



Non Confidential Report

Project Name:

Valorizing Industrially Produced CO₂: A reliable and cost effective solution for carbon capture and its conversion to marketable products

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Executive Summary:

Enerkem has successfully achieved the original research objective of identifying industrial CO₂ sources and synthesizing a marketable chemical such as acrylic acid that could sequester CO₂ directly in the molecule. Two sources of industrial CO₂ were identified in Alberta and the data obtained were used to conduct a techno-economic analysis aimed to develop the dry methane reforming (DMR) process to produce syngas from CO₂ and methane. The techno-economic analysis for dry reforming process indicates that it has a good potential in CO₂ capture for CO production. This reforming approach therefore provides an alternative technology that converts CO₂ emission problem into an opportunity by using the CO and the H₂ generated as raw materials for the chemical synthesis. A robust dry reforming catalyst system (E20) has been developed that has been tested for more than 3000 h time-on-stream under different conditions. Furthermore, the E20 catalyst has been tested for over 470 hours continuously during kinetics evaluation. Under certain operating conditions during this testing, the catalyst could consume between 28.8 – 35.4 kg of CO₂ per kg of catalyst while yielding between 2.81 - 3.38 kg of H₂. The kinetic model developed on the catalyst was utilized for running simulations in HYSYS for scale up evaluation. Use of syngas such as the dry reformed syngas for direct production of chemicals was evaluated for the production of dimethyl ether (DME) in a single step process at the pilot scale. DME is a biofuel unto itself and is an important intermediate for the production of other chemicals.

Several other catalytic processes were developed over the course of the project to produce chemicals that utilize the syngas and maximize carbon capture. The preliminary data generated on three different chemicals are methyl acetate, acetic acid and acrylic acid. These chemicals are also identified as high potential products for future Enerkem commercial development. Among these chemicals both methyl acetate and acetic acid are currently being made from methanol on standard technology that utilizes the syngas with appropriate H₂/CO ratio and methyl-iodide as a co-catalyst. During the course of this project a stable and regenerable catalyst for iodide-free DME carbonylation process for methyl acetate synthesis has been identified and tested. The fact that the new process is iodide-free improves certain economic aspects of the process while improving environmental performance of the process. In addition to the iodide free carbonylation catalyst, Enerkem also developed or repurposed two other catalyst formulations that now lay a solid foundation for the production of chemicals that could sequester CO₂ using green chemistry; Hydrolysis of methyl acetate to Acetic Acid (New Formulations) and Aldol condensation of Formaldehyde and Acetic Acid to Acrylic Acid (New Formulations).

The developed Carbonylation catalyst (Catalyst 1) is a bimetallic iodide-free zeolite based catalyst with immense potential for scale up. The preliminary data on methyl acetate hydrolysis (Catalyst 2) to produce iodide-free acetic acid process has also been evaluated on an in-house metal free zeolite catalysts. Furthermore, a novel aldol condensation catalyst for direct one-step acrylic acid synthesis from acetic acid and formaldehyde has been developed and tested under different conditions. The results on acrylic acid yields obtained are comparable to the results from literature and are indicative that yield and selectivity targets for commercialization could be obtained. The greenhouse gas (GHG) emission reduction potential of a manufacturing plant using these processes has also been estimated. It has been assumed that such chemical plants will be a bolt-on process to an existing Enerkem bio-

refinery that has a CO₂ source that is currently being released to the atmosphere. This cost estimate includes a catalytic dry reforming process to syngas followed by a chemical conversion of syngas to DME and further converting DME to acetic acid by using a novel iodide-free catalytic system. Methanol formed is further converted to acrylic acid via formaldehyde and acetic acid using a novel aldol condensation catalyst. These alternative routes have shown significant impact on GHG emission reduction based on the materials balance.

For an integrated process that uses methanol from 1 Enerkem module (144 tpd) combined with additional syngas from externally sourced CO₂ (111 tpd) to make acrylic acid (173 tpd) through intermediates such as acetic acid (143 tpd) and formaldehyde (72 tpd), the GHG estimates were completed. All the carbon monoxide (CO) thus generated from CO₂ reforming from fossil based CO₂ are consumed by utilizing the entire methanol through intermediates. The total estimated GHG emission reduction was projected to be significant for an integrated process scaled to use the methanol and syngas from a single Enerkem commercial module. One megatonne CO₂ reduction could be achievable by putting together 4-5 Enerkem modules for acrylic acid with the best internal rate of return (IRR). Based on Alberta's demographics, there is potential for 6 – 8 Enerkem modules when considering waste from Edmonton and Calgary.

Project Description

Current technologies sequester industrially produced CO₂ leading to its capture, via the underground formation of stable inorganic carbonates/bicarbonates. However, this approach is dependent on available geological CO₂ sinks and appropriate infrastructure and energy for compressing, piping, and injecting the CO₂ into the geological formation. Enerkem is proposing an alternate approach that converts the CO₂ into valuable organic products having commercial markets. Such approach can be implemented on a distributed basis independently of geological formations and pipeline locations, and can become an economically attractive route for long term CO₂ and methane carbon capture. It is also an important step towards further development of the chemical sector in Alberta aimed to export into Global markets. Enerkem has taken this approach since the planning of the first commercial biofuel plant in Edmonton (Enerkem Alberta Biofuel or EAB) using municipal solid waste as carbon feed source to make both methanol and ethanol. The incorporation of CO₂ as a carbon source material with which to expand the platform is part of the Enerkem strategy aiming to further improve the use of Carbon from waste (biogenic Carbon, recycled Carbon or Carbon in CO₂ from industrial processes). Such strategy is deployable across Alberta where carbon from waste and CO₂ are readily available.

a) Introduction and Background

Enerkem has developed a robust, low severity gasification technology that can convert non-homogeneous carbonaceous materials into clean synthetic gas (“syngas”). Enerkem, in the period 2003 – 2005, proved, at the pilot level (200 kg feed/h dry basis), that such synthetic gas could be conditioned and subsequently converted into methanol using novel three phase reactor technology. As methanol is a building-block molecule, other products could be produced from it. This would enable the emergence of an innovative “green chemicals” sector using renewable biomass-rich feedstocks ranging from municipal solid wastes to agro-residues and forest residues. Enerkem’s innovative technology is now used in the world’s first full-scale commercial biomass to ethanol plant on the site of the Edmonton Waste Management Centre (EWMC). In parallel to full-scale commercial development, Enerkem continues to extend its technology development capabilities with the inauguration of the AERF (Advanced Energy Research Facility) plant in Edmonton. Operated jointly with the EWMC, this laboratory and pilot facility has become a dynamic center of excellence in research and development for Enerkem as well as for other technology development companies.

b) Technology Description

The catalytic chemical technology that converts carbon from CO₂ to intermediate carbon monoxide (CO) could be used to implement a carbonylation strategy that leads to marketable chemical products. Enerkem plans to use CO₂ from major emitters such as (i) steam methane reforming operations in Alberta that produce hydrogen for refineries and (ii) synthetic crude oil from oil sands operations for upgrader applications. Both these operations have emissions or process streams that have high concentrations of CO₂ that would be suitable for dry reforming use with minimal pre-treatment. Such CO₂ will be recovered and converted to CO using a reforming route that would also use the abundant natural gas available in Alberta. We estimate that for a given installation, we could reduce CO₂ emissions

by about 45% by converting industrial CO₂ to CO and the latter subsequently used in “building” added value marketable molecules as end product functional chemicals. The awarded project has the following four key objectives:

- Identify the specific CO₂ industrial sources to be used as CO₂ feedstock for the catalytic conversion process to produce CO and H₂ as syngas;
- Test the catalyst formulations of Enerkem successfully tested at the lab level for sensitivity to potential poisons present in the identified CO₂ streams and establish appropriate purification strategies;
- Use the CO produced in carbonylation-related strategies, beginning with Methanol, (or DME) and Ethanol as initial prototype reactant(s) to synthesize value added oxygenated chemicals aiming at acetic acid, acetaldehyde, acrolein and acrylic acid;
- With the results obtained, develop a techno-economic model that quantifies the dual value proposition of such strategy: GHG emissions reduction and marketable chemicals.

c) Project Goals (Original goals & changes made throughout the project)

The project goals are built in 2 phases:

Phase 1 will have two years duration (Years 1 and 2) and comprise three tasks:

(Task 1) will focus on

- I. pre-conditioning CO₂ streams in terms of purity, contaminant removal and compression for downstream requirement and
- II. cost evaluation of the CO₂ – conditioned stream thus obtained;

(Task 2) will optimize the CO₂ reforming catalyst and will focus on

- I. gathering kinetic data with which to construct and develop a functional model for scale up;
- II. build a high pressure carbonylation reactor

(Task 3) will focus on CO valorization and conversion to products via carbonylation catalysis

- I. Carbonylation of DME to Methyl acetate (New Formulations)
- II. Hydrolysis of methyl acetate to Acetic Acid (New Formulations)
- III. Aldol Condensation of Formaldehyde and Acetic Acid (New Formulations)

Task 1 - Outcomes and Learning

Three different types of CO₂ sources (raw gas) were identified and studied in details:

- a) Waste treatment section from bio-sources
- b) Oil Sand Mining and Upgrading (Shell Canada Energy Limited)
- c) AERF Rectisol Process for CO₂ recovery and use

a) Waste treatment section from bio-sources

Bio-waste to Energy for Canada Integration Initiative (BECii) is a bio-sourced technology using grains (wheat, corn or mix) to produce ethanol and is located in rural Hairy Hill near Vegreville, Alberta. The company produces 40M liters per year of ethanol and 2.5 MWH electricity from processing over 260 ktons per year of bio-waste including manure, agricultural, and municipal source separated organics (SSO) waste. Currently, the company releases about 35,000 tonne CO₂ to the atmosphere at atmospheric pressure per year. The technology is based on anaerobic degradation of particulate organic material. The process can be categorized to four steps: 1) pre-treatment to de-structure the feed stock, 2) hydrolysis, 3) fermentation and 4) product separation. During the hydrolysis step, the cellulosic part of the feedstock is converted to sugar using acid treatment, typically sulfuric acid. Bio-ethanol is produced during fermentation using microorganisms such as yeast. As a result of the fermentation process, glucose sugar (C₆H₁₂O₆) is converted to alcohol (C₂H₅OH) and carbon dioxide gas (CO₂) ^[1].



Currently, the company releases this CO₂ to the atmosphere which is considered biogenic and is carbon neutral. The gas stream was analyzed by CO₂ analyzer at the site. In addition, samples were taken and were also analyzed by Gas chromatography (GC). Analysis of the results revealed that the gas stream contains more than 98% CO₂ and the rest is nitrogen and hydrogen. It should be noted that the pressure of CO₂ is atmospheric. The flow rate of the carbon dioxide being released to the atmosphere is 107 kmol/ h (111 tonne CO₂/d). Based on these analyses this CO₂ rich stream could be a good source of further processing into syngas using appropriate reforming technology.

b) Oil Sand Mining and Upgrading (Shell Canada- Scotford Upgrader)

The Shell Scotford upgrader is located about 40 km northeast of Edmonton, Alberta and consists of an upgrader, oil refinery and chemicals facility. The refinery produces 100,000 barrels per day of marketable products; mainly diesel, gasoline, jet fuel and propane in addition to about 3 million tonnes of CO₂ per year.⁽²⁾ Currently, Shell Canada Energy, located at Scotford Upgrader and Expansion, operates two existing Hydrogen Manufacturing Units (HMUs) which are the primary sources of CO₂ produced. It is expected that another hydrogen manufacturing unit (HMU 3) which is under construction will be operated in 2016 to expand the hydrogen production. In the hydrogen manufacturing unit, the feedstock used is a mixture of natural gas with hydrocarbon feeds (low pressure and high pressure hydrocarbon streams). The composition of these streams is presented in Table 1.1.⁽³⁾

Table 1.1: Component composition of feedstock for hydrogen manufacturing units at Shell ⁽³⁾

Stream No.		1.a	1.b	1.c
Component		LP-HC Feed	HP-HC Feed	HP Natural Gas
CH ₄	%	22.82	14.67	93.87
C ₂ H ₆	%	9.21	9.54	2.88

C ₃ H ₈	%	6.31	14.76	0.75
i-C ₄ H ₁₀	%	0.90	2.82	0
n-C ₄ H ₁₀	%	2	2.81	0.18
n-C ₅ H ₁₂	%	1	0.88	0.02
n-C ₆ H ₁₄	%	0.5	0.45	0.01
H ₂	%	57.16	51.35	0
N ₂	%	0.1	2.71	1.6

During operation of HMU 1+2 units (100% loads), feed stream containing hydrocarbon and hydrogen is preheated to reach 540 °C and mixed with steam. Subsequently, this stream is reformed through steam-methane reforming (SMR) using well established Ni-based catalyst to produce syngas (H₂ and CO). The main by-product of this reaction is CO₂.

The main unit operation during the process is presented in simple schematics (Figure 1.1). It can be seen that the reformed gas is routed to the cooler followed by a high temperature (HT) shift conversion reactor. The temperature of the feed stream fed in is 340°C. In this reactor, most of the CO gas component is reacted with water to produce more hydrogen. The raw hydrogen is passed through several coolers and heat exchangers to cool and condense water. Currently, Shell Canada Quest Project is planning to capture 1 million tonnes of CO₂ produced from syngas using Amine CO₂ extraction followed by Carbon capture and Sequestration (CCS) technology. In the plant, three absorbers are planned to be operated. Finally, the treated gas will be fed to pressure swing adsorption (PSA) to separate hydrogen. In this unit, hydrogen with high purity of 99.9% is produced. Currently, the off-gas of PSA which contains hydrogen and CO₂ (Stream 5) is directed to the reformer burner.

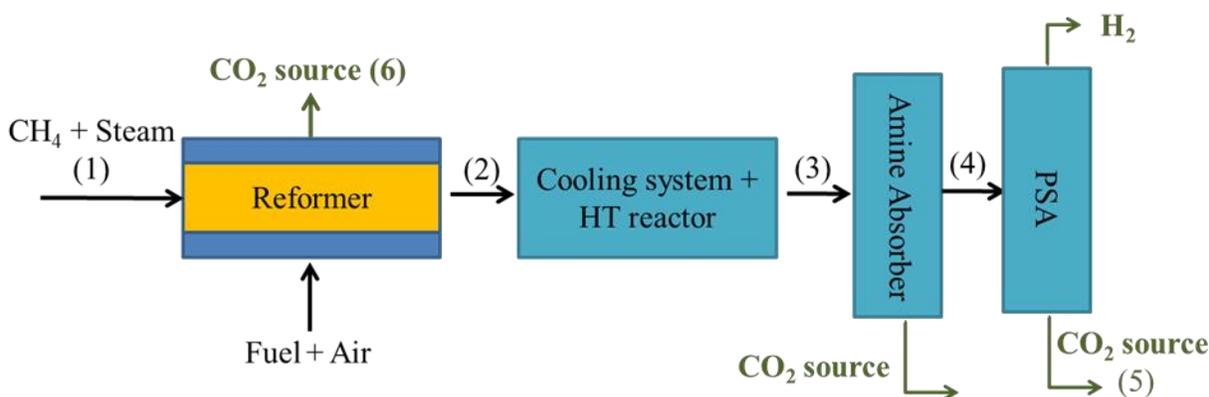


Figure 1.1: Simplified process flow diagram (PFD) of Shell Upgrader HMU 1 at Scotford

According to the released report by Shell, 1.5 million tons per year (3,891 kmol/h) of CO₂ will be produced during the reforming as a by-product of steam methane reforming reactions.⁽²⁾ Besides, CO₂ is generated as a result of burning of fuel gas to produce energy for reformers, compressor and other equipment. Based on the analysis of the gas streams in the Hydrogen Manufacturing Unit (HMUs) indicated that 3 streams as depicted on Figure 1.1 were suitable sources of CO₂ from the SMR process to be used in Dry Reforming.

Table 1.2: Recognized CO₂ sources at Shell –Scotford Upgrader

Stream Name and #		Striper product from Amine unit	PSA Off gas (5)	Burner flue gas (6)
CO ₂	Kmol/h	975	213	455
Temperature	°C	35	35	25
Pressure	kPa(abs)	147	130	120
Suitability for dry reforming		yes	yes	no

Based on this study it can be concluded that in a typical hydrogen manufacturing plant that uses steam methane reforming operation to produce hydrogen, the above streams (Table 1.2) could be potential candidate sources for Enerkem if external the CO₂ is required. Currently, at Shell, PSA off gas is sent to burner and the CO₂ obtained from Amine unit, is planned to be used for carbon capture sequestration Shell Quest project.

Further a techno-economic analysis of utilizing the PSA feed gas and integrated to a dry reformer for syngas production followed by a standard separation unit to generate pure streams of H₂ and CO were evaluated. The preliminary evaluation indicated that the total capex for a 1 Million Tonne CO₂ capture plant could be in the excess of 300 Million USD with OPEX at about 93.5 Million USD per year. The CO₂ avoidance and capture cost are calculated as 163 USD/Tonne and 124 USD/Tonne respectively. If we compare the CO₂ capture and sequestration (CCS) cost for various operations as proposed on fossil-based industry the CO₂ avoidance cost range from 60 CAD /Tonne to 230 CAD/Tonne and are comparable to the cost associated with other processes prevalent in power, oil sands and chemical emission points in Alberta.

	CAD / Tonne CO ₂ Abated
Coal/Coke Gasifier	60 - 150
Coal Post Combustion	50 - 150
Coal- Oxy Fired	85 -130
H2- PSA (Process)	110 - 165
H2- PSA (Flue)	140 - 180
SAGD Boilers	175 – 230

CO₂ Capture Cost Estimates (Alberta Carbon Capture and Storage Development Council, 2009)

Based on the techno-economic analysis it can be concluded that the dry reforming process could be a possible option for both CO₂ capturing and utilizing the CO for downstream carbonylation process to manufacture value added chemicals.

c) AERF Rectisol Process

The current design at AERF uses chilled methanol as a physical absorption solvent at high pressure to separate CO₂ from syngas at low temperature (Rectisol process). Rectisol process uses chilled methanol as a physical solvent to separate CO₂. Industrially, this process is used in syngas treatment and in natural gas industry. Due to the high vapour pressure of methanol, the process must be carried out between -35 to -70°C. Some of the main advantages of the Rectisol process can be listed as follows: high thermal and chemical stability, non-corrosive, miscibility of the solvent with water. Other main advantages of Rectisol process is that regeneration of solvent is achieved by low pressure flashing without using any process heat. At AERF, methanol is regenerated by two flashed separators working at 4 and 1 bar respectively. Based on the experimental data and simulation results showed that, high purity of CO₂ (>96%) is produced due to the reduced solubility of CO₂ in methanol at lower pressure. The experimental data on Rectisol Process collected during gasification process for syngas production has proven the efficiency to remove both the acid gases present in the syngas.

- ✓ 86% CO₂ removal efficiency at -15°C
- ✓ 87% H₂S removal efficiency at -15°C

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Task 2 - Outcomes and Learning

Dry reforming integration in the current Enerkem technology is designed to use CO₂ directly in a reducing environment to increase the yield of usable syngas. This in turn reduces the Greenhouse Gas (GHG) emissions directly and reduces the energy load of steam generation used in the reforming process and eventually may lead to a reduction in CAPEX. This task was accomplished on a small reformer to evaluate the impact of CO₂ in syngas formation when mixed with natural gas without any steam. A stable catalyst formulation was established. The structure characterization and performance evaluation indicates that the developed catalyst can be used for dry reforming reaction under established reaction condition. In addition a kinetic model for the Dry Methane Reforming system was developed based on experimental studies. The kinetic model provided a sufficiently good fit and was utilized for running simulations in HYSYS. The DMR system has immense carbon capture potential, capturing over twice the amount of CO₂ that is emitted by CH₄ combustion for providing energy to the process. But when compared with a Steam Methane Reforming system, the DMR appears generally less

favourable as a source of pure hydrogen gas, on the basis of energy consumption. If, however, we consider CO to also be a desirable product, the DMR system is much more favourable than the SMR system. The E20 catalyst has been tested for over 470 hours continuously. Under certain operating conditions, in this duration, the catalyst could consume between 28.8 – 35.4 kg of CO₂ per kg of catalyst while yielding between 2.81 - 3.38 kg of H₂. Evaluation of the process economics clearly exhibited the advantages in terms of process economics, energy consumption as well as CO₂ capture. For 100 kg moles of CO produced per hour, there was a reduction of 6789.7 kg of CO₂ per hour.

In another analysis the cost evaluation of generating syngas from dry reforming process and further separating the gases to appropriate H₂/CO ratio to make methanol and CO is estimated. Since dry reforming produces H₂/CO ratio less than 1 and is hydrogen deficit. The analysis considers that the excess CO will be utilized for downstream carbonylation step to generate acrylic acid. The methanol yield thus produced will be significantly improved if integrated with the current projected capacity of EAB plant. Based on this it can be concluded that methanol is a good platform from which higher value chemicals such as acrylic acid can be made when integrated with a plant like EAB. The external CO₂ from fossil based industries could be utilized to generate more syngas that could improve the total methanol production by adjusting the H₂/CO ratio. The additional CO obtained from dry reforming could be utilized to make acetic acid. Formaldehyde is also manufactured from the methanol obtained by using commercial process. The acrylic acid obtained thus utilized all the methanol and CO and effectively captured the carbon present in CO₂. The techno-economic analysis reveals that the dry reforming process could be a possible option for generating revenue with a healthy rate of return when integrated with one Enerkem module. Profitability improves further when multiple Enerkem modules are considered in such integration.

Task 3 - Outcomes and Learning

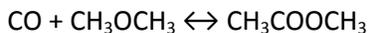
Biofuels production (1st Gen) which includes biodiesel, bio-ethanol, and biogas, are characterized by their ability to easily fit in with current fuels and technology. They are easily blended with current fuels and can be burned in current internal combustion engines. However, the first generation of biofuels, which are produced primarily from food crops, including grains, sugar beets and oil seeds, and compete directly with other food crops for land use is not sustainable as it may accelerate deforestation, competes for water resources and provide only limited greenhouse gas reduction. Several of the issues brought forth by the use of first generation biofuels can be resolved by using agricultural, forest residues and non-food feedstocks instead of edible feedstocks. These residues and non-food feedstocks, otherwise known as biomass, are broken down to produce lignocellulose, which can undergo a number of possible reactions to produce bio-ethanol and other biofuels, but may also serve as a precursor to other carbon-containing chemicals (2nd Gen). Lignocellulosic biomass is also more abundant, sustainable, and more economical to produce when compared to edible feedstocks. However, lignocellulosic feedstocks are more difficult to convert to other chemicals, and processing costs are higher compared to first generation biofuels. Moreover, due to processing difficulties as well as feedstock availability, the search for a sustainable biofuel is ongoing. This has led to the utilization of other potential feedstocks, one of which is municipal solid waste (MSW). Enerkem has taken this route

to make biofuels such as methanol and ethanol and other chemicals using gasification technology and catalytic processes. Catalysis can be used to dramatically reduce the amount of waste and by-products produced in the course of chemical reactions, some of which are difficult to dispose of or may be environmentally hazardous. Since more than 90% of chemical industrial processes currently use a catalyst so a successful production of biofuels and other chemicals from sustainable sources is likely rooted in the development of novel catalysts and processes.

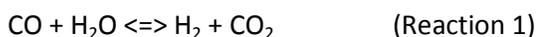
Production of methyl acetate and acetic acid

Acetic acid is mostly produced via methanol carbonylation, which accounts for approximately 65% of global acetic acid production of which the two main processes are the Monsanto and BP Cativa™ processes. The Monsanto process was first designed in 1966, and the first commercial installation started up in 1970. The process used rhodium and iodide-based homogeneous catalysts and operated at pressures of 30 atm and temperatures of 423-473 K. The advantage over previous processes was higher selectivity, which led to simpler purification resulting in savings on both operating and capital expenses. BP Chemicals later acquired the licensing rights to the Monsanto process, and further developed it to create the Cativa™ process in 1996, which was based on an iridium/iodide homogeneous catalyst and operated at a temperature of 463 K and pressures of 20-40 atm. While the selectivity towards acetic acid is very high, harsh halides are formed during the course of the reaction. These halides are very corrosive, and require that process equipment be made from exotic materials. The final acetic acid product must also be purified of these halides. Halides also pose a significant environmental hazard, and must be disposed of in a safe manner. While the Monsanto and BP Cativa™ processes are significantly more efficient when compared to previous methanol carbonylation processes, the presence of halides still translates into increased capital and operating expenditures, as well as the taking on of some risk to the environment. The metals used for the catalysts, rhodium and iridium, are also precious metals, both of which have significant cost.

One of the coproducts in methanol carbonylation is methyl acetate (MA). MA is also the main product of methanol carbonylation when methanol is in excess and acid catalysts are present. MA serves as a popular solvent, but may also be used in the production of other chemicals, mostly in esterification reactions. MA has the lowest boiling point of all organic acetates, and is useful in applications where rapid evaporation is a necessity. Currently most, if not all, MA is produced via methanol carbonylation. For true sustainable and environmentally friendly MA production, the original reactants should come from sustainable sources (such as methanol) and any catalyst used should not require the use of a harmful co-catalyst and preferably be synthesized from inexpensive, common metals. One such alternative to conventional methanol carbonylation for MA production is dimethyl ether (DME) carbonylation utilizing solid acid catalysts. DME is non-carcinogenic, and non-toxic, but is an extremely volatile organic compound. For those reasons, the principal application of DME has been as a clean, high efficiency compression ignition fuel with reduced nitric and sulphuric oxide emissions and particulates. However, in recent years it has been identified as a base chemical for the production of many other chemicals. MA can also be formed by DME carbonylation as well as depicted below:



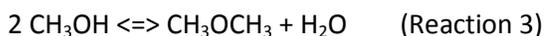
There has also been extensive work conducted on the synthesis of DME from syngas. Predominantly, there is a two-step synthesis using two different catalysts and a one-step synthesis using a bifunctional catalyst. Conversion of synthesis gas to DME requires three steps. Conventionally, synthesis gas is produced by gasification or reforming. Too rich CO would require an adjustment of the synthesis gas via the water-gas shift reaction:



Once the ratio of hydrogen to carbon oxides has been adjusted, the gas is reacted to produce methanol (MeOH):



Finally, methanol is dehydrated to form DME:



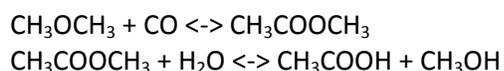
All three reactions are thermodynamically equilibrium-limited and exothermic. Moreover, the catalysts for shift and methanol synthesis reactions are subject to severe deactivation when overheated. To avoid thermodynamic limitations and excessive catalyst deactivation, conventional gas-phase reactors must be run at low per-pass conversions to maintain reactor temperature. Consequently, overall conversion of carbon monoxide to DME is reduced. Commercially, DME is produced from multiple reactors in series and with high recycle rates. The large capital investment and operating costs offer a significant opportunity for cost reduction. Multistep processes, which use separate reactors for each reaction, cannot exploit the potential synergy of the three reactions. If these three reactions are conducted simultaneously, methanol synthesis drives forward the shift reaction and DME synthesis drives both the methanol and shift reactions. Consequently, a one-step process is more flexible and can operate under a wider range of conditions than a multistep process [2]. However, a single-step gas-phase process would still experience a large reactor exotherm from the high net heat of reaction.

Air Products [3] has been conducting laboratory investigations into the synthesis of DME since 1986, initially in an effort to improve syngas conversion per pass in the slurry LPMEOH reactor. Removing methanol by converting it to DME within the same reactor overcomes the usual equilibrium constraints imposed by operating temperature and pressure. A slurry reactor for the direct DME synthesis has many merits compared with a fixed-bed reactor because the existence of a liquid medium makes it easier to remove reaction heat, to achieve almost isothermal conditions. Enerkem has also conducted a bench scale investigation on direct DME synthesis from syngas in a single liquid phase stirred-tank catalytic reactor on bi-functional catalysts composed of copper-based methanol synthesis catalysts and a solid acid such as $\gamma\text{-Al}_2\text{O}_3$ with good results.

Enerkem has further initiated an effort to explore how the carbonylation could effectively proceed without iodine in the reaction system. This is conceptually possible should a catalyst be designed to form the appropriate ligands with CO and insert such CO into the DME molecule. While designing the catalyst,

the importance of a structured solid (such as zeolites) with the “right acidity” was chosen for this research as it could do the work of the I-Rh ligand replacing the Iodine. Current catalysts based on zeolites may have high activity but deactivate quite quickly due to the formation of heavy organic compounds in the pores and channels of the zeolite framework, blocking the reactants access to active sites. Through simple process of elimination and activity measurements, it was determined that the 8 MR provided the highest selectivity towards MA and validated further from the literature data. The data as prevalent in literature also suggest that the some zeolites and metal loaded zeolites could be a good catalyst for MA synthesis from DME very similar to what has been observed during our research. A judicious choice on a combination of metals has been made during the progress of the work for better activity with the ability to regenerate. Operating conditions were optimized so as to limit the formation of coke by-products or to favour desorption of coke precursors. We synthesized and tested a large variety of bi-functional catalysts based on commercial and modified zeolites, with different pre-treatment conditions. The catalyst synthesis, pre-treatment and any modifications are performed in-house based on the original commercially available zeolite. The procedures do not require specialized equipment, may be performed in air atmosphere, they are simple, reproducible and easily scalable. Multiple batches of different catalysts were prepared, stored under wet or dry conditions that showed reproducible catalytic behavior. Conversion is substantially improved on a bi-metallic system compared to monometallic system. The productivity is also found to be improved at an appropriate ratio of the metals associated. The regeneration of the catalyst was accomplished in situ without the use of air, so that the production safety is not compromised. It was observed that after regeneration the selectivity towards methyl acetate was maintained at very high level (approximately 100%) with the only other by – product being very low levels of methanol.

Acetic acid was synthesis during the work (iodide free process) by methyl acetate hydrolysis in presence of another heterogeneous acid catalyst in a fixed bed to acetic acid and methanol with very conversion.



Furthermore, in order to deal with the azeotropes of methyl acetate-methanol and methyl acetate-water existing in the system, a separation process that would require multiple columns can be sued used.

Production of acrylic acid

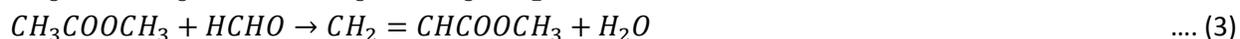
Acrylic acid is a high value chemical used for the synthesis of a variety of plastics, coatings, paints and polishes etc. Presently, the oxidation of propylene oxidation is the major industrial method for synthesis of acrylic acid. However, the numerous oxidation by-products, along with the limitations of the availability of propylene as an abundant raw material outside the sphere of petrochemical industries, make the possibility of alternative catalytic processes very lucrative. Formaldehyde and acetic acid have been found to participate in an aldol condensation reaction to form acrylic acid. As the pathways for formation of either of these starting materials is well established in industry, the aldol condensation route holds promise of delivering an economically feasible process for acrylic acid formation, without dependence on the petrochemical industries. Literature suggests the possibility of achieving high acrylic

acid selectivity as well as over 80 % yields based on formaldehyde conversion. Commercial performance achieving similar values would allow manufacture of acrylates without dependence on the fossil fuel industry, and with immense carbon capture potential.

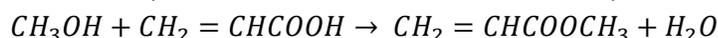
The aldol condensation reaction of the acetic acid with formaldehyde results in the formation of acrylic acid. This reaction has been observed to take place in the region of 280 – 400°C.



There are however a variety of side reactions possible in the system as well. Esterification of acetic acid with methanol from formalin results in the formation of methyl acetate, the reaction of which with formaldehyde can lead to the formation of methyl acrylate.



Alternatively, the methanol can also react with acrylic acid directly to form the methyl acrylate.



Carbon dioxide and acetone are formed by the decomposition of acetic acid.



The decomposition of formaldehyde can also result in formation of methanol and carbon dioxide as well.



Furthermore, the acrylic acid produced in the system may undergo polymerization to form polyacrylates.



All the experiments were completed on a fixed bed plug flow reactor consisted of a tube of diameter 1.27 cm in a furnace heater. The catalyst bed was topped with a layer of alumina to create a preheating zone so as to allow the liquid feed mixture to vaporize. A condenser and a collector tank were placed downstream of the reactor for product collection. Under the established operating conditions various catalysts were tested with differing Acetic Acid – to – Formaldehyde – to – Water – to – Nitrogen ratios, differing residence times, and operating temperatures (from 300 to 420°C). The liquid products were analyzed using an Agilent 7820A Gas Chromatography system with a FID and DBWax column, while a Haysep column was utilized for the effluent gases. The water content in the product was determined by using a Mettler Toledo V20 Volumetric Karl Fischer Titrator.

The analysis data indicate that the selectivity to acrylic acid on the basis of formaldehyde conversion varies between 3-4 % to over 50 %. However, generally the higher selectivity has been associated with lower conversions. In the case of catalyst H101 however, a selectivity of 49 % was

observed with a conversion of 42 % similar to the reported data from literature. The experiments when operating at higher $\text{CH}_3\text{COOH}:\text{HCHO}$ ratios enhance the selectivity of Acrylic Acid by limiting the extents of side reactions emanating from formaldehyde. In such a case, the conversion of acetic acid would be less in a single pass through the reactor, but the unreacted acetic acid can be separated from the product stream and recycled back into the reactor.

Overall Conclusions:

The original research objective of identifying and synthesizing the marketable products from CO_2 has been achieved. The techno-economic analysis for dry reforming process indicated that the dry reforming has a good potential in CO_2 capture for CO generation. However, the CO utilization downstream is the key to move forward. A robust dry reforming catalyst system has been developed that has been tested for more than 3000 h under different conditions for syngas production. The feasibility of direct one step dimethyl ether (DME) synthesis using syngas has been established. Further, the catalysts developed during this research maintains high selectivity towards there chemicals that were of interest; methyl acetate, acetic acid and acrylic acid. All these chemicals are synthesized on a bench unit using more environment friendly and novel catalytic processes. If the syngas produced is derived from renewable sources such as MSW with biogenic carbon content then it offers a means to recycle carbon from these wastes into chemicals, reducing in significant GHG emission compared to conventional petrochemical production. Using locally available wastes to produce chemicals also addresses the issue of scarce raw materials in certain regions, leading to benefits such as reduced costs and emissions from shipping over long distances, and increased reliability of supply. An integrated bolt-on approach to manufacture acrylic acid has an excellent GHGs emission reduction and good economics that would support commercialization of such a process. This research, if supported could lead to an opportunity to develop a proprietary position for acrylic acid manufacturing from waste (via DME) in Alberta.