



Energy Research and Development Division FINAL PROJECT REPORT

# **Carbon Dioxide-Based Coproducts for Commercially Viable Renewable Natural Gas Production**

Gavin Newsom, Governor March 2020 | CEC-500-2020-014

#### **PREPARED BY**:

#### **Primary Authors:**

Chan Seung Park Arun S.K. Raju Joseph M. Norbeck Sean Franco Partho Roy Junior Castillo

CE-CERT/ University of California, Riverside 1084 Columbia Avenue Riverside, CA 92507

Contract Number: PIR-12-020

## PREPARED FOR:

California Energy Commission

Pilar Magaña Project Manager

Jonah Steinbuck, Ph.D. Office Manager ENERGY GENERATION RESEARCH OFFICE

Laurie ten Hope
Deputy Director
ENERGY RESEARCH AND DEVELOPMENT DIVISION

Drew Bohan Executive Director

#### DISCLAIMER

This report was prepared as the result of work sponsored by the California Energy Commission. It does not necessarily represent the views of the Energy Commission, its employees or the State of California. The Energy Commission, the State of California, its employees, contractors and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the uses of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the California Energy Commission passed upon the accuracy or adequacy of the information in this report.

## ACKNOWLEDGEMENTS

The authors acknowledge the funding from the California Energy Commission under Contract PIR-12-020.

## PREFACE

The California Energy Commission's Energy Research and Development Division manages the Natural Gas Research and Development program, which supports energyrelated research, development, and demonstration (RD&D) not adequately provided by competitive and regulated markets. These natural gas research investments spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution and transportation.

The Energy Research and Development Division conducts this public interest natural gas-related energy research by partnering with RD&D entities, including individuals, businesses, utilities and public and private research institutions. This program promotes greater natural gas reliability, lower costs and increases safety for Californians and is focused in these areas:

- Buildings End-Use Energy Efficiency.
- Industrial, Agriculture and Water Efficiency
- Renewable Energy and Advanced Generation
- Natural Gas Infrastructure Safety and Integrity.
- Energy-Related Environmental Research
- Natural Gas-Related Transportation.

*Carbon Dioxide-Based Coproducts for Commercially Viable Renewable Natural Gas Production* is the final report for the project (Contract Number PIR-12-020) conducted by the University of California Riverside. The information from this project contributes to the Energy Research and Development Division's Natural Gas Research and Development Program.

For more information about the Energy Research and Development Division, please visit the <u>Energy Commission's research website</u> (www.energy.ca.gov/research/) or contact the Energy Commission at 916-327-1551.

## ABSTRACT

The California Energy Commission has identified renewable natural gas as an important alternative fuel that can contribute to California's goals to diversify fuels and reduce emissions in the transportation sector. Removing carbon dioxide ( $CO_2$ ) allows renewable natural gas to be used as a transportation fuel, and this project studied converting the removed  $CO_2$  into a commercially viable coproduct to increase the competitiveness of renewable natural gas in the marketplace.

Researchers demonstrated a process for converting CO<sub>2</sub> into dimethyl ether (another alternative fuel that can be used in a variety of sectors), along with a combined CO<sub>2</sub> separation and conversion technology to convert CO<sub>2</sub> into another commercially valuable coproduct, in a laboratory-scale flow reactor. This process can be applied directly to an existing renewable natural gas system. The results showed 17 percent carbon conversion efficiency from the CO<sub>2</sub> into the product. The process was also studied using the Aspen Plus Process Simulation model, estimating 79.8 percent thermal efficiency (or thermal energy used) under optimum process conditions. Thermal efficiency is an important metric used when evaluating the commercial potential of the processes.

Researchers also demonstrated formation of potassium carbonate (a commercially valuable coproduct) from CO<sub>2</sub> and found that when potassium hydroxide concentrations are 20 percent or higher, more than 80 percent CO<sub>2</sub> absorption is possible. Potassium carbonate has commercial value if produced with adequate quality, and the additional revenue stream from producing high quality potassium carbonate can contribute to the economic viability of renewable natural gas production projects.

For dimethyl ether, economic analysis showed that reductions in renewable natural gas production costs depend strongly on the required hydrogen feed cost. According to the analysis, viable renewable natural gas production cost reduction requires hydrogen cost to be equal or below the U.S. Department of Energy's long-term cost target of \$1 per kilogram from renewable sources. Also, revenue from creating CO<sub>2</sub> coproducts alone will not decrease the production cost of renewable natural gas.

**Keywords:** renewable natural gas, carbon dioxide, dimethyl ether, methanol, potassium carbonate, potassium hydroxide, production cost.

Please use the following citation for this report:

Park, Chan Seung, Arun S.K. Raju, Joseph M. Norbeck, Sean Franco, Partho Roy and Junior Castilo. University of California, Riverside. 2020. *Carbon Dioxide-Based Coproducts for Commercially Viable Renewable Natural Gas Production*. California Energy Commission. Publication number: CEC-500-2020-014.

## **TABLE OF CONTENTS**

ACKNOWLEDGEMENTS1
PREFACEii
ABSTRACTiii
EXECUTIVE SUMMARY1
Introduction1
Project Purpose1
Project Process2
Project Results2
Benefits to California3
Technology/Knowledge Transfer/Market Adoption (Advancing the Research to Market)
CHAPTER 1: Introduction
Contaminants and Compounds in Process Gases5
Sulfur Compounds5
Halogenated Compounds7
Ammonia7
Siloxanes and Other Silicon Compounds7
Particulate Matter7
Moisture Content7
Carbon Dioxide8
Project Goals12
Technical Performance Objectives13
Deliverables13
CHAPTER 2: Methanol and Dimethyl Ether Production from Carbon Dioxide13
Background14
Task 2 Objective16
Test Plans and Reports17
Test Plans17
Test Report (Process Simulation)18

Test Report (Laboratory Demonstration)	21
CHAPTER 3: Potassium Carbonate Synthesis from Carbon Dioxide	27
Background	27
Task 3 Objective	28
Test Plans and Reports	28
Test Plans	28
Test Report (Laboratory Demonstration Result)	30
CHAPTER 4: Economic Assessment of Proposed Technologies and Recommendation Optimized Carbon Dioxide Recovery and Use Technology	۱ of 33
Background and Methods	33
Methods and Assumptions	35
Capital Cost Estimation	39
DME production cost	40
	40
Extra Revenue Estimation	40 41
Extra Revenue Estimation Recommendation of Optimized Carbon Dioxide Recovery and Utilization Technolog (Task 5)	40 41 Iy 43
Extra Revenue Estimation Recommendation of Optimized Carbon Dioxide Recovery and Utilization Technolog (Task 5) CHAPTER 5: Summary of Results	40 41 Iy 43 44

## LIST OF FIGURES

	Page
Figure 1: Carbon Dioxide Capture Technology Options	9
Figure 2: Process Flow Diagram at Optimum Process Condition (265C, 660 psi)	20
Figure 3: Flow Controller System	21
Figure 4: Top Part of Reactor System	22
Figure 5: Process Controller	22
Figure 6: Gas Analysis System	23
Figure 7: Heated Oven for Inlet Capillary of Residual Gas Analyzer	23
Figure 8: Overall Experimental Setup	24
Figure 9: Typical Experimental Chart with Methanol Production from Carbon Dioxid	de26
Figure 10: Hot Carbonate Absorption Column Setup	29

Figure 11: Percent CO <sub>2</sub> Absorbed versus Liquid Hourly Space Velocity at 10 percent Potassium Hydroxide Concentration
Figure 12: Percent Carbon Dioxide Absorbed versus Gas Hourly Space Velocity at 10 percent Potassium Hydroxide Concentration and Reactant Gases at 60 percent Methane and 40 percent Carbon Dioxide
Figure 13: Percent Carbon Dioxide Absorbed versus Potassium Hydroxide Concentration
Figure 14: Process Block Diagram for Carbon Dioxide to Dimethyl Ether Process (Carbon Dioxide Separation Section)
Figure 15: Process Block Diagram for Carbon Dioxide to Dimethyl Ether Process (Carbon Dioxide Utilization Section)
Figure 16: Yearly Cash Flow for Carbon Dioxide-to-Dimethyl Ether Plant (million\$ vs Year)42

## **LIST OF TABLES**

Table 1: Current California Air Resources Board Compressed Natural Gas Fuel         Specifications	.6
Table 2: Comparison of Carbon Dioxide Capture Technology Options	LO
Table 3: Project Deliverables and Related Section in Report	L3
Table 4: Separator Mass Input Condition for the Aspen Process Simulation	18
Table 5: Hydrogen Supply to Methanol Synthesis Reactor, Mass Input Condition	18
Table 6: Final Product Composition	۱9
Table 7: Renewable Natural Gas Production Cost Estimates for Different Technologies	34
Table 8: Description of Unit Operations	39
Table 9: Capital Cost Estimation	<del>1</del> 0
Table 10: Average Hydrogen Production Cost	11
Table 11: Estimated Reduction of the Renewable Natural Gas Production Price4	12

## **EXECUTIVE SUMMARY**

### Introduction

For more than a decade, California has committed to reducing statewide greenhouse gas emissions to help avoid the impacts of climate change. In 2006, the state passed the landmark California Global Warming Solutions Act of 2006 (Assembly Bill 32, Núñez, Chapter 488, Statutes of 2006) to reduce statewide greenhouse gas emissions to 1990 levels by 2020. Ten years later, Senate Bill 32 (Pavley, Chapter 249, Statutes of 2016) put into law a statewide goal to reduce greenhouse gas emissions 40 percent below 1990 levels by 2030. In 2018, then-Governor Edmund G. Brown, Jr. issued Executive Order B-55-18 to set a statewide goal to achieve carbon neutrality by 2045 and negative greenhouse gas emissions afterward.

Renewable natural gas (RNG) is an important alternative fuel that can contribute to achieving these and other goals set by California related to conventional fuel replacement and emissions reduction in the state's transportation sector. The major challenges facing the use of RNG on a large scale include the lack of economic viability of potential projects and technological options to upgrade RNG to achieve the fuel standards required by most vehicle manufacturers. Solutions to these challenges will help achieve California's conventional fuel replacement and emissions reduction goals.

RNG production projects typically generate considerably less fuel compared to conventional fuel projects, including fossil-based natural gas. Most sources of RNG, such as landfill gas, digester gas, and syngas (an energy source created by subjecting carbonaceous materials to high temperatures, contain several contaminants as well as large amounts of moisture and carbon dioxide ( $CO_2$ ). The  $CO_2$  must be removed from the gas stream to increase the energy content of the RNG and allow its use as a transportation fuel, with the  $CO_2$  typically vented to the atmosphere. Existing  $CO_2$  separation methods can negatively affect the economic viability of RNG projects because the cost of  $CO_2$  separation can potentially be a major capital and operating cost. Moreover, a considerable amount of carbon in the feedstock is lost as vented  $CO_2$ , thereby reducing the net efficiency of conversion.

This project studied the use of removed  $CO_2$  converted into a commercially valuable coproduct to help improve the commercial competitiveness of RNG processes in the marketplace.

## **Project Purpose**

This project aimed to develop a cost-effective technology for converting  $CO_2$  into a commercially valuable co-product such as methanol or dimethyl ether, as well as a combined  $CO_2$  separation and conversion technology to convert  $CO_2$  into another commercially valuable coproduct such as potassium carbonate, which can be used in pharmaceutical laboratories, fire extinguishers, soap or glass making, and water softeners. These technologies would reduce the production cost of the RNG

transportation fuel by at least \$0.50 per million British thermal units (MMBtu) compared to the current preferred production methods for the specific feedstocks. Furthermore, the technologies will improve the total efficiency of RNG production processes while increasing the commercial viability through the revenue stream generated from the coproducts.

### **Project Process**

In a laboratory-scale flow reactor, the project demonstrated a process for converting  $CO_2$  into a dimethyl ether co-product with a combined  $CO_2$  separation. Researchers used the Aspen Plus Process Simulator to verify the experiment, which estimated 79.8 percent thermal efficiency under optimum process conditions. This simulation was important as it provides information about the viability of this method when commercialized.

Researchers also demonstrated the formation of potassium carbonate from  $CO_2$  in a laboratory-scale flow reactor. The experimental setup consisted of an absorption column where an aqueous solution of potassium hydroxide comes in contact with a gas stream containing methane,  $CO_2$  and other components. Researchers collected the output gas in gas sampling bags and analyzed it using a residual gas analyzer. The project team used data from the first two tasks of this project to evaluate the commercial viability of the technology options and the potential for widespread adoption of these technology options.

To analyze the commercial viability of this project, the research team chose a typical landfill site with 4 megawatts electricity generation or 15 metric tons (tonnes) per day of dimethyl ether product throughout (equivalent to daily generation of 5.3 million cubic feet of gas) of RNG as the model size for the application of the technology.

## **Project Results**

The two experiments performed successfully and provided data that can be used for future analysis. The first experiment resulted in a 17 percent carbon conversion efficiency from  $CO_2$  into dimethyl ether, and the second resulted in more than 80 percent  $CO_2$  absorption when potassium hydroxide concentrations are 20 percent or more.

For the dimethyl ether process, economic analysis showed that the estimated RNG production cost reduction depends heavily on the required hydrogen feed cost and dimethyl ether sale price. With a hydrogen cost scenario of \$1-\$6 per kilogram, researchers found that the average dimethyl ether production cost ranges from \$408 to \$1,314 per tonne. For a dimethyl ether sale price of \$500 per tonne, the results showed an estimated price reduction in the RNG production cost of \$0.26 per MMBtu at a hydrogen cost of \$1 per kilogram. According to this analysis, CO<sub>2</sub> use through creation of co-product revenue will not decrease the production cost of RNG. The required hydrogen cost must equal or be below the U.S. Department of Energy's long-term

target cost of \$1 per kilogram for hydrogen from renewable sources to contribute to the viable cost reduction of RNG production.

## **Benefits to California**

This project benefits California by advancing RNG technology as a whole, setting milestones for future RNG production. The project shows that the methods demonstrated can be used with existing RNG manufacturing methods to make RNG a more viable commercial product. In addition, analysis from the project provides conditions that must be met for RNG to be a commercially viable fuel source.

The research is significant to ratepayers because it is aimed at developing a technology that is cost-effective and reducing the production cost of RNG transportation fuel by at least \$0.50 per million British thermal units. While decreasing costs, the technology will improve the total efficiency of RNG production processes. In addition, by 2020, the cost of production of hydrogen from water electrolysis using renewable power estimated to be reduced to less than \$2.00 per kilogram at plant gate. Another benefit is that the technology can be used in conjunction with any RNG production processes and therefore will result in maximizing benefits in terms of enabling existing and new RNG production processes to be commercially competitive.

## Technology/Knowledge Transfer/Market Adoption (Advancing the Research to Market)

The technology showed the potential for successful commercial implementation but has not yet reached the point where pilot demonstration followed by commercialization is warranted. The specific challenge is to optimize these technology options for small-scale commercial implementation. Since there are no plans in place for commercialization, there are not yet well-defined markets for this technology.

According to the results, the two experiments performed successfully and provided data that can be used for future analysis. The U.S. Department of Energy will be using these results to see if its target cost of \$1 per kilogram for hydrogen from renewable sources will contribute to the viable cost reduction of RNG production. If the hydrogen is produced directly using renewable sources of energy, then carbon dioxide hydrogenation will become a great strategy for renewable energy use in power generation.

## CHAPTER 1: Introduction

Renewable natural gas (RNG) can be produced from carbonaceous and renewable feedstocks through various technologies including anaerobic digestion, landfill waste decomposition, gasification and pyrolysis. These methods, however, can be inefficient and the qualities of these gas products are inferior to the quality of fossil-based natural gas products. Thermochemical pathways with high conversion efficiency that convert renewable feedstocks such as biomass, sewage sludge, and carbonaceous matter into RNG are under development.<sup>1</sup> These different methods produce product streams of varying fuel composition, calorific value and quantities depending on a number of parameters. Irrespective of the technology chosen, the product gas stream must undergo considerable conditioning to upgrade the quality of the final product and meet fuel specifications for use in transportation applications. Table 1 summarizes the current compressed natural gas (CNG) transportation fuel specifications under the California Air Resources Board (CARB) regulations.<sup>2</sup>

### **Contaminants and Compounds in Process Gases**

Although the product gas compositions from different technologies vary widely, there are certain contaminants and compounds that are commonly found in most process gases: sulfur compounds, halogenated compounds, ammonia, silicon compounds and siloxanes, particulate matter, moisture, and carbon dioxide (CO<sub>2</sub>).<sup>3,4</sup>

#### **Sulfur Compounds**

Landfill gases and biogases typically contain sulfur compounds such as sulfides, disulfides, and thiols. Examples of sulfide species include hydrogen sulfide, dimethyl sulfide, diethyl sulfide, and so on. Examples of thiols include methyl mercaptan, and ethanethiol. The sulfur content of synthesis gas (syngas) streams from gasification and other thermochemical processes depends on the sulfur content of the feedstock. While the sulfur content of plant and vegetable biomass based syngas is negligible, syngas from waste matter feedstocks like biosolids can exhibit higher sulfur content. Sulfur compounds are corrosive and can harm downstream equipment and materials, including catalysts, so these compounds must be reduced to acceptable levels

<sup>&</sup>lt;sup>1</sup> Norbeck JM, Park CS, Raju ASK, Vo C., *Report on Potential Application of Using the Steam Hydrogasification Process to Convert Biomass Materials Prevalent in Southern California into Synthetic Fuels*, September 2008.

<sup>&</sup>lt;sup>2</sup> Light Duty CNG Vehicle Fuel Composition Study, Gas Technology Institute, April 2006.

<sup>&</sup>lt;sup>3</sup> Landfill Gas Energy Technologies, Instytut Nafty i Gazu, 2010.

<sup>&</sup>lt;sup>4</sup> *Guidance on Gas Treatment Technologies for Landfill Gas Engines,* Environmental Agency, August 2004.

depending on the intended application. For transportation purposes, the sulfur content must be lowered to 16 parts per million (ppm) or less (Table 1).

Specifications		Value			
Hydrocarbons	Methane	88.0% (min.)			
Hydrocarbons	Ethane	6.0% (max.)			
Hydrocarbons	C <sub>3</sub> and higher HC	3.0% (max.)			
Hydrocarbons	C <sub>6</sub> and higher HC	0.2% (max.)			
Other Species	Hydrogen	0.1% (max.)			
Other Species	Carbon Monoxide	0.1% (max.)			
Other Species	Oxygen	1.0% (max.)			
Other Species	Inert Gases (Sum of				
	CO <sub>2</sub> and N <sub>2</sub> )	1.5-4.5% (range)			
Other Species	Sulfur	16ppmv (max.)			
Other Species	Water	The dewpoint at vehicle fuel storage container pressure shall be at least 10F below the 99.0% winter design temperature listed in Chapter 24, Table 1, Climatic Conditions for the United States, in the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE) Handbook. 1989 fundamentals volume. Testing for water vapor shall be in accordance with ASTM D 1142-90, utilizing the Bureau of Mines apparatus.			
Other Species	Particulate Matter	The compressed natural gas shall not contain dust, sand, dirt, gums, oils, or other substances in an amount sufficient to be injurious to the fueling station equipment or the vehicle being fueled.			
Other Species	Odorant	The natural gas at ambient conditions must have a distinctive odor potent enough for its presence to be detected down to a concentration in air or not over 1/5 (one-fifth) of the lower limit of flammability.			

Table 1: Current California Air Resources Board Compressed Natural GasFuel Specifications

Hydrocarbons expressed as mole percent; Other species expressed as mole percent unless otherwise indicated.

Source: Gas Technology Institute 2006

#### **Halogenated Compounds**

Halogenated compounds such as carbon tetrachloride, chlorobenzene, chloroform and trifluoromethane are often found in landfill gases and occasionally in other RNG production processes. Halogen species can lead to the formation of acid gases such as hydrochloric acid and hydrofluoric acid which can result in corrosion and other issues. The presence of significant quantities of halogen species in feedstocks can cause problems in thermochemical processes as well.

#### Ammonia

Ammonia is formed from nitrogen-containing species and must be below specified levels. Ammonia forms nitrous oxide upon combustion.

#### **Siloxanes and Other Silicon Compounds**

Siloxanes and silicon species are primarily found in landfill gas and are derived from silicon-containing consumer product wastes including cosmetics. Siloxanes are recognized as a major problem in various landfill gas applications and often form harmful deposits in downstream equipment.

#### **Particulate Matter**

Different types of particulate matter are found in landfill gases and biogas streams and are often removed by means of filters or cyclones (removal by centrifugal or inertial forces).

#### **Moisture Content**

Landfill gas and biogas streams contain sizeable quantities of moisture that can have a detrimental effect on pipes, lines, and other equipment. Syngas from thermochemical processes often contains steam and is subjected to water knockout steps to eliminate the moisture content. Gas streams are often passed through knockout drums that reduce the gas velocity so that any liquid drops out and is drained. The next step in moisture removal is to eliminate foam from gas streams by means of coalescing meshes. Cyclones can also be used to capture liquid droplets.

Uncondensed water vapor in the gas stream is eliminated using one of the following dehumidification methods.<sup>5,6</sup>

 Refrigeration drying: The most common technique used to eliminate water vapor from landfill gas and biogas streams is refrigeration. The gas stream is cooled to 2°C in a heat exchanger causing the water to condense. The condensed liquid is separated from the gas stream. More effective drying can be achieved by cooling gas streams to -18 °C. In this case, glycol must be used to prevent ice formation in the pipework. The glycol must then be removed from the dry gas stream.

<sup>&</sup>lt;sup>5</sup> Landfill Gas Energy Technologies, Instytut Nafty i Gazu, 2010.

<sup>&</sup>lt;sup>6</sup> *Guidance on Gas Treatment Technologies for Landfill Gas Engines,* Environmental Agency, August 2004.

- Deliquescent bed absorption: Alternatively, deliquescent dryers containing moisture-absorbing materials, such as common salt, silica gel or aluminium oxide, can be used to remove moisture from the gas streams. The drying agents are loaded in towers and regenerated during the process using appropriate techniques. These processes can be conducted at elevated pressures to improve the capture efficiency.
- Glycol stripping: Glycol stripping techniques are primarily used in facilities that produce large quantities of gas. The gas stream is passed through a contact tower containing material such as triethylene glycol that can be recovered for reuse.

The water recovered from the gas streams is often acidic and requires treatment before disposal.

#### **Carbon Dioxide**

All processes for producing RNG generate substantial quantities of CO<sub>2</sub>. The RNG is upgraded to remove most of the CO<sub>2</sub> to increase the calorific value (energy content) of the final gas stream and avoid operational issues. As noted in Table 1, the total inert gas content, including nitrogen-containing species, of RNG transportation fuel is between 1.5 percent and 4.5 percent.

#### **Carbon Dioxide Removal Technologies**

Several CO<sub>2</sub> removal technologies have been developed and can be broadly classified into the following categories:

- Physical and chemical absorption methods
- Water scrubbing techniques
- Membrane separation methods
- Pressure swing adsorption (PSA)
- Cryogenic separation

Figure 1 compares these methods and shows their approximate development timelines.<sup>7,8</sup>

<sup>&</sup>lt;sup>7</sup> Ciferno JP, Marano JJ, Munson RK., *CCS Technology Integration Challenges*. Chemical Engineering Progress, August 2011.

<sup>&</sup>lt;sup>8</sup> Esposito RA, Irvin N. *Demonstrating CCS Integration,* Chemical Engineering Progress, August 2011.



Figure 1: Carbon Dioxide Capture Technology Options

Source: University of California, Riverside

- Physical and chemical absorption methods: A number of organic solvents have been developed for the physical absorption-based removal of CO<sub>2</sub> and other contaminants from gas streams. Commercially available solvents include:
  - Selexol: Selexol is a commercial solvent derived from the dimethyl ether of polyethylene glycol and used for the removal of CO<sub>2</sub> and hydrogen sulfide. Although Selexol is commercially available, its high cost prevents widespread usage, especially in small-scale projects.
  - Amine-Based Solvents: Diethanolamine (DEA) and Monoethanolamine (MEA) and other amine based solvents have been successfully used to remove CO<sub>2</sub>. The use of DEA requires pretreatment of the gas stream to remove sulfur compounds and other hydrocarbons, whereas the use of MEA is restricted due to the high rate of loss of the solvent during regeneration.

The primary application for these technologies is in large scale industries and chemical plants. CO<sub>2</sub> removal technologies are thus often adopted from these

industries for use in RNG production. Table 2 compares the basic properties of these technologies. $^{9,10}$ 

	Low-Partial Pressure Application	High-Temp Application	Selectivity	Large-Scale Applications	Mechanical Simplicity
Absorption	Chemical solvents: yes Physical Solvents: may be difficult	Aqueous solvents: no	Chemical solvents: high Physical solvents: moderate	Yes	Yes for low- viscosity solvents
Adsorption	Chemisorption: yes Physisorption: may be difficult	Yes	Chemisorption: high Physisorption: moderate	Limiting: costs scale linearly with capacity	No if solids handling is required
Membrane Separation	No	Polymer membranes: no	Dense inorganic membranes: high Polymeric membranes: variable Microporous membranes: high	Limiting: costs scale linearly with capacity	Yes without compression
Cryogenic Separation	No	No	Yes	Yes	No if solids condense

#### Table 2: Comparison of Carbon Dioxide Capture Technology Options

Source: University of California, Riverside

The key characteristics required for effective solvents are:

- High affinity for acid gases (in particular CO2).
- $\circ$   $\;$  Low bond strength with absorbed gases.
- $\circ$   $\;$  Low affinity for alkanes.
- $\circ$   $\;$  Low vapour pressure at ambient temperatures.
- Low viscosity.

<sup>&</sup>lt;sup>9</sup> Ciferno JP, Marano JJ, Munson RK., *CCS Technology Integration Challenges*, Chemical Engineering Progress, August 2011.

<sup>&</sup>lt;sup>10</sup> Esposito RA, Irvin N., *Demonstrating CCS Integration,* Chemical Engineering Progress, August 2011.

- Water scrubbing techniques: CO<sub>2</sub> and hydrogen sulfide exhibit a higher degree of solubility in water compared to methane. The compressed gas stream is brought into contact with counter-current columns designed to maximize the contact surface between the gas and the liquid. The enriched gas stream is then dried to remove the residual water. The CO<sub>2</sub>-enriched water is then passed through flash tanks where depressurization results in the release of the CO<sub>2</sub>. The process can be enhanced by air stripping or by vacuum. Water scrubbing is an attractive method for small scale projects due to the absence of expensive organic solvents.<sup>11</sup> However, water scrubbing often requires high levels of power consumption to handle the circulating flows. A cost effective alternative for water scrubbing is the use of an aqueous solution of potassium carbonate, referred to as the "hot carbonate" process. Hot carbonate is a potentially attractive option that can enrich the RNG to transportation fuel standards while capturing CO<sub>2</sub> in the form of a chemical with commercial value. This option is discussed in detail in later sections of this report.
- Membrane separation: The differential permeability of CO<sub>2</sub> and methane through polymeric membranes can be used to convert the gas stream into transportation grade RNG. The membranes can be operated with the gas phase on both sides or by using a liquid such as a solvent to absorb the CO<sub>2</sub> that permeates through the membrane. Membranes with the gas phase on both sides are referred to as 'dry membranes.' Single stage membranes typically result in low levels of methane recovery. Consequently, multistage processes are needed to achieve RNG quality necessary to meet transportation fuel standards.
- Pressure swing adsorption: PSA processes remove the CO<sub>2</sub> from the gas stream by means of selective adsorption on the surface of porous solid adsorbents. The adsorption takes place under elevated pressures and the CO<sub>2</sub> is released during depressurization. The process involves four steps:
  - High pressure adsorption
  - Depressurization
  - Vacuum stripping of CO<sub>2</sub>
  - Product re-pressurization

Two types of sorbents have been used in landfill gas clean-up projects: molecular sieve type materials and activated carbon beds. PSA processes require a dry gas stream and the removal of hydrogen sulfide before the process can begin.

• Cryogenic separation: The boiling point of methane under atmospheric pressure is -160°C whereas the boiling point of CO<sub>2</sub> is -78°C. Cryogenic processes cool the gas stream to temperatures low enough to allow the separation of CO<sub>2</sub> as a

<sup>&</sup>lt;sup>11</sup> Rasi S, Lantela J, Veijanen A, Rintala J., *Landfill Gas Upgrading with Countercurrent Water Wash*, 2008;28(9):1528–1534.

liquid. The methane is recovered either as a gas or as a liquid. Compression and refrigeration is normally achieved in several steps. Although the process yields a highly enriched RNG, it is energy intensive and not suitable for small-scale projects.

Commercially available CO<sub>2</sub> separation methods are primarily suited for large-scale industrial processes and not for RNG production technologies. RNG production by nature is limited to small to medium scale projects. This is due to the limited concentration of feedstocks at a single location or by the gas production capability of landfills. In turn, these feedstock characteristics affect the commercial viability of RNG projects since the gas conditioning step is often capital intensive and technologically demanding. Consequently, while RNG has the potential to make a significant contribution as a transportation fuel and help California achieve its fossil fuels replacement and emissions reduction goals in the transportation sector, the realization of this potential is contingent on the development of cost-effective and technologically robust CO<sub>2</sub> separation methods. Furthermore, CO<sub>2</sub> separation methods must be capable of being implemented in small- to medium-scale RNG production projects without negatively affecting their commercial viability.

Even if cost-effective  $CO_2$  separation methods are available, it is highly unlikely that RNG will be competitive with fossil CNG or petroleum-based fuels for transportation. As mentioned earlier, this is due to the loss of a major portion of carbon from the feedstock in the form of  $CO_2$  that is either vented into the atmosphere or captured and sequestered. Therefore, for RNG processes to be commercially competitive, it is critical that the carbon lost as  $CO_2$  be converted into a co-product with commercial value.

This report addressed the two major issues emphasized above by developing cost effective and robust  $CO_2$  recovery and utilization options that can be implemented in RNG production projects. Experimental and simulation work was successfully conducted and demonstrated for  $CO_2$  conversion technology options that can be used in combination with existing  $CO_2$  capture technologies.

## **Project Goals**

The goal of this agreement is to develop a cost-effective technology for: (1)  $CO_2$  conversion into a commercially valuable co-product such as methanol or dimethyl ether (DME); and (2) a combined  $CO_2$  separation and conversion technology that converts  $CO_2$  into a commercially valuable co-product such as potassium carbonate. An important benefit of this approach is that the technology can be used in conjunction with any RNG production process and therefore will result in maximizing the benefits in terms of enabling a number of existing and new RNG production processes to be commercially competitive.

The ultimate goal of this project is to develop a CO<sub>2</sub>-based co-product synthesis technology that will reduce the production cost of the RNG transportation fuel by a minimum of \$0.50 per MMBtu compared to the current preferred production methods

for the specific feedstocks. The technologies will improve the total efficiency of RNG production processes while increasing the commercial viability through the revenue stream generated from the co-products.

## **Technical Performance Objectives**

The objective of this agreement was to develop and optimize a technology for the costeffective synthesis of methanol, DME and/or potassium carbonate from  $CO_2$  recovered from RNG fuel production processes.

## Deliverables

Table 3 lists the technical tasks and deliverables covered in each chapter of the report.

Task	Deliverables	Chptr
Task 2: Methanol	Modeling Test Plan	3
and DME	DME Synthesis Test plan	
production from	Modeling Evaluation Report	
CO <sub>2</sub>	<ul> <li>Optimal Process Parameters Report</li> </ul>	
	Process Metrics Report	
Task 3:	Hot Carbonate Test Plan	4
Potassium	Hot Carbonate Simulation Report	
Carbonate	<ul> <li>CO<sub>2</sub> Recovery Report</li> </ul>	
Synthesis from	Results and Metrics Report	
CO <sub>2</sub>		
Task 4:	CO <sub>2</sub> -to-Methanol Conversion Modeling and Analysis	5
Economic	Test Plan	
Assessment of	DME-to-Methanol Conversion Modeling and Analysis	
Proposed	Test Plan	
rechnologies	<ul> <li>Potassium Carbonate CO<sub>2</sub> Capture and Conversion Test Plan</li> </ul>	
	<ul> <li>Final CO<sub>2</sub>-to-Methanol Viability Report</li> </ul>	
	Final CO <sub>2</sub> -to-DME Viability Report	
	Final CO <sub>2</sub> -to-Potassium Carbonate Viability Report	
Task 5:	Final Report	5
Recommendation		
of Optimized CO <sub>2</sub>		
Recovery and		
Utilization		
Technology		

 Table 3: Project Deliverables and Related Section in Report

Source: University of California, Riverside

## CHAPTER 2: Methanol and Dimethyl Ether Production from Carbon Dioxide

## Background

Methanol is manufactured commercially for several applications, and can also be used as an alternative transportation fuel. Demand is expected to grow for methanol to transport energy cost-effectively and efficiently and for use in its various commercial applications. With half the energy density of gasoline but a higher octane rating of 100, methanol has been used as a fuel in modified vehicles and in flexible fuel vehicles that can use a blend of methanol and gasoline, such as M15 (15 percent methanol) and M85 (85 percent methanol).<sup>12</sup> The methanol is treated as a co-product that can be sold in the open commercial market.

A major challenge with methanol is its toxicity, although it is highly toxic only when ingested in large quantities (30-100 milliliters). It has long been used in various consumer products including windshield washer fluids, deicing fluids, and antifreezes without major problems. In 2010, approximately 45 million metric tonnes or 15 billion gallons of methanol were used worldwide, roughly equivalent to global demand for ethanol fuel. The methanol market price has varied from \$200-400 per tonne over the last few years.<sup>13</sup>

Dimethyl ether (DME) is a clean oxygenated synthetic fuel that can be made from any carbonaceous feedstock. It is relatively inert, non-corrosive, non-carcinogenic, and almost non-toxic and does not form peroxides upon prolonged exposure to air.<sup>14</sup> DME is a potential alternative fuel to replace diesel due to its high cetane number (55-60)<sup>15</sup> and clean burning characteristics. The fuel can be stored as a liquid by subjecting it to mild pressurization.<sup>16</sup> DME can be used as a substitute for liquefied petroleum gas in domestic applications such as cooking, and as a fuel for power plants. There is also interest in DME-to-gasoline conversion; ExxonMobil uses a mixture of methanol and

<sup>&</sup>lt;sup>12</sup> Olah GA, Goeppert A, Prakash GKS. Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons. December 8, 2008.

<sup>13</sup> Ibid.

<sup>&</sup>lt;sup>14</sup> Williams RH, Larson ED. A comparison of direct and indirect liquefaction technologies for making fluid fuels from coal. December 2003 2003;7(4):103–129.

<sup>&</sup>lt;sup>15</sup> Cetane number is a measurement of the quality or performance of diesel fuel, similar to the octane rating for gasoline. The higher the number, the better the fuel burns within the vehicle engine.

<sup>&</sup>lt;sup>16</sup> Adachi Y, Komoto M, Watanabe I, Ohno Y, Fujimoto K. Effective utilization of remote coal through dimethyl ether synthesis. February 2000 2000;79(Issues 3–4):229–234.

DME to produce gasoline using its methanol-to-gasoline process. DME can be reformed into hydrogen ( $H_2$ ) as easily as methanol and is suitable for use as a hydrogen source for fuel cell vehicles. The market price of DME has varied from \$500-\$800 per ton over the last few years, with demand increasing significantly over the last decade.

Traditionally, DME has been produced by dewatering methanol over a dehydration catalyst such as  $\gamma$ -Alumina. The methanol is typically produced from syngas, which can be derived from any carbonaceous feedstock. The synthesis of methanol from syngas is carried out over a catalyst (for example, CuO, ZnO or Al<sub>2</sub>O<sub>3</sub>).<sup>17</sup>

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (-90.7 \text{ KJ/mol}) \tag{1}$$

This methanol is then converted to DME in the next step.

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (-23.4 \text{ KJ/mol}) \tag{2}$$

By combining dehydration and methanol synthesis catalysts in the same reactor, these two reactions proceed simultaneously, resulting in direct synthesis of DME from syngas in a single step process. When the syngas is rich in carbon monoxide (CO), as in coal gasification, the methanol catalyst also promotes the water gas shift (WGS) reaction.

$$H_2O + CO \leftrightarrow H_2 + CO_2 \quad (-40.9 \text{ KJ/mol}) \tag{3}$$

Therefore, in a single-step reactor the methanol is reacted away as it is formed, thereby bypassing the equilibrium results of reaction 1. The water gas shift reaction provides a further synergistic effect because the water formed by dehydration (reaction 2) drives hydrogen production, which in turn increases the methanol production by reaction 1. This also avoids the water limiting the extent of reaction 2. Hence, the single step synthesis of DME allows higher syngas conversion per pass compared to the traditional two-stage processes.<sup>18</sup>

The single step DME synthesis from syngas can be represented by the single reaction given below, which needs a  $H_2$  to CO ratio of 1.<sup>19</sup>

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \quad (-40.9 \text{ KJ/mol}) \qquad (4)$$

Since all the reactions above are exothermic, effective heat removal is an important aspect of DME synthesis reactor design. Both fixed bed and slurry phase reactors are being used. The temperature is controlled in a fixed bed reactor by either limiting the initial concentration of CO entering the reactor (to 10-15 volume percent) or by using a staged reactor design with cooling in between the stages. The limited initial

<sup>&</sup>lt;sup>17</sup> Larson ED, Tingjin R. Synthetic fuel production by indirect coal liquefaction. December 2003 2003;7(4):79–102.

<sup>&</sup>lt;sup>18</sup> Guidance on Gas Treatment Technologies for Landfill Gas Engines: Environmental Agency; August 2004.

<sup>&</sup>lt;sup>19</sup> Peng XD, Toseland BA, Tijm PJA. Kinetic understanding of the chemical synergy under LPDMETM conditions—once-through applications. July 1999 1999;54(Issues 13–14):2787–2792.

concentration of CO can be achieved by recycling the unconverted  $H_2$ -rich syngas. In the liquid phase reactors, syngas is bubbled through an inert mineral oil in which the powdered catalyst is suspended.<sup>20</sup>

DME can also be produced by the hydrogenation of CO<sub>2</sub> through two pathways, in a manner similar to DME synthesis from syngas discussed above. The first pathway is a two-step process: first, methanol is synthesized from CO<sub>2</sub> on a methanol synthesis catalyst, followed by the dehydration of methanol into DME over a dehydration catalyst. The second pathway directly converts the CO<sub>2</sub> into DME on a bifunctional DME synthesis catalyst that is composed of both methanol synthesis and methanol dehydration catalyst components. This direct pathway has the potential to be economically more competitive than the two-step process.<sup>21,22</sup>

The main reactions taking place during CO<sub>2</sub> to DME conversion are:

$$CO_{2} + 3H_{2} \rightleftharpoons CH_{3}OH + H_{2}O$$

$$2CH_{3}OH \rightleftharpoons CH_{3}OCH_{3} + H_{2}O$$

$$CO_{2} + H_{2} \rightleftarrows CO + H_{2}O$$
(6)
(7)

Besides the methanol synthesis and the DME synthesis reactions, the reverse water gas shift (RWGS) is also an important reaction taking place during the catalytic hydrogenation of CO<sub>2</sub>. A number of catalysts have been shown to have high methanol synthesis activity, including CuO–ZnO, CuO–ZnO–Al<sub>2</sub>O<sub>3</sub>, CuO–ZnO–CrO<sub>3</sub>, and CuO–TiO<sub>2</sub>–ZrO<sub>2</sub>, among others. Preferred methanol dehydration catalysts include  $\gamma$ -Alumina or ZSM-5 zeolite. The RWGS reaction is promoted by catalysts such as ZnO that promote the WGS reaction.<sup>23</sup>

## Task 2 Objective

The bifunctional catalysts such as 6CuO–3ZnO–1Al<sub>2</sub>O<sub>3</sub>/HZSM-5 have shown the potential for high conversion of CO<sub>2</sub> and high selectivity for DME in fixed bed and slurry bed reactors. Although these catalysts and processes have shown the potential to lead towards a synthesis technology that can be commercialized, they have not yet reached the point where pilot demonstration followed by commercialization is warranted. A specific challenge is that these technologies are often intended for very large-scale commercial facilities using syngas from coal and are not optimized for small scale projects that are typical for RNG production. Therefore, it is critical to optimize these

<sup>&</sup>lt;sup>20</sup> Landfill Gas Energy Technologies: Instytut Nafty i Gazu;2010.

<sup>&</sup>lt;sup>21</sup> Omata K, Watanabe Y, Umegaki T, Ishiguro G, Yamada M. Low-pressure DME synthesis with Cu-based hybrid catalysts using temperature-gradient reactor 3. 8 July 2002 2002;81(Issues 11–12):1605–1609.

<sup>&</sup>lt;sup>22</sup> Brown DM, Bhatt BL, Hsiung TH, Lewnard JJ, Waller FJ. Novel technology for the synthesis of dimethyl ether from syngas. 17 January 1991 1991;8(3):279–304.

<sup>&</sup>lt;sup>23</sup> Naik SP, Ryu T, Bui V, Miller JD, Drinnan NB, Zmierczak W. Synthesis of DME from CO2/H2 gas mixture. 15 February 2011 2011;167(1):362–368.

technology options for small scale commercial implementation. Researchers considered typical RNG project sizes with ~5 million standard cubic feet per day (MMSCFD) landfill gas throughput or with ~4 megawatts (MW) electricity generation in this report, and evaluated the contribution of revenue streams from co-products of methanol and DME.

This study focused on the synthesis of methanol and DME from CO<sub>2</sub>. The hydrogen necessary for the methanol and DME synthesis is planned to be delivered from other commercial sources with various production scenarios.

The objective of Task 2 was is to perform experimental and simulation work to optimize the production of methanol and DME from  $CO_2$  by:

- Modeling evaluation of the various process configurations and parameters of methanol synthesis from CO<sub>2</sub> and DME synthesis from CO<sub>2</sub> to identify the process conditions for the experimental condition. The Aspen Plus Process Simulator was used to perform the modeling of the process.
- Identifying the optimal process parameters to allow the cost-effective and efficient synthesis of methanol from CO<sub>2</sub> using experimental and simulation methods.
- Identifying the optimal process parameters to allow the synthesis of DME from CO<sub>2</sub> to be achieved in a cost effective and efficient manner using experimental and simulation methods
- Identifying the process metrics to be used as input parameters in the commercial evaluation of the processes.

## **Test Plans and Reports**

#### **Test Plans**

The research team carried out methanol synthesis over a commercially available CuO– ZnO based catalyst and DME synthesis over two sets of catalysts: (1) the methanol synthesis catalyst followed by a methanol dewatering catalyst such as  $\gamma$ -Alumina; (2) direct DME synthesis catalyst such as 6CuO–3ZnO–1Al<sub>2</sub>O3/HZSM-5.

The experimental setup consisted of an externally heated packed bed reactor that contained the catalyst along with the necessary instrumentation. The researchers evaluated the impact of the following process parameters on the overall efficiency and process performance for both methanol and DME syntheses.

- The reaction temperature varied from 200-300°C for both syntheses.
- The reaction pressure varied from atmospheric pressure to 15 bar.
- The impact of the residence time of the reactor was evaluated.

• A number of other variables such as feed gas flow rates, composition, and temperature were analyzed using the Aspen Plus Process Simulator before experimental work was conducted

The criteria for optimization of the synthesis technology are:

- The feedstock (CO<sub>2</sub>) conversion efficiency of the process must be greater than 95 percent by mole.
- The production of the methanol or DME co-product must generate enough revenues to reduce the production cost of the RNG transportation fuel by a minimum of \$0.50 per million British thermal units (MMBtu). The economic evaluation (discussed in Chapter 5) indicates that the target is achievable and an improved RNG fuel production cost reduction is feasible. Data from the experimental and simulation work was used in conjunction with the process economic and technological analysis methods also described in Chapter 5 to estimate the RNG fuel price reduction through co-product revenue streams.

#### **Test Report (Process Simulation)**

To find out the optimum process condition, the researchers performed process simulation with the Aspen Plus Process Simulator. Biogas, which contains  $CH_4$  and  $CO_2$ , is fed into the separator. The  $CO_2$  output from the separator goes to the methanol synthesis and subsequent DME synthesis reactor. An external source of hydrogen is added to these processes.

Mass and heat input condition used for the simulation are summarized in Table 4 and Table 5.

Components	Mole Flow Kmole/sec	Composition (mole %)
CH <sub>4</sub>	0.74	60
CO <sub>2</sub>	0.50	40
Total	1.25	100.00

#### Table 4: Separator Mass Input Condition for the Aspen Process Simulation

Source: University of California, Riverside

## Table 5: Hydrogen Supply to Methanol Synthesis Reactor, Mass Input Condition

Components	Mole Flow Kmole/sec	Composition (mole %)
H <sub>2</sub>	0.35	100
Total	0.35	100.00

Source: University of California, Riverside

The optimum process conditions for the methanol synthesis reactor and DME synthesis reactor maximizing carbon conversion yield to methanol and final product were found to be 265°C for the temperature and 660 pounds per square inch (psi) for the reactor pressure. Table 6 summarizes the final product composition at the optimum process condition.

Components	Mole Flow Kmole/sec	Composition (mole %)
H <sub>2</sub> O	0.75	75
DME	0.25	25
Total	0.41	100.00

**Table 6: Final Product Composition** 

Source: University of California, Riverside

As shown in Figure 2, the biogas with 40 percent  $CO_2$  content (A) is fed into the process.  $CH_4$  content of the biogas is separated in the separator and provided to the grid as a final RNG product (C). Separated  $CO_2$  (D) is fed into the methanol synthesis reactor (E) and subsequently fed into the DME reactor to produce the final product (F) from  $CO_2$ . Hydrogen input for the methanol synthesis reactor is assumed to come from renewable electricity through hydrolysis. This overall process concept was also used for the basic process diagram for the economic analysis in Chapter 5.

Process thermal efficiency, defined in the equation below, of the entire process (CO<sub>2</sub> separation, reactant compression and DME synthesis) was estimated to be 79.8 percent.

Process thermal efficiency where HHV represents the higher heating value of the chemical species =

( $\Sigma$  (HHV of products) + Heat generated) / ( $\Sigma$  (HHV of reactants) + Energy added)

The process thermal efficiency was identified as an important metric that will be used as an input parameter in the commercial evaluation of the processes.

The overall process flow diagram with mass and heat balance is provided in Figure 2.

#### Mole Flow kmol/sec composition (mole % Components CH4 0.75 100.00 RNG to the grid (C) Mole Flow kmol/sec:omposition (mole % Components 0.75 60.00 CH4 0.50 40.00 CO2 1.25 100.00 Total (A) Biogas Feed separator Mole Flow kmol/sec:omposition (mole % Components Product methanol composition (D) 0.18 100.00 Mole Flow kmol/sec composition (mole % CO2 Components 100.00 Total 0.18 H2O 0.75 75.00 Mole Flow kmol/sec:omposition (mole % 0.25 25.00 Components DME 100.00 1.00 100.00 H2 0.35 Total 0.35 100.00 Product DME Total Syngas С 660 265 265 С 660 psi ps (E) (F) External Hydrogen s (B) DME reactor Methanol synthesis & distillation Recycle Recycle gas Components Mole Flow kmol/sec composition (mole %) MeOH product to DME reactor CO2 9.50 25.00 Components Mole Flow kmol/sec composition (mole % 28.50 75.00 H2O 0.50 50.00 H2 Total 38.00 100.00 CH3OH 0.50 50.00 Total 1.00 100.00

#### Figure 2: Process Flow Diagram at Optimum Process Condition (265C, 660 psi)

Source: University of California, Riverside

#### Test Report (Laboratory Demonstration)

#### **Experimental Setup for Carbon Dioxide-to-Methanol Production**

#### Reactor Design

From the simulation study result of overall process, conversion of CO<sub>2</sub> to methanol process was demonstrated in the laboratory scale flow-through reactor.

The reactor was converted from an existing water-gas shift reactor. The feed flow direction was redesigned to adequately handle the collection of liquid products. The reactor had a catalyst holding section in the middle to prevent the catalyst from leaving the chamber.

#### Flow Controllers Systems

Sierra Smart Trak 100 controllers (Figure 3) were purchased to accurately control the gas flow through the system. Flow controllers were installed and linked to the control mainframe. A flow meter was installed and calibrated using a biosmeter, which measures the total gas volume at the reactor exhaust. Flow exhaust pipes were installed to vent the system.



#### Figure 3: Flow Controller System

Source: University of California, Riverside

#### Sensors/Electronics

Thermocouples and pressure sensors were installed at the top and bottom of the reactor to monitor the reactor temperature and pressure. The top of the reactor is shown in Figure 4. These sensors are wired to National Instrument's field points

(Figure 5). A LabView program was created to graph, record and display the values of the thermocouples, flow meter and pressure sensors.



Figure 4: Top Part of Reactor System

Note: The pressure sensors are the blue components to the left and the upper right of the reactor; the yellow sensors are the thermocouples.

Source: University of California, Riverside



#### Figure 5: Process Controller

#### Gas Analysis System

The researchers chose the Residual Gas Analyzer, model QMS200 (RGA) from Stanford Research Systems to analyze the products of the reactor (Figure 6). The RGA is connected with a capillary tube to the bottom of the reactor and then purged with dry and inert gas to remove residual water from the system before the measurement. The

Source: University of California, Riverside

capillary shown in Figure 7 was installed in an oven and insulated to maintain a temperature to prevent the condensation of liquid product from the reactor effluent.



Figure 6: Gas Analysis System

Source: University of California, Riverside



Figure 7: Heated Oven for Inlet Capillary of Residual Gas Analyzer

Source: University of California, Riverside

#### Overall Reactor System

As illustrated in Figure 8, the reactor system apparatus has a (1) Watlow heater that encases a Swagelok filter containing the activated Cu-Zn catalyst. Gas is introduced to the catalyst from (2) compressed gas tanks that are regulated by (3) Sierra flow

controllers. Pressure is controlled using (4) a backpressure regulator and monitored above and below the catalyst by (5) pressure transducers. After the catalyst a small amount of gas is sampled using a capillary line which is then sent to an (6) RGA while the remaining gas is cooled in an ice bath (9). The remaining dry gas is measured using a brooks gas flow meter (7) and exhausted.

An oven (10) is used to ensure that the gas sampled for the RGA remains above methanol's boiling temperature, so all products remain in gas phase. Temperatures are recorded throughout the reactor using k-type thermocouples (8). Gas pressures, gas temperatures and catalyst temperatures are recorded by LABVIEW and compiled with RGA data in excel.



Figure 8: Overall Experimental Setup

Source: University of California, Riverside

#### **Experimental Results for Carbon Dioxide-to-Methanol Production**

The RGA was calibrated every time before a test was conducted. The gases used for calibration were composed of varying mixtures of  $H_2$ , CO, CO<sub>2</sub>, air, and dimethyl ether. Air was in the calibration to mimic methanol because methanol is liquid at STP and air contains  $O_2$  which has the same atomic weight as methanol. The regression coefficient of the calibration curve was always statistically significant at a confidence interval greater than 0.95.

#### Test Procedures

- Activation of the Cu-Zn catalyst before every run.
- Once the activation process was completed, the reactor was heated to the desired temperature and pressurized to the desired pressure.
- Once the reactor reached steady state the flow was then switched to the reactant gases.
- The experiment was run for a duration of 1-2 hours.
- Data was collected and then analyzed in Excel.

#### Controlled Tests Parameters

The optimum input conditions found in the simulation study were used for the experimental input condition of the laboratory test:

- Hydrogen flow rate from (.24-2) SLPM
- Carbon monoxide flow rate at (0-.3) SLPM
- Carbon dioxide flow rate at (.08-.8) SLPM
- Temperature varied at (240- 300)C
- Catalyst loading of (100-500) mg

#### Data Analysis

The pressure of the reactor system was set around 660 psi and the temperature was set to 270°C, which are suggested as the optimum conditions from the catalyst provider and Aspen Plus Process Simulation study in the previous section.

Figure 9 shows the typical experimental result. From the second mark of 1700, the feed gas was routed to the reactor from the bypass position. The feed gases ( $CO_2$  and  $H_2$ ) begin to decrease and the products such as CO and methanol increase. In this test, 17 percent of the carbon in the  $CO_2$  was converted into methanol. In the laboratory scale reactor, the "wall effect" was predominant, in which most of the feed gases passes through the wall of the reactor instead of the catalyst bed however, maximum  $CO_2$  conversion achieved in this type of reactor.



Figure 9: Typical Experimental Chart with Methanol Production from Carbon Dioxide

Source: University of California, Riverside

## CHAPTER 3: Potassium Carbonate Synthesis from Carbon Dioxide

### Background

Removing CO<sub>2</sub> by scrubbing with potassium hydroxide (KOH) solution results in the formation of aqueous potassium carbonate known as the "hot carbonate" process. This process has been known for many years but has not been implemented widely due to various issues. It is particularly well-suited for gases with low hydrogen sulfide content and moderate CO<sub>2</sub> concentrations. The overall efficiency of the process can be improved by means of additives that enhance the rate of absorption. There is revived interest in this process recently and laboratory and pilot scale studies have been conducted in both the United States and Europe.

The major advantage of this technology is the ability to recover the potassium carbonate from the process in aqueous or crystalline form. Potassium carbonate has commercial value if produced with adequate quality. The additional revenue stream from this commercially valuable co-product can contribute to the economic viability of RNG production projects.

The key reaction in the hot carbonate process is the absorption of  $CO_2$  by KOH resulting in the formation of an aqueous solution of  $K_2CO_3$ :

$$2 \text{ KOH} + \text{CO}_2 \leftrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \tag{1}$$

The presence of excess KOH during this reaction leads to an increased production of potassium carbonate, while excess CO<sub>2</sub> leads to the undesired formation of KHCO<sub>3</sub>.

The hot carbonate process is integrated through drying and crystallization steps that allow the potassium carbonate to be recovered as a solid. This report does not include the crystallization of potassium carbonate in the experimental section.

As with Task 2, the hot carbonate and related processes for  $CO_2$  separation and use have shown potential for successful commercial implementation, but have not yet reached the point where pilot demonstration followed by commercialization is warranted. As discussed earlier, the specific challenge for such processes is that these technologies are often intended for very large-scale commercial facilities using syngas from coal and are not optimized for small-scale projects that are typical for RNG production. Therefore, it is critical to optimize these technology options for small scale commercial implementation. This report considered RNG plant sizes with ~5 MMSCFD landfill gas throughput or with ~4 MW electricity generation.

## Task 3 Objective

The goal of Task 3 was to develop and optimize a technology for the cost-effective separation of  $CO_2$  from RNG fuel and the subsequent production of potassium carbonate from the  $CO_2$ .

The specific objectives under this task were:

- Modeling evaluation of various process configurations and parameters of the hot carbonate process in order to identify the process conditions that will be experimentally studied. The Aspen Plus Process Simulator was used to model the process.
- Experimental evaluation of optimal process parameters for the recovery of CO<sub>2</sub> sufficient enough to upgrade the RNG to transportation fuel specifications. The parameters studied are discussed below.
- Identification of process metrics that to be used as input parameters in the commercial evaluation of the processes.

## **Test Plans and Reports**

### Test Plans

The experimental setup consisted of an absorption column similar to the setup used in recent efforts reported in literature.<sup>24,25</sup> The reactor was comprised of a packed column where an aqueous solution of KOH comes into contact with the gas stream containing methane,  $CO_2$  and other components.

A schematic of the reactor setup along with a photograph is given in Figure 10. The apparatus used for the potassium carbonate experiments includes a SS316 1" tube that is 5' long (1). The reactor column was filled with glass beads in order to increase the time the potassium hydroxide solution would take to flow through the reactor. Heating tape (2) was wrapped around the column and was controlled by a PID controller through LABVIEW software (3). A pump (4) was used to feed the KOH solution to the top of the column while the speed was regulated by an AC tech controller (5). The KOH supply feed was held in a 5 gallon polypropylene container (6). The liquid product was also stored in a 5 gallon polypropylene container (7). Mass flow controllers (8) were used to regulate the gas inlet. Temperature was monitored by thermocouples (9) and recorded with LABVIEW. The pressure was monitored with a pressure transducer (10) and recorded with LABVIEW. A condensation trap (11) was used to remove any remaining liquid in the product gas line. A control valve (12) was used to control the output gas flow direction (bypass/vent/sample collection).

<sup>&</sup>lt;sup>24</sup> *GreenHouse Effect Reduction from Landfill*, GHERL, 2011.

<sup>&</sup>lt;sup>25</sup> Lombardi L, Corti A, Carnevale E, Baciocchi R, Zingaretti D. *Carbon Dioxide Removal and Capture for Landfill Gas Up-grading*, Energy Procedia, 2011;4:465-472.



Figure 10: Hot Carbonate Absorption Column Setup

Source: University of California, Riverside

The output gas was collected in gas sampling bags and analyzed with the RGA. The RGA was calibrated every time a test was done. The gas used for calibration was  $CH_4$  and  $CO_2$  that was mixed together at varying compositions. The calibration curve's R2 value was always found to be greater than 0.95.

#### Tests Parameters

The impact of the following process parameters on the overall efficiency and process performance was evaluated.

- Total gas flow rates were varied between 1, 1.75, 2.5, and 3.5 liters per minute.
- Temperature was varied between 25, 40, 55, and 70°C.
- KOH concentrations were varied between 5, 10, 20, and 25 percent KOH.
- Gas composition was varied between 60/40, 40/60, and 20/80 percent CH<sub>4</sub>/CO<sub>2</sub>. The 60/40 gas composition was used the most because it best represented the gas composition of landfill gas.
- KOH was varied between 10, 20, 30, and 40 milliliters per minute.

#### Test Report (Laboratory Demonstration Result)

Results from the experiment are shown in Figures 11 through 13. The results show that a higher percentage of the  $CO_2$  was absorbed at higher liquid hourly space velocity (LHSV) and lower gas hourly space velocity (GHSV). The LSHV and GHSV were calculated by taking the volumetric flow rate of the gas feed and liquid feed and dividing it by the volume of the reaction zone in the reactor.

The results also showed that the amount of  $CO_2$  absorbed is linearly proportional to the concentration of the potassium hydroxide.

Figure 11 correlates the percentage of  $CO_2$  absorbed with respect to the LHSV. This correlation is based on a 10 percent concentration of potassium hydroxide used for the KOH flow rates ranging from 10-40 mL/min. As LHSV increases, the percentage of  $CO_2$  absorbed increases. At higher than 0.001 (hour <sup>-1</sup>) of LHSV, nearly 100 percent of the  $CO_2$  can be absorbed. Increased absorption was expected since high LHSV allows a larger amount of KOH in the reactor.





Source: University of California, Riverside

Figure 12 shows the relationships between the percent  $CO_2$  absorbed with varying GHSV. The result is based on a 10 percent concentration of potassium hydroxide as the reactant gas mixture flow rate ranged from 1-3.5 L/min. As the GHSV increases, the percentage of  $CO_2$  absorption decreases. In order to achieve maximum absorption of 100 percent, GHSV should be maintained at less than 0.002 (hour <sup>-1</sup>).

This decrease of  $CO_2$  absorption was expected since at higher GHSV, the residence time of  $CO_2$  in the KOH solution is decreased, so there is not enough time for the absorption reactions to take place.





Source: University of California, Riverside

Figure 13 shows the effect of KOH concentration to the absorption of  $CO_2$ . The trend seen here is as the concentration of  $CO_2$  in the feed gas increases, the  $CO_2$  absorption efficiency decreases. This is anticipated due to the fact that lowering the  $CO_2$ concentration in the feed gas increases the ratio of  $CO_2$  to KOH in the reactor.

By increasing the concentration of the KOH solution, the percentage of  $CO_2$  absorbed increases, since it lowers the ratio of  $CO_2$  to KOH in the reactor. A  $CO_2$  absorption of 80 percent or more can be achieved when KOH concentrations are 20 percent or greater.

In conclusion, it was found that a CO<sub>2</sub> absorption of more than 80 percent is achievable at less than 0.02 GHSV (hour<sup>-1</sup>), with a minimum KOH concentration of 20 percent.



Figure 13: Percent Carbon Dioxide Absorbed versus Potassium Hydroxide Concentration

Source: University of California, Riverside

## CHAPTER 4: Economic Assessment of Proposed Technologies and Recommendation of Optimized Carbon Dioxide Recovery and Use Technology

## Background

The objective of Task 4 was to use the experimental and simulation data from the first two project tasks to evaluate the commercial viability of the technology options and the potential for widespread adoption of these technology options.

RNG has the potential to have a meaningful impact on the current energy mix in the transportation sector in the United States by reducing fossil fuel use and greenhouse gas emissions. The practical potential for RNG production in the United States for 2035-2050 is approximately 4.7 trillion cubic feet or 40 billion gasoline gallon equivalents per year.<sup>26</sup>

Although RNG has tremendous potential as a transportation fuel, widespread commercial production over the next few decades is not guaranteed due to a number of challenges, primarily associated with the economic viability of potential projects. RNG production cost varies widely depending on a wide range of parameters including feedstock availability, conversion technology, project scale, and market competitiveness. Table 7 provides an overview of RNG production costs for a number of different technology options.

<sup>&</sup>lt;sup>26</sup> An Overview of the Feedstock Capacity, Economics, and GHG Emission Reduction Benefits of RNG as a Low-Carbon Fuel, National Petroleum Council, March 2012.

## Table 7: Renewable Natural Gas Production Cost Estimates for DifferentTechnologies

RNG Cost Summary	Biomass	Conversion (	to pipeline qualit	ty RNG)	Delivery	Other / Co- Products	RNG Cost Estima Pipe	tes (Delivered to line)		
Biomass / Case	Biomass Cost (\$/dry ton)	Digestion / Gasification (\$/MMBTU/d input)	Upgrading and Cleanup (\$/mmcfd input)	Yield (gge/dry ton and % of Energy Input)	Pipeline Injection (\$/MMBTU delivered)	Any other costs or co-product credits.	\$/MMBTU	\$/gge		
Landfill Gas		LFG collection system costs (\$0.9 average, range: \$0.6 - \$1.2)	Biogas	~ 85% of Energy Content in collected Landfill Gas	Requires compressors, connection and	Could get credits	\$5 - \$9	\$0.6 - \$1.1		
Livestock Manure - Large Dairy	Waste already collected. MSW may	Covered Iagoon (\$1- \$7) or Anaerobic Digester (\$2 - \$25) Anaerobic Digester (\$2	Upgrading and Cleanup (\$0.5 - \$25). Costs depend on scale.	ading and hup (\$0.5 - i). Costs pend on Typically 48 - 64 scale. (35% - 46%)	monitoring equipment, and pipe (typically \$50/ft installed) to the pipeline injection point. (\$0.2 - \$30 depending on scale) For	for tipping fees, carbon credits for avoided emissions, value of co-products including digestate other	\$5 - \$9	\$0.6 - \$1.1		
Livestock Manure - Medium	require sorting						\$7 - \$13	\$0.8 - \$1.6		
MSW - Digestable - Large	or creating.						\$4 - \$12	\$0.5 - \$1.5		
Wastewater Sludge		on scale and type.					pir	pipeline multiply by	non-RNG	\$5 - \$11
Large Plant (ag waste, energy crops, &/or forest waste)	\$30 - \$150	Thermo-Chemical Conversion (e.g., Gasification and Methanation with Clean up) (\$5 - \$40/MMBTU) Costs depend on scale.	Typically 70 - 95 (50% - 70%)	urban costs per mile can be much higher than in agricultural areas.	district heating, excess power delivered to grid.	\$8 - \$20	\$1.0 - \$2.5			
Medium Plant (ag waste, energy crops, &/or forest waste)	\$10 - \$50					\$15 - \$25	\$1.9-\$3.1			

Source: University of California, Riverside

As the data shows, the price varies widely, from \$4 to \$25 per MMBtu. The broad range of prices demonstrates the inherent risks and uncertainties associated with RNG production projects. For most technologies, the lowest production cost possible is around \$4 per MMBtu, although this varies between \$4-\$7. Even at the lowest estimated production cost of \$5 per MMBtu, RNG will not be able to compete with fossil natural gas in the open market. Current natural gas spot prices are in the range of \$3.00 to \$3.50 per MMBtu and the prices are not expected to increase significantly over the next decade. The production of shale gas in the United States is expected to contribute to increased natural gas production, resulting in low-to-moderate prices for the foreseeable future.

Government subsidies and other incentives such as renewable fuel credits and tipping fees for waste feedstocks can help reduce the price of RNG, but will not in themselves make commercial viability feasible. A critical step that can help reduce the price of RNG further is to create additional revenue streams by producing co-products that are commercially valuable. The co-product technology demonstrated here provides two distinct advantages:

- The technology improves the total feedstock use efficiency of RNG production processes by converting the otherwise wasted CO<sub>2</sub> to commercially valuable products.
- The technologies considerably increase the commercial viability of potential projects through the revenue stream generated from the co-products.

The technologies developed in the program show the potential for successful commercial implementation, but have not yet reached the point where pilot

demonstration followed by commercialization is warranted. The specific challenge is to optimize these technology options for small scale commercial implementation. This report considered RNG project sizes of typical landfill gas projects with ~5 MMSCFD throughput or with ~4 MW electricity generation. One of the key challenges is the hydrogen requirement for methanol and DME synthesis. A number of hydrogen procurement options were evaluated as part of this task.

Current United States Department of Energy cost targets are \$3.10/kg for central hydrogen plants and \$3.70/kilogram (kg) for distributed hydrogen plants.<sup>27</sup> Further reduction of the cost from central production of hydrogen from water electrolysis using renewable power is anticipated to be lowered to \$3.00/kg at plant gate. By 2020, the cost of central production of hydrogen from water electrolysis using renewable power is estimated to be reduced to  $\leq$ \$2.00/kg at plant gate. Some technology options, such as the steam hydrogasification process generate excess hydrogen as a co-product along with RNG.<sup>28</sup> This hydrogen is typically used for power generation or is recycled back into the process. These technologies are ideally suited for the co-product synthesis options.

### **Methods and Assumptions**

A model for process economic assessment was developed using the Aspen Plus Process Simulator. The process was divided into two sub-processes:  $CO_2$  separation from the existing RNG infrastructure and  $CO_2$  use.

The assumptions made on this calculation were:

- CO<sub>2</sub> is separated from the RNG production site. The CO<sub>2</sub> composition in RNG is 40 percent.
- Gas pressure is increased with an isentropic multistage compressor to the desired pressure. The mechanical efficiency of the compressor is 70 percent and pump is 65 percent.
- Produced gas from the RNG site goes through a separator before entering the methanol synthesis system.
- Separated CO<sub>2</sub> passes through a multistage compressor and cooler before entering the methanol synthesis reactor.
- Product from the methanol synthesis reactor is a mixture of unreacted feed gas, steam, and methanol which is fed to a distillation column. The distillation column

<sup>&</sup>lt;sup>27</sup> Department of Energy, Multi-Year Research, Development and Demonstration Plan (Hydrogen Production), 2015.

<sup>&</sup>lt;sup>28</sup> Raju ASK, Park CS, Norbeck JM. Production of Synthesis Gas for Liquid Fuel Synthesis Using a Steam Hydrogasification and Reforming Process. 15th European Biomass Conference & Exhibition. Berlin, Germany2007.

separates the CH<sub>3</sub>OH mixed with water from the unreacted syngas containing CO,  $CO_2$  and  $H_2$ .

- Methanol synthesis reactor; 265°C, 660 psi, CO<sub>2</sub> converted to CH<sub>3</sub>OH.
- The produced methanol goes to the DME synthesis reactor at 265°C, 45 bar. 100 percent conversion.
- Heat supplied to the steam generator is from the combustor and the heat recovery from the process.
- Heat generated from the methanol synthesis reactor is utilized in the distillation column or separator.
- The model uses the Peng-Robinson equation of state for thermodynamic calculations.

The complete process is diagrammed in Figure 14 and Figure 15. Table 8 describes the unit operations labeled in the block diagram.





Source: University of California, Riverside

## Figure 15: Process Block Diagram for Carbon Dioxide to Dimethyl Ether Process (Carbon Dioxide Utilization Section)



Source: University of California, Riverside

Label	Unit Description
B9	Methanol distillation column
CPRNG2	Multistage compression for RNG to store at the existing Natural Gas infrastructure
MEOHREAC	Reactor for methanol synthesis
CPRNG1	Multistage compression for RNG to store at the existing Natural Gas infrastructure
B13	RNG cooling after compression
CPCO21	Multistage compression for CO <sub>2</sub> before sending to the methanol synthesis reactor
DMEREACT	DME synthesis reactor
CPCO22	Multistage compression for CO <sub>2</sub> before sending to the methanol synthesis reactor
B14	RNG cooling after compression
COOLER1	CO <sub>2</sub> cooling after compression
CPH2	H <sub>2</sub> compression before sending to the methanol synthesis reactor
COOLER2	CO <sub>2</sub> cooling after compression
BGASSEPA	CH4 (RNG) separator from Biogas

#### Table 8: Description of Unit Operations

Source: University of California, Riverside

El Sobrante SLF site was chosen for the standard model size for the economic simulation. The details of the El Sobrante SLF site is located in the City of Corona, Riverside County in southern California, operated by Waste Management Inc. The site produced 4MW of electricity from the 5.27 MMSCF of landfill gas or (3.2 MMSCF of CH<sub>4</sub>). For the CO<sub>2</sub> utilization scenario, 15 tonnes per day (TPD) of DME can be produced additionally.

### **Results and Discussion**

#### **Capital Cost Estimation**

The researchers estimated the capital cost of the entire process with the assumptions described in the previous section using the Aspen Plus Process Simulator. Table 9 summarizes the results.

	CO <sub>2</sub> Separation	CO <sub>2</sub> Utilization (to DME)	Total Process
Capital Cost (MM\$)	10	8	18
Operating Cost (MM\$/Year)	1	0.8	1.8
Utility Cost (\$/Year)	8,500	1,000	9,500

#### Table 9: Capital Cost Estimation

Source: University of California, Riverside

#### **DME Production Cost**

The researchers used the following assumptions when estimating production cost.

- Plant design basis: Same as capital cost estimation, 15 metric tonnes per day (TPD) of DME produced
- Plant on-stream percentage: 91.3 percent (8,000 hours of operation per year)
- Location: Corona, California
- Capital cost for the plant: \$18 million
- Debt/Equity: 70/30 percent (loan period 10 years)
- Plant life: 30 years
- Loan interest rate: 5 percent
- Inflation rate: 3 percent
- Construction: 2 years
- Start up : 3rd year
- Production in nominal capacity : 4th year
- Annual operating & maintenance costs: \$ 1.8 million, which is 10 percent of EPC costs (Fixed operating and maintenance [O&M] plus variable O&M)
- Fixed O&M costs: 6 percent of EPC costs; variable O&M costs: 4 percent of EPC costs
- DME sales price: \$500 \$/metric tonne.
- DME prices are based on past and projected prices for worldwide average.
- Hydrogen cost: \$1 to \$ 6 per Kg. The 2015 United States Department of Energy cost targets are \$3.10/kg for central hydrogen plants and \$3.70/kg for distributed hydrogen plants.<sup>29</sup> For compression, storage, and dispensing costs, an additional

<sup>&</sup>lt;sup>29</sup> Department of Energy, Multi-Year Research, Development and Demonstration Plan (Hydrogen Production), 2015.

cost of \$2/kg has to be considered. Further reduction of the cost of central production of hydrogen from water electrolysis using renewable power was estimated to \$3.00/kg at plant gate. By 2020, the cost of central production of hydrogen from water electrolysis using renewable power to is expected to be  $\leq$ \$2.00/kg at plant gate. Long term target price for the hydrogen production was \$1.00/kg.

Table 10 summarizes the average production cost with different Hydrogen cost scenarios. As shown in the table, only the case with a hydrogen cost of \$1/kg, shows the investible Return on Investment (ROI) of 12 percent with the \$408/kg of average DME production cost.

Table 10: Average invalogent roduction cost					
	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Hydrogen Cost (\$/kg)	1	2	3.1	3.7	6
Average DME Production Cost (\$/Tonne)	408	589	789	897	1,314
ROI* (%)	12	n/a	n/a	n/a	n/a

**Table 10: Average Hydrogen Production Cost** 

\* Return On Investment, for 15 years and terminal value.

Source: University of California, Riverside

#### **Extra Revenue Estimation**

Figure 16 shows yearly cash flow for the model CO<sub>2</sub> to DME plant. It shows positive cash flow from the third year due to the product start up to the nominal level. It also shows the step up at the tenth year due to completion of the loan payment. Hydrogen cost for this scenario was \$1/kg, which is the United States Department of Energy's long-term hydrogen cost target from renewable sources.





Source: University of California, Riverside

When the hydrogen costs more than \$2/kg, the model did not show any meaningful ROI that is worthy to invest. It was found the sale price of DME has to be more than \$600 per tonne to generate the positive value of ROI. This extra cash flow from the co-product (DME) production must generate enough revenue to reduce the production cost of the RNG transportation by a minimum of \$0.50 per MMBtu, which is the main objective of this study.

An estimated price reduction in the fourth year operation of the plant, at which fullscale production of DME started, was \$2.29 per mmBtu for the typical landfill project scenario such as the El Sobrante landfill site located in Corona. The site produces 5.27 MMSCF of landfill gas daily. It was also assumed that the landfill gas contains 60 percent  $CH_4$  and 40 percent  $CO_2$  and 15 tonnes per day of DME is produced.

Final reduction of the RNG price for varying hydrogen cost scenarios is presented in Table 11.

Table 11: Estimated Reduction of the Renewable Natural Gas ProductionPrice

	Scenario 1	Scenario 2	Scenario 3
Hydrogen Cost (\$/kg)	1	2	3.1
Fourth Year Cash Flow (MM\$)	0.31	-1.63	-3.76
Reduction of RNG production cost (\$/mmBtu)	0.26	-1.37	-3.15

Source: University of California, Riverside

As shown in the table, only the case with the hydrogen cost of 1/kg creates the revenue to reduce the RNG production cost to 0.26 per mmBTU. The economic evaluation indicates that the RNG fuel production cost reduction by co-product development from CO<sub>2</sub> is only achievable in the limited case.

# **Recommendation of Optimized Carbon Dioxide Recovery and Utilization Technology (Task 5)**

This task consisted of developing conclusions and recommendations on optimized CO<sub>2</sub> recovery and utilization technology for RNG projects. Based on the results gathered from tasks 2 through 4, the research team makes the following recommendations:

- Recovery and utilization technology from the RNG project site, such as DME production from the waste CO<sub>2</sub>, will not decrease the production cost of RNG through the benefit of co-product sales in most cases. The required hydrogen cost has to meet the long-term United States Department of Energy target cost of \$1/kg for hydrogen from renewable sources to achieve the viable RNG production cost reduction.
- This extra cash flow from the co-product (DME) production generates revenues to reduce the production cost of the RNG by \$0.26 per MMBtu, at the above hydrogen cost scenario.
- The anticipated reduction in RNG production cost is strongly dependent on the hydrogen delivery cost to the site and DME sales price.
- The RNG project sizes selected were based off a typical landfill site of 4MW electricity generation from the 5.3 MMCFG of daily landfill gas production. The proposed site will have 15 TPD of DME product throughput.

## CHAPTER 5: Summary of Results

The project demonstrated a cost-effective technology for  $CO_2$  conversion into a commercially valuable co-product such as methanol or DME with a combined  $CO_2$  separation, which is directly applicable to the existing RNG project evaluated.

The research team carried out DME synthesis over two sets of commercially available catalysts: (1) the methanol synthesis catalyst followed by a methanol dewatering catalyst with  $\gamma$ -Alumina; (2) direct DME synthesis catalyst such as 6CuO-3ZnO-1Al<sub>2</sub>O3/HZSM-5.

The optimum process conditions for the methanol and DME synthesis reactors that maximizes the carbon conversion yield of methanol and final product were found to be 265°C for the temperature and 660 psi for the reactor pressure. Process thermal efficiency, defined as the ratio of the percentage of heating value of all products to that of input (including heat supply), was found to be 79.8 percent under these conditions. A laboratory scale bench reactor was built to demonstrate the conversion of  $CO_2$  to methanol, which confirmed that 17 percent of the  $CO_2$  was converted to methanol in the laboratory flow reactor.

For the potassium carbonate formation, a laboratory scale flow reactor was developed. It was found that the  $CO_2$  absorption of 80 percent or more can be achieved when KOH concentrations are 20 percent or greater.

Process economic analysis of the  $CO_2$  to DME process in the typical RNG project site was performed. Typical sites considered were RNG landfill gas projects with daily production of ~5 MMSCF throughput or with ~4 MW electricity generation.

One of the key challenges of the project was the hydrogen requirement for the DME synthesis. The team evaluated several hydrogen procurement options. With a hydrogen cost scenario of \$1-\$6/kg, results showed that the average DME production cost ranged from \$408 to \$1,314 per tonne. For the DME sale price of \$500 per tonne, estimated price reduction in the RNG production cost was \$0.26 per MMBTU with a hydrogen cost of \$1/kg.

## LIST OF ACRONYMS

Term	Definition
ASHRAE	American Society of Heating, Refrigeration, and Air Conditioning Engineers
С	Centigrade
CE-CERT	College of Engineering – Center for Environmental Research and Technology
CH4	Methane
CNG	Compressed natural gas
СО	Carbon monoxide
CO2	Carbon dioxide
DEA	diethanolamine
DME	Dimethyl ether
GHSV	Gas hourly space velocity
H2	Hydrogen
HC	Hydrocarbons
HHV	Higher heating value
Kg	Kilogram
КОН	Potassium hydroxide
L/min	Liters per minute
LSHV	Liquid hourly space velocity
M15	Fuel blend consisting of 85 percent gasoline and 15 percent methanol
M85	Fuel blend consisting of 15 percent gasoline and 85 percent methanol
MEA	Monoethanolamine
mL/min	Milliliters per minute
MMBtu	Million British thermal units
MMCFG	Million cubic feet of gas

Term	Definition
MMSCFD	Million standard cubic feet per day
MW	Megawatts
02	Oxygen
PSA	Pressure swing adsorption
Psi	Pounds per square inch
Ppm	Parts per million
SLPM	
RD&D	Research, development, and demonstration
RGA	Residual Gas Analyzer
RNG	Renewable natural gas
ROI	Return on investment
TPD	Tonnes per day
WGS	Water Gas Shift
ZnO	Zinc oxide