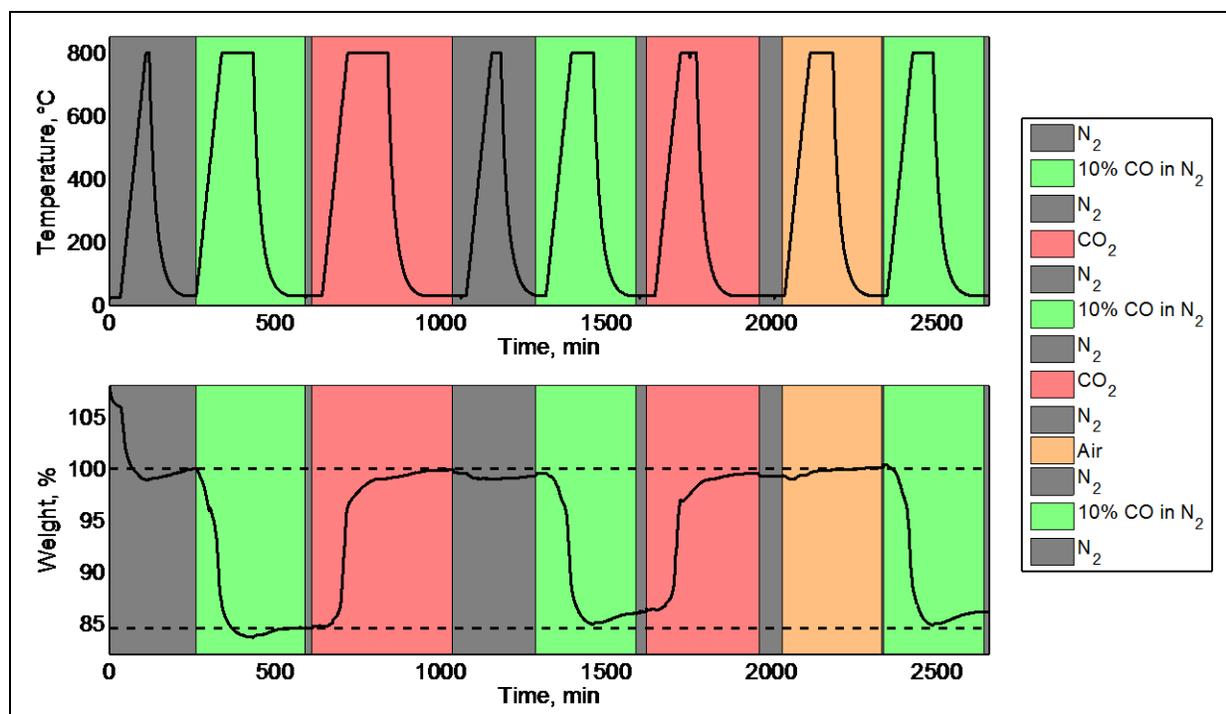


Figure 4. Percent weight change of catalyst during thermo-gravimetric analysis (bottom) and the corresponding temperature (top).

Weight changes observed in the absence of a reductant (grey) are most likely because of desorption of adventitious adsorbates (i.e., water [H₂O], CO₂, possibly O₂) from the surface of the catalyst. In the presence of a reductant (green), both tin(IV) oxide (SnO₂) and iron(III) oxide (Fe₂O₃) sites are reduced when heated to 800°C, but the alumina (Al₂O₃) sites do not appear to be reduced. The observed weight loss (15.5%) agrees well with the amount of oxygen calculated to be associated with SnO₂ and Fe₂O₃ (16.7%). The weight is regained in the presence of an oxidant (red), indicating that the oxygen transfer is reversible. The repeated reduction and oxidation steps indicate that the process is reproducible. Lastly, the sample is treated with air (orange) after the catalyst has been oxidized with CO₂, and there is little observable change in weight during this event, signifying that the catalyst is effectively oxidized by CO₂.

We conducted MS experiments with isotopically labeled C¹⁸O₂. The study reveals details about the fate of the oxygen abstracted from CO₂ and the capability of the catalyst to transfer metal-oxide-associated oxygen to external carbon sources. First, we reduced the catalyst in CO. Next, we introduced isotopically labeled C¹⁸O₂, removed heavy oxygen (¹⁸O), and produced ¹⁸O-labeled CO (C¹⁸O) as the primary product. This process labeled the reduced catalyst with ¹⁸O, and the labeled catalyst could then be reduced again with CO with the resulting production of C¹⁶O¹⁸O as shown in **Figure 5**. In addition, we also observed CO₂, C¹⁸O, and C¹⁸O₂ during this

step. This result of this study indicates that oxygen is highly mobile within the catalyst and is able to move between species.

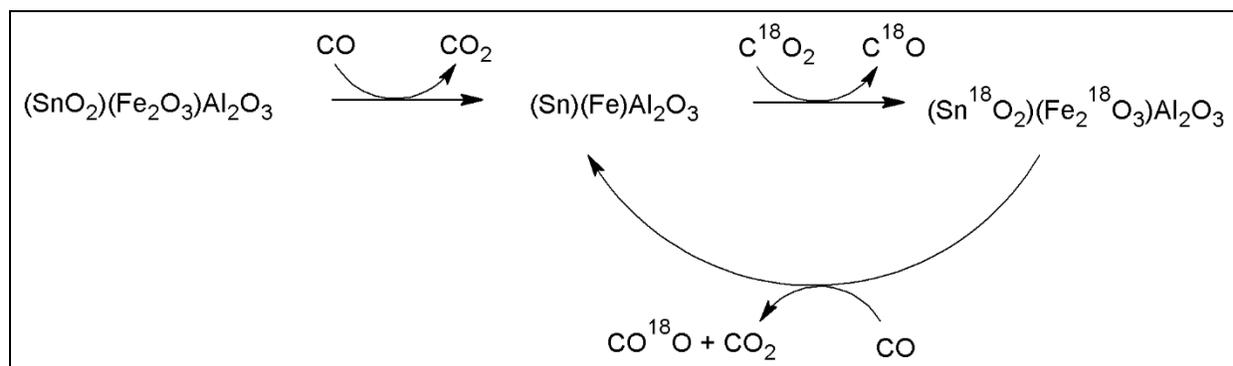


Figure 5. Labeling of $(\text{SnO}_2)(\text{Fe}_2\text{O}_3)\text{Al}_2\text{O}_3$

In summary, the mechanistic investigation of the CO_2 utilization catalyst $(\text{SnO}_2)_{1.41}(\text{Fe}_2\text{O}_3)(\text{Al}_2\text{O}_3)_{1.82}$ confirmed that the reduced catalyst abstracts oxygen from CO_2 and transfers it to another carbon. Thermogravimetric evidence suggests that oxygen from Fe_2O_3 and SnO_2 is mobile and can be removed from the catalyst by reductants. Side reactions involving rapid exchange of oxygen by the catalyst easily occur, resulting in overall high mobility of oxygen between the catalyst and CO_2 .

Development of Catalysts Performing at Lower Temperatures

Building on the promising performance of $\text{SnO}_2\text{Fe}_2\text{O}_3$ -based catalysts, we investigated the potential for using this and similar mixed-metal oxide materials for other CO_2 utilization applications. As an oxygen carrier, the catalyst could be used for the selective oxidation reactions of hydrocarbons, such as alkene epoxidations.⁵

Previous studies on $(\text{SnO}_2)_{1.41}(\text{Fe}_2\text{O}_3)(\text{Al}_2\text{O}_3)_{1.82}$ indicated that it required a high temperature (approximately 700°C) to reduce CO_2 . To effectively make reactive oxidation products such as EtO, the current formulation would need to operate in a CO_2 utilization process with a large temperature swing between a catalyst reducing zone and a catalyst oxidizing zone. It seemed likely that a more active catalyst would be needed that can strip oxygen from CO_2 and oxidize hydrocarbons, such as ethylene, at lower reaction temperatures. To accomplish this, we prepared an alternative catalyst. We then used thermogravimetric analysis–mass spectrometry (TGA-MS) to characterize these catalysts, and then compared them to determine whether an improvement could be made with respect to the following:

- Lower reduction temperature compared with $(\text{SnO}_2)_{1.41}(\text{Fe}_2\text{O}_3)(\text{Al}_2\text{O}_3)_{1.82}$
- Ability to abstract oxygen from CO_2 , preferably at a lower temperature.

The results of TGA-MS testing are shown in **Figure 6** in terms of the rates of weight change versus temperature. The negative values correspond to weight loss during reduction of the catalyst with CO, where oxygen is removed from the catalyst, whereas the positive values correspond to weight gains when the catalyst removes oxygen from CO₂ (verified by MS). We performed these experiments by first degassing, then reducing the mixed-metal oxide catalysts with 20% CO in nitrogen, and then with a treatment of the reduced catalyst with 100% of CO₂. We ramped the temperature from ambient to 800°C for the (SnO₂)_{1.41}(Fe₂O₃) (Al₂O₃)_{1.82} catalyst and from ambient to 450°C for the alternative catalyst. The temperature ranges were previously identified by using temperature-programmed reduction with hydrogen.

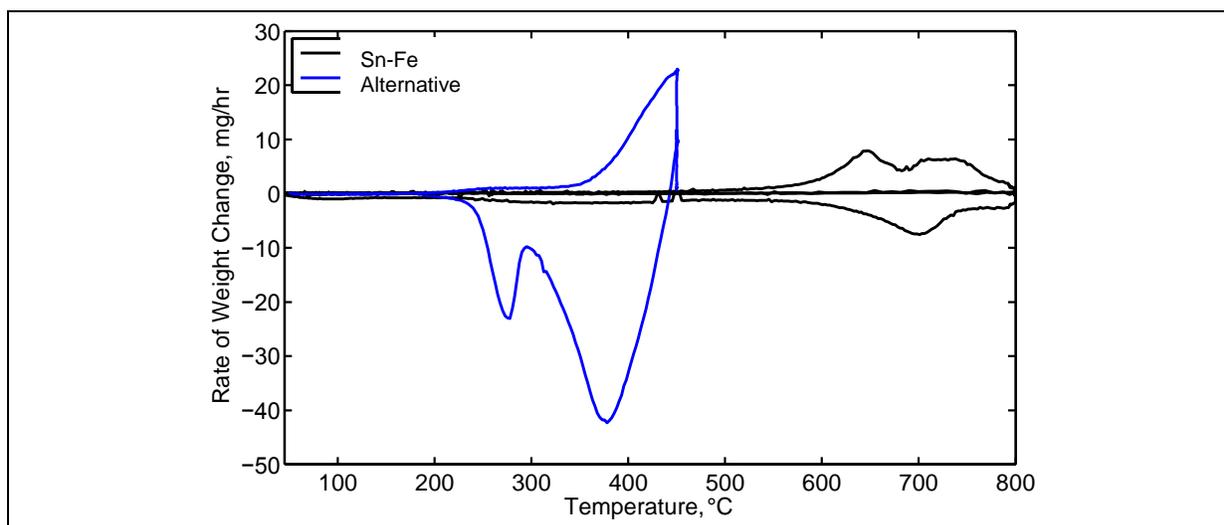


Figure 6. Oxidation and reduction rates of weight changes for (SnO₂)_{1.41}(Fe₂O₃) (Al₂O₃)_{1.82} and the improved catalyst.

When comparing these two catalysts, we clearly see a significant improvement. The (SnO₂)_{1.41}(Fe₂O₃) (Al₂O₃)_{1.82} catalyst is reduced starting at greater than 500°C, whereas the improved catalyst is reducible at approximately 250°C, with a second reduction at approximately 375°C. There are two distinct types of reducible sites in the improved catalyst. In the (SnO₂)_{1.41}(Fe₂O₃) (Al₂O₃)_{1.82} catalyst, there is primarily one type of reducible sites, occurring at almost 600°C. The major difference is observed when the reduced catalysts are oxidized with CO₂. The improved catalyst removes oxygen rapidly from CO₂ at 400°C, whereas (SnO₂)_{1.41}(Fe₂O₃) (Al₂O₃)_{1.82} has two peaks at 600°C and 700°C. The ability to remove oxygen from CO₂ at a much lower temperature shows a promising direction for further development of the catalyst for ethylene epoxidation at lower temperature.

Potential for Application to Ethylene Epoxidation

RTI has patented the previously mentioned CO₂ utilization technologies, which are based on catalysts that catalyze the conversion of CO₂ into CO. Catalysts of this type have the potential to combine the abstracted O₂ with ethylene to selectively form EtO on a catalyst surface. The (SnO₂)_{1.41}(Fe₂O₃) (Al₂O₃)_{1.82} material catalyzes the transfer of the extracted oxygen to a solid carbonaceous feedstock (e.g., coal, biomass, petcoke) through a reverse-Boudouard-type reaction to produce CO [CO₂ + C = 2CO].⁷ The second catalyst abstracts an oxygen atom from CO₂ and transfers it to methane to form syngas (a CO and H₂ mixture) through the dry reforming reaction at fairly moderate temperatures.

Initial Findings

Early in the project, the application of these catalysts for ethylene epoxidation was studied. Without modification, the catalysts are not selective for ethylene epoxidation, and a new metal oxide phase must be added to the catalyst to achieve this selectivity. The new phase must be active for the addition of oxygen across the carbon-carbon π -bond of ethylene. The obvious phase to consider first for this application is silver oxide (Ag₂O) because it is used commercially and is known to be active for ethylene epoxidation.⁸ As Step 1 in our catalyst development, we tested the addition of Ag₂O to our iron-tin catalyst previously mentioned.⁷ We doped the (Fe₂O₃)(SnO₂)_{1.41}(Al₂O₃)_{1.82} catalyst with 15% Ag₂O. Our doping procedure was to simply take calcined (Fe₂O₃)(SnO₂)_{1.41}(Al₂O₃)_{1.82} and to impregnate it with silver nitrate salt, followed by calcination at 450°C. To distinguish the activity of Ag₂O from the remainder of the mixed-metal oxide, we prepared, and later tested, a catalyst of 15% silver on γ -alumina (typical commercial formulation). **Table 2** compares the behavior of the three catalysts by using thermogravimetric analysis (TGA).

Table 2. Comparison of Weight Change due to Reduction by CO and Oxidation by CO₂ for Conventional Ethylene Oxidation Catalyst (AgO) (Al₂O₃), RTI's Gen 1 CO₂ Utilization Catalyst (Fe₂O₃)(SnO₂) (Al₂O₃), and an Early RTI Gen 2 CO₂ Utilization Catalyst for Epoxidation AgO(Fe₂O₃)(SnO₂) (Al₂O₃)

Catalyst	% Weight Loss by CO Reduction	Temperature of Peak Reduction (°C)	% Weight Gain by CO ₂ Oxidation	Temperature of Peak Oxidation (°C)
(Ag ₂ O) (Al ₂ O ₃)	0.60	700	1.30	700
(Fe ₂ O ₃)(SnO ₂) (Al ₂ O ₃)	9.16	600	9.85	700
Ag ₂ O(Fe ₂ O ₃)(SnO ₂) (Al ₂ O ₃)	5.99	500	7.35	600

The data in Table 2 compare the weight loss or weight gain observed for each catalyst under CO reducing (weight loss) and CO₂ oxidizing (weight gain) conditions. The commercial catalyst analog, (Ag₂O) (Al₂O₃), is reduced by CO near 700°C with a low capacity of available oxygen and is reoxidized by CO₂ to a small extent. The CO₂ utilization catalyst (Fe₂O₃)(SnO₂) (Al₂O₃) is substantially reduced by CO near 600°C and is oxidized by CO₂ near 700°C with an appreciable capacity. The doped Ag₂O(Fe₂O₃)(SnO₂) (Al₂O₃) catalyst is reduced at lower temperatures near 500°C and is oxidized by CO₂ near 600°C, also with approximately 5.5 times higher capacity than Ag₂O alone. This finding reveals that the addition of silver does not inhibit the CO₂ utilization ability of the tin-iron formulation and that a CO₂ utilization catalyst can be modified for ethylene epoxidation without the loss of the CO₂ utilization functionality. The primary focus of our work in Round 1 was to develop catalysts with the two metal oxide phases that work together.

We further tested Ag₂O(Fe₂O₃)(SnO₂) (Al₂O₃) to determine whether it was selective for ethylene epoxidation. We found that it was not selective for ethylene epoxidation and never observed the production of EtO when using this formulation. With this result, we revisited our catalyst formulation strategy and developed other CO₂ utilization catalysts that are selective for ethylene epoxidation by using different metal-oxide phases. The Catalyst Results section of this report describes these efforts.

Project Objectives

RTI staff have developed a Research Plan that will effectively build on our extensive knowledge of CO₂ and ethylene reactions and of catalysis chemistry to complete a pre-commercial demonstration of this novel catalytic technology. The Research Plan is divided into three rounds. The project objectives in Round 1 focused heavily on the improvement of the current catalyst formulation. The improvement criteria include conversion and selectivity for EtO, GHG reduction performance, and process economics. To support this optimization process, additional Round 1 activities included developing necessary data for process design, conducting a preliminary economic analysis and preliminary life-cycle analysis (LCA). During Round 2, the key objective will be to successfully scale-up catalyst production and process testing equipment to enable pilot plant testing of the technology. In addition, the catalyst formulation will be further optimized for increased EtO yield along with long-term stability of the catalyst. At the current stage of development, a catalyst has been developed that is selective for EtO by using only CO₂ and ethylene as feedstocks with EtO yields very comparable to conventional EtO catalysts used in air or O₂-based processes. However, catalyst degradation pathways have not been studied. We will use the knowledge and data collected during Round 2 to reduce the technical and design

assumptions employed in the techno-economic analysis and the LCA. During Round 3, the goal is to complete a pre-commercial demonstration that would reduce the technical and economic risks associated with the technology to allow for successful commercial deployment. The roadmap for this Research Plan is shown in **Figure 7**.

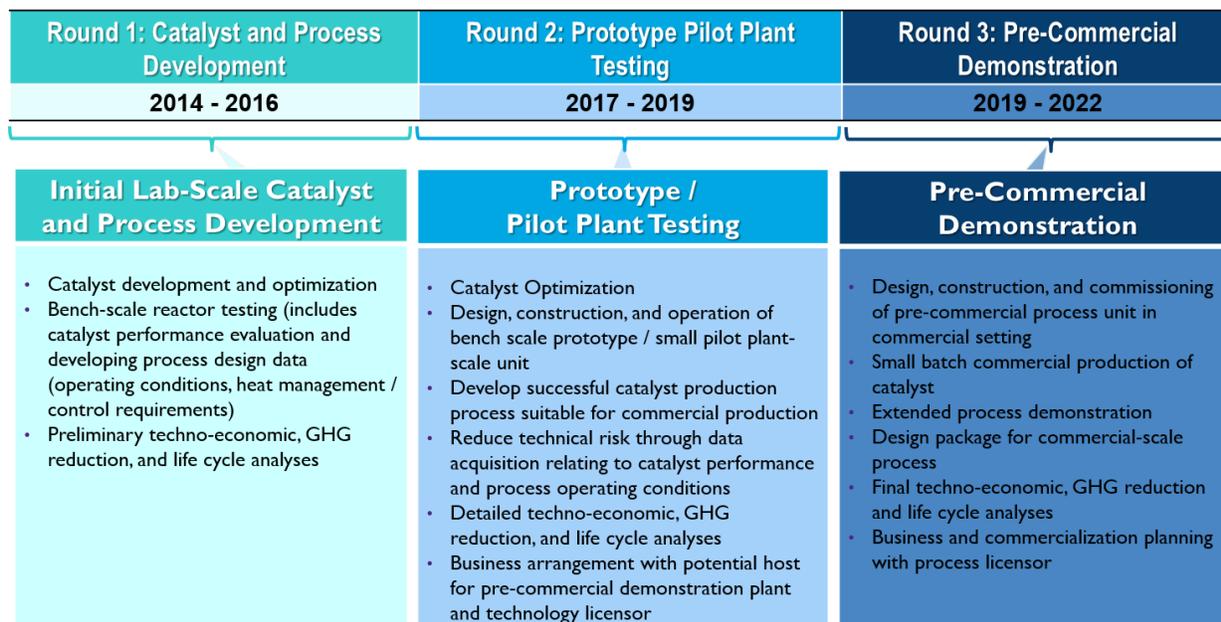


Figure 7. Technology roadmap for improving the catalytic production of EtO from ethylene and CO₂.

METHODOLOGY

Catalyst Preparation

We used two methods for preparing the catalysts: wet deposition and co-precipitation. Each preparation method has merit. Wet deposition has the merit of concentrating all of the active catalyst phase on the surface of the support, but it does not have as many phase interfaces, which could be important to the catalysis. Co-precipitation has more phase interfaces, but it could lead to some of the catalyst phases being in the bulk of the material and not exposed to the surface where gas–solid interactions take place. The two methods are further described in the following subsections of this report.

Wet Deposition Method

Wet deposition is a catalyst preparation method during which the surfaces of inert support materials are doped with small amounts of transition-metals. The transition-metals are deposited on the surface of the support as decomposable inorganic salts. After deposition, the inorganic salts are calcined at a high temperature (between 300°C and 550°C) to make the

transition-metal oxide, or mixed-metal oxides, when more than one transition metal is used. An advantage of using a wet deposition preparation is that the active catalyst materials are concentrated at the surface of the catalyst rather than elsewhere in the bulk. In a round-bottomed flask with a ground-glass neck, metal salt was dissolved in H₂O. We used a gravimetric balance to weigh out support, and then the support was added to the round-bottomed flask containing the salt solution. H₂O was added to completely cover all solids. We used rotovary evaporation to dry the solution. When the sample was air dried, we performed calcination by heating the solid at high temperature to obtain a calcined powder.

Co-Precipitation Method

Co-precipitation is a catalyst preparation method during which an aqueous solution of metal salts is created, typically containing more than one metal salt, followed by adding an aqueous base to the solution, which raises the pH of the aqueous solution, resulting in precipitation of the metal species in solution as insoluble metal hydroxides. The species often precipitate together and form solids that are filtered from the solution, are dried, and then are calcined to convert the metal hydroxides into the corresponding metal oxides. We used this method to prepare several catalysts. In a beaker, we added two metal salts, and then dissolved these in H₂O. With a Pasteur pipette, we added ammonium hydroxide to the solution until the pH was greater than 8. Next, we filtered and washed the solid precipitate thoroughly. After the solid precipitate was air dried, we further dried and calcined it to obtain a calcined powder.

Catalyst Testing

We tested the catalysts in three systems to evaluate their ability to abstract an oxygen from CO₂ and to transfer an oxygen to ethylene to produce EtO. The three systems used for testing included an atmospheric thermogravimetric analyzer, a high-pressure thermogravimetric analyzer (HP-TGA), and an automated microreactor. Each system is described further in the following subsections of this report.

Atmospheric Thermogravimetric Analyzer

A TA Instruments TGA Q500 thermogravimetric analyzer is a tool used to accurately



Figure 8. The TGA Q500 (TA Instruments) that was used to test catalyst performance.

investigate the effects of different process variables (e.g., temperature, feed composition) on adsorbate (e.g., CO₂) loading capacity, uptake rate, and desorption rate in new sorbent and catalyst materials (see **Figure 8**).

High-Pressure Thermogravimetric Analyzer

The HP-TGA is a tool used to accurately investigate the effects of different process variables (e.g., temperature, pressure, feed composition) on adsorbate (e.g., CO₂) loading capacity, uptake rate, and desorption rate in new sorbent and catalyst materials (see **Figure 9**). This laboratory system is also used to conduct detailed kinetic and equilibrium studies as well as cyclic (regenerability) and long-term performance stability studies. This system is fully automated for unattended, continuous operation. The heart of this HP-TGA reactor system is a Cahn microbalance that accurately measures the weight change of the catalyst or sorbent sample in reactive or nonreactive, dry or humidified, single or multicomponent gas flows at high temperatures and high pressures. We used this system during Round 1 to provide detailed weight change data to evaluate the material performance between approximately 300°C and 600°C and 10 to 30 bar.



Figure 9. HP-TGA for catalyst performance testing.

Automated Microreactor

We selected an automated microreactor to evaluate catalyst performance for conversion of CO₂ and ethylene to EtO. The microreactor system has the ability to run various reaction conditions unattended and is a good way to screen new catalyst formulations.

Safety

The microreactor packed-bed system has been designed to operate in an unattended manner with limited user involvement. Such automated systems require adequate safety measures because the reaction testing involves the use of electrical heaters, high-pressure gases, asphyxiating and poisonous gases, and potentially hazardous chemical materials. The system has been designed and equipped with software temperature limits, hardware temperature limits, three pressure relief valves, and fail-closed MFCs to mitigate the adverse effects of unexpected incidents such as run-away temperature and over-pressurizing the system.

Experiments have been conducted by using CO (a toxic gas) as a reducing feed gas with a maximum flow rate of approximately 100 sccm. The desired product, EtO, is a toxic gas and is expected to be produced at no more than 10% in the effluent amounting to a maximum of 50 sccm. Because EtO has an Occupational Safety and Health Administration (OSHA) time-weighted average exposure limit of 1 ppm for an 8-hour day, the microreactor system operates fully enclosed inside a walk-in fume hood (see **Figure 10**), which eliminates any possible exposure of EtO and CO from fugitive leaks. After a test, the system is purged for 30 minutes to ensure that all harmful gases are removed from the system. In addition, the hot box is purged with nitrogen to ensure that there is no buildup of EtO and CO from a leak.

Testing Programs

The catalyst screening experiment test programs consists of multiple cycles. Each cycle follows five fixed steps (i.e., feed test, analytical purge, oxidation, purge, and reduction), which are each described in the following paragraphs.

Step 1. Feed test—This step involves bypassing the reactor and purging the analytical system downstream with the feed gas containing a known concentration of oxidant (CO_2 or air). This step allows for verification of the exact composition of the feed gas prior to each experiment. In addition, this provides a check on the calibration of the gas analyzer and MFCs. To avoid exposing the catalyst to oxidation gas prior to the oxidation step, this step was achieved in two stages. The microreactor is first purged with nitrogen, and then placed on bypass. During the next stage, oxidation gas mixture is fed to the system to allow for a steady composition to be recorded in the analyzer. The oxidation gas mixture is fed until a steady composition is recorded for 5 minutes.

Step 2. Analytical purge—With the six-port valve in the bypass mode, the feed gas mixture is switched to nitrogen to purge off the oxidizing gas from the microreactor system and analytics. Step 2 continues for a duration of 5 minutes until the gas analyzers indicate the absence of active feed gas constituents.

Step 3. Oxidation—This step ensures that the catalyst surface is fully oxidized and that any carbon deposits are burned off that may have formed during the previous reaction. Nitrogen is directed to the microreactor, which is then heated to the oxidation temperature (between 300°C and 500°C). Then, the oxidant is directed to the microreactor catalyst bed. The duration for this step is based on the effluent CO and CO_2 concentration. Step 3 continues until CO and CO_2 are



Figure 10. The microreactor packed-bed system in a walk-in hood.

no longer produced, indicating that the catalyst is fully oxidized. Then, the microreactor is cooled to the reducing temperature (between 250°C and 450°C) while under oxidizing gas.

Step 4. Purge—During this step, the microreactor is purged with nitrogen. Then, the microreactor is bypassed and the desired reducing gas mixture is fed to the system to purge the reactor downstream lines, condenser, and analytical system, which allows for the reducing gas mixture to be recorded in the analyzer. The reducing gas mixture is fed until a steady composition is recorded for 5 minutes.

Step 5. Reduction—This step begins by directing the reducing gas mixture (ethylene or CO) directly to the microreactor. The time allowed for Step 5 is 45 minutes or until the catalyst is fully reduced. When this step has ended, the microreactor system is purged with nitrogen.

Depending on the Test Plan, Steps 1 through 5 are repeated to measure the effects of changing conditions as a function of the cycle number. We developed two types of test modes (i.e., transfer and cofeed) to simulate conditions of two different reactor types. These two test modes are further described as follows:

Transport mode—This Test Plan simulates a transport reactor by first oxidizing the catalyst surface with CO₂ or air during Step 3 (Oxidation). Then, ethylene is fed to the reactor during Step 5 (Reduction) to react with the oxidized catalyst surface to form EtO. This Test Plan completes one transport cycle following Steps 1 through 5 as previously mentioned.

Cofeed mode—This Test Plan follows a cofeed fixed-bed reactor setup in which both CO₂ and ethylene are fed to the reactor during Step 5 (Reduction) previously mentioned. In this test mode, the CO₂ replenishes the catalyst surface with oxygen, and the ethylene reacts with the oxygen forming EtO.

Although the proposed technology is represented by testing in transport mode, we also investigated the cofeed mode because this may allow for a simpler process arrangement. It was believed that this arrangement would not be possible because CO₂ and EtO may form into ethylene carbonate. In addition, process conditions that would allow for both the abstraction of oxygen from CO₂ and the epoxidation of ethylene may not exist. However, as discussed in the Results section of this report, EtO was found to be produced for various catalysts in cofeed mode.

We used the microreactor to screen 28 of the developed catalyst formulations in more than 460 cycles for EtO production under a range of test conditions, each in both cofeed and

transport test modes. For these tests, we diluted 5 g of catalyst in silicon carbide to fill a 15-mL heated reactor zone. The feed gas volume was between 100 and 600 sccm for each test condition at 19 barg, with varying amounts of feed gas compositions and reactor temperatures. We used design of experiments and response surface methods to vary the possible parameters that may affect the production of EtO in the minimal number of experiments. This approach also allowed us to investigate any two-factor interactions that may exist between the parameters that would not be found while varying each one at a time. We used a central composite design to vary CO₂ partial pressure, ethylene partial pressure, and temperature. The ranges investigated of the parameters are summarized in **Table 3**. During each experiment, we repeated the center points five times to increase the statistical power of the results and investigate any catalyst deactivation during the course of each testing cycle.

Table 3. Design of Experiments Parameters for Testing

Varied Parameter	Range
Temperature (°C)	300–450
CO ₂ partial pressure (bar)	5–10
Ethylene partial pressure (bar)	2.5–10

Catalyst Performance Metrics

The desired elementary reaction for formation of EtO from ethylene is shown as follows (Equation 2):



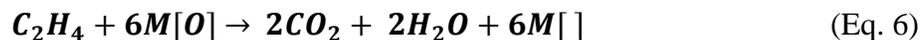
Where M[O] represents an oxidized metal catalyst site, and M[] represents a reduced metal catalyst site. We compared each reaction by using the three reaction metrics shown in the following equations: ethylene conversion (Equation 3), EtO yield (Equation 4), and EtO selectivity (Equation 5), which are presented as follows:

$$X_{Et} = \frac{\dot{n}_{Et,in} - \dot{n}_{Et,out}}{\dot{n}_{Et,in}} \quad (\text{Eq. 3})$$

$$Y_{EtO} = \frac{\dot{n}_{EtO,out}}{\dot{n}_{Et,in}} \quad (\text{Eq. 4})$$

$$S_{EtO} = \frac{\dot{n}_{EtO,out}}{\dot{n}_{Et,in} - \dot{n}_{Et,out}} \quad (\text{Eq. 5})$$

The major competing side reaction to EtO formation (i.e., complete oxidation of ethylene) is undesired and is shown as follows (Equation 6).



For each test, we quantified the reaction H₂O yield and H₂O selectivity to compare catalyst activity for the undesired reaction. Because the stoichiometric ratio of ethylene to H₂O in the undesired reaction is 1:2, the H₂O yield is defined in Equation 7 and the selectivity is presented as Equation 8 as follows:

$$Y_{H_2O} = \frac{\dot{n}_{H_2O,out}}{\dot{n}_{Et,in}} \times \frac{1}{2} \quad (\text{Eq. 7})$$

$$S_{H_2O} = \frac{\dot{n}_{H_2O,out}}{\dot{n}_{Et,in} - \dot{n}_{Et,out}} \times \frac{1}{2} \quad (\text{Eq. 8})$$

Gas Analysis

An FTIR multigas analyzer (MKS Instruments) is used to analyze the gas effluent stream from the reactor. The effluent is diluted by adding 750 sccm of nitrogen before the analyzer to allow for enough flow to purge the sample cell and to not saturate the detector. We developed a method to quantify the effluent composition of the following components: CO, CO₂, ethylene, EtO, and H₂O. Calibration data for CO, CO₂, EtO, and H₂O were available in the MKS spectra library to develop calibration curves for each component within the expected volume percent ranges and verified with known gas mixtures. We developed a custom calibration curve for the ethylene feed at high concentrations (see **Figure 11**).

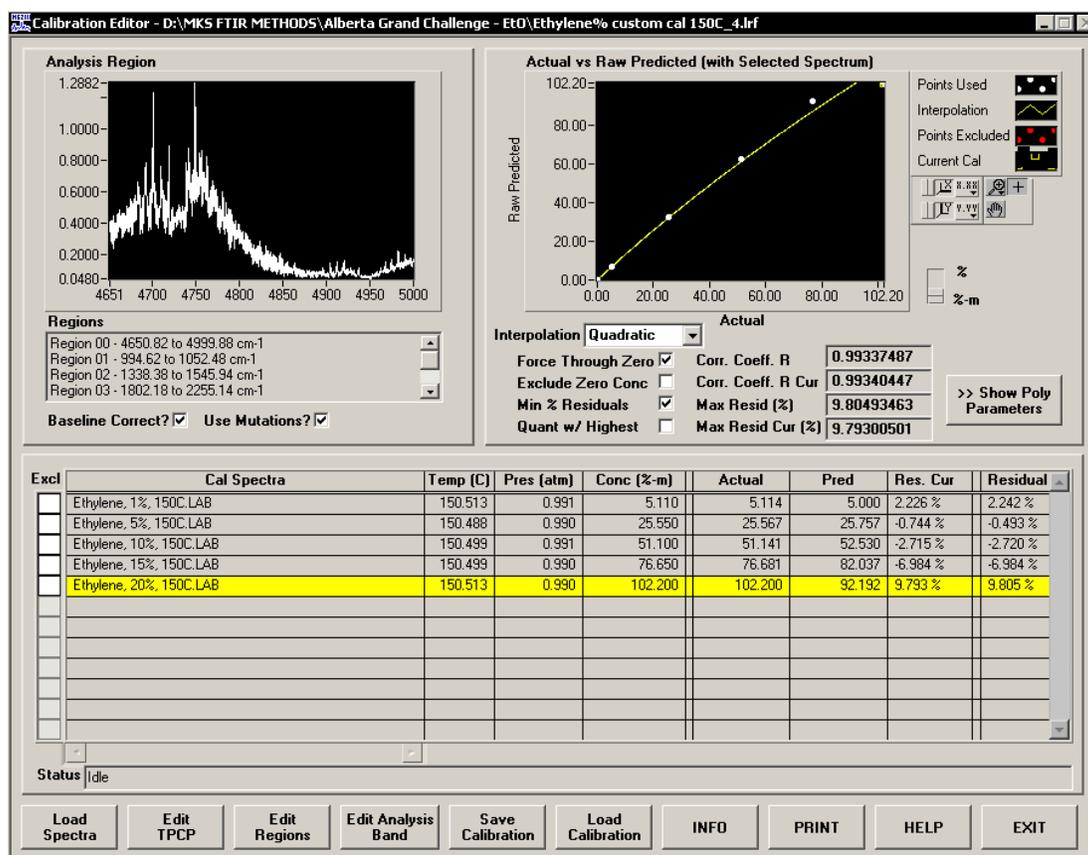


Figure 11. The custom ethylene calibration at high concentrations.

We identified unique spectral bands for each component to minimize analytical interference with other components. For example, **Figure 12** shows the ethylene spectrum (white) overlapping the EtO interference spectrum (red), with the quantification band for ethylene highlighted in blue.

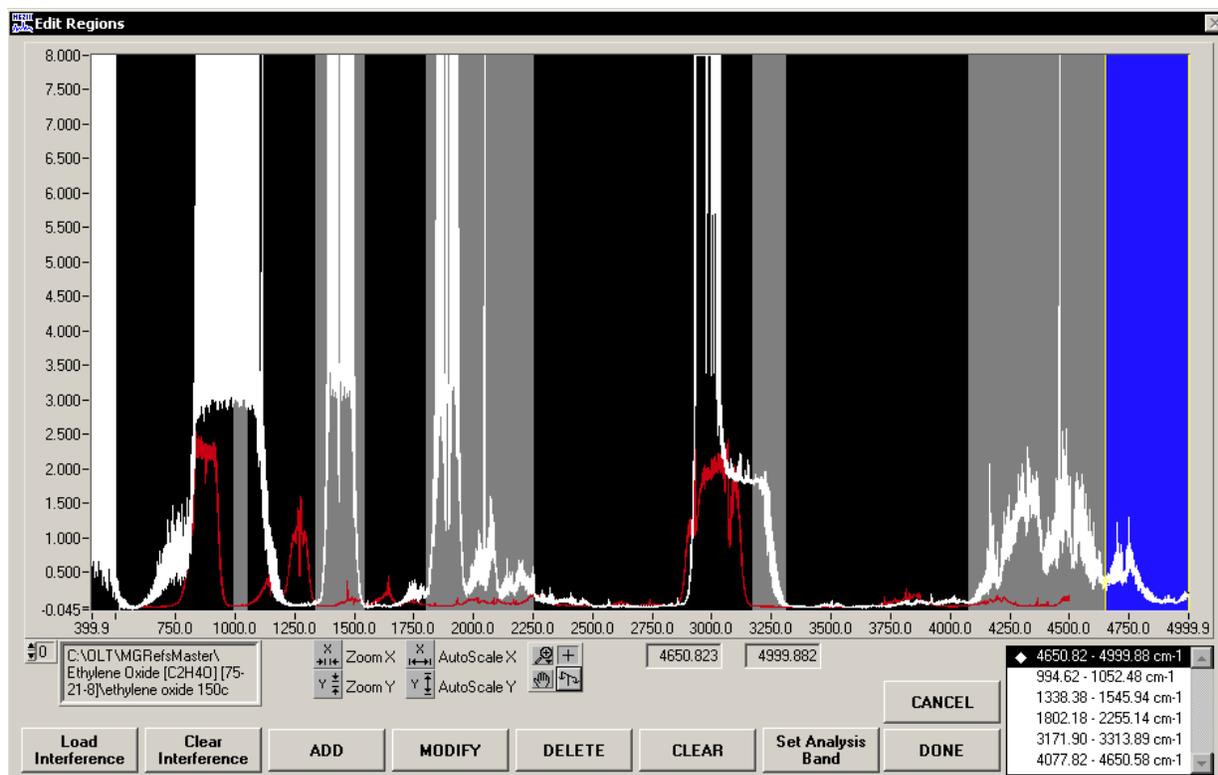


Figure 12. Ethylene (white) and EtO (red) overlapping spectra.

CATALYST RESULTS

When designing a catalyst for CO₂ utilization by ethylene epoxidation, there are three main hurdles to overcome. The first hurdle is the low thermodynamic stability of EtO relative to most reduced metals. The second hurdle is the high thermodynamic stability of CO₂ relative to most reduced metals. The third hurdle is formulation of a catalyst that includes a combination of phases which can overcome the first two hurdles under similar reaction conditions.

As previously mentioned, we have developed an advanced iron mixed-metal oxide catalysts that can abstract oxygen from CO₂ at moderate temperatures (400°C, see **Figure 13**) compared to other iron mixed-metal oxides (>600°C). Definitive mechanistic evidence has not been obtained about this point; however, as discussed in the Results section of this report, the reduced catalyst is capable of gaining nearly 20 wt% oxygen from CO₂. This is a promising catalyst material for CO₂ utilization, but in order to use it for the purpose of ethylene epoxidation, it must be able to selectively transfer oxygen to ethylene to produce EtO. We spent some time investigating this during catalyst development, but observed that the advanced iron is not selective for EtO. We tried numerous combinations, but there was little evidence of EtO formation.

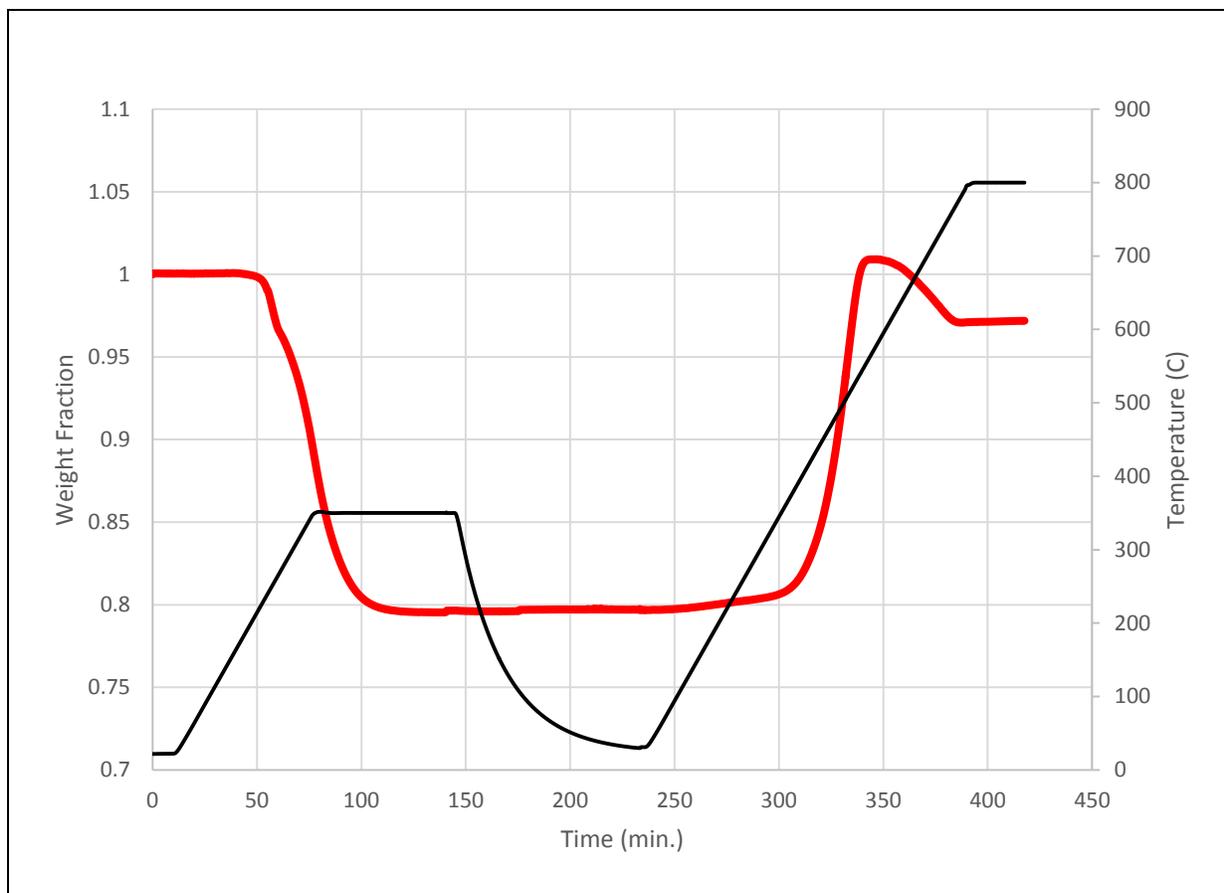


Figure 13. TGA testing of CO reduction and CO₂ oxidation of improved catalyst up to 800°C at atmospheric pressure.

Having observed good reactivity with CO₂ by using an advanced iron mixed-metal oxide, we hypothesized that we should see similar CO₂ reactivity from other metal oxides. We hypothesized that a different metal oxide phase might be more selective for EtO compared to iron. We formulated several new catalysts and the first investigations of the catalysts involved testing for oxygen abstraction at moderate temperatures with the effect of pressure. Initial catalysts were able to show weight gain at 575°C and 19.3 barg (280 psig) in the HP-TGA (see **Figure 14**).

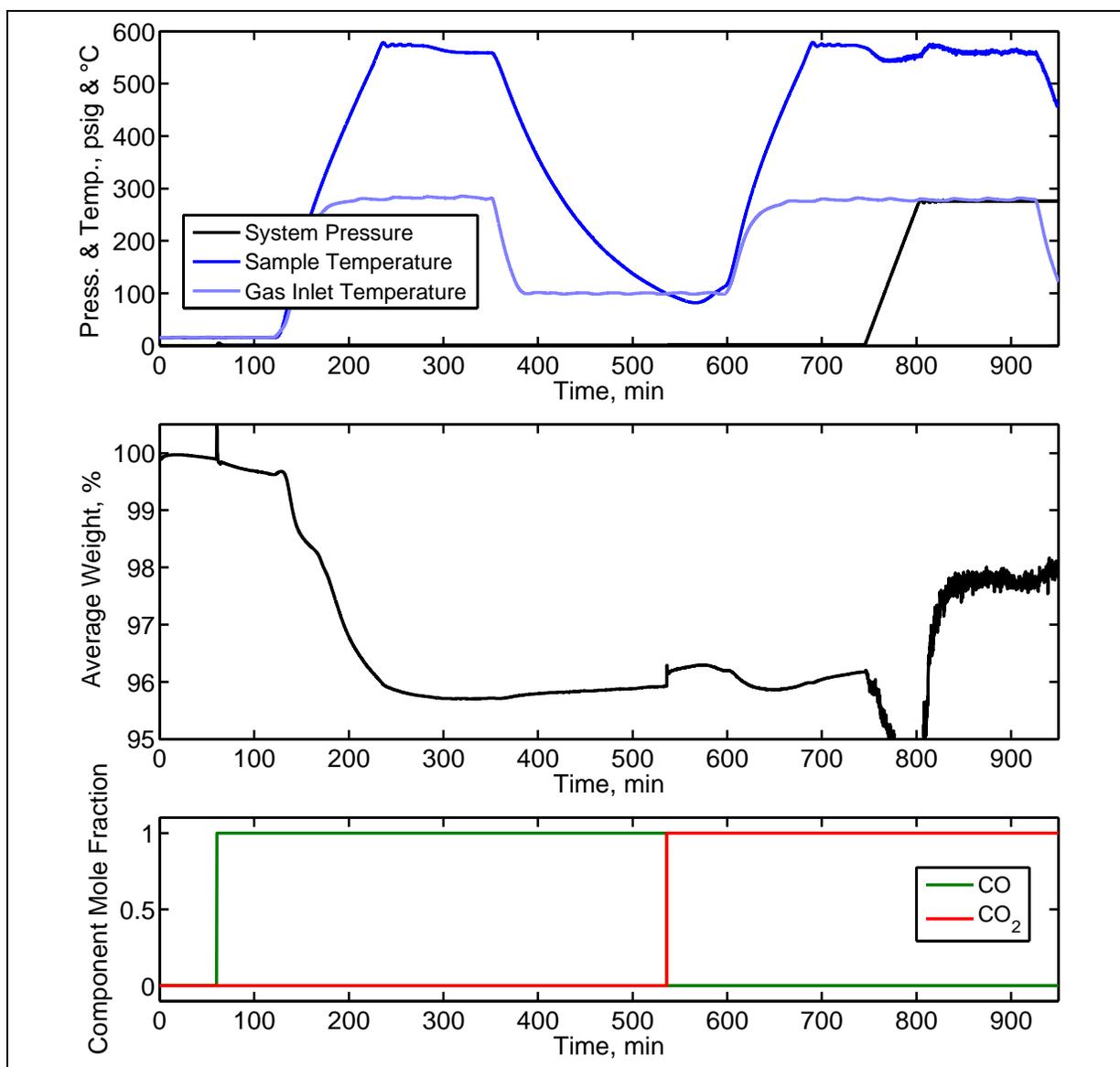


Figure 14. HP-TGA testing of CO₂ oxidation on a catalyst at 575°C and up to 19.3 barg (280 psig).

Further catalyst optimization sought to test oxygen abstraction at ambient pressures with the possibility of up to 800°C temperatures. One catalyst was found to be able to use more than 10% of the oxygen in the catalyst as shown in **Figure 15** (Task 3). We observed that the combination led to the observation of EtO under several test conditions involving either simultaneous or sequential exposure of the catalyst to ethylene and CO₂. This was one of the first observations of a catalyst system in which the reduced form of the catalyst can react with CO₂ to remove an oxygen, while the oxidized catalyst can transfer an oxygen to ethylene to make EtO. The mechanistic pathway by which the EtO is formed is not clearly understood at this point.

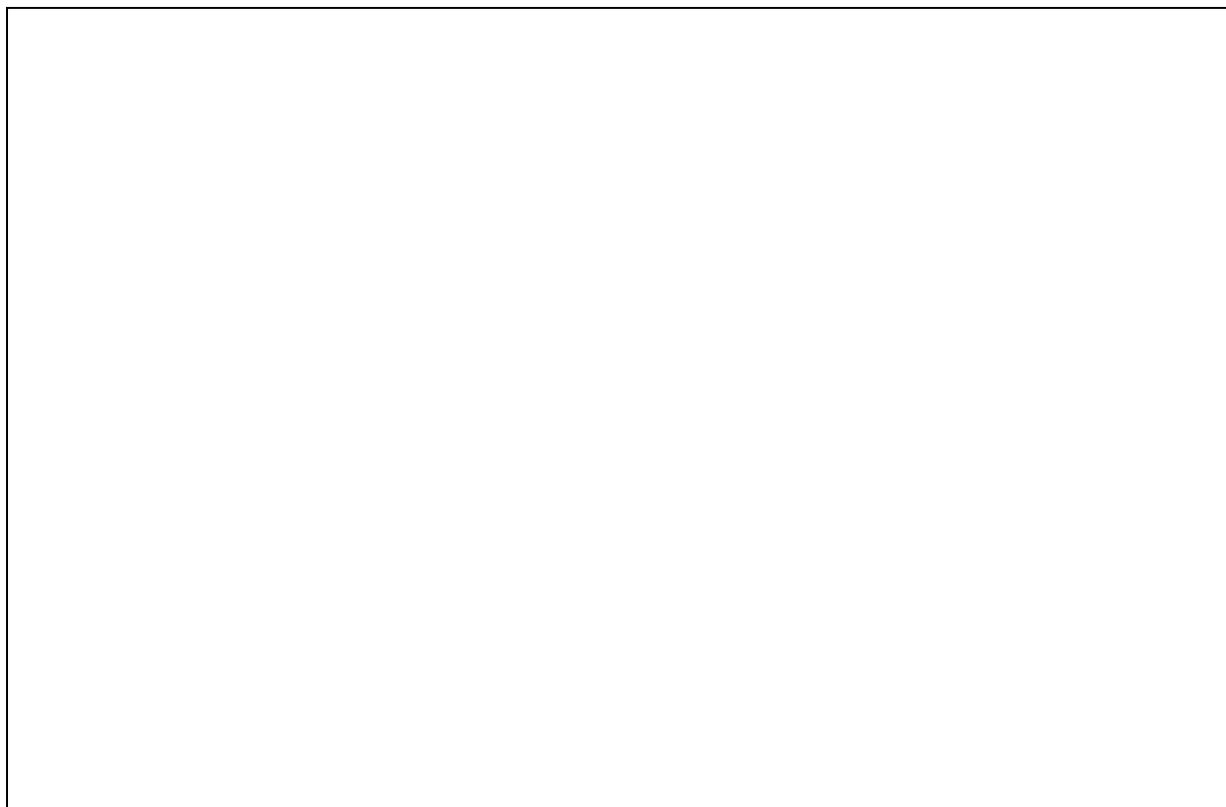


Figure 15. TGA testing of CO reduction and CO₂ oxidation of a catalyst up to 800°C at atmospheric pressure.

Microreactor Results Summary

The catalyst screening test results under cofeed and transport test conditions demonstrated cofeed mode produced the best results. While multiple catalyst families were capable of producing EtO in both transport and cofeed modes, EtO yields were limited to less than 1% in transport mode. However, catalysts were able to produce EtO yields greater than 5%. As a result, we performed further optimization of the best performing catalysts from cofeed mode tests as detailed in the following sections.

Catalyst Support Modification

Although support materials are often mentioned as being inert, there can be synergistic properties as a result of support and catalyst interaction. We studied the effect of the support by preparing catalysts on several different supports. We found that the support plays a significant role in the catalyst activity. For example the highest EtO effluent in the product stream is observed when it is supported on a certain support. The catalyst activity, however, is different when the same formulation is supported on others. When the same catalyst formulation is supported on other supports, the reactivity decreases by two orders of magnitude. The connection

at this time is not completely understood. Additional factors that should be considered in the support comparison are the pore size and surface area.

Variations in the results based on support are shown in **Table 4**. However, the lower H₂O yields indicated lower selectivity towards complete oxidation of ethylene, which significantly improves the economics of the process as described in the Techno-economic Analysis section of this report. The EtO:H₂O ratio is an important metric to distinguish the relative selectivity of ethylene conversion to EtO as compared to forming H₂O by the side reaction of combustion. The data reported are collected during the maximum average amount of EtO produced over a 1-minute period.

Table 4. Comparison of a Catalyst on Two Different Supports

Catalyst	Reduction Feed Conditions				Results					
	Total Flow (sccm)	CO ₂ (vol%)	Ethylene (vol%)	Reactor (°C)	Ethylene Conv.	EtO Sel.	EtO Yield	H ₂ O Sel.	H ₂ O Yield	EtO/H ₂ O Yield
Cat 1 on Support A	300	15-35	5-25	300-450	13	45	5.7	78	9.9	0.58
Cat 1 on Support A	300	15-35	5-25	300-450	15	39	5.7	78	11.5	0.50
Cat 1 on Support A	300	15-35	5-25	300-450	15	37	5.4	91	13.3	0.41
Cat 1 on Support B	300	15-35	5-25	300-450	12	44	5.3	64	7.6	0.69
Cat 1 on Support B	300	15-35	5-25	300-450	13	41	5.2	62	7.8	0.66
Cat 1 on Support B	300	15-35	5-25	300-450	13	39	5.0	56	7.0	0.71

Catalyst Formula Optimization

We performed a statistical ANOVA test of the best performing cycles from the catalyst screening tests to optimize the catalyst formulation. The analysis found that the variable that had the most significant impact on EtO yield and the EtO/H₂O yield ratio was the percentage of certain metals in the catalyst. We developed variations of the best performing catalyst from the screening tests with higher and lower concentrations. We employed the same set of conditions used to test the support variations to test the variations. One catalyst formula produced the highest EtO yields measured thus far, ranging from 6.2% to 8.5%. The H₂O yield was higher at 21.7% for the experiment that resulted in an 8.5% EtO yield; however, the other experiments resulted in more comparable H₂O yields. To further optimize the catalyst, higher compositions may result in even better EtO to H₂O yield ratios. The results are shown in **Table 5**.

Table 5. Comparison of Various Compositions of Catalyst

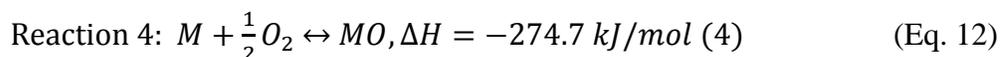
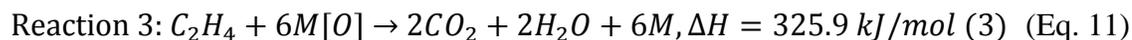
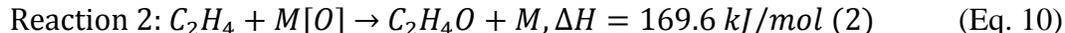
Catalyst	Reduction Feed Conditions				Results					
	Total Flow (sccm)	CO ₂ (vol%)	Ethylene (vol%)	Reactor (°C)	Ethylene Conv.	EtO Sel.	EtO Yield	H ₂ O Sel.	H ₂ O Yield	EtO/H ₂ O Yield
Cat A	300	15-35	5-25	300-450	25	34	8.5	87	21.7	0.39
Cat B	300	15-35	5-25	300-450	35	21	7.5	28	9.9	0.76
Cat C	300	15-35	5-25	300-450	20	36	7.0	51	10.0	0.69
Cat D	300	15-35	5-25	300-450	16	42	7.0	78	12.9	0.54
Cat E	300	15-35	5-25	300-450	41	17	6.8	25	10.3	0.66
Cat F	300	15-35	5-25	300-450	18	35	6.2	48	8.6	0.72
Cat G	300	15-35	5-25	300-450	13	45	5.7	78	9.9	0.58
Cat H	300	15-35	5-25	300-450	15	39	5.7	78	11.5	0.50
Cat I	300	15-35	5-25	300-450	15	37	5.4	91	13.3	0.41
Cat J	300	15-35	5-25	300-450	46	11	4.9	23	10	0.47
Cat K	300	15-35	5-25	300-450	46	11	4.9	23	10.5	0.47
Cat L	300	15-35	5-25	300-450	39	12	4.6	21	8.3	0.55

Although the catalyst shows promising results already in terms of EtO yield, catalyst optimization will lead to even better performance. Calcination temperature is a variable in the synthesis procedure, which could prove to be impactful on catalyst activity, but at this point in the development, this aspect has not been optimized.

PROCESS MODELING

RTI has developed a novel catalytic process for producing EtO from ethylene by using CO₂ as the oxidizing agent. With the aim of understanding the economic and technical feasibilities and the environmental impact of this process, we developed a process model using Aspen Plus, a commercial process simulation software from AspenTech™, and performed a detailed analysis of the process. We developed the process models to depict the overall process to produce 250,000 tonnes/yr of EtO.

The main reactions that define this process are presented in Equations 9 through 12 as follows:



Reaction 1 (Equation 9) defines the oxidation of the metal catalyst, where the metal catalyst in its initial state is denoted by “M” and in its oxidized state is denoted by “M[O].” Reaction 2 (Equation 10) is the oxidation of ethylene by the oxidized metal catalyst to produce EtO. Reaction 3 (Equation 11) is the undesirable side reaction, which is the combustion of ethylene, where the combustion agent is the oxidized metal catalyst. It is important to note that this reaction is endothermic, mainly due to the simultaneous metal oxide reduction. In this reaction, each mole of ethylene is oxidized by 6 moles of metal oxide. Although ethylene combustion is exothermic, the simultaneous endothermic reduction of 6 moles of the metal oxide makes the overall side reaction endothermic in nature.

Based on the experimental studies in the project, two modes of the process have been developed. The first mode is referred to as the transport mode, in which the oxidation and

reduction reactors are carried out in separate reactors. In the oxidation reactor, the reaction in Equation 12 occurs in which the metal catalyst is oxidized. This oxidized metal catalyst is separated from the gas stream containing a CO and CO₂ mixture in a cyclone, and the catalyst is sent to the reduction reactor where Reactions 2 and 3 (Equations 10 and 11, respectively) take place. The reduced metal catalyst is then recycled to the oxidation reactor for another cycle of the redox reactions.

The second operating mode is referred to as the cofeed mode. Like the name suggests, both the main reactants CO₂ and ethylene are fed together into the main reactor where the oxidation and reduction reactions occur sequentially in the same reactor.

The block flow diagrams and the process description for the two operating modes are discussed in the next section.

Model Architecture

During this process, the main reactants are CO₂ and ethylene. The inlet conditions for CO₂ are considered to be 151 barg and 25°C assuming that CO₂ is procured from the Alberta Carbon trunk line, in this scenario.¹¹ The inlet conditions are similar to CO₂ available from the Souris Valley Pipeline in North Dakota.^{12,12} Ethylene is assumed to be available at 102 barg and 25°C from the Ethylene Distribution System operated by Nova Chemicals.¹³

Transport Mode

The block flow diagram of the transport mode is shown in **Figure 16**. The main reactants (i.e., CO₂ and ethylene) are first heated to 200°C by using steam and then expanded to 20.7 barg. CO₂ is heated to 700°C and is then sent to the oxidation reactor, where the catalyst is oxidized and CO is produced. The reactions in Equations 9 through 11 (Reactions 1, 2, and 3, respectively) are net endothermic, and the heat of reaction is supplied by preheating the feed inlet gases to the oxidation and reduction reactors and additionally supplying external heat to the reactors. A wide range of reaction conversions have been evaluated in this study, and to ensure convergence for the different reaction scenarios, the reactors have been assumed to be isothermal in the process model, and the heat duty requirement of the reactors was used to estimate the thermal energy requirement of the process. The outlet gas from the oxidation reactor contains CO, CO₂, and the oxidized metal catalyst. This gas-solid mixture is sent to a cyclone, where the oxidized catalyst is separated and sent to the reduction reactor, while the gas stream containing CO₂ and CO is sent to the purification section. This stream is sent to an amine treatment system for separating CO₂ present in this stream. The purified CO stream is a by-product in the process, and the captured CO₂ is recycled back to the oxidation reactor.

Ethylene is heated to a temperature of 450°C and sent to the reduction reactor. The oxidized catalyst sent to the reduction reactor reacts with ethylene to form EtO. In the reduction reactor, an undesirable side reaction between ethylene and oxygen from the oxidized catalyst results in ethylene combustion and produces CO₂ and H₂O. The outlet stream from the reduction reactor is sent to a cyclone where the reduced catalyst is separated, heated, and sent back into the oxidation reactor. The gas stream containing EtO, ethylene, CO₂, and H₂O is sent to a scrubbing column where the gas stream is scrubbed with H₂O. EtO dissolves in the H₂O and exits with the water stream while the gas stream exiting the scrubber contains ethylene and CO₂. The EtO-water stream is sent to a distillation column to separate the product EtO from the H₂O. The EtO separation from the product gas using water scrubbing and subsequent distillation is a common practice and is employed in the conventional direct oxidation process as well.¹⁴ . The unreacted ethylene and CO₂ mixture is sent to an amine absorber for CO₂ capture and the unconverted ethylene is recycled to the reduction reactor.

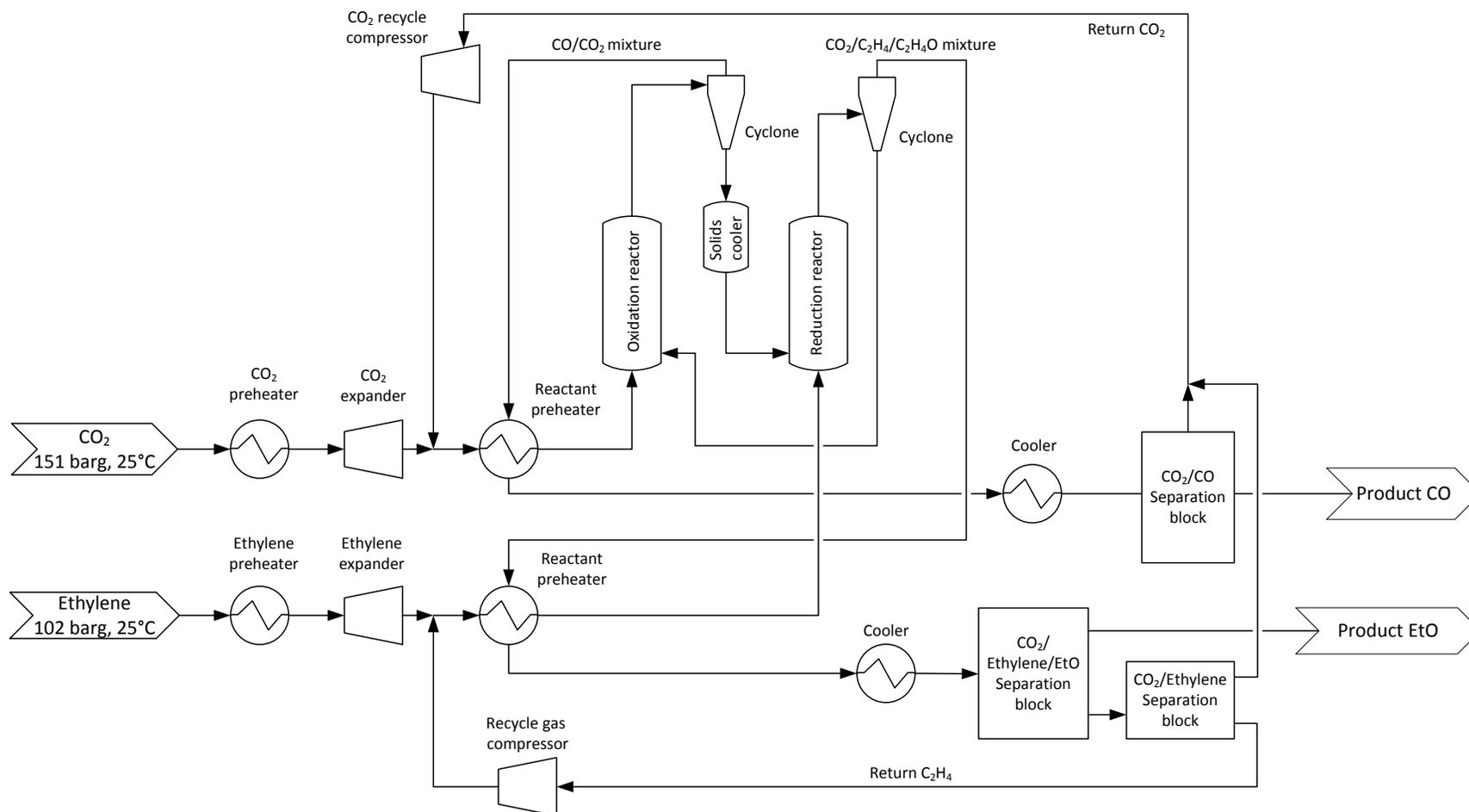


Figure 16. Block flow diagram of the transport mode.

Cofeed Mode

The block flow diagram for the cofeed mode of operation is shown in **Figure 17**. Ethylene and CO₂, after heating and expansion to 20.7 barg, are mixed and heated to 700°C to provide the heat required for Reactions 1, 2, and (Equations 9 through 11, respectively). Additional external heat is supplied to the reactors to provide the heat required for the reactions to take place. A wide range of reaction conversions were evaluated in this study and to ensure process model convergence, the cofeed reactor was assumed to be isothermal in the process model, and the heat duty of the reactor was considered in the TEA to estimate the cost of the thermal energy requirement for this process.

The feed mixture is sent to the cofeed reactor, where the oxidation and reduction reactions take place over the metal catalyst to produce CO and EtO. Some CO₂ is also formed as a by-product of the undesirable combustion reaction. The outlet gas stream contains a mixture of products (CO, EtO, and H₂O), as well as the unreacted CO₂ and ethylene. This stream is used for partial reheating of the feed gases and is sent to a scrubbing section that uses H₂O as the scrubbing agent. Product EtO is recovered in the water stream exiting this section, and the H₂O and EtO mixture is distilled to recover EtO as the product similar to the transport mode process. The gas stream leaving the scrubbing section with CO, CO₂, and unconverted ethylene is sent to a carbon capture system, where CO₂ is captured and recycled to the cofeed reactor. The CO₂ free gas stream is a mixture of CO and ethylene at this point and is sent to a cryogenic separation unit to condense ethylene from the mixture and obtain a pure product stream of CO. The separation may be able to be achieved in a cold box unit instead of requiring cryogenic separation, which would further lower the energy requirement. As a conservative estimate, the cryogenic separation unit was used in the process model. Unconverted ethylene is recycled to the cofeed reactor.

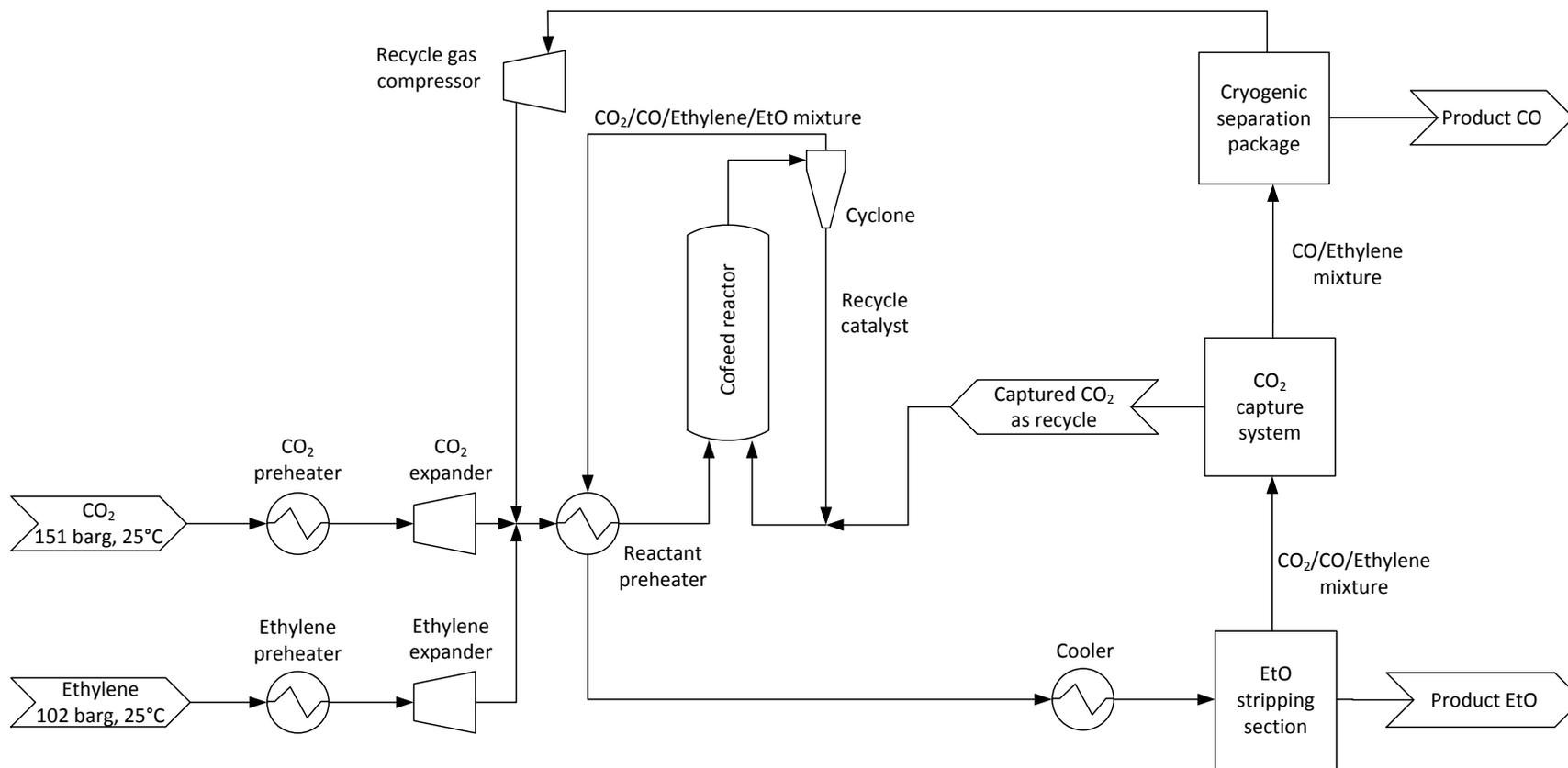


Figure 17. Block flow diagram of the cofeed mode.

Model Assumptions

Specific assumptions were made during the process of developing the models on Aspen Plus. The assumptions were made based on conservative results from the experimental analysis of the process. The assumptions considered are listed as follows:

- In the transport mode of operation, the operating conditions for the oxidation reactor are 19 barg and 600°C, and 19 barg and 450°C for the reduction reactor.
- In the cofeed mode, the operating conditions in the cofeed reactor are assumed to be 19 barg and 450°C.
- In both the operating modes, the reactors are considered to be isothermal to accommodate the wide range of reaction conversions evaluated. The heat duty of the reactors was considered to estimate the total thermal energy requirement for the process.
- The conversion for the side reaction, Reaction 3 (Equation 11) was assumed to be 10%.
- To enable development of the process model simultaneously while screening catalysts for the best performing combination, the metal to metal oxide conversion has been assumed to be iron to Fe₂O₃. Thus, heat of reactions for the three key reactions in the process are based on the iron catalyst oxidation reduction cycle.

Techno-economic Analysis

We performed a techno-economic evaluation on both the modes of operation of the C3-PEO technology. The assumptions, approach, and the results from this study are discussed in the following few subsections of this report.

Techno-economic Analysis Architecture

The economic model assumptions made for the process are summarized in **Table 6**. All of the costs considered in the study are in 2015 U.S. dollars.

Table 6. Summary of Economic Assumptions Considered for the C3-PEO Process

Parameter	Assumption
Taxes	38%
Capacity factor	85%
Interest rate	8%
Capital depreciation	20 years; 150% double declining method
% of Total capital that is depreciated	100%
Total debt financed	60%

Parameter	Assumption
Term of loan	20 years
Capital expenditure period	3 years (2015–2017)
Operational period	20 years (2017–2037);
Economic analysis period (for calculating internal rate of return [IRR])	23 years (capital expenditure period + plant operational period); (2015–2037)
Escalation of revenue, operating and maintenance costs, and fuel costs	3%
Repayment term of debt	20 years
Grace period on debt repayment	0 years

Other information required to calculate the yearly cash flows would be the raw material and product price information. For all the cases, the product or raw material prices considered in the economic evaluation are summarized in **Table 7**.

Table 7. Summary of Product and Raw Material Cost Assumptions

Feed and Product Pricing	
<i>Product</i>	
Carbon monoxide, \$/MMBtu	\$12.50
Ethylene oxide, \$/tonne	\$990.00
<i>Raw Materials</i>	
Carbon dioxide, \$/tonne	\$0.00
Ethylene, \$/tonne	\$600.00

For evaluating the cash flow of any process, it is essential to know the capital costs and the operating costs for the process. We used the Aspen Process Economic Analyzer to estimate the capital cost for both cases. From the process models developed for both the cases, we then listed and sized all the equipment. Using the sizing information, we then estimated the capital costs of the plant. The process model serves as the basis for estimating the operating costs. We determined the operating costs of the process by estimating the total raw material, labor, and utility costs.

Using the estimated capital costs and operating costs information, we calculated the yearly cash flow values for each of the cases. Starting from the year when construction began (2015) to the end of the economic analysis period (2037), we calculated the taxable income, the net revenue after taxes, and the operating cash flow for every year. Using the operating cash

flow values for the entire economic evaluation period, we calculated the internal rate of return (IRR) for each case.

For each year in the economic analysis period, we calculated the earnings before interest and taxes (EBIT) as the difference between the total annual revenue and the total annual expenses. While estimating EBIT, it is important to note that depreciation is also considered as an expense. We then calculated the taxable income as the difference between the total annual revenue and the total annual expenses, less the depreciation and the interest payment. As shown in Table 9, 38% of the taxable income was assumed to be taxes. We then calculated the net revenue as the difference between EBIT and the taxes plus interest payment. Because depreciation is not a tangible cost or a real cash flow, the annual depreciation amount is added back to the net revenue to estimate the operating cash flow for a year. The operating cash flows for the entire economic evaluation period are considered to calculate the IRR for each case. The cash flow analysis assumptions are included in **Error! Reference source not found. A**.

Model Results

RTI used the Aspen Process Economic Analyzer from the AspenTech Suite of process simulation software to estimate the capital costs for the two cases. We used the information from the process models developed on Aspen Plus to size the equipment, and then utilized the sizing data in the Aspen Process Economic Analyzer to estimate the total capital costs. The capital costs for the two cases are presented in **Table 8**. The capital costs for the two cases are similar. In the transport mode, the number of equipment components are higher in the reaction area of the process, and the separation zone of the process is fairly straightforward. In the cofeed mode, the reaction zone is fairly straightforward and has fewer equipment components, and the separation of the mixture containing both the products and the unconverted reactants is complex. In addition to the CO₂ separation and scrubbing towers, the separation zone also includes a cryogenic separation unit to separate the unconverted ethylene from the product CO. Overall, the capital costs for the two process cases are estimated to be approximately \$100 million for a plant producing 250,000 tonnes/yr of EtO.

Table 8. Capital Costs for the Two Cases

	Transport Mode	Cofeed Mode
Total capital cost (2015 U.S. dollars)	\$101,004,002	\$105,371,798

We performed the cash flow analysis for both the transport and cofeed modes, and the results are presented in **Figure 18**. We evaluated the ethylene to EtO conversion that is required for each case in order to have an IRR of 15%. For cofeed case, we estimated that a main reaction conversion of 9% is needed with the assumptions previously discussed to achieve an IRR of 15%. For the transport case, however, the main reaction conversion must be at least 12% for an IRR of 15%. The experimental results for ethylene oxidation by CO₂ in the transport mode do not appear to be capable of achieving the required conversion value. Therefore, we performed a sensitivity analysis only for the cofeed mode of operation to better understand the impacts of various process parameters on the economics.

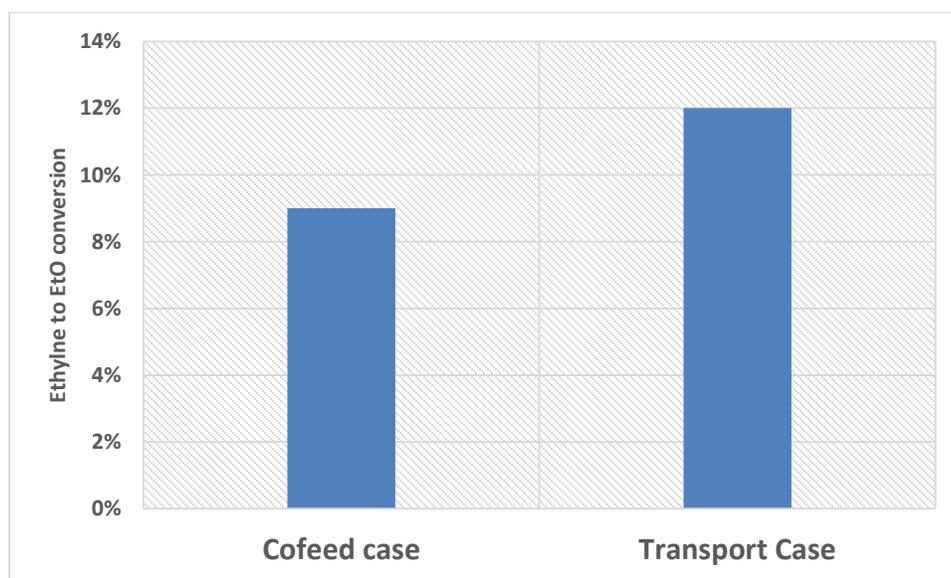


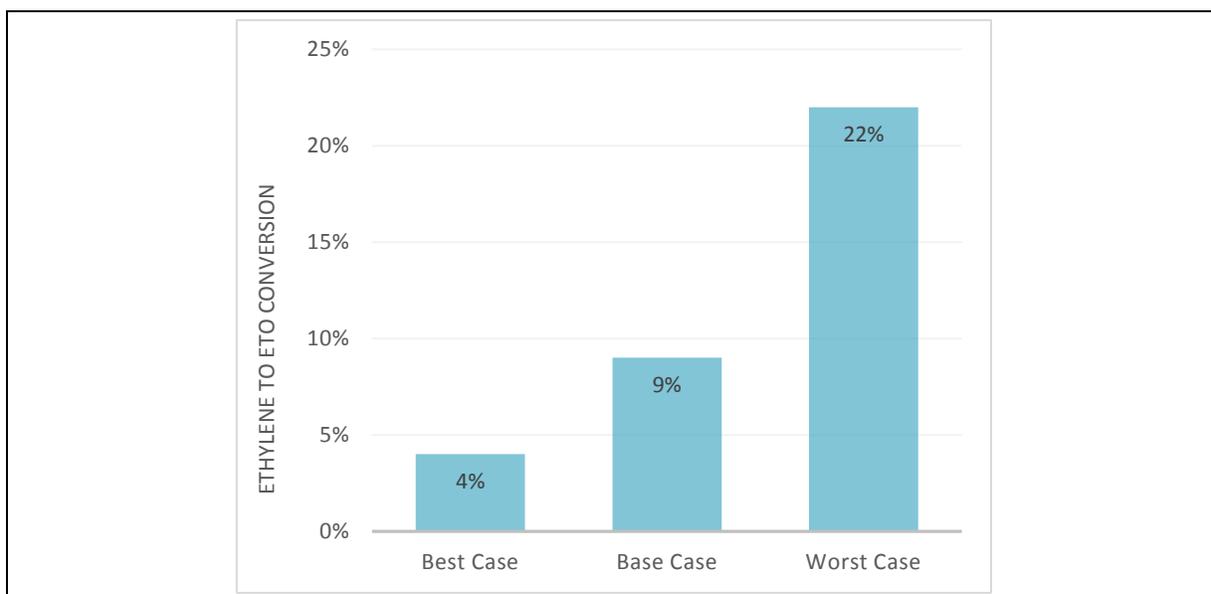
Figure 18. Comparison of main reaction conversion required to achieve an IRR of 15% for the two cases.

The economic analysis results previously discussed are based on current product and raw material prices. To understand the impact of the prices, we developed the process economics for best, base, and worst case scenarios. The assumptions for the best and worst case scenarios are presented in **Table 9**. For the best case scenario, a credit of \$15/tonne of CO₂ is considered.

Table 9. Summary of Process Costs for the Three Scenarios

	Best Case	Base Case	Worst Case
<i>Products</i>			
Carbon monoxide, \$/MMBtu	\$20.00	\$12.50	\$5.00
Ethylene oxide, \$/tonne	\$1,090.00	\$990.00	\$890.00
<i>Raw Materials</i>			
Carbon dioxide, \$/tonne	-\$15.00	\$0.00	\$15.00
Ethylene, \$/tonne	\$500.00	\$600.00	\$770.00

For these three scenarios (i.e., best, base, and worst case), we estimated the ethylene to EtO reaction conversion with the objective of achieving an IRR of 15%. We kept the side reaction conversion for the three scenarios constant at 10%. The results are shown in **Figure 19**. In the best case scenario listed in Table 12, for 4% of the ethylene converting to EtO, an IRR of 15% is obtained, whereas in the worst case scenario with unfavorable raw material and product costs, a reaction conversion of 22% is required to achieve an IRR of 15%.

**Figure 19. Main reaction conversions for the three scenarios.**

Process Sensitivity Analysis

Techno-economic Analysis

Furthermore, it is important to understand the impacts of the various process parameters on the process economics. RTI varied the impacts of various parameters (e.g., the ethylene

price, the CO₂ price, the product values) one at a time to understand their individual impact on the process economics. The objective was to determine which of these parameters had the most impact on the economic feasibility of the process. We varied each of the process parameters, and then determined the main reaction conversion required to achieve an IRR of 15%. The results of this exercise are summarized in **Figure 20**. As previously discussed, with the base case assumptions, a minimum conversion of 9% is required, which is the median value.

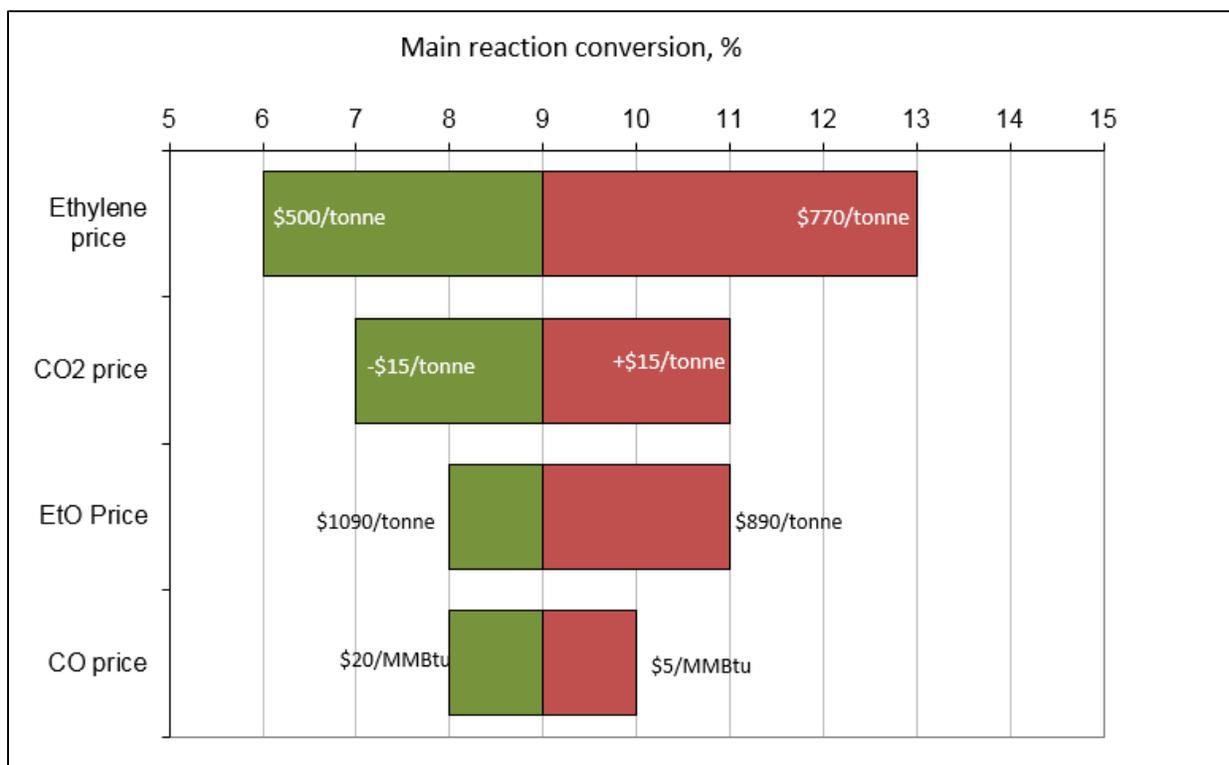


Figure 20. A tornado chart for process sensitivity analysis.

From the analysis, it was evident that the ethylene price has the most impact on the process economics. In addition to the conversion of ethylene to EtO, some ethylene is also converted to CO₂ and H₂O. The overall consumption of ethylene is found to have the most impact on the process economics. Therefore, it is of very high value to improve the catalyst properties so that the side reaction is minimized. The price of CO₂ was found to have the next highest impact, due to its high consumption, to provide the oxidized catalyst for EtO production, as well as the undesirable side reaction. EtO price was found to have a moderate impact, and CO price was found to have the least impact on the economics. This analysis shows that it is very important to inhibit the side reaction and to effectively use the two reactants, ethylene and CO₂.

The next task was to evaluate the production cost of EtO and understand the factors that have the most impact on the production cost. The previous sensitivity analysis focused on estimating the minimum EtO yield under different scenarios. The current analysis aims to understand the impact of various process factors on the EtO production cost, while keeping the EtO yield constant. In this evaluation the ethylene to EtO yield has been considered to be 5%, while the side reaction yield was assumed to be 7% to match the best performance case from the experimental runs. The EtO selectivity was estimated to be 41% in this case. The EtO production cost for this base case is estimated to be \$980/tonne. The base case assumptions used for this analysis are listed in **Table 10.** Base Case Assumptions for Production Cost Sensitivity Analysis . The variation in EtO production cost with a change in each of these process parameters is shown in **Figure 21.** .

Table 10. Base Case Assumptions for Production Cost Sensitivity Analysis

Parameter	Assumption
EtO selectivity	41%
Ethylene price, \$/tonne	\$500
CO ₂ credit, \$/tonne	\$15
CO price, \$/MMBtu	\$10
EtO production cost	\$980

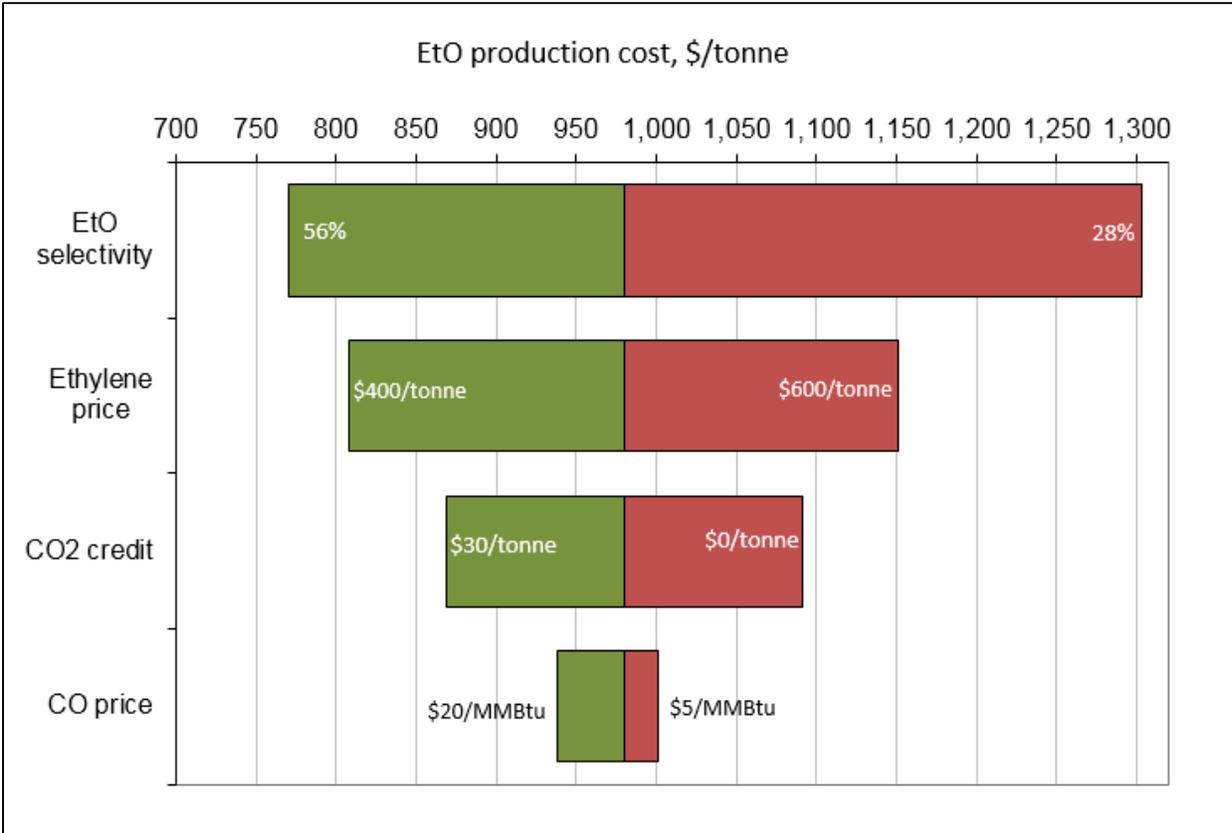


Figure 21. A tornado chart for process sensitivity analysis.

Out of all the factors listed, EtO selectivity has the biggest impact on the process economics. A 15 percentage-point increase in EtO selectivity from the current selectivity of 41% to 56% reduces the production cost of EtO by as much as 21%. The production cost at 56% selectivity is estimated to be \$770/tonne. Similarly, a 15 percentage-point reduction in selectivity has a detrimental effect on the process economics, increasing the production cost by approximately 33%. As discussed in the previous sensitivity analysis, ethylene consumption is the next biggest impact factor, as it is the key raw material. A \$100/tonne increase or decrease in ethylene price, results in a 17% increase or decrease in the EtO production cost. CO price does not significantly impact the production cost of EtO, while an increase in the CO₂ credit to \$30/tonne reduces the EtO production cost by 11%.

GHG LCA

One of the key advantages of the C3-PEO process is that CO₂ is effectively used to oxidize ethylene to make EtO, which is a valuable product. It is very important to understand the environmental benefits of this process by performing a GHG LCA. To enable a fair comparison, RTI compared the GHG impact of the C3-PEO process to the conventional EtO

manufacture process, and we estimated the GHG benefits in producing a tonne of EtO. A preliminary LCA was completed during the proposal stage of the project and was updated with the process model results to include an increased level of detail. A cradle-to-gate approach for analyzing the GHG benefits for the C3-PEO process compared to the conventional process is outlined in the following subsections of this report.

Various studies have documented the resources required in the production of EtO in cradle-to-gate type approaches.¹⁵ In such approaches, the GHG emissions associated with each precursor and inputs into the process are included, along with the impact of the EtO production process. The analysis concluded with the desired product of EtO, independent of how it may be used or disposed of beyond that step. Following the production of EtO, its subsequent use either as an end product or more commonly as an intermediate in further chemical production and associated emissions will be the same regardless of the production method used. Therefore, the cradle-to-gate analysis of the current production methods of EtO, compared with that of the C3-PEO technology, will help distinguish the possible GHG benefits.

The block diagram of the conventional EtO manufacture process is shown in **Figure 22**. In the conventional process ethylene (95–98% purity) and O₂ (95 mole %) are mixed in a ratio of 1:10 by weight and are passed over a catalyst consisting of Ag₂O deposited on an inert carrier such as corundum or α -alumina. Generally, an anti-catalyst such as ethylene dichloride (approximately 2% based on the weight of ethylene) is added to the ethylene feed to suppress the formation of CO₂.¹⁴

The pure O₂ stream is produced on site by using an air separation unit, which is energy intensive. During the conventional process, the side reaction conversion is approximately 5.6%. The EtO purification step is similar in both the conventional and the C3-PEO processes.

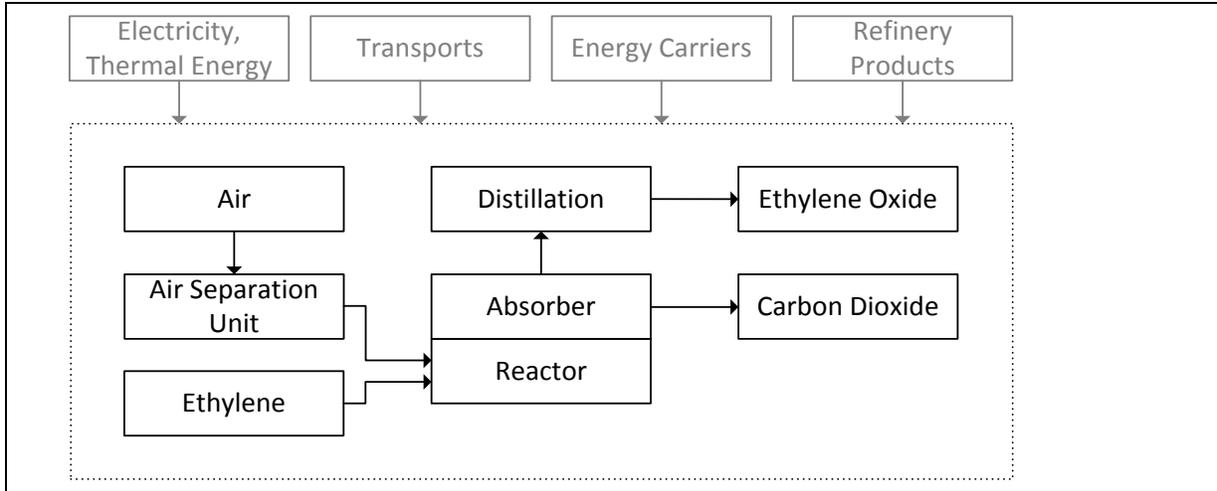


Figure 22. A block diagram of the conventional ethylene oxidation process from a GHG perspective.

A block flow diagram of the process layout for the transport mode is shown in **Figure 23**. The blocks in blue represent the units implemented in the process model that were not previously considered in the preliminary GHG analysis previously developed. In addition, compressors and pumps, when required, have been considered in this analysis.

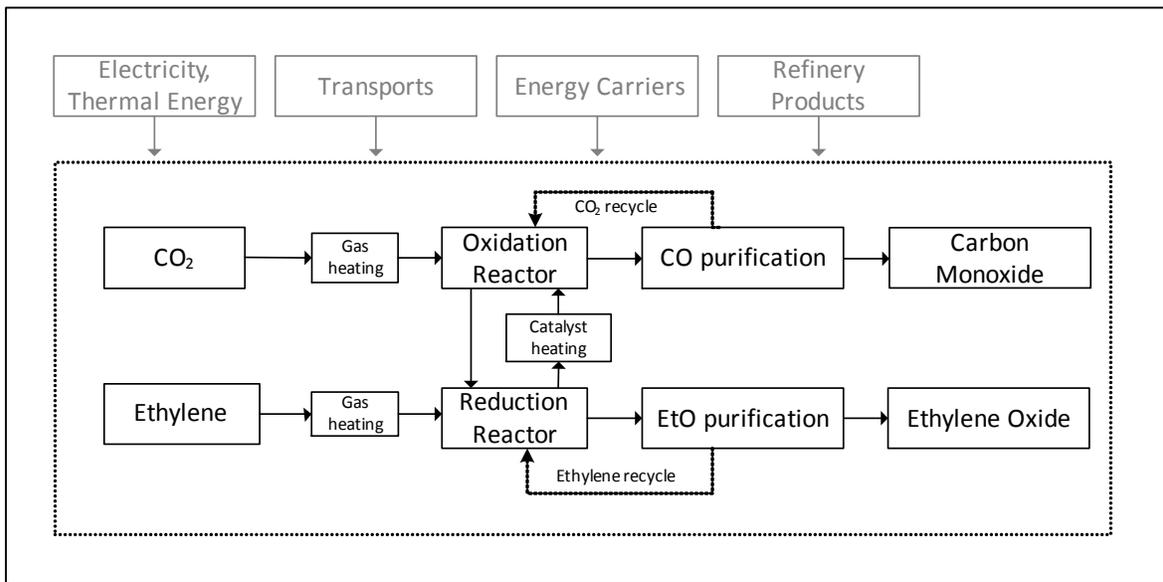


Figure 23. A block flow diagram of the C3-PEO process, transport mode from a GHG perspective.

The block diagram for the cofeed mode is shown in **Figure 24**. Using the process model, RTI estimated the electricity consumption, amount of CO₂ used and heat input to the system. We used these estimates in the GHG analysis to estimate the total amount of CO₂ emitted per tonne of EtO produced. Estimating the CO₂ emissions, allows us to calculate the amount of CO₂

emissions that can be potentially avoided if EtO was produced by using the C3-PEO process instead of the conventional direct oxidation process. The main contributions to the LCA are outlined in the following subsections.

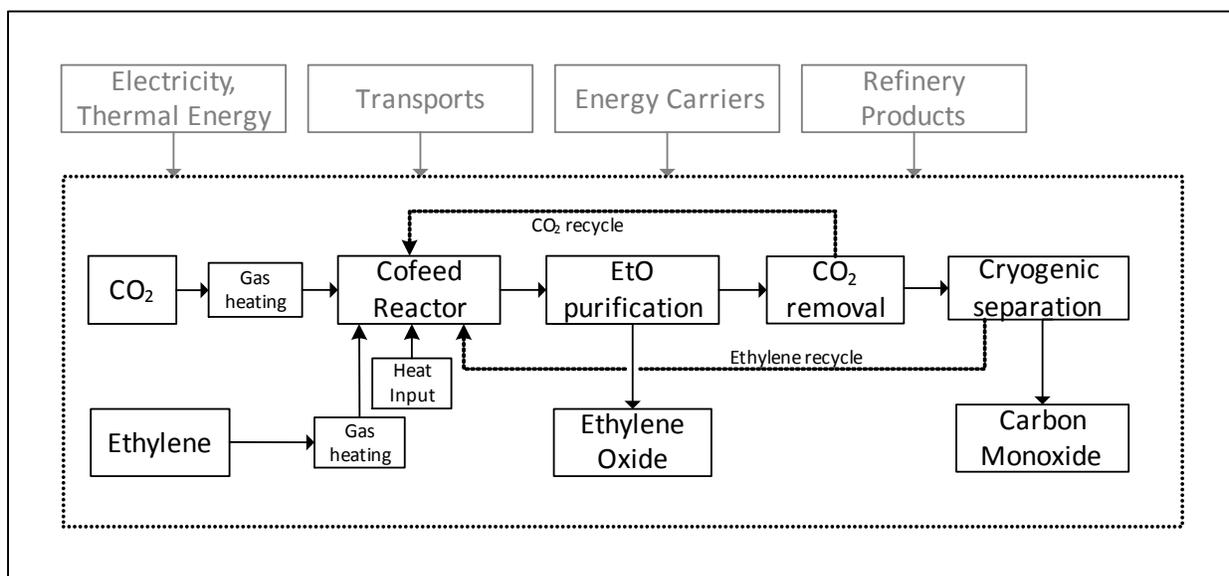


Figure 24. A block flow diagram of the C3-PEO process, cofeed mode from a GHG perspective.

Air separation unit

CO₂ is the main oxidizing agent in the C3-PEO process; however, for the conventional process, O₂ is the main oxidizing agent, for which an air separation unit would be necessary. The CO₂ generated during the production of electricity used for the air separation unit is considered in estimating the total tonnes of CO₂ produced per tonne of EtO produced in the conventional process.

Carbon dioxide (CO₂) input

In the C3-PEO process, CO₂ is consumed, and the benefit of reducing GHG gases should be considered in this analysis. Some CO₂ is produced as a by-product from the undesirable combustion of ethylene, but the net CO₂ that is consumed in the process is essential to estimate the GHG benefits of the novel process. The source of the CO₂ was not considered in this analysis and any GHG impacts from the CO₂ consumed in the process must be integrated depending on the source.

Electricity

The electricity consumed for compression, pumping, and conveying is determined for the conventional and the C3-PEO processes and are considered when estimating the GHG produced per tonne of EtO produced in these two processes.

Natural gas

The cradle-to-grave impacts for the natural gas consumed for heating purposes in the two processes are considered in the evaluation of GHG produced. RTI estimated the natural gas required to supply the heat of reaction for all the key reactions in the process for each case and took into account the CO₂ emissions from burning the natural gas when determining the GHG emissions for the C3-PEO process.

Carbon monoxide (CO)

CO is a by-product in the C3-PEO process. A cradle-to-gate GHG impact for CO produced conventionally was considered in this analysis. This impact would be total GHG emissions that are avoided by producing CO by using the C3-PEO process instead of through conventional processes and hence, considered as a GHG benefit. This gas manufacture typically occurs through the processing of syngas that may originate from a number of different hydrocarbon resources. Although the GHG impact of syngas may be minimized with the use of biomass, steam methane reforming of natural gas is more likely suited for use in Alberta.¹⁶ We used ThinkStep's proprietary LCA software, GaBi, to calculate the GHG emissions for conventionally producing CO.

CO Purification

In both of the process modes, CO in the exit stream from the reactor is present in a mixture of other components in the system. In the transport mode, it is a CO and CO₂ mixture, whereas in the cofeed mode, it is in a mixture of CO, CO₂, and ethylene. To separate CO₂, the gas mixture is sent to an amine separation unit; to recover CO₂ from the amine solvent, the solvent is subjected to thermal regeneration. To account for the heating requirements in the CO purification step, RTI considered the CO₂ thermal regeneration energy.

We determined the previously described factors for the conventional EtO production and the C3-PEO process in the two modes of operation. All other factors such as transport and refinery products would be similar for the conventional and C3-PEO processes and hence can be ignored to estimate the GHG benefits. The results are discussed further in the next section of this report.

LCA Results

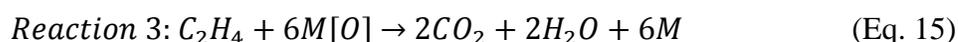
The LCA results for the two cases are summarized in **Table 11**. RTI used the GHG emissions from the conventional ethylene direct oxidation in the GHG benefit evaluation. The GHG emissions for the two process modes were evaluated from the process model and were used to determine the amount of CO₂ avoided by each of these processes per tonne of EtO produced.

The EtO yield for the transport and cofeed modes was assumed to be 12% and 9%, respectively, and the side reaction conversion was assumed to be 10% for both the cases. The amount of CO₂ consumed per tonne of EtO produced is in the same range for both the modes of operation of the C3-PEO process. However, the consumption of electricity and natural gas is higher for the transport mode compared to the cofeed mode mainly because of the intermediate catalyst heating and additional recycle compression in the transport mode case. However, because CO₂ is one of the main reactants, in both the modes of operation of the C3-PEO process, the amount of CO₂ avoided is greater than 2 tonnes per tonne of EtO produced. The amount of CO₂ avoided for the cofeed mode was found to be higher at 3.2 tonnes per tonne EtO produced.

Table 11. Results of GHG Benefit Analysis for the Two Cases

	Traditional Production (tonne/tonne of EtO)	Transport Mode		Cofeed Mode	
		C3-PEO Production (tonne/tonne of EtO)	GHG Benefit (tonne/tonne of EtO)	C3-PEO Production (tonne/tonne of EtO)	GHG Benefit (tonne/tonne of EtO)
Air separation unit	0.035	—	0.035	—	0.035
Carbon dioxide input	—	-5.080	5.080	-5.172	5.172
Electricity	0.064	0.225	-0.161	0.171	-0.107
Natural gas	0.390	2.550	-2.160	1.967	-1.577
Carbon monoxide	—	-3.214	3.214	-3.108	3.108
Carbon monoxide purification	—	-3.965	-3.965	-3.416	-3.416
Transports	—	—	—	—	—
Energy carriers	—	—	—	—	—
Refinery products	—	—	—	—	—
Total			2.043		3.215

To understand the effects of various parameters on the GHG emissions, RTI performed a sensitivity analysis for various scenarios of main reaction and side reaction conversions. However, we found that the higher the side reaction conversion was, the higher the GHG avoided as well. This can be better understood by studying the following key reactions involved (Equations 13 through 15):



Only 1 mole of the oxidized metal catalyst is required to convert 1 mole of ethylene to EtO in the main reaction, Reaction 2 (Equation 14). However, for the undesirable side reaction, every mole of ethylene participating in the side reaction consumes 6 moles of the oxidized metal catalyst. These 6 moles of the oxidized catalyst require 6 moles of CO₂ to get to the oxidized state from the initial state. Therefore, a combination of Reactions 1 and 3 (Equations 13 and 15, respectively) would show that every mole of ethylene participating in the side reaction indirectly consumes 4 moles of CO₂ and hence, the overall GHG benefits are higher when the side reaction is dominant, though valuable products are not generated, and the ethylene reactant is consumed. As a result, this side reaction has a positive effect on the GHG benefits, but would have a negative effect on the economics of the process.

This analysis suggests that although it is important to understand the GHG savings using the novel process, the GHG benefit analysis should be tightly integrated to the techno-economic analysis of the overall process. The results of the integrated analysis are presented in the next few subsections of this report.

GHG Benefit Analysis

From the LCA, it was evident that the GHG benefits that could be realized by the C3-PEO process should be evaluated with integration into the process economics. With this objective, we evaluated the base case process economics at different side reaction conversions. The results are presented in **Figure 25**.

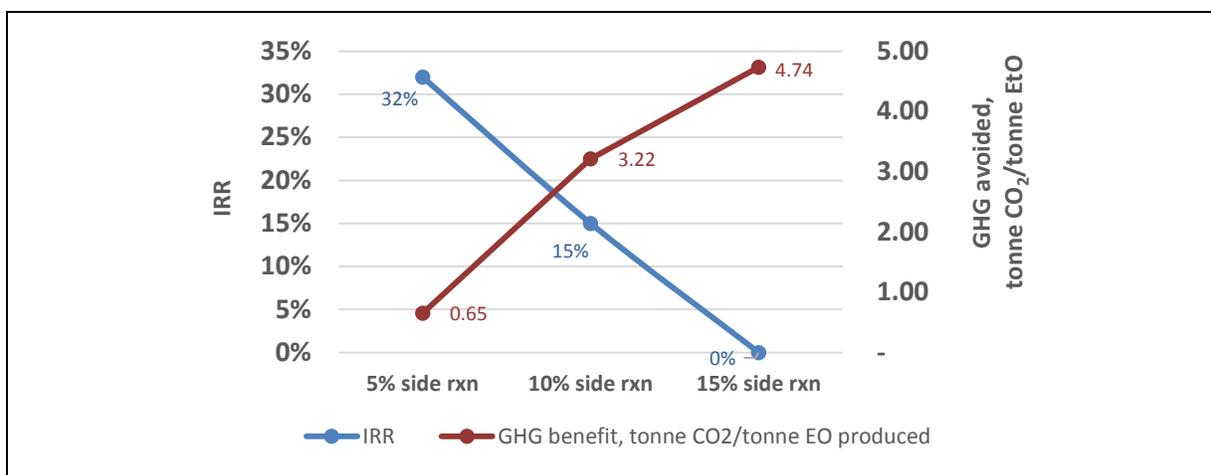


Figure 25. IRR and GHG variations with different side reaction conversions.

From the LCA, we concluded that the higher the side reaction conversion, the higher were the GHG benefits. The main reaction conversion was maintained constant at the base case value of 9%, and the process economics and GHG benefits were estimated at three different side reaction conversions of 5%, 10%, and 15%. From Figure 35, for a 5% side reaction, the IRR is estimated to be 32%, and only 0.65 tonnes of CO₂ are avoided per tonne of EtO produced. However, at a 15% side reaction conversion, 4.7 tonnes of CO₂ are avoided per tonne of EtO produced, and the IRR is 0%, which shows that the process is not promising in this scenario. For the base case scenario, 3.2 tonnes of CO₂ are avoided per tonne of EtO produced, and the IRR is 15%. Figure 35 clearly shows that there is a tradeoff between the GHG benefits and the process economics, and it is very important to understand the integrated environmental and economic performance of the process for different economic and process scenarios.

Techno-economic Analysis and GHG Benefit Analysis for Current Catalyst Performance

The sensitivity analyses previously described show the importance of balancing the EtO and H₂O yields of the C3-PEO catalyst. **Table 12** lists the calculated IRR and GHG benefit for three of the top performing catalysts developed in Round 1 of the Climate Change and Emissions Management Corporation (CCEMC) Grand Challenge. We calculated each of the IRR values by using the best case scenario values previously listed. While Figure 35 shows a major variability in the IRR and GHG benefit as the side reaction conversion is varied, Table 15 shows that both a high IRR and GHG benefit may be achieved as long as the EtO:H₂O yield ratio is approximately 3:4.

Table 12. IRR and GHG Benefit of Three Top Performing Catalysts

	Catalyst 1	Catalyst 2	Catalyst 3
EtO yield	7.5	6.2	5
H ₂ O yield	10	8.6	7
IRR	27%	23%	21%
GHG benefit, tonne/tonne of EtO produced	4.20	4.31	4.33

The total GHG reduction benefit for the C3-PEO process in Alberta, Canada, is estimated at 4.33 tonnes of CO₂-e per tonne of EtO produced. Therefore, to achieve a minimum emission reduction of 1 Mt of CO₂-e, 0.23 Mt of EtO would need to be produced by the C3-PEO process per annum, or approximately 1 plant sized at 250 kt. This value is approximately 20% of the current market size in Canada and less than 1% of the expected global market size of 24.5 Mt in 2017.¹⁷ Conservative market penetration rates were assumed to determine the expected GHG reduction from C3-PEO deployment. With the EtO market growing between 3% and 4% per annum, we assumed an average global market penetration rate of 2% and a higher penetration rate for Alberta of 4%, given the ideal market for the technology and products.¹⁷⁻¹⁸ As a result, following the demonstration of the process in 2020, the cumulative GHG reductions of C3-PEO can be calculated in 10- and 20-year increments as shown in **Table 13**. This technology has an expected GHG benefit of 32 Mt of CO₂-e by 2036 in Alberta and 356 Mt of CO₂-e reductions globally. With the annual global demand of EtO expected to grow to nearly 50 Mt by 2050 and 2.3 Mt in Alberta, there is a potential GHG emission reduction of more than 200 Mt of CO₂-e per annum if the entire global supply adopted the C3-PEO process and 10 Mt of CO₂-e per annum in Alberta.

Table 13. Cumulative Emissions Reductions from C3-PEO Market Penetration

	10-Year Increment 2016–2026	20-Year Increment 2016–2036
Alberta	5.8 Mt of CO ₂ -e	32 Mt of CO ₂ -e
Global	65 Mt of CO ₂ -e	356 Mt of CO ₂ -e

PRELIMINARY DESIGN PACKAGE

The process flow diagram for the C3-PEO pilot system to be built during Round 2 of the CCEMC Grand Challenge is shown in **Figure 26**. The reactant gas consisting of ethylene, nitrogen, CO₂, and a tracer gas, is preheated before entering the fluidized bed reactor, which can be operated as a fixed or fluidized bed. The product gas is then filtered and reduced to near

atmospheric pressure in a BPR. The effluent stream then enters a heat exchanger to cool the product gas to the scrubber operational temperature (73°C), and the EtO is converted to ethylene glycol. The remaining products are combusted in a thermal oxidizer.

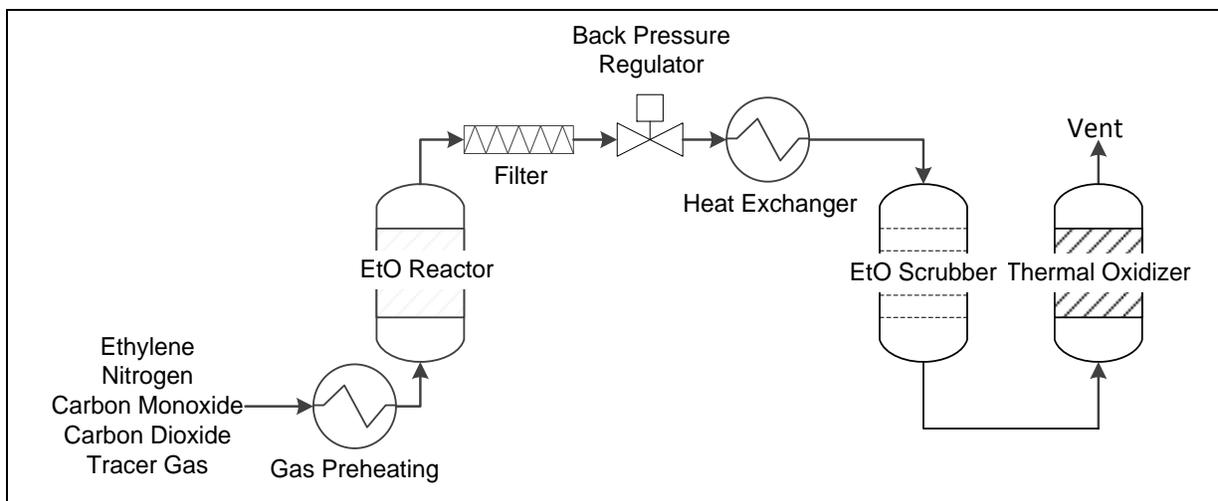


Figure 26. Process flow diagram for the C3-PEO pilot system.

GHG Emissions Reductions Status

This project is not projected to begin reducing GHG emissions until commercial development begins after the end of Round 3 of the CCEMC Grand Challenge.

CONCLUSIONS

During Round 1, RTI has improved on its previous catalyst formulations and developed families of catalysts that can both remove oxygen from CO₂ and transfer the oxygen to ethylene to make EtO. Although previous work focused on iron in terms of reacting with CO₂, we determined that it was not selective for ethylene epoxidation. Instead, other catalyst families were found to have higher EtO selectivity. We have made improvements regarding the production of EtO by incorporating promoters, by investigating the catalyst support, and observing the impacts of dispersion. We evaluated the technology to obtain long-term catalyst activity and stability data and to develop an optimum process design.

RTI developed catalysts that have been shown to be able to produce EtO in both a cofeed mode and a transport mode of operation. However, after incorporating experimental data into a process model, it was determined that the cofeed mode of operation is the most economical embodiment for a complete process. While the catalyst is not optimized, the current experimental results have achieved yields comparable to the conventional process with a yield of EtO between 5% and 8%. The TEA results have indicated that the C3-PEO technology could

be economically viable given favorable market conditions. Optimization of the catalyst during continued development could increase the economic advantage of the C3-PEO technology beyond the conventional process. RTI also used the modeled system to perform a detailed analysis of the potential GHG reductions of the process. The LCA shows that greater than 4.3 Mt of CO₂-e may be avoided for each 1 Mt of EtO produced. One standard-sized 250 kt EtO plant in Alberta would be able to achieve greater than 1 Mt of CO₂ emissions avoidance per annum. Finally, we developed a preliminary design package for testing of the novel catalyst in a scaled-up process in Round 2 of the CCEMC Grand Challenge for Innovative Carbon Uses.

SCIENTIFIC ACHIEVEMENTS

RTI presented the results of the project at various conferences over the course of the project including the following:

- Mobley, P. D., & Lail, M. A. (Invited Speaker). (2014, April). *Captured-CO₂ Catalyst for the Production of Ethylene Oxide (C3-PEO)*. Presented at Zero14, Alberta, Canada.
- Lail, M. A., Mobley, P. D., & Peters, J. E. (Invited Speaker). (2015, May). *Carbon dioxide utilization for the production of ethylene oxide*. Poster presented at Gordon Research Conference on Carbon Capture, Utilization, and Storage, Easton, MA
- Mobley, P. D., Lail, M. A., & Peters, J. E. (Invited Speaker). (2015, November). *CO₂ Utilization for the Production of Ethylene Oxide*. Presented at AIChE Annual Meeting, Salt Lake City, UT.

In addition, a patent application is in progress to secure the intellectual property of the C3-PEO technology and will be submitted after completion of Round 1 of the project.

NEXT STEPS

RTI is seeking to secure continued funding through CCEMC during Round 2 of the Grand Challenge for Innovative Carbon Uses to continue development of the C3-PEO technology. An industrial project partner and pilot-scale testing host site is currently being negotiated to accelerate the development path toward commercialization. We have developed presentation slides outlining the project findings and development path for the next several years. Multiple industry representatives have visited RTI to discuss the progress of the

technology and the potential role they may play as a partner in the development into a commercial process.

REFERENCES

1. Chongterdtoonskul, A.; Schwank, J. W.; Chavadej, S., Comparative study on the influence of second metals on Ag-loaded mesoporous SrTiO₃ catalysts for ethylene oxide evolution. *Journal of Molecular Catalysis A: Chemical* **2013**, *372* (175-182).
2. Kolb, K. E.; Kolb, D., Organic Chemicals from Carbon Monoxide. *Journal of Chemical Education* **1983**, *60* (1), 57-59.
3. Dellamorte, J. C.; Lauterbach, J.; Barteau, M. A., Rhenium promotion of Ag and Cu-Ag bimetallic catalysts for ethylene epoxidation. *Catal. Today* **2007**, *120*, 182-185.
4. (a) Maier, J.; Gopel, W., Investigations of the bulk defect chemistry of polycrystalline tin(IV)oxide. *Journal of Solid State Chemistry* **1988**, *72*, 293-302; (b) Mizusaki, J.; Koinuma, H.; Shimoyama, J.-I.; Kawasaki, M.; Fueki, K., High-temperature gravimetric study on non-stoichiometry and oxygen-adsorption of SnO₂. *Journal of Solid State Chemistry* **1990**, *88*, 443-450.
5. (a) Sutton, D.; Parle, S. M.; Ross, J. R. H., The CO₂ reforming of the hydrocarbons present in a model gas stream over selected catalysts. *Fuel Processing Technology* **2002**, *75* (1), 45-53; (b) Wu, W. Q.; Jiang, H. F., Palladium-Catalyzed Oxidation of Unsaturated Hydrocarbons Using Molecular Oxygen. *Accounts of Chemical Research* **2012**, *45* (10), 1736-1748; (c) Lee, J. K.; Lee, H.; Hong, U. G.; Yoo, Y.; Cho, Y. J.; Lee, J.; Chang, H.; Song, I. K., Oxidative dehydrogenation of n-butane over Mg-3(VO₄)(2)/MgO-ZrO₂ catalysts: Effect of oxygen capacity and acidity of the catalysts. *Journal of Industrial and Engineering Chemistry* **2012**, *18* (5), 1758-1763; (d) Zhang, F.; Miao, C. X.; Yue, Y. H.; Hua, W. M.; Gao, Z., Dehydrogenation of Propane to Propylene in the Presence of CO₂ over Steaming-treated HZSM-5 Supported ZnO. *Chinese Journal of Chemistry* **2012**, *30* (4), 929-934; (e) Yasuda, K.; Masui, T.; Miyamoto, T.; Imanaka, N., Catalytic combustion of methane over Pt and PdO-supported CeO₂-ZrO₂-Bi₂O₃/gamma-Al₂O₃ catalysts. *Journal of Materials Science* **2011**, *46* (11), 4046-4052.
6. Jakobsen, J. G.; Jorgensen, T. L.; Chorkendorff, I.; Sehested, J., Steam and CO₂ reforming of methane over a Ru/ZrO₂ catalyst. *Applied Catalysis a-General* **2010**, *377* (1-2), 158-166.
7. Shen, J. P.; Mobley, P. D.; Douglas, L. M.; Peters, J. E.; Lail, M.; Norman, J. S.; Turk, B., Mechanistic Study of CO Formation from CO₂ Using a Mixed-Metal Oxide of Tin, Iron, and Aluminum. *RSC Advances* **2014**, *4* (85), 45198-45206.
8. Chongterdtoonskul, A.; Schwank, J.; Chavadej, S., Comparative Study on the influence of second metals on Ag-loaded mesoporous SrTiO₃ catalysts for ethylene oxide evolution. *Journal of Molecular Catalysis A: Chemical* **2013**, *372*, 175-182.
11. The Alberta Carbon Trunk Line Project Fact Sheet. http://www.enhanceenergy.com/pdf/ACTL/actl_fact_sheet.pdf.
12. (a) Gas Pipeline. In *Dakota Gasification Company*; (b) Living and Working Near CO₂ Pipelines. https://www.dakotagas.com/files/pdf/Brochures_Displays/Living-and-Working-near-CO2-Pipelines-Souris-Valley-brochure-SVPL.pdf.

13. Chemicals, N. Taking CAER along the pipelines we operate: A guide for landowners and neighbours.
http://www.novachem.com/ExWeb%20Documents/joffre/NOVA_CAER_Jan2014_web.pdf.
14. Rebsdats, S., Mayer, Dieter, Ethylene Oxide. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2000.
15. (a) International, P., Organic Intermediates Database: Ethylene Oxide (EO) via O₂/methane; oxidation of ethylene with oxygen. PE International: 2012; Vol. GaBi Databases 2011 Version 6; (b) *Cradle-to-Gate Live Cycle Inventory of Nine Plastic Resins and Four Polyurethane Precursors*; Franklin Associates.: Prairie Village, Kansas., 2011
16. Marano, J. J.; Ciferno, J. p., Life-cycle green-house gas emissions inventory for Fischer-Tropsch fuels. Energy, U. D. o., Ed. 2001.
17. *Ethylene Oxide, A Global Strategic Business Report*; Global Industry Analysts Inc: San Jose, CA, 2011.
18. (a) Szulczyk, K. R.; McCarl, B. A.; Cornforth, G. *Market Penetration of Ethanol*; Texas A&M University: 2006; (b) Lund, P., Market Penetration Rates of New Energy Technologies. *Energy Policy* **2006**, *34*, 3317-3326.
19. . Taking CAER along the pipelines we operate *Nova Chemicals* [Online].
http://www.novachem.com/ExWeb%20Documents/joffre/NOVA_CAER_Jan2014_web.pdf.

DISCLAIMER

CCEMC and Her Majesty the Queen in right of Alberta and each of them make no warranty, express or implied, nor assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information contained in this publication, nor that use thereof does not infringe on privately owned rights. The views and opinions of the author expressed herein do not necessarily reflect those of CCEMC and Her Majesty the Queen in right of Alberta and each of them. The directors, officers, employees, agents, and consultants of CCEMC and the Government of Alberta are exempted, excluded, and absolved from all liability for damage or injury, howsoever caused, to any person in connection with or arising out of the use by that person for any purpose of this publication or its contents.