



## **TECHNICAL GROUP**

### **CO<sub>2</sub> Utilization Options Task Force Phase 1 Report**

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## CSLF IS GOING GREEN\*

### CO<sub>2</sub> UTILIZATION OPTIONS TASK FORCE PHASE 1 REPORT

*Note by the Secretariat*

#### Background

At the 4<sup>th</sup> CSLF Ministerial Meeting, at Beijing, China in September 2011, the Technical Group approved a new multi-year Action Plan. “CO<sub>2</sub> Utilization Options” is one of the twelve Actions that comprise the Action Plan, and the United States is leading a new Task Force that will focus on CO<sub>2</sub> utilization options that have the potential to yield a significant, net reduction of CO<sub>2</sub> emissions in sufficient volumes to make a meaningful contribution to global warming and climate change objectives. This document is the Task Force’s Phase 1 Report, which provides a summary of current knowledge of the use and re-use of CO<sub>2</sub>.

#### Action Requested

The Technical Group is requested to review the Task Force’s Phase 1 report.

\* **Note:** This document is available only electronically. Please print it prior to the CSLF meeting if you need a hardcopy.

# **CO<sub>2</sub> Utilization Options - Phase 1 Report**

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**Draft Version**

August 23, 2012

**Prepared for Carbon Sequestration Leadership Forum**

**CO<sub>2</sub> Utilization Options Task Force**

# CO<sub>2</sub> Utilization Options - Phase 1 Report

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## List of Acronyms and Abbreviations

Acronym/Abbreviation	Definition
AMSO	American Shale Oil
ANL	Argonne National Laboratory
ANS	Alaska North Slope
ARI	Advanced Resources International
ARRA	American Recovery and Reinvestment Act
ASTM	American Society for Testing and Materials
bbl	Barrel (of crude oil, 42 U.S. gallons)
bbl eq	Barrel equivalent
BD	Biodiesel (fatty acid alkyl esters)
BOE	Barrels of oil equivalent
CaCO <sub>3</sub>	Calcite
CaMg(CO <sub>3</sub> ) <sub>2</sub>	Dolomite
CBM	Coalbed Methane
CCS	Carbon Capture and Storage
CF	Critical Fluid
CH <sub>4</sub>	Methane
CMAP	Carbonate Mineralization by Aqueous Precipitation (Calera)
CO <sub>2</sub> CRC	Cooperative Research Centre for Greenhouse Gas Technologies
COE	Cost of Electricity
CO <sub>2</sub>	Carbon Dioxide
CO <sub>2</sub> -EOR	Carbon Dioxide-Enhanced Oil Recovery
CSLF	Carbon Sequestration Leadership Forum
DOE	U.S. Department of Energy
ECBM	Enhanced Coalbed Methane
EGR	Enhanced Gas Recovery
EGHR	Enhanced Gas Hydrate Recovery
EOR	Enhanced Oil Recovery
EPA	U.S. Environmental Protection Agency
EtOH	Ethanol
FAME	Fatty Acid Methyl Esters
gal	gallon (unit of volume, 3.8 liters)
GGBFS	Ground Granulated Blast Furnace Slag
GHG	Greenhouse Gas
GT	Giga tonne (1 billion metric tonnes)
H <sub>2</sub> O	Water
H <sub>2</sub> S	Hydrogen Sulfide

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<b>Acronym/Abbreviation</b>	<b>Definition</b>
HCPV	Hydrocarbon Pore Volume
HRBP	HR BioPetroleum
HTGR	Very High Temperature Gas Reactor
IABR	Integrated Algal Biorefinery
IEA	International Energy Agency
IEA GHG	IEA Greenhouse Gas R&D Programme
IGCC	Integrated Gasification Combined Cycle
INL	Idaho National Laboratory
KCl	Potassium chloride
KGS	Kentucky Geological Survey
LICADO	Liquid Carbon Dioxide (Process)
LLNL	Lawrence Livermore National Laboratory
MCF	Thousand cubic feet (10 <sup>3</sup> ft <sup>3</sup> )
MDS	Marine Desalination Systems, LLC
MgCO <sub>3</sub>	Magnesium Carbonate
MIT	Massachusetts Institute of Technology
MT	Million Metric Tonnes
MTPA	Million Metric Tonnes per Annum
MW	Mega Watt
N <sub>2</sub>	Nitrogen
NA	(Data) Not Available
Na <sub>2</sub> CO <sub>3</sub>	Sodium Carbonate (soda ash, washing soda)
NaHCO <sub>3</sub>	Sodium Bicarbonate (baking soda)
NEA	Nuclear Energy Agency
NETL	U.S. DOE National Energy Technology Laboratory
NO <sub>2</sub>	Nitrogen Dioxide
NO <sub>x</sub>	Nitrogen Oxides (NO, NO <sub>2</sub> )
O <sub>2</sub>	Oxygen
ORNL	Oak Ridge National Laboratory
PBR	Photobioreactor
PC	Propylene Carbonate
PPC	Polypropylene Carbonate
RCSP	U.S. DOE Regional Carbon Sequestration Partnership
RF	Radio Frequency
RFS2	revisions to the National Renewable Fuel Standard
SCF	Standard Cubic Feet
SCM	Supplementary Cementitious Material
SFE	Supercritical Fluid Extraction

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<b>Acronym/Abbreviation</b>	<b>Definition</b>
SOTA	State of the art
SO <sub>x</sub>	Sulfur oxides (sulfur dioxide, sulfur trioxide)
TAG	Triacyl glycerol
TBD	To Be Determined
TCF	Trillion cubic feet (10 <sup>12</sup> ft <sup>3</sup> )
TPD	Metric tonnes per day
UIC	Underground Injection Control (Program)
VES	Viscoelastic Surfactant



## Definitions

1. **Beneficial use:** A process, technology, or application which generates valuable chemicals, fuels, raw materials, or has considerable environmental or economic advantages over the status quo.
2. **Hydrocarbon resource recovery applications:** Applications where CO<sub>2</sub> is used to enhance the production of hydrocarbon resources.
3. **Re-use (non-consumptive) applications:** Applications where CO<sub>2</sub> is not consumed directly, but re-used or used only once while generating some additional benefit (compared to sequestering the CO<sub>2</sub> stream following its separation).
4. **Consumptive applications:** These applications involve the formation of minerals, or long-lived compounds from CO<sub>2</sub> which results in carbon sequestration by '*locking-up*' carbon.
5. **Nominal-net benefit:** The value realized from the use of CO<sub>2</sub> less the costs of raw materials involved in the CO<sub>2</sub>-use process. This approach does not account directly for the capital costs of CO<sub>2</sub> utilization, which are process-specific. The costs of CO<sub>2</sub> capture and compression are aggregated as the cost of high-pressure, pure CO<sub>2</sub> (assumed to be 40 \$/T). Relative comparisons of net benefits from various beneficial uses are more relevant than the absolute values themselves.
6. **Direct benefit:** A beneficial use which, by itself, leads to the reduction of CO<sub>2</sub> emissions over a given time period, without considering other related processes.
7. **Indirect benefit:** A beneficial use which, by itself does not reduce CO<sub>2</sub> emissions, but mitigates CO<sub>2</sub> when considered in conjunction with several related processes, as a part of a particular lifecycle, or a system-wide analysis.
8. **Indirect CO<sub>2</sub> emissions:** CO<sub>2</sub> emitted during a CO<sub>2</sub>-use process, as a result of energy consumption in the application, or arising as CO<sub>2</sub> emissions from energy expended in forming or processing the raw materials used in the application.
9. **Cost of CO<sub>2</sub> reduction:** Nominal net cost (or benefit). If it is less than zero, it is the nominal net-positive benefit.
10. **Indirect-carbon avoidance:** CO<sub>2</sub> emissions avoided as a result of the indirect-application, or use of CO<sub>2</sub>. Typical examples include reduction in CO<sub>2</sub> emissions from gains in process efficiency, single- or multiple-reuse or recycling of CO<sub>2</sub> which displaces the use of fossil fuel-derived energy in a particular application or process.

## Executive Summary

This document provides a summary of current knowledge of the use and re-use of carbon dioxide (CO<sub>2</sub>). Simply put, use or reuse options provide a value to the end-user which creates a market for CO<sub>2</sub> producers. The use of CO<sub>2</sub> in various applications may have economic and/or environmental benefits. Historically, the market for the use of CO<sub>2</sub> has been relatively small compared to anthropogenic CO<sub>2</sub> emissions. However, there is an impetus to explore additional uses and benefits of CO<sub>2</sub> to mitigate CO<sub>2</sub> emissions. All processes discussed here provide incremental advantages resulting from using CO<sub>2</sub>, when compared to present day consumption. No single process will mitigate all anthropogenic CO<sub>2</sub>. However, with continued support of research and development, the number of applications is increasing. In combination with geologic sequestration these applications could lead to significant benefits.

The metrics utilized in this summary considered the following:

- Total amount of CO<sub>2</sub> permanently sequestered
- Unit value (benefit) or cost of application
- Energy consumed by the application (or net-CO<sub>2</sub> savings from the technology)
- Market Potential of primary CO<sub>2</sub> use and any by-products

These considerations were used to establish more detailed metrics to compare each of the various technologies. This summary provides more detailed discussion on the technologies found and provides summary tables for the various categories.

Various CO<sub>2</sub> use applications were classified into three categories: resource recovery, non-consumptive uses, and consumptive uses. To make a meaningful impact, a CO<sub>2</sub> use process should use large quantities of CO<sub>2</sub>, or result in a large net-benefit, or preferably both.

Resource recovery applications include the use of CO<sub>2</sub> for enhanced oil recovery (EOR), enhanced gas recovery (EGR), fracturing, enhanced coalbed methane production (ECBM), and oil shale recovery. Among the resource recovery applications, CO<sub>2</sub>-EOR has a significant potential to mitigate CO<sub>2</sub> (16-22 billion T CO<sub>2</sub> by 2050) with a relatively high-net benefit (~\$100 /T CO<sub>2</sub> economic margin, 167 to 243 \$/T net-benefit). This analysis assumed an oil price of \$85/bbl and CO<sub>2</sub> price of \$40/T. The use of CO<sub>2</sub> to recover natural gas from depleted gas reservoirs, CO<sub>2</sub>-enhanced gas recovery (CO<sub>2</sub>-EGR) has the technical potential to use up to 3,200 to 7,800 MT CO<sub>2</sub>/y till 2050 (or 160 to 390 giga tons of CO<sub>2</sub>). The technical, U.S. potential for CO<sub>2</sub> use in enhanced-coalbed methane (CO<sub>2</sub>-ECBM) production over 50 years is about 60 to 117 GT CO<sub>2</sub> (1,200 to 2,340 MT CO<sub>2</sub>/y). Up to 2.2 MCF of natural gas could be produced for every metric tonne of CO<sub>2</sub> stored. Assuming a nominal natural gas price of \$2/MCF, the nominal-net benefit would be approximately \$4.4/T CO<sub>2</sub>. About 0.4 T of CO<sub>2</sub> could be used per vertical-well completion, if employed as a fracturing agent. Approximately 18 MT CO<sub>2</sub>/y would be required for a facility to produce 1 million bbl/d of syncrude from in situ processing of oil shale. CO<sub>2</sub>-EGHR and use for oil shale recovery are also beneficial, but the amount of CO<sub>2</sub> which could potentially be used in these applications is relatively uncertain. The benefits from resource recovery could partly offset the costs of carbon capture. Unlike CO<sub>2</sub>-EOR which is relatively more mature, oil recovery from oil shale using CO<sub>2</sub>, CO<sub>2</sub> fracturing, CO<sub>2</sub>-EGR, CO<sub>2</sub>-ECBM, and CO<sub>2</sub>-EGHR are processes still being developed or tested in pilot-scale tests.

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Non-consumptive CO<sub>2</sub>-use applications have an indirect-CO<sub>2</sub> reduction benefit in the form of production of fresh water or valuable minerals, higher efficiency, or the displacement of fossil fuels. Seven non-consumptive uses were discussed in the report: desalination, beneficiation, slurry transport, heat transfer fluid, freight pipelines, solvent extraction, and the conversion of CO<sub>2</sub> to fuels and chemicals. Of these, 'closed-loop' re-use applications where CO<sub>2</sub> is used to produce minerals, or higher process efficiency may have limited potential demand for CO<sub>2</sub>. Income from the sale of fresh water may offset some of the cost of CO<sub>2</sub> capture. The use of CO<sub>2</sub> for supercritical fluid extraction is a commercial-scale process. The rest of the non-consumptive, 'closed-loop' re-use applications are relatively less-technologically mature, and require research and development.

Nominal-net benefit analysis indicates that the conversion of CO<sub>2</sub> to fuels such as diesel, gasoline and methanol (approximately -200 \$/T) is less 'beneficial' than CO<sub>2</sub> to chemicals (formic acid, acrylic acid, plastics: approximately 750 to 2,000 \$/T). However, the potential CO<sub>2</sub> demand for producing chemicals is small (~millions of tonnes per year overall) compared to amount of CO<sub>2</sub> demand from its conversion to fuels (billions of tonnes per year). Both of these applications recycle carbon from fossil fuels. It is to be noted that the production of urea and certain other chemicals from CO<sub>2</sub> is occurring on a commercial-scale. However, the conversion of CO<sub>2</sub> to fuels requires large-scale demonstrations, and the integration of multiple proven steps (e.g., methanol-to-gasoline process, CO<sub>2</sub> conversion to methanol). Similarly the conversion of CO<sub>2</sub> to high-value chemicals also requires pilot-scale testing and development.

Various consumptive uses, or applications where CO<sub>2</sub> is converted into products with a long-life, form the basis for the third category of CO<sub>2</sub> uses. Several processes currently being developed to convert CO<sub>2</sub> to sodium or calcium/magnesium carbonates/bicarbonates were evaluated. In general, consumptive uses may have the potential to use or mitigate large quantities (billions of tonnes per year globally) of CO<sub>2</sub>. However, larger scale demonstration pilots are needed to evaluate their feasibility. In addition to mineral carbonates, other by-products from consumptive-use processes include chlorine, hydrogen, soil amendments, fertilizers, and building materials. Nominal-net benefits from consumptive uses vary from \$10 to \$300/T CO<sub>2</sub> depending on the product.

The table on the following page provides a summary of various applications which are further discussed in various sections of the document.

		<b>CO<sub>2</sub> considered permanently sequestered, (global, MT CO<sub>2</sub>/yr)</b>	<b>Benefit</b>	<b>Impact (nominal-net benefit, \$/T CO<sub>2</sub>)<sup>1</sup></b>
<b>Resource Recovery</b>	<b>CO<sub>2</sub>-EOR (mainly miscible)</b>	320 to 446 <sup>2*</sup> , Net: 246 to 343*	Crude oil	Gross impact: 167 to 243*
	<b>CO<sub>2</sub>-EGR</b>	3,200 to 7,800 <sup>3</sup>	Natural gas	NA
	<b>CO<sub>2</sub> Fracturing</b>	NA	Natural gas	NA
	<b>CO<sub>2</sub>-ECBM</b>	1,200 to 2,340 <sup>4</sup>	Natural gas	NA
	<b>CO<sub>2</sub>-Enhanced Gas Hydrate Recovery</b>	NA	Natural gas	NA
	<b>Oil Shale Recovery</b>	NA	Hydrocarbons/syncrude	Less than CO <sub>2</sub> -EOR
<b>Non-Consumptive Uses</b>	<b>Desalination</b>	Indirect	Fresh water	NA
	<b>Beneficiation</b>	Indirect	Minerals such as rare earths	NA
	<b>Feed solids to gasifiers or for slurry transport</b>	Indirect	Increased efficiency	NA
	<b>Heat transfer fluid</b>	Indirect	Increased efficiency	NA
	<b>Freight pipelines</b>	Indirect	Increased efficiency	NA
	<b>Solvent Extraction</b>	Indirect	Increased efficiency	NA
	<b>Fuels and chemicals</b>	Indirect	Displaces fossil fuels	2,000* to -200*
<b>Consumptive Uses (carbonation)</b>	<b>Skyonic</b>	20 to 4,842 <sup>5</sup>	Sodium carbonate, bicarbonate	10* to 300*
	<b>Alcoa</b>	2.6 to 23*	Soil amendment, fertilizer	10* to 300*
	<b>Calera</b>	12 to 1,500*	Aggregate, supplementary cementitious material (SCM)	14* to 100*
	<b>Concrete Carbonation</b>	1.8 to 8*	Precast concrete	NA
	<b>Slag Carbonation</b>	6.5 to 18*	Soil amendment	NA
	<b>Novacem</b>	54*/ 2,130	SCM	NA
	<b>Cambridge Carbon Capture</b>	Similar in scale to Novacem & Calera	Carbonate building materials	NA

\* indicate U.S.-specific estimates or values.

In the development of this summary some conclusions became apparent:

1. No single application is capable of consuming major fractions of current or projected CO<sub>2</sub> emissions. However, large potential beneficial impacts (\$/T CO<sub>2</sub>eq) could be realized over the next few decades.

<sup>1</sup> The net-positive benefit is explained in the 'Definitions' section.

<sup>2</sup> Economic margin: 100 \$/T, time period: 30 years, from ARI analyses, economic margin of CO<sub>2</sub>-EOR is \$15 to \$25/bbl.

<sup>3</sup> Time period: 50 years. 160 to 390 GT CO<sub>2</sub> globally can be sequestered via CO<sub>2</sub>-EGR (technical storage capacity)

<sup>4</sup> Time period: 50 years. 60 to 117 GT CO<sub>2</sub> can be stored in unmineable coalbeds in North America (technical storage capacity).

<sup>5</sup> 100% market share, or total available markets

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2. Currently hydrocarbon resource recovery holds the greatest potential for CO<sub>2</sub> use, in terms of amount of CO<sub>2</sub> used annually. Generally, these applications are better understood and closest to practical application at a large scale.
3. Using CO<sub>2</sub> to produce fuels is also a potentially high capacity re-use of CO<sub>2</sub> if there was a high-market penetration, but is limited by the cost of hydrogen, or the relatively-high cost of producing fuels from photosynthetic microorganisms. Producing chemicals is a less costly re-use but the amount of CO<sub>2</sub> used is considerably lower than the CO<sub>2</sub>-to-fuels applications.
4. Other consumptive uses hold potential to provide a sustainable sink for carbon but the market size for these applications is far more limited, based on current markets, than resource recovery options and important aspects of the various relevant process chemistries need to be proven at scale.
5. Carbonation approaches which produce building materials or aggregates, still need to be demonstrated at a scale sufficient to prove their commercial viability.
6. A number of other uses for carbon dioxide might offer indirect benefits through improved energy efficiency, through production of potable water from produced, saline waters, or simply by raising the efficiency of power cycles. These applications could improve overall efficiency from a system point of view.

It is essential to apply sound analytic methodologies to assess both the potential for use of any concept and to estimate the full range of benefits, in terms of the net carbon dioxide removed from the atmosphere, the duration of such storage (if it is not consumed), the potential market value of a use, and finally, the net energetic impact. In the metrics tables in the body of the document, we refer to the need to apply sound life cycle assessment methodologies to appreciate the benefits of many of the candidate beneficial uses.

The beneficial uses of CO<sub>2</sub> are worthy of continued research, development and demonstration. Proper incentives will lead to commercial, large-scale applications. CO<sub>2</sub> use or re-use technologies which are current and being developed are summarized in this paper.

## **1 Introduction and Scope**

This report has been developed to provide a summary of currently known uses and re-use applications for carbon dioxide (CO<sub>2</sub>). A beneficial use of CO<sub>2</sub> is a process, an operation, or a function which adds value by creating a salable product, or by improving process efficiency. The quantities of CO<sub>2</sub> used in some beneficial use applications may be small compared to the potential for CO<sub>2</sub> mitigation from geologic carbon capture and storage (CCS). However, beneficial use processes offer the benefits of value-addition (e.g., hydrocarbon resource recovery) and lower-risk perceptions (e.g., applications where carbon dioxide is consumed). Furthermore, geologic storage of CO<sub>2</sub> may not be suitable in all geographic locations, and requires the presence of suitable seals, access to pore space, and optimal permeability and porosity in the subsurface. Income from high-value products produced from the beneficial use of a slipstream of captured CO<sub>2</sub> could offset a portion of the capital and operating costs for CCS. The higher-value potential and lower-risk perception may also accelerate the development of CO<sub>2</sub> pipeline networks and the deployment of novel technologies, in turn, enhancing prospects for geologic CO<sub>2</sub> storage. For instance, CO<sub>2</sub> used for enhanced oil recovery may also be injected into suitable saline formations adjacent to the oil reservoir, thereby reducing the need for additional infrastructure (wells, pipelines, equipment) at such locations. In other cases, if the produced CO<sub>2</sub> would be used within an industrial complex, only small modifications to existing pipeline networks may be needed.

No single beneficial use technology solution would fully mitigate global CO<sub>2</sub> emissions. However, if a holistic approach is taken, and all options are considered, the sum of the applications could have a significant beneficial impact.

Further, there might be enhanced opportunities to apply these beneficial uses globally, and therefore developing such beneficial use applications may lead to competitive advantage in the short term. Low-carbon intensity products may enjoy an advantage in global trade under policies that limit GHG emissions. Therefore, developing reuse options to lower carbon intensity could lead to a competitive advantage in international trade.

The objectives of this assessment were:

- To conduct a literature survey and research previous studies on the beneficial uses or re-use of CO<sub>2</sub>
- To evaluate and quantify current and potential future beneficial uses of CO<sub>2</sub>
- To develop metrics to be used to evaluate beneficial use concepts

## **2 Overview**

This summary is designed to document processes that use and re-use of CO<sub>2</sub> and to present this information in a format that can be used as a reference tool. There are numerous applications where CO<sub>2</sub> could be used in existing or future industrial processes. Compared to the re-use options, hydrocarbon resource recovery applications have the potential to use larger quantities of CO<sub>2</sub>. Furthermore, some hydrocarbon resource recovery applications have the potential to sequester CO<sub>2</sub> in geologic formations during, or at the end of the resource recovery.

The technologies discussed in the hydrocarbon resource recovery with CO<sub>2</sub> section (Table 2) are:

1. CO<sub>2</sub>-enhanced oil recovery (CO<sub>2</sub>-EOR) and,
2. Recovery of unconventional hydrocarbons (gas, gas hydrate, oil shale, coal bed methane) with CO<sub>2</sub>
3. Improved recovery of hydrocarbons with CO<sub>2</sub> fracturing of reservoirs

The technologies discussed in the re-use section are:

1. CO<sub>2</sub>-clathrate based desalination process (Table 6),
2. Use of CO<sub>2</sub> as a working fluid (heat transfer fluid, freight pipelines, beneficiation, solvent extraction and as a medium for gasifier solid feed transport) (Table 6)
3. Production of fuels and chemicals from CO<sub>2</sub> (Table 7)<sup>6</sup>.

We note that some applications may be classified under several categories. For example, the use of CO<sub>2</sub> for geothermal energy recovery, may be considered as a resource recovery application and also as an application where CO<sub>2</sub> is re-used as a working fluid. In contrast to CO<sub>2</sub>-reuse applications, where CO<sub>2</sub> may be recycled or reused, the consumptive use applications involve the formation of minerals which contribute directly to carbon sequestration by ‘locking-up’ carbon. Various means to form mineral carbonates from CO<sub>2</sub> are discussed in the ‘consumptive use’ section. Applications described in Table 8 include Skyonic, Alcoa, Calera, Novacem, concrete carbonation and slag carbonation processes. Finally, a complete bibliography of source documents is provided.

### 3 Metrics Overview

Comparison of the various applications for CO<sub>2</sub> recovery, and their relative costs and benefits helps to identify challenges and opportunities for the increased use of CO<sub>2</sub>. An objective of this task was to develop a list of metrics to evaluate various beneficial use concepts. Performing a comparative or quantitative ranking of these options is a challenge. CO<sub>2</sub>-use technologies in this document are at varying levels of readiness and not all of the processes can be ranked against all the criteria. That stated, the primary criteria for the relative comparison of various CO<sub>2</sub> applications include:

- Total amount of CO<sub>2</sub> permanently sequestered
- Unit value (benefit) or cost of application
- Energy consumed by the application, or net-energy saved by implementing this technology ( net-CO<sub>2</sub> savings from the technology)
- Market potential of primary CO<sub>2</sub> use and any by-products

The costs of CO<sub>2</sub> separation, compression, and delivery may be accounted in various ways, depending on the allocation of the CO<sub>2</sub> allowances/credits. In this Summary, the use of CO<sub>2</sub> is treated as a cost to the operator of the CO<sub>2</sub>-use process and a benefit to the seller of the CO<sub>2</sub> offsets, possibly a CO<sub>2</sub> capture project developer. High-pressure, high-purity CO<sub>2</sub> is assumed to have a cost of 40 \$/T (consistent with NETL/ESPA [2011] analyses). We do not directly account for the cost of purifying, cooling, and compressing the flue gas in applications where it is used without CO<sub>2</sub> separation (ex: Calera, Skyonic). The nominal benefit is estimated as the value derived from the use of CO<sub>2</sub> less the costs of raw material inputs to the process<sup>7</sup>. We note that this

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<sup>6</sup> The production of organic polymers from CO<sub>2</sub> is classified as a re-use, but could also be considered as a consumptive use depending on the lifetime of the polymer. For example, organic carbonates and polyurethanes have decades-to-centuries lifetimes (see Styring et al., 2011, Carbon Capture and Utilisation in the Green Economy, Centre for Low Carbon Futures, Report 501) . For simplicity, all CO<sub>2</sub>-to-chemical processes have been classified as *re-use applications*.

<sup>7</sup> The prices of hydrogen, and other chemical inputs are accounted for in the CO<sub>2</sub>-to-fuels/chemicals application. The price of brine or seawater is not accounted for in Calera or Skyonic processes. It is expected that they would be considerably lower than the unit cost of CO<sub>2</sub> or the unit value of the product. Similarly, the alkaline earth metal silicate raw material inputs for the Calera and Novacem processes are also not assigned a price, and this may be refined in the future.

nominal benefit is a preliminary metric, and the actual benefits and costs may be estimated by a full life cycle analysis, which is out of the scope of the current task.

Another metric of relevance to CO<sub>2</sub>-use processes is the net-CO<sub>2</sub> mitigation, closely related to the amount of energy consumed in the process. Typical examples are the use of electrical, thermal, or chemical energy in applications which convert, compress, or use CO<sub>2</sub>. The net-CO<sub>2</sub> used in the process, or mitigated per unit of process output (product) would therefore be the gross-amount of CO<sub>2</sub> used per unit of product, less the amount of CO<sub>2</sub> emitted during the process per unit of product. Because (fossil) energy use and CO<sub>2</sub> emissions are correlated, emissions from the CO<sub>2</sub>-use process can also be deduced by energy consumption, energy required for capture and/or disposal, energy penalty or energy gain, and the energy use avoided.

A primary constraint on the adoption of certain technologies which use CO<sub>2</sub> is the dearth of pipeline-quality low-cost CO<sub>2</sub> supply. In hydrocarbon resource recovery applications, the cost of CO<sub>2</sub> may be a major factor driving the economics. For example, data from the NETL/ESPA (2011) analysis indicate the cost of CO<sub>2</sub> to be 11 to 17% of the cost of the recovered crude oil. In other applications such as CO<sub>2</sub>-ECBM and CO<sub>2</sub>-EGR, the proportional cost of CO<sub>2</sub> may be even higher because natural gas trades at a lower unit energy cost (\$/MMBTU) compared to crude oil. Such constraints would incentivize higher recycling and lower unit-utilization of CO<sub>2</sub>. In applications where CO<sub>2</sub> is converted to a fuel such as gasoline or diesel using hydrogen, the cost of CO<sub>2</sub> is still a considerable percentage of the value of fuel, but is outweighed by the cost of hydrogen. Therefore, the cost and the availability of hydrogen derived from CO<sub>2</sub>-free energy sources would determine the rate of adoption of technologies where hydrogen is used as a feedstock. As discussed in the Introduction, market saturation may not be a significant factor affecting the development of first-of-a-kind applications such as the conversion of CO<sub>2</sub> to fuels, chemicals and raw materials.

The tables in each of the following sections summarize the metrics and the results of an objective evaluation. Not all applications are mature enough to provide information in each category. Table 1 lists the metrics considered when comparing the applications.

Table 1 - Metric Summary

<i>CO<sub>2</sub> Mitigation</i>	<b>Amount of CO<sub>2</sub> reduced (total : direct + indirect)</b>
	<b>Amount of Captured CO<sub>2</sub> utilized (direct reduction)</b>
	<b>Amount of CO<sub>2</sub> consumed</b>
	<b>Is capture an intrinsic part of the process?</b>
<i>Benefits</i>	<b>Cost of CO<sub>2</sub> reduction/ tonne (total system basis)</b>
	<b>Cost of CO<sub>2</sub> capture and processing</b>
	<b>Value of by-products</b>



*Draft*

<i>Energy Consumption</i>	<b>Energy penalty/ gain for total system (LCA)</b>
	<b>Energy required for capture and disposal</b>
	<b>Energy penalty/ gain for byproduct process</b>
	<b>Energy use avoided (without chemical transformation of CO<sub>2</sub>)</b>
<i>Market Potential</i>	<b>Market size (potential tonnage removed from atmosphere)</b>
	<b>CO<sub>2</sub> subjected to capture and storage</b>
	<b>CO<sub>2</sub> sold to commercial markets for consumption or resource recovery</b>
	<b>Market size of by-products</b>
	<b>(Nominal Benefit (Negative cost)) x Market size</b>

## 4 Hydrocarbon Resource Recovery

### 4.1 Introduction: Hydrocarbon Resource Recovery

CO<sub>2</sub>-enhanced oil recovery (CO<sub>2</sub>-EOR), enhanced coal bed methane production (ECBM), enhanced gas recovery (EGR), enhanced gas hydrate recovery (EGHR), hydrocarbon recovery from oil shale, and the fracturing of reservoirs to increase oil/gas recovery are some of the specific applications for CO<sub>2</sub>-enhanced hydrocarbon recovery. The common characteristics of CO<sub>2</sub>-enhanced hydrocarbon recovery processes include:

- Recovery of conventional and unconventional hydrocarbon resources (oil, conventional gas, shale gas, coal bed methane, oil shale and tar sands),
- Recycling, or once-through use of CO<sub>2</sub> in conjunction with hydrocarbon recovery,
- The need for high-pressure CO<sub>2</sub> and/or appropriate surface infrastructure such as wells, compressors, and pipelines. CO<sub>2</sub> purity required for each application may vary depending on the specific application.

In addition, some hydrocarbon recovery applications may enable sequestration of CO<sub>2</sub> in the hydrocarbon formation at the end of the project lifetime. The actual mechanisms involved in enhanced hydrocarbon recovery are distinct in each case, and include stripping the light-hydrocarbon components (CO<sub>2</sub>-EOR), density/pressure drive (EGR), and more favorable thermodynamics (EGHR, ECBM). The benefits in enhanced hydrocarbon recovery applications accrue from the sale of produced hydrocarbons, suitability to certain (water-sensitive or shallow) reservoirs, and the CO<sub>2</sub> offsets (to CO<sub>2</sub> emitters) resulting from sequestration over the project lifetime.

### 4.2 Metrics: Hydrocarbon Resource Recovery

Resource recovery applications include the use of CO<sub>2</sub> for enhanced oil recovery (EOR), enhanced gas recovery (EGR), fracturing, enhanced coalbed methane production (ECBM), and oil shale recovery. Among the resource recovery applications, CO<sub>2</sub>-EOR has a significant potential to mitigate CO<sub>2</sub> (16-22 billion T CO<sub>2</sub> by 2050) with a relatively high-net benefit (~\$100 /T CO<sub>2</sub> economic margin, 167 to 243 \$/T net-benefit). This analysis assumed an oil price of \$85/bbl and CO<sub>2</sub> price of \$40/T. The use of CO<sub>2</sub> to recover natural gas from depleted gas reservoirs, CO<sub>2</sub>-enhanced gas recovery (CO<sub>2</sub>-EGR) has the technical potential to use up to 3,200 to 7,800 MT CO<sub>2</sub>/y till 2050 (or 160 to 390 giga tons of CO<sub>2</sub>). The technical, U.S. potential for CO<sub>2</sub> use in enhanced-coalbed methane (CO<sub>2</sub>-ECBM) production over 50 years is about 60 to 117 GT CO<sub>2</sub> (1,200 to 2,340 MT CO<sub>2</sub>/y). Up to 2.2 MCF of natural gas could be produced for every metric tonne of CO<sub>2</sub> stored. Assuming a nominal natural gas price of \$2/MCF, the nominal-net benefit would be approximately \$4.4/T CO<sub>2</sub>. About 0.4 T of CO<sub>2</sub> could be used per vertical-well completion, if employed as a fracturing agent. Approximately 18 MT CO<sub>2</sub>/y would be required for a facility to produce 1 million bbl/d of syncrude from in situ processing of oil shale. CO<sub>2</sub>-EGHR and use for oil shale recovery are also beneficial, but the amount of CO<sub>2</sub> which could potentially be used in these applications is relatively uncertain.

Unlike CO<sub>2</sub>-EOR which is relatively more mature, oil recovery from oil shale using CO<sub>2</sub>, CO<sub>2</sub> fracturing, CO<sub>2</sub>-EGR, CO<sub>2</sub>-ECBM, and CO<sub>2</sub>-EGHR are processes still being developed or tested in pilot-scale tests.

An overview of various applications for the recovery of crude, natural gas and syncrude using CO<sub>2</sub> is presented in Table 2. Values preceding asterisks are specific to the United States.

Table 2. Hydrocarbon Resource Recovery Applications (excluding CO<sub>2</sub>-EOR)

Draft

	CO <sub>2</sub> Mitigation		Benefits	Energy penalty/CO <sub>2</sub> emissions	Market Potential		Overall Benefits
	(A) CO <sub>2</sub> Reduced (total)	(B) Captured CO <sub>2</sub> used	(C) Value of by-products		(D) Market size (potential tonnage removed from atmosphere)	(E) Potential for commercial sales	
CO <sub>2</sub> -EGR	NA	160 to 390 GT CO <sub>2</sub> by 2050	TBD	Could be similar to CO <sub>2</sub> -EOR <sup>8</sup>	A fraction of value in (B)	High	
CO <sub>2</sub> Fracturing	NA	~0.4 T CO <sub>2</sub> /well for vertical wells <sup>9</sup>	TBD	TBD	Determined by economics & regulations		
CO <sub>2</sub> -ECBM	Technical: 60 to 117 billion T, economic: ~30 billion T	2.2 MCF NG/T CO <sub>2</sub> <sup>10</sup>	Maximum benefit: 4.4 \$/T CO <sub>2</sub> <sup>11</sup>	TBD, gas compression	NA		U.S. (2003): 66 billion \$ total*
CO <sub>2</sub> -EGHR	TBD* <sup>12</sup>	TBD	TBD	TBD	TBD		
Oil shale, tar sands	TBD	0.05 T CO <sub>2</sub> /bbl of produced hydrocarbon	less than 167 to 243* \$/T CO <sub>2</sub> for EOR <sup>13</sup>	TBD	~18 million tons (CO <sub>2</sub> )/yr (see note to B) <sup>14</sup>	High	

<sup>8</sup> Life-cycle CO<sub>2</sub> emissions from DOE/NETL-2010/1433: 71 to 95 kg CO<sub>2</sub>e/bbl oil, using 0.23 to 0.21 T CO<sub>2</sub>/bbl oil. This is lower than the 0.3 to 0.4 T CO<sub>2</sub>/bbl oil used in the NETL/ESPA (2011) study. 0.23 to 0.31 T net-CO<sub>2</sub> stored/bbl oil, or 0.23 T CO<sub>2</sub> emitted per T CO<sub>2</sub> purchased for injection .

<sup>9</sup> Fracturing fluid volumes can reach up to 200 m<sup>3</sup> (0.4 T CO<sub>2</sub>) for vertical well completions. Horizontal shale (e.g. Marcellus shale) gas wells typically have multiple fracturing stages and may require larger quantities of CO<sub>2</sub> if it is used as a fracturing fluid.

<sup>10</sup> ARI 2003 report

<sup>11</sup> Assumes nominal natural gas price of \$2/MCF

<sup>12</sup> A fraction of the 85 TCF technically recoverable Alaskan gas hydrate resource may be produced.

<sup>13</sup> By-product hydrocarbons require upgrading compared to crude oil

<sup>14</sup> Tar sands: 1 to 5 million barrels/day (bbl/d). In-situ processing of 1 MM bbl/da would require 18 million T CO<sub>2</sub>/y

### **4.3 CO<sub>2</sub>-EOR**

Enhanced oil recovery (EOR) refers to the introduction of heat, chemicals, and/or gases to stimulate the production of oil unrecovered during primary and secondary oil production. CO<sub>2</sub>-EOR has been used extensively in mature light- and medium-oil and gas reservoirs. The CSLF EOR working group is developing a summary dedicated to CO<sub>2</sub>-EOR. The scope of this report is focused on utilization options other than EOR.

### **4.4 CO<sub>2</sub> Use for Unconventional Hydrocarbon Recovery**

The potential of using CO<sub>2</sub> for EOR has been investigated extensively. In addition to CO<sub>2</sub>-EOR, unconventional hydrocarbon recovery processes include CO<sub>2</sub> injection for enhanced gas recovery, the use of CO<sub>2</sub> as a fracturing medium for conventional gas/oil reservoirs and shale formations, the production of coal-bed methane from CO<sub>2</sub>, and the use of CO<sub>2</sub> as a transport medium and solvent for extracting hydrocarbons from oil shale and tar sands. The gas is typically recovered and re-compressed at the end of the process.

The use of CO<sub>2</sub> for unconventional hydrocarbon recovery involves a variety of considerations, some of which are distinct from those for CO<sub>2</sub>-EOR. Some of these questions are:

1. Is CO<sub>2</sub> locally available at a moderate price? Is the project economically feasible at the price of supplied CO<sub>2</sub>?
2. Is the process energy efficient, or does it consume more energy than it would produce?
3. Does the injected CO<sub>2</sub> contaminate the hydrocarbon being produced?
4. Do the impurities in CO<sub>2</sub> (such as SO<sub>x</sub>, H<sub>2</sub>S, N<sub>2</sub>) affect the product quality, and would any of these gases need to be separated from CO<sub>2</sub> before its use?
5. Would the use of CO<sub>2</sub> affect the water/resource consumption or production in the process (ECBM, extraction)?
6. Is surface infrastructure needed to separate and re-inject the produced CO<sub>2</sub> already in place?

#### 4.4.1 CO<sub>2</sub>-Enhanced Gas Recovery (CO<sub>2</sub>-EGR) and CO<sub>2</sub> Sequestration EGR (CSEGR)

Gas reservoirs suitable for CO<sub>2</sub>-EGR include both conventional (i.e. 'tight' sandstone or carbonate reservoirs) and unconventional shale-gas reservoirs. The mechanism of CH<sub>4</sub> recovery is different in both cases. In conventional reservoirs, CO<sub>2</sub> displaces the methane present in the pore space. In contrast, CO<sub>2</sub> in shale reservoirs adsorbs on the organic surfaces and desorbs methane which flows through natural and artificial fractures to the wellbore. Reservoirs containing high amounts of acid gases (CO<sub>2</sub>, H<sub>2</sub>S) may be suitable candidates for injecting CO<sub>2</sub>, especially because of existing gas separation infrastructure. Examples of CO<sub>2</sub> injection into (conventional) gas reservoirs are shown in the following table.

Table 5. CO<sub>2</sub> Injection Projects in Gas Reservoirs

Project	Features	Purpose	Injection Rate
K12-B offshore gas field, North Sea (Netherlands)	CO <sub>2</sub> separated from natural gas (13% CO <sub>2</sub> ) from a nearly-depleted gas reservoir and injected into the same sandstone formation at a depth of 4,000 m	Storage, EGR	NA
CO2CRC Otway Storage Project, Victoria, Australia	80% CO <sub>2</sub> , 20% CH <sub>4</sub> injection into a depleted gas formation underlying the active-gas producing formation) at a depth of 2,100 m	Storage	150 TPD
Altmark gas field, Germany (Vattenfall AB and Gaz de France)	Proposed CO <sub>2</sub> injection in a nearly-depleted gas field, CO <sub>2</sub> captured from oxycombustion plant	EGR	NA
In Salah, Algeria	CO <sub>2</sub> injection into a deep saline aquifer, part of the same formation and lower than ('down-dip' of) the natural gas reservoir	Storage	548 TPD/well

**Tight Gas Sandstone Reservoirs:** Compared to oil fields, gas reservoirs have higher primary recovery rates (~55-90%), and therefore, the amount of additional CH<sub>4</sub> produced may not justify the economics of CO<sub>2</sub> pressurization and injection. Rapid CO<sub>2</sub> breakthrough to the natural gas producing wells would lead to an increase in the CO<sub>2</sub> content of the produced gas, increasing separation costs and eventually making reinjection economically unfeasible<sup>15</sup>. On the other hand, injection into the gas reservoirs would indirectly pressurize the existing natural gas, thereby enhancing methane production and preventing water ingress<sup>16</sup>. CO<sub>2</sub>-EGR is economical in cases where a significant portion of the original gas in place is yet to be recovered, and where the gas reservoir has considerable vertical extent.

<sup>15</sup> CSLF, 2010. 2010 Carbon Sequestration Leadership Forum Technology Roadmap, Available at: [http://www.cslforum.org/publications/documents/CSLF\\_Technology\\_Roadmap.pdf](http://www.cslforum.org/publications/documents/CSLF_Technology_Roadmap.pdf) [Accessed November 10, 2010].

<sup>16</sup> Benson, S. et al., 2004. GEO-SEQ Best Practices Manual. Geologic Carbon Dioxide Sequestration: From Site Selection to Implementation, 9/30/2004: Lawrence Berkeley National Laboratory, Available at: <http://escholarship.org/uc/item/27k6d70j>

**Gas Shales:** Organic-rich shales (such as carbonaceous shales occurring throughout the Appalachian Basin and other parts of the world), are relatively non-porous and impermeable compared to conventional gas and tight sandstone gas reservoirs. Methane is adsorbed on clay and kerogen shale surfaces. The organic-rich shale often serves as the seal for underlying hydrocarbon formations, is a source-rock in itself, for hydrocarbons, and may also serve as a means to sequester CO<sub>2</sub>. Similar to coal beds, organic shales adsorb CO<sub>2</sub> and preferentially desorb methane. The common technique of fracturing leads to the formation of high-permeability pathways for fluid transport in the shale, resulting in enhanced CO<sub>2</sub> sequestration concomitant with methane production.

The potential for CO<sub>2</sub> storage in conventional gas reservoirs and regional organic-rich shales in the U.S. has been estimated by IEA GHG, NETL and Kentucky Geological Survey (KGS). A depleted gas fields study, using regional GIS-based source-sink matching was conducted for IEA GHG in 2008<sup>17</sup>. Capacity calculations were made with reference to the CSLF “resource pyramid” classification scheme. The IEA GHG study estimated that the available, matched, global-depleted gas field CO<sub>2</sub> storage capacity up to 2050 is 156 billion (metric) tonnes (GT) CO<sub>2</sub>. More recent IEA GHG studies indicate a global capacity of 160 to 390 GT CO<sub>2</sub><sup>18,19</sup> or enough capacity to store 30 to 70 years of U.S. energy-related CO<sub>2</sub> emissions. In the U.S.A., KGS evaluated the organic-rich shales of Kentucky to have the potential to sequester 28 billion tons of (28 GT) CO<sub>2</sub><sup>20</sup>. Similarly, a recent NETL study noted that the Marcellus Shale Formation had the potential to store 17 to 166 GT CO<sub>2</sub><sup>21</sup>. Note that some of these estimates are technical capacity estimates and do not account for the economics of natural gas production.

Estimates for CO<sub>2</sub> storage and methane production in shale reservoirs are subject to high uncertainties because they were calculated based on the adsorption isotherm data collected in the laboratory. At the reservoir scale, multiple techno-socio-economic factors, such as low-permeability, shale swelling, operator concerns about CO<sub>2</sub> diluting the produced methane, or negative public perceptions may lower this potential.

#### 4.4.2 CO<sub>2</sub>-EGR Factsheet

<b>Estimated impact /Net CO<sub>2</sub> considered permanently sequestered (US)</b>	Estimates vary from 160 to 390 GT CO <sub>2</sub> for conventional depleted gas reservoirs worldwide, and tens of GT CO <sub>2</sub> for each of the various regional shale gas plays in North America
<b>Gross current CO<sub>2</sub> consumption in this use MT/year</b>	TBD –K12-B: 0.48 MT/y, see Figure 2
<b>Game-changing events/scenarios favorable</b>	Adoption of technologies that use (impure) natural gas close to

<sup>17</sup> IEA GHG, 2009. Storage in Depleted Gas Fields, IEA GHG Technical Report, 2009/1, Available at: <http://www.ieaghg.org/index.php?/technical-reports-2009.html>

<sup>18</sup> Wildgust, N., 2009, Global CO<sub>2</sub> geological storage capacity in hydrocarbon fields, presented at IEA GHG Weyburn-Midale Monitoring Project PRISM meeting, June 2009, Regina, Canada

<sup>19</sup> Wildgust, N., 2009, Global mapping of CO<sub>2</sub> sources and sinks, presented at NACAP Workshop, 22-23 June 2009, Pittsburgh, USA

<sup>20</sup> Nutall, B. C., J. A. Drahovsal, C. Eble and R. M. Bustin, 2005, CO<sub>2</sub> Sequestration in Gas Shales of Kentucky, Search and Discovery Article #40171, Available at: [www.searchanddiscovery.net/documents/2005/nutall/index.htm](http://www.searchanddiscovery.net/documents/2005/nutall/index.htm), Accessed November 10, 2010.

<sup>21</sup> NETL, 2010. Impact of the Marcellus Shale gas play on current and future CCS activities, Available at: [http://www.netl.doe.gov/technologies/carbon\\_seq/refshelf/Marcellus\\_CCS.pdf](http://www.netl.doe.gov/technologies/carbon_seq/refshelf/Marcellus_CCS.pdf).

<p><b>for this process</b></p>	<p>the wellhead (either for electricity or chemicals), significantly increased demand for natural gas, GHG legislation</p>
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Figure 2. The K12-B offshore platform in the North Sea where CO<sub>2</sub> is injected into a sandstone formation containing natural gas. Source: [co2geonet.com](http://co2geonet.com)

<p><b>Gross/net CO<sub>2</sub> reduction per tonne of primary CO<sub>2</sub></b></p>	<p>TBD, impacts apply to both conventional depleted gas reservoirs and shale gas formations</p>
<p><b>Estimated scale of single application (i.e. plant size or field size)</b></p>	<p>Economics would determine minimum size of installation that would be feasible.</p>
<p><b>Number of deployments at maturity</b></p>	<p>TBD</p>
<p><b>Estimated time to full deployment/ market saturation</b></p>	<p>5 to 30 years depending upon whether an economic driver exists for this purpose.</p>
<p><b>Estimated duration of significant impact</b></p>	<p>Dependent on the availability of pore space, and pressure decline in the gas reservoir</p>
<p><b>Special requirements on CO<sub>2</sub> (purity, etc.)</b></p>	<p>Pure CO<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub> or CO<sub>2</sub>/CH<sub>4</sub> mixtures can be used, but CO<sub>2</sub> transported over pipeline should be purified to relevant specifications</p>
<p><b>Process/Technology Input Raw Materials and/or Energy</b></p>	<p>Carbon dioxide, electricity</p>
<p><b>Process/Technology Outputs</b></p>	<p>Methane, any co-produced water and CO<sub>2</sub></p>
<p><b>Any concomitant advantages?</b></p>	<p>Produces natural gas</p>
<p><b>Legal/regulatory framework governing/impacting deployment of this option</b></p>	<p>UIC Class II regulations for future wells in the U.S., framework to permit acid-gas injections in Canada.</p>

### 4.4.3 CO<sub>2</sub> Fracturing

CO<sub>2</sub> fracturing refers to the creation of high-permeability pathways for increased natural gas recovery. CO<sub>2</sub> fracturing is one example of ‘energized-fluid fracturing, where a gas component is added to reduce the water content of the fracturing fluid. Energized fractures are used in almost all hydraulic fracturing treatments in depleted tight gas sand formations of North America<sup>22</sup>. They are used in water-sensitive formations (e.g. shale formations containing clays which may swell in the presence of water), depleted or shallow reservoirs. CO<sub>2</sub> has been used in hydraulic fracture stimulation since the 1960's. In energized-fluid fracturing, after completion of the fracturing, reduction of the fluid pressure leads to a rapid increase in the gas permeability because of the lower liquid content of the fracturing fluid, enhancing fluid flowback while the sand particles ‘proppants’ transported by CO<sub>2</sub> into the formation prevent fracture closure. CO<sub>2</sub>-based fracturing fluids minimize the use of viscosity-enhancing polymers in the fracturing fluid. Fluid recoveries in energized-fluid fracturing are considerably higher than that for hydraulic fracturing. CO<sub>2</sub> fracturing is applicable to both conventional ‘tight sandstone’ reservoirs and the ‘tighter’, less-permeable organic shale formations. Kargbo et al.<sup>23</sup> note that nitrogen may also be needed to reduce the formation of ice in the wellbores and to reduce the overall treatment cost.

The issue of fracturing formations to release underground hydrocarbons that can then be recovered has been, and continues to be contentious for the risk it may pose to drinking water supplies, for inducing seismicity, and for other environmental impacts of fluid mixtures used in this process. There have been attempts to bring all of these activities under the aegis of the Safe Drinking Water Act and the Community Right to Know regulations. The changes in practice that might occur if CO<sub>2</sub> (particularly supercritical carbon dioxide) were widely used in lieu of other fluids is not clear at this time. Whether the existing concerns would be ameliorated by this change in practice remains an active question.

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<sup>22</sup> Freihauf, K.E., 2009. Simulation and Design of Energized Hydraulic Fractures. Ph.D. Thesis. Austin, TX: The University of Texas at Austin. Available at: <http://www.pge.utexas.edu/theses09/friehauf.pdf>.

<sup>23</sup> Kargbo, D.M., Wilhelm, R.G. & Campbell, D.J., 2010. Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environmental Science & Technology*, 44(15), pp.5679-5684.



4.4.3.1 *Dry-Frac CO<sub>2</sub>/sand stimulation Factsheet*

<p><b>Estimated impact /Net CO<sub>2</sub> considered permanently sequestered (US)</b></p>	<p>Uses CO<sub>2</sub>, does not permanently store it</p>
<p><b>Gross current CO<sub>2</sub> consumption in this use (US), MT/year</b></p>	<p>TBD. A typical tight gas vertical well completion in the Western Canadian Sedimentary Basin (WCSB) can require a volume of fluids exceeding 200 cubic meters<sup>24</sup>. Upto 0.4 T of CO<sub>2</sub> could be used per well completion.</p>
<p><b>Projected growth in CO<sub>2</sub> demand for this process</b></p>	<p>TBD. Depends on the rate of maturation of gas reservoirs, and additional demand growth from shale gas drilling</p>
<p><b>Game-changing events/scenarios favorable for this process</b></p>	<p>Regulations that limit the use of water in hydraulic fracturing, limited availability of fresh water, or recycling produced water, increased exploration of shale gas plays and ‘tighter’ conventional sand gas reservoirs</p>



Figure 3. Liquid CO<sub>2</sub> from the truck and the solid proppant are mixed in a closed vessel and used for subsequent fracturing in the Dry-Frac stimulation. Source: Mazza, 2001

In this process, liquid CO<sub>2</sub> is used as the fracturing fluid for proppant transport. Upon fracturing, with the reduction in pressure, the liquid CO<sub>2</sub> vaporizes within the formation leaving no residual fluids and minimizing formation damage. This is useful for fracturing of low-pressure reservoirs, where the hydraulic fracturing flowbacks to the surface can take a long time, increasing water treatment costs. CO<sub>2</sub> fracturing minimizes the

<sup>24</sup> Liao, S., Brunner, F. & Mattar, L., 2009. Impact of Ignoring CO<sub>2</sub> Injection Volumes on Post-Frac PTA. In Proceedings of Canadian International Petroleum Conference. Available at: <http://www.onepetro.org/mslib/servlet/onepetropreview?id=PETSOC-2009-124&soc=PETSOC> [Accessed November 22, 2010].

volume of liquid to be 'swabbed' or treated, prevents clay swelling because it stabilizes the pH to around 3, and allows rapid clean-up of treating fluids. Because dissolved CO<sub>2</sub> is acidic, it may also enhance the permeability of the formation. Trican Well Service in Canada<sup>25</sup> and Universal Well Services in the U.S.A. supply the technology to blend the proppant with liquid CO<sub>2</sub> in a closed container under pressure. In the Dry-Frac stimulation process, liquid CO<sub>2</sub> from a tanker is mixed with the proppant without any additional additives and pumped at high rate into the formation. The Dry-Frac process is best applicable to tighter (less permeable), lower-pressure, dry gas reservoirs (where other stimulation liquids may reduce gas permeability), and also in higher-permeability reservoirs to reduce near-wellbore damage. Nitrogen may also be needed to reduce the formation of ice in the wellbores and to reduce the overall treatment cost. The lack of infrastructure to transport CO<sub>2</sub> and N<sub>2</sub> from their sources (air separation plants, cement plants, power plants) to the fracturing site is an impediment to this process.

#### **4.4.3.2 CO<sub>2</sub>-Based Fracturing Fluids, Schlumberger**

Other variations in the use of CO<sub>2</sub> as a fracturing fluid include polymer-CO<sub>2</sub> mixtures (e.g. ThermoFOAM<sup>26</sup>) and polymer-free CO<sub>2</sub> fracturing fluids such as ClearFRAC CO<sub>2</sub> viscoelastic surfactant (VES)<sup>27</sup> from Schlumberger. The ClearFRAC CO<sub>2</sub> surfactant was developed for wells requiring 'energized-fluid fracturing' for added fluid flowback and the pressure benefits of hydraulic fracturing with CO<sub>2</sub>. The ClearFRAC CO<sub>2</sub> fluid has low friction pressure and high proppant-carrying capacity, minimizes formation damage and creates longer, more effective fracture half-lengths compared to polymer-CO<sub>2</sub> fracturing fluids. The low-viscosity, high-elasticity features of the fluid are suited for efficient proppant (sand particle) transport into the formation. The ClearFRAC CO<sub>2</sub> stimulant is prepared with 2% potassium chloride (KCl) solution and supercritical CO<sub>2</sub>. An encapsulated emulsion 'breaker', designed for the proppant-laden fracturing stages is added in the slurry stage. Upon pressure release subsequent to fracturing, the foam is destabilized by the breaker and the gas formed enhances fluid flowback to the surface, minimizing damage to the structure of the injected proppant (proppant pack).

#### **4.4.3.3 Other CO<sub>2</sub> Fracturing Technology Providers**

Other technology providers include Halliburton, and Linde. Linde supplies CO<sub>2</sub> for fracturing fluid formulation in the U.S.A.<sup>28</sup>

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<sup>25</sup> <http://www.trican.ca/Services/technologyfracturingliquidco2.aspx>

<sup>26</sup> [http://www.slb.com/services/stimulation/tight\\_gas\\_stimulation/thermafoam.aspx](http://www.slb.com/services/stimulation/tight_gas_stimulation/thermafoam.aspx)

<sup>27</sup> [http://www.slb.com/resources/other\\_resources/product\\_sheets/stimulation/clearfrac\\_co2.aspx](http://www.slb.com/resources/other_resources/product_sheets/stimulation/clearfrac_co2.aspx)

<sup>28</sup> [http://www.lindegasbenelux.com/international/web/lg/us/likelgus30.nsf/docbyalias/nav\\_frac\\_co2#1](http://www.lindegasbenelux.com/international/web/lg/us/likelgus30.nsf/docbyalias/nav_frac_co2#1)

#### 4.4.4 Enhanced Coal-Bed Methane (ECBM) Recovery

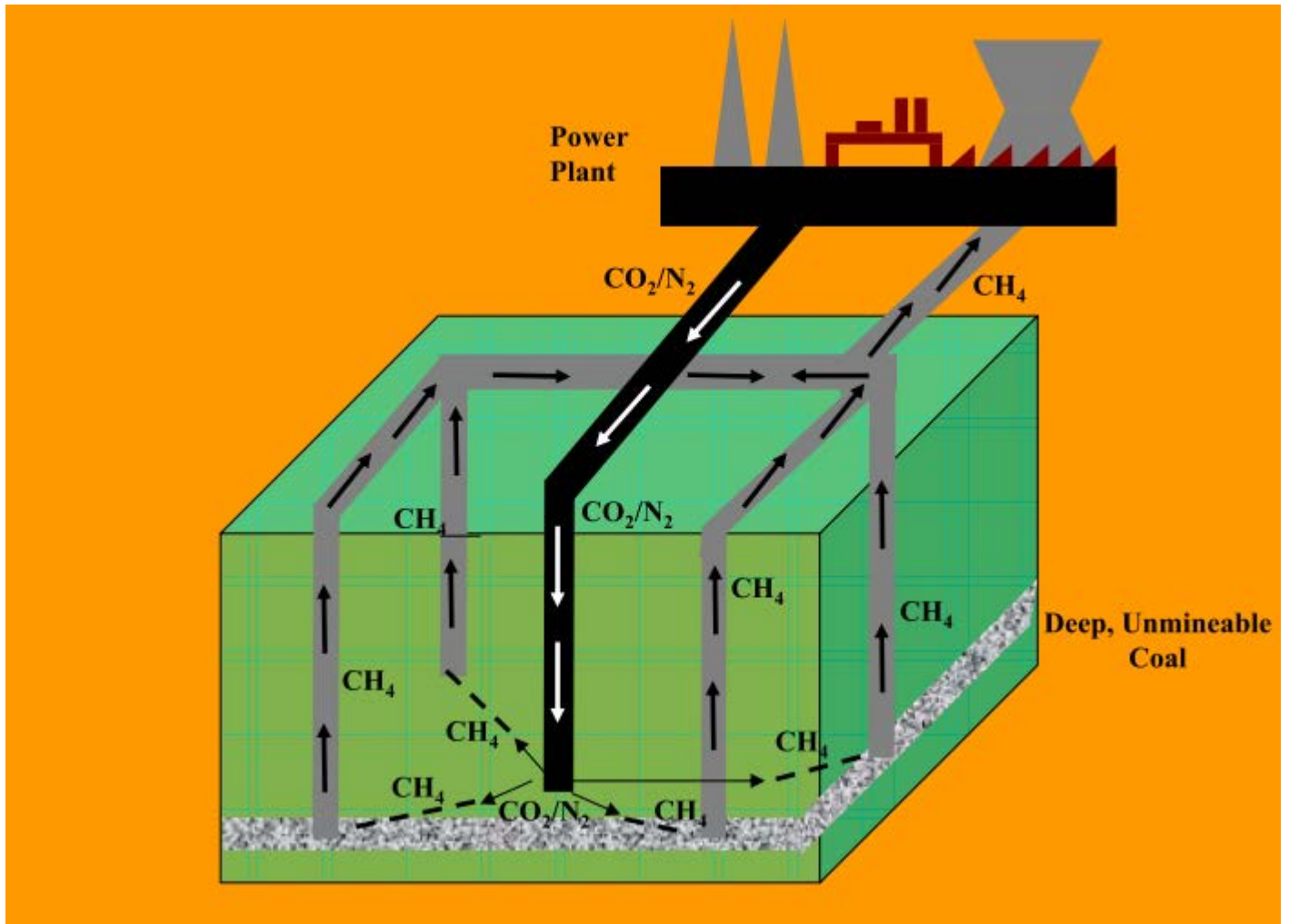
ECBM refers to the production of methane (CH<sub>4</sub>) by injecting gases such as CO<sub>2</sub> and N<sub>2</sub>. The injection of CO<sub>2</sub> into unmineable coal seams results in methane production because CO<sub>2</sub> interacts more strongly with the coal matrix than CH<sub>4</sub>. The definition of what coal seams are unmineable may vary, but coal-bed depths of 100 to 1,500 m and thin coal seams (less than 10 m) are usually considered for CO<sub>2</sub>-ECBM. Methane not recovered by primary recovery techniques such as dewatering and depressurization can be recovered by sweeping the coal bed with CO<sub>2</sub>. Although natural gas prices in the U.S. are currently low, coal bed methane recovery has economic potential in other parts of the world, and could offset CO<sub>2</sub> storage costs. A 2003 study<sup>29</sup> (Reeves, 2003) on the storage potential of U.S. coal beds noted a capacity of 90 GT CO<sub>2</sub> (90 billion metric tonnes). Reeves further noted that approximately a third of this potential storage capacity of CO<sub>2</sub> could be stored at a net benefit to the operator (excluding CO<sub>2</sub> capture and transportation cost). A large portion of the U.S. ECBM potential is in Alaska (38 GT CO<sub>2</sub>). More recent assessments indicate a technical CO<sub>2</sub> storage potential of 60 to 117 billion tonnes of CO<sub>2</sub><sup>30</sup>. Also, storage in marginal coal bed prospects (at a net cost to the operator) perhaps may not constitute a beneficial use of CO<sub>2</sub>. Finally, there is significant variability in the estimates of CBM, and by extension, ECBM, because the amount of methane in the coal and the fraction of that methane displaced by CO<sub>2</sub> is not quantified using consistent methodologies. CO<sub>2</sub>-ECBM has been tested at pilot scale in the U.S. (San Juan Basin), Canada (Alberta Basin), Poland (RECOPOL project), China (Qinshui Basin) and Japan (Hokkaido). The permeability of the coal matrix to fluid flow decreases upon swelling due to CO<sub>2</sub> injection. Pilot-scale tests indicate that the swelling-shrinkage phenomena have considerable effects on the transport of CO<sub>2</sub> and methane in the coal bed.

##### 4.4.4.1 CO<sub>2</sub>-Enhanced Coal Bed Methane Recovery Factsheet

<b>Estimated impact /Net CO<sub>2</sub> considered permanently sequestered (US)</b>	U.S. estimates of CO <sub>2</sub> storage range from 60 to 110 billion T CO <sub>2</sub> . Net CO <sub>2</sub> beneficially stored (at a profit) would be lower, ~30 billion T CO <sub>2</sub> could be beneficially stored.
<b>Gross current CO<sub>2</sub> consumption in this use (US), MT/year</b>	Pilot tests, no current large-scale operations
<b>Projected growth in CO<sub>2</sub> demand for this process</b>	TBD
<b>Game-changing events/scenarios favorable for this process</b>	Overcoming coal swelling

<sup>29</sup> Reeves, S.R., Assessment of CO<sub>2</sub> Sequestration and ECBM Potential of US Coalbeds, Topical Report, DOE Contract No. DE-FC26-00NT40924, February 2003.

<sup>30</sup> [http://www.netl.doe.gov/technologies/carbon\\_seq/refshelf/atlasIII/](http://www.netl.doe.gov/technologies/carbon_seq/refshelf/atlasIII/), Accessed November 2010.

Figure 4. Illustration of  $\text{CO}_2$ -ECBM operation

<b>Estimated scale of single application (i.e. plant size or field size)</b>	Economics would determine minimum size of installation that would be feasible.
<b>Number of deployments at maturity</b>	May be limited to fields proximate to $\text{CO}_2$ pipelines or sources
<b>Special requirements on <math>\text{CO}_2</math> (purity, etc.)</b>	Pure $\text{CO}_2$ , $\text{CO}_2/\text{N}_2$ mixtures may be used. $\text{N}_2$ flushes $\text{CH}_4$ and results in quicker breakthrough
<b>Process/Technology Input Raw Materials and/or Energy</b>	Carbon dioxide, electricity
<b>Process/Technology Outputs</b>	Methane, co-produced water and $\text{CO}_2$
<b>Any concomitant advantages? (For example, Does this process eliminate the need for other pollution control equipment?)</b>	Produces natural gas, has indirect $\text{CO}_2$ reduction impacts
<b>Legal/regulatory framework governing/impacting deployment of this option</b>	UIC Class II regulations for future wells in the U.S.A.

#### 4.4.5 Recovery of Natural Gas from Gas Hydrate Using CO<sub>2</sub>

Clathrate hydrates are solid crystalline inclusion compounds formed when water is contacted with small molecules (guests) under certain temperature and pressure conditions. When the guests are comprised of methane or other natural gas components, clathrate hydrates are referred to as gas hydrates. Clathrate hydrates are comprised of a guest molecule encapsulated in a cage-like structure of water ice. They occur both onshore (shallow permafrost settings) and offshore (continental margins). Estimates of global methane hydrate resources are of the order of 10<sup>15</sup> cubic meters. Within the continental U.S., the USGS estimated that the Alaska North Slope (ANS) contains 590 trillion cubic feet (TCF) (or 17x10<sup>12</sup> m<sup>3</sup>) of gas-in-place<sup>31</sup>. Of this, approximately 85 TCF may be technically recoverable by being in close proximity to existing oil and gas production infrastructure. The dissociation of methane hydrates requires energy, and is self-limiting if depressurization is employed as the only recovery technique. Various thermal stimulation techniques including hot brine injection, steam injection, and microwave-enhanced recovery have been proposed to extract methane. All of them are at a conceptual level and may incur significant energy penalties to heat and dissociate the methane hydrate.

A wide range of values for the amount of methane-in-place recovered have been reported by previous laboratory-scale experimental studies. Recent modeling studies (based on data from pilot tests) on the 'Eileen' gas hydrate accumulation in Alaska indicate that up to 2.5 TCF of the 33 TCF of gas-in-place at 'Eileen' may be produced in 20 years if depressurization was successfully employed<sup>32</sup>. One technique which is relevant for the purposes of this discussion is the injection of CO<sub>2</sub> to form CO<sub>2</sub> hydrate by displacing methane. Both CO<sub>2</sub> and CH<sub>4</sub> form 'Structure I' hydrates, although the number of water molecules encapsulating the guest molecule may vary from 5 to 7<sup>33</sup>. Each molecule of methane produced would be substituted by a molecule of CO<sub>2</sub>. This is advantageous, because the formation of CO<sub>2</sub> hydrate releases more energy than that consumed by the breakup of CH<sub>4</sub> hydrates<sup>34</sup>. This concept has been a subject of various journal articles<sup>35,36</sup> and patents<sup>37,38</sup>. One

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<sup>31</sup> Hunter R., Lewis, S., Resource Characterization and Quantification of Natural Gas Hydrate and Associated Free-Gas Accumulations in the Prudhoe Bay – Kuparuk River Area on the North Slope of Alaska, 2Q2010-3Q2010 Semi-Annual Progress Report, Available at: [http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/2010Reports/NT41332\\_SemiAnnApr-Sep2010.pdf](http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/2010Reports/NT41332_SemiAnnApr-Sep2010.pdf), [Accessed December 2, 2010].

<sup>32</sup> Wilson, S.J. et al., Alaska North Slope regional gas hydrate production modeling forecasts. Marine and Petroleum Geology, In Press, Corrected Proof. Available at: <http://www.sciencedirect.com/science/article/B6V9Y-4YMPXBH-1/2/6a47c6322e7c6c18fab05573d2c1e270> [Accessed December 3, 2010].

<sup>33</sup> Birkedal, K.A., 2009. Hydrate Formation and CH<sub>4</sub> Production from Natural Gas Hydrates - Emphasis on Boundary Conditions and Production Methods. Master's Thesis. Norway: University of Bergen. Available at: <https://bora.uib.no/bitstream/1956/3425/1/56365022.pdf> [Accessed December 3, 2010].

<sup>34</sup> McGrail, B.P. et al., 2007. Using Carbon Dioxide to Enhance Recovery of Methane from Gas Hydrate Reservoirs: Final Summary Report, PNNL-17035, Available at: <http://www.osti.gov/bridge/servlets/purl/929209-jP39G7/> [Accessed December 2, 2010].

<sup>35</sup> See for example: Baldwin, B.A. et al., 2009. Using magnetic resonance imaging to monitor CH<sub>4</sub> hydrate formation and spontaneous conversion of CH<sub>4</sub> hydrate to CO<sub>2</sub> hydrate in porous media. Magnetic Resonance Imaging, 27(5), pp.720-726.

<sup>36</sup> See for instance: Ikegawa, Y. et al., 2010. SS: Hydrates: Experimental Results for Long Term CO<sub>2</sub> Injection Near Methane Hydrate Formations. In Proceedings of Offshore Technology Conference. Offshore Technology Conference. Available at: <http://www.onepetro.org/mslib/servlet/onepetropreview?id=OTC-20575-MS&soc=OTC> [Accessed December 2, 2010].

<sup>37</sup> See for example: Sivaraman, A., 2005. Process to sequester CO<sub>2</sub> in natural gas hydrate fields and simultaneously recover methane. Available at: <http://uspto.gov> [Accessed December 3, 2010].

<sup>38</sup> See for instance: Lyon, R.K., 2004, United States Patent: 6733573 - Catalyst allowing conversion of natural gas hydrate and liquid CO<sub>2</sub> to CO<sub>2</sub> hydrate and natural gas. Available at: <http://uspto.gov> [Accessed December 3, 2010].

*Draft*

proposed process involves the injection of microemulsions of liquid CO<sub>2</sub> and water into gas hydrate-bearing formations resulting in the breakup of methane hydrate and the formation of CO<sub>2</sub> hydrate, thereby storing CO<sub>2</sub> and producing methane. McGrail et al. note that injection of liquid CO<sub>2</sub>-water emulsion at high pressures (~1,000 psia) results in a three-fold increase in methane production compared to the injection of cold water alone. If natural gas beneath the gas hydrate accumulation contains appreciable quantities of CO<sub>2</sub>, and can be easily processed, the separated CO<sub>2</sub> could possibly be injected into the hydrate zone to enhance the production of methane<sup>39</sup>. Many parameters of this process critical to pilot, or experimental investigations are poorly understood, because the concept is in the developmental stage.

The U.S. DOE, ConocoPhillips and Japan Oil, Gas and Metals National Corporation (JOGMEC) are currently conducting a test of hydrate production by injecting CO<sub>2</sub> into gas hydrate reservoirs. Approximately 210,000 standard cubic feet (scf) of CO<sub>2</sub>/N<sub>2</sub> gas blend was injected into the hydrate-bearing Sagavanirktok "C" sandstone at the Ignik Sikumi #1 well. Initial injection rate was ~11,000 scf per day, and gradually increased to ~21,000 scf per day during thirteen days of injection. The primary test target, the Sagavanirktok "Upper C" sandstone (2,214 to 2,274 ft below the rig floor) contains 44 feet of clean, high-porosity sandstone rock with very high concentrations of gas hydrate in the optimal pressure-temperature conditions. Post-injection flowback operation is being continued at Ignik Sikumi #1<sup>40</sup>.

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<sup>39</sup> Goel, N., 2006. In situ methane hydrate dissociation with carbon dioxide sequestration: Current knowledge and issues. *Journal of Petroleum Science and Engineering*, 51(3-4), pp.169-184.

<sup>40</sup> [http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/rd-program/ANSWell/co2\\_ch4exchange.html](http://www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/rd-program/ANSWell/co2_ch4exchange.html)



#### 4.4.6 Oil Shale

##### Process Discussion: Use of Supercritical CO<sub>2</sub> in oil shale and tar sands

Extracting hydrocarbons from either Canadian tar sands or from oil shale formations represent significant commercial or near-commercial activities amongst a number of unconventional hydrocarbon extraction processes. There is on-going commercial production of heavy liquids from the tar sands deposits in Canada. Recent announcements in the U.S. indicate that commercial development of oil shale in the U.S. won't occur for some time – perhaps 15 years or longer<sup>41</sup>. Oil shale deposits have been used to produce hydrocarbon liquids in Estonia for many years and Brazil has continued to develop surface retorting technology applicable to the deposits found there<sup>42</sup> (see Figure 5). Oil shale deposits are found in many places in the world, although the greatest known concentrations occur in the United States. One location in China, the Ordos basin, is also being actively examined as a location for carbon sequestration sites. It is also necessary, for clarity, to point out the distinction between crude oil found in shale deposits (including the Bakken shale in the upper Midwest and central Canadian Province, and the Eagle Ford deposit in southwest Texas) and oil shale, rock formations containing kerogen. Kerogen is an organic precursor to petroleum, composed of algae and woody plant material that have been geologically trapped<sup>43</sup>.

There are several connections between tar sands or oil shale and the use or storage of carbon dioxide. First, patents have been granted for various processes which use supercritical carbon dioxide to release and react with the kerogen within the formation to produce hydrocarbon liquids that can then be extracted from oil shale formations. US patent US7500517, describes a process involving the use of liquid and solid carbon dioxide to extract hydrocarbons from kerogens. As described in the patent, one possible approach would be to fracture and rubblize subsurface shale formations in order to enhance permeability of the formation. This effect can be produced by drilling a well into the formation and injecting a slurry of liquid carbon dioxide and solid carbon dioxide then sealing the injection well. Once sealed, the two forms of carbon dioxide are to interact to form a single supercritical phase and to pressurize the well. Subsequent depressurization of the well produces adiabatic expansion of the carbon dioxide which cools the subsurface formation. The resulting thermal and mechanical stresses are claimed, in the patent, to occur and to fracture the formation facilitating subsequent extraction. The patent also claims that in some embodiments, the hydrocarbon so released can be chemically reacted (cracked) in ways that render it mobile and readily extracted<sup>44</sup>.

In 2008, Schlumberger acquired the technology developed by Raytheon and CF Technologies for production of liquids from oil shales<sup>45</sup>. The technology developed to be used in oil shale processing combines radio frequency (RF) technology with critical fluid (CF) technology.

Raytheon has projected that the same process could also be used to retrieve oil from Canadian oil sands and to reprocess spent wells. Carbon dioxide is commonly considered as the supercritical fluid<sup>46</sup> to be used.

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<sup>41</sup> Huffington Post article, February 2010

<sup>42</sup> See: [http://www.searchanddiscovery.com/documents/2009/30083nummedal/ndx\\_nummedal.pdf](http://www.searchanddiscovery.com/documents/2009/30083nummedal/ndx_nummedal.pdf)

<sup>43</sup> See both <http://seekingalpha.com/article/235257-oil-shale-shale-oil-and-6-ways-to-play-the-difference> and <http://www.glossary.oilfield.slb.com/Display.cfm?Term=kerogen>

<sup>44</sup> US patent 7500517, Looney, et al., March 10, 2009

<sup>45</sup> See: <http://www.greencarcongress.com/2008/01/schlumberger-ac.html> as cited in <https://alum.mit.edu/discuss/thread.jspa?messageID=8737&tstart=0>

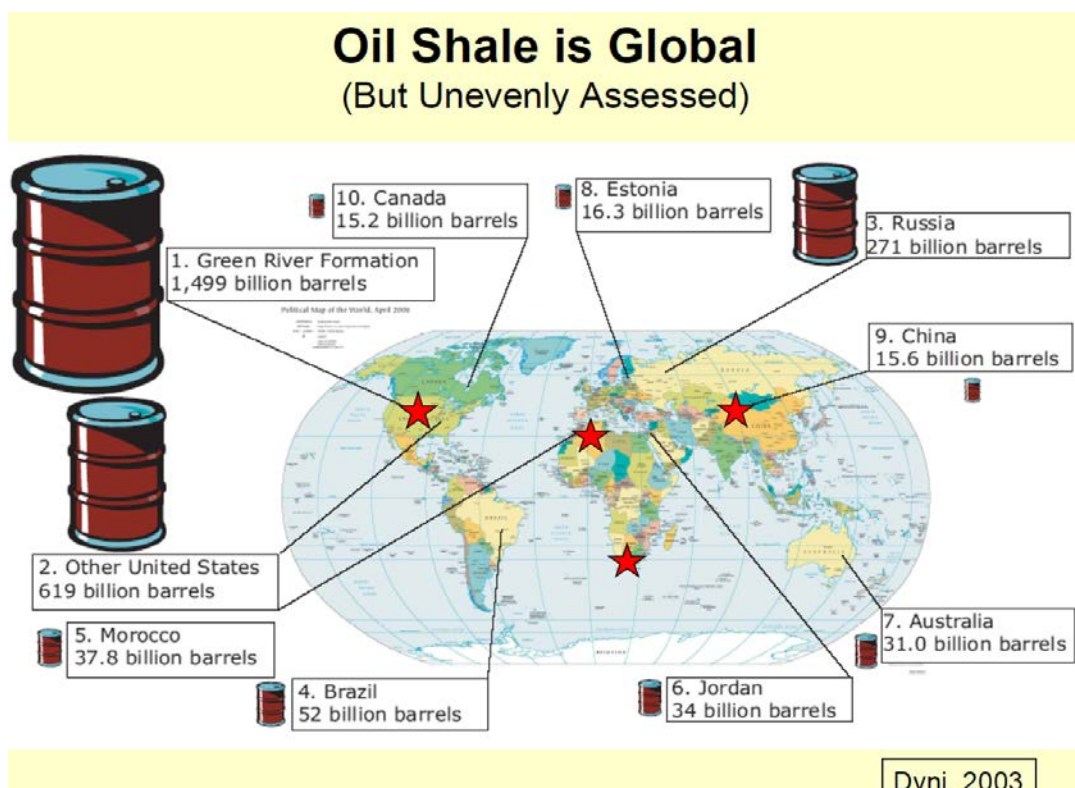


Figure 5. Global oil shale formations (see Nummedal, et al, 2009)

Carbon dioxide has also been studied for its action as a recently developed solvent capable of this chemical transformation. A paper from 2001<sup>47</sup> describes the potential role of carbon dioxide compared to other organic solvents in treatment of oil shale samples. According to the authors, “Supercritical fluid extraction (SFE) with carbon dioxide is particularly effective for the isolation of substances of medium molecular weight and relatively low polarity. At elevated temperatures it is possible to unite the breaking chemical bonds in the kerogen organic matter and convert the former into oil with extraction using supercritical fluids.”

Similarly, there are patents in the literature for means to process tar sands. For instance, U.S. patents 4341619<sup>48</sup> and 4565248<sup>49</sup> describe methods for extracting liquids from tar sands using either direct injection of supercritical fluids (such as carbon dioxide) or of a mixture of carbon dioxide and steam. Neither of these patents discusses the fate of the carbon dioxide after recovery of the bitumen. However, it is likely that much of the carbon dioxide could return to the surface with the bitumen and would need to be reinjected into a formation to be sequestered.

<sup>46</sup> See: Raytheon brochure: Radio Frequency/Critical Fluid Oil Extraction Technology (2006)

<sup>47</sup> M. Koel, S. Ljovin, K. Hollis, and J. Rubin, Using neoteric solvents in oil shale studies, *Pure Appl. Chem.*, Vol. 73, No. 1, pp. 153–159, 2001

<sup>48</sup> US patent 4341619, Poska, July 27, 1982

<sup>49</sup> US patent 4565249, Pebdani and Shu, January 21, 1986



*Draft*

In 2008, Lawrence Livermore National Laboratory (LLNL) and American Shale Oil (AMSO) announced a technical cooperation agreement to explore development of carbon sequestration technologies applicable to in-situ shale-oil production processes. The organizations agreed to partner in a study of means to permanently store carbon dioxide generated during the oil shale extraction process in depleted underground oil shale formations<sup>50</sup>.

In order to develop a sense for the quantities of carbon dioxide that could be involved in recovery of either oil shale liquids or bitumen, the Pebdani patent<sup>51</sup> discusses some typical results from limited field tests for tar sands: an article by L.C. Leung<sup>52</sup> based on simulation studies reported that for a series of steam injection rates, injection of carbon dioxide at a ratio of 400 SCF/bbl of steam (cold water equivalent) yielded a 36% improvement in recovery. And an article by Redford (1982)<sup>53</sup> reported that the optimum CO<sub>2</sub> to steam ratio, based on injection tests, was approximately 197 SCF/bbl of steam (cold water equivalent). The Pebdani patent reported data from limited tests using steam and carbon dioxide in a “huff and puff” approach and showed optimum increases in liquid recovery when injecting 300 SCF of carbon dioxide per barrel of steam (estimated on equivalent liquid water volume). Using these data, one can estimate that approximately 0.05 tons of carbon dioxide would be used per barrel of hydrocarbon liquid produced (see the figure below).

Estimating average values for the amount of kerogen per ton of rock, threshold values start at 15 gallons per ton. Very rich deposits can have up to 100 gallons per ton. Estimates of water usage for processing vary but could be in the range of 1 (or less) to 3 barrels of cold water per barrel of hydrocarbons produced for the in-situ extraction step. Coupling these estimates with the carbon dioxide/steam ratios given above, the amount of carbon dioxide per barrel of liquid might range from 150 SCF/barrel of liquid to 1,000 SCF/ barrel. This does not include the injection of carbon dioxide for any other purpose (such as creating a frozen barrier to ground water intrusion).

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<sup>50</sup> See: <http://www.businesswire.com/news/home/20081203005851/en>

<sup>51</sup> Ibid Pebdani, page 3

<sup>52</sup> L.C. Leung, Numerical Evaluation of the Effect of Simultaneous Steam and CO<sub>2</sub> Injection on the Recovery of Heavy Oil, *J. Pet. Tech.*, p. 1591 (September 1983)

<sup>53</sup> D.A. Redford, The Use of Solvents and Gases with Steam in the Recovery of Bitumen from Oil Sands, *J. Can. Pet. Tech.*, p. 45 (January-February 1982)

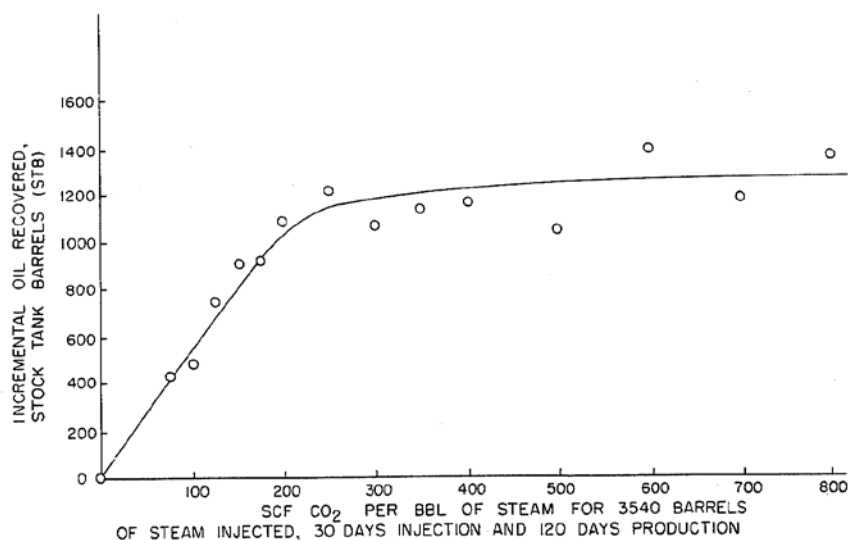


Figure 6. Field test data from Pebdani, et al.

Researchers at the University of Victoria, Canada (Fadaei et al., 2012)<sup>54</sup> report the development of a microfluidics-based rapid testing methodology for evaluating the behaviour of CO<sub>2</sub> in bitumen reservoirs, such as Canada's oil sands. Supplementing steam injection by CO<sub>2</sub> for the extraction of crude from bituminous oil sands has the potential to lower the CO<sub>2</sub> emissions directly and indirectly.

At present, closed loop applications that would employ carbon dioxide in any of the processes described above have not been engineered or studied in terms of life cycle emissions. Such an analysis would need to include: (a) carbon dioxide used as a solvent then released during separation of the hydrocarbon liquids from the solvents and other production fluids; and, (b) any carbon dioxide generated from energy production facilities needed to supply either electricity (for example for the RF technologies) or to produce steam.

#### 4.4.7 Enhanced Recovery of Shale Gas Using CO<sub>2</sub>

The use of CO<sub>2</sub> to enhance the recovery of methane trapped in gas shales has some similarities with ECBM in that CO<sub>2</sub> is adsorbed preferentially compared to methane. However, this is a relatively less-mature process. Capacity estimates and preliminary reservoir modeling studies are being conducted for various gas shales. A study by ARI (Petrusak, 2011)<sup>55</sup> provides preliminary estimates of gas production and CO<sub>2</sub> storage by CO<sub>2</sub> injection in the Marcellus and Utica shales of New York state. The gas-in-place (GIP) was estimated to be 579 Tcf, and theoretical maximum CO<sub>2</sub> storage capacity was calculated to be 519 Tcf. Preliminary reservoir modeling results indicate methane recovery would be 1 to 11% of GIP, and CO<sub>2</sub> storage capacity to be 3 to

<sup>54</sup> Fadaei, H., Scarff, B. & Sinton, D., 2011, Rapid Microfluidics-Based Measurement of CO<sub>2</sub> Diffusivity in Bitumen, *Energy Fuels*, 25(10), pp.4829–4835.

<sup>55</sup> Petrusak, R., 2011, Assessing Factors influencing CO<sub>2</sub> storage capacity and injectivity in gas shales – Review of current activities, Presented at the 7<sup>th</sup> International Forum on Geological Sequestration of CO<sub>2</sub> in Coal Seams and Gas Shale Reservoirs, March 7-8, 2011, Houston, TX, Available at: [http://coal-seq.com/proceedings2011/presentations/8\\_Robin%20Petrusak\\_ARI.pdf](http://coal-seq.com/proceedings2011/presentations/8_Robin%20Petrusak_ARI.pdf) [Accessed: 10/19/2011].

20% of the theoretical maximum for both Marcellus and Utica shale plays. This is equivalent to 17 to 111 MT/y of CO<sub>2</sub> storage in the Marcellus shale and 10 to 68 MT/y CO<sub>2</sub> storage in the Utica shale (over 30 years). These quantities are likely to be revised as shale gas operators develop a better understanding of CO<sub>2</sub> storage and enhanced gas recovery from shales.

## **5 Reuse (Non-Consumptive) Applications**

### **5.1 Introduction: Re-use (Non-Consumptive) Applications**

Applications where CO<sub>2</sub> is not consumed directly, but re-used or used only once are categorized as CO<sub>2</sub>-reuse. The main applications in this category are:

- Use of CO<sub>2</sub> for desalination,
- Use of CO<sub>2</sub> as a working fluid,
- Production of fuels and chemicals.

The CO<sub>2</sub>-desalination process for brackish or saline water is based on the principle of exclusion of large dissolved ions when CO<sub>2</sub> hydrates are formed. In the gas hydrate structure, water molecules form a network of cages that are occupied by individual gas molecules, eliminating all other dissolved ions. The salt content of the water forming the hydrate phase is lowered considerably in the process. Formation and subsequent dissociation of CO<sub>2</sub> hydrates in saline water leads to the reduction of salinity and the production of fresh water. High-pressure and relatively high-purity CO<sub>2</sub> would likely be needed for this process. The benefits from CO<sub>2</sub>-desalination processes result from the production of fresh water for general plant use and sale in areas otherwise lacking fresh water supplies, and any potential CO<sub>2</sub> offsets generated by geologic or oceanic sequestration. The value of generating potable water is two-fold. Firstly, the economic value could be substantial, offsetting a portion of the CCS costs. Secondly, potable water shortages are a significant concern in various parts of the world, and generating potable water may provide a means to adapt to climate change.

CO<sub>2</sub> can also be used as a ‘working fluid’ in freight pipelines, for the beneficiation and recovery of valuable metals such as rare earths, as a superior heat transfer fluid in power plants, as a ‘green’ solvent (for example as an alternative to some current tar sands processing technologies), and as a slurry transport medium for gasifier solid feeds. The primary benefits from this category of applications include avoided-CO<sub>2</sub> emissions, and concomitant cost savings resulting from higher efficiencies.

Finally, CO<sub>2</sub> can also be used to produce fuels and chemicals such as methanol, formaldehyde, and other polymer precursors. Unlike the other applications in the non-consumptive use category, the production of fuels and chemicals chemically transforms CO<sub>2</sub>. The primary benefits from this application involve avoided-CO<sub>2</sub> emissions as a result of carbon recycling, the value of the produced chemical, and any potential long-term sequestration in inert organic polymers.

### **5.2 Metrics: Non-Consumptive Applications**

Non-consumptive CO<sub>2</sub>-use applications have an indirect-CO<sub>2</sub> reduction benefit in the form of production of fresh water or valuable minerals, higher efficiency, or the displacement of fossil fuels. Seven non-consumptive uses were discussed in the report: desalination, beneficiation, slurry transport, heat transfer fluid, freight pipelines, solvent extraction, and the conversion of CO<sub>2</sub> to fuels and chemicals. The use of CO<sub>2</sub> for

supercritical fluid extraction is a commercial-scale process used commercially. The rest of the processes are relatively less-technologically mature, and require research and development.

Table 6 provides a summary of the processes and applications that were reviewed. Where more information was available a “factsheet” was developed to provide a summary of information.

Table 6. Non-Consumptive Applications: Use of CO<sub>2</sub> for Desalination and as a Working Fluid

	CO <sub>2</sub> Mitigation		Benefits	Energy penalty/CO <sub>2</sub>	Market Potential
	(A) CO <sub>2</sub> Reduced (total)	(B) Captured CO <sub>2</sub> used	Value of by-products		(4) Market size (potential tonnage removed from atmosphere)
<b>Desalination</b>	See (A). Primary reductions from indirect-carbon avoidance	5 kg of supercritical CO <sub>2</sub> would produce 50 kg of potable water. <sup>56</sup>	Excess potable water could be sold.	To be assessed on a case-by-case basis	Market potential to be determined by indirect reductions in CO <sub>2</sub> emissions
<b>Freight Pipelines</b>		Amount consumed or sequestered ~zero	NA		
<b>Beneficiation</b>					
<b>Heat Transfer Fluid</b>		Solvent recycled	Solvent extraction can yield commercially valuable materials such as rare earths		
<b>Solvent Extraction</b>					
<b>Feed solids to gasifiers or for slurry transport</b>		Amount consumed or sequestered ~zero	NA		

<sup>56</sup> Sheps, preliminary data

### 5.3 CO<sub>2</sub> Clathrate-Based Process for Desalination of Brackish/Saline Water

It has long been known that clathrates can be formed by a variety of compounds, including refrigerants, light hydrocarbons and carbon dioxide. This property has been seized on to develop concepts for purification of seawater and brackish waters. A number of reports have been written and several patents have been filed on processes to treat waste water, brackish water, and to desalinate sea water. A report by McCormack and Anderson<sup>57</sup> examined a number of options including the use of refrigerants, such as R141B and R22, several hydrocarbons, and carbon dioxide. They evaluated the refrigerants in particular, dismissing carbon dioxide largely due to the costs involved in compressing CO<sub>2</sub> to the necessary operating pressure for clathrate formation – 900 psia.

With the heightened interest in carbon dioxide capture, transportation and sequestration, the compression issue has potentially become a less-critical barrier as carbon dioxide compression would be part of the CCS process, and this may be taken advantage of. However, the process development step is still challenging and typically involves hydrate ice formation, a crystallization process that is difficult to carry-out reliably in continuous, high throughput reactors. The report, Desalination Utilizing Clathrate Hydrates (LDRD Final Report), from Sandia (SAND2007-6565)<sup>58</sup> provides a literature survey of recent research studies and process issues as does the McCormack and Anderson paper (up to 1995).

Among recent patents, US 6,991,722 B2 (Michael Max)<sup>59</sup> and US 2007/0004945 A1 (ORNL)<sup>60</sup> detail approaches to develop a practical process. MDS, a company working to commercialize the Max patent, received FE funding to pursue their approach and built a bench-scale unit. They provide a chart of the relationship between the amount of water that could be processed per cycle and the amount of carbon dioxide utilized (Figure 7).

The primary conclusion of the McCormack and Anderson study was that a clathrate-based process could be attractive if key issues were resolved. Secondary to that conclusion was their assessment that most work to date rushed to the pilot-scale too quickly before the critical processes steps could be developed and refined sufficiently to meet the required commercial performance criteria. For the refrigerants they considered, there were several probable benefits compared to flash desalination and to reverse osmosis. In general, this pathway is still in the early developmental stage although at least one company appears to be moving ahead based on their patented approach (MDS, see <http://www.mdswater.com/OurTechnology.html> and <http://www.aquaventus.com/>).

The MDS technology does not include the capture of carbon dioxide from the gas stream in an energy system. It reuses pressurized CO<sub>2</sub> to purify either waste water or saline waters - including sea water – and to produce a by-product of commercial value.

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[http://www.netl.doe.gov/technologies/carbon\\_seq/core\\_rd/storage.html](http://www.netl.doe.gov/technologies/carbon_seq/core_rd/storage.html)

Desalination Plant – Preliminary Research Study, Water Treatment Technology Program Report No. 5, U.S. Department Of The Interior, Bureau of Reclamation, Technical Service Center, Water Treatment Engineering and Research Group.

<sup>58</sup> Simmons, B.A. et al., 2008. Desalination utilizing clathrate hydrates (LDRD final report, SAND2007-6565, Sandia National Laboratories), Available at: <http://www.osti.gov/bridge/servlets/purl/934586-mQC25H/> [Accessed October 26, 2010].

<sup>59</sup> Max, M.D., 2006. Hydrate Desalination for Water Purification. US 6,991,722 B2

<sup>60</sup> Phelps, T.J. et al., 2005. Method for excluding salt and other soluble materials from produced water. US 2007/004945 A1, [Accessed October 26, 2010].

One industrial application of the ion exclusion during the formation of hydrates is the treatment of wastewater produced in a power plant. In integrated gasification combined cycle (IGCC) power plants, a stream of sour water containing chloride, and traces of ammonia, hydrogen sulfide and other compounds is produced from synthesis gas scrubbing and further acid-gas recovery steps. Another industrial application of this technology is the treatment of brackish brines produced during mining, hydrocarbon recovery, or CO<sub>2</sub> sequestration to produce fresh water which could be used for human consumption or for process uses. James and McGurl (2004)<sup>61</sup> discussed a scenario where a small portion of the desalinated water could be used for wet cooling, general plant consumption, and the rest could be sold as potable water...

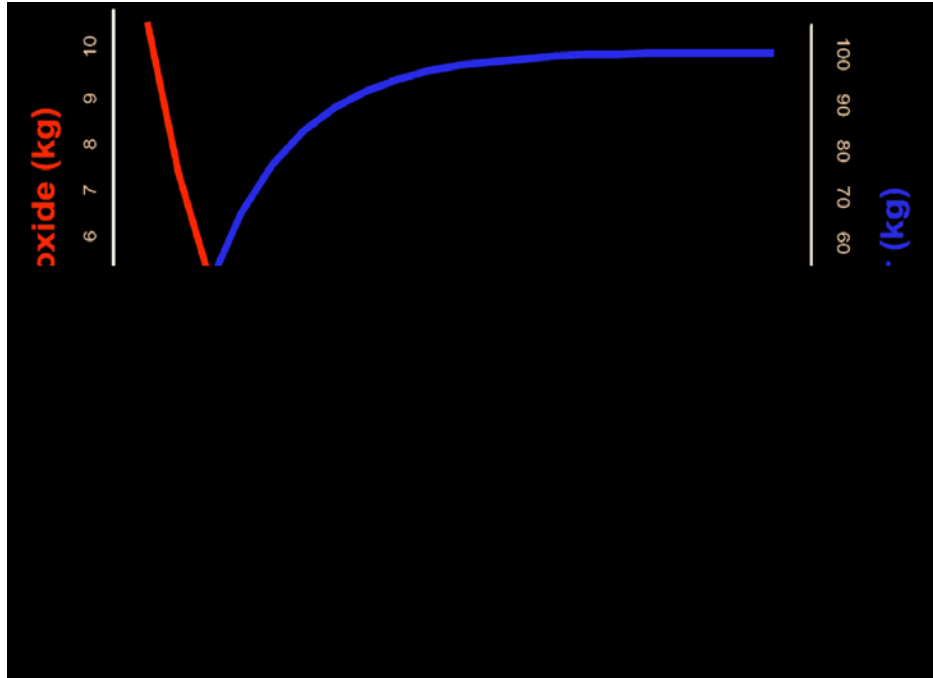


Figure 7. Relationship between the amount of CO<sub>2</sub> utilized and the desalinated water processed per cycle.  
Source: MDS

The impact of this technology depends on whether the deep ocean storage version of this concept, in which the clathrates are formed and broken at depth, providing pressure control over the small range of pressure and temperature swings needed to drive the key step, can be pursued. Alternately, terrestrial applications present a different set of challenges that would need to be overcome prior to deployment of any of the nascent concepts. One non-technical issue that would need to be addressed deals with ownership of the produced water and whether a power plant could discharge the potable water into a stream and sell the rights to pump the water out downstream. This water would not be considered natural water and might not fall under either state or EPA regulations.

In order to develop a rough sense of the potential benefits, the paper by James and McGurl can serve as a point of reference. This system study sought to utilize all of the captured CO<sub>2</sub> (at 90% rate of capture) from a nominal

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<sup>61</sup> James, R.E. & McGurl, G.V., 2004. IGCC System Analysis Utilizing Various Condenser Cooling Platforms, Including CO<sub>2</sub> Sequestration and Water Desalination. Proceedings of the Water Environment Federation, 2004, pp.720-737(18).

425 MWe IGCC unit (based on gross fuel input), producing 23.6 million gallons of water per day. , The sale of excess potable water could offset all costs involved in the production of the water (including costs for the additional equipment and any energy costs associated with the unit). Water production costs using this method are marginally less than costs for a comparable reverse osmosis unit at the time of this study and could offset some of the increased costs for the addition of the carbon capture and storage system, which is beneficial in arid regions.

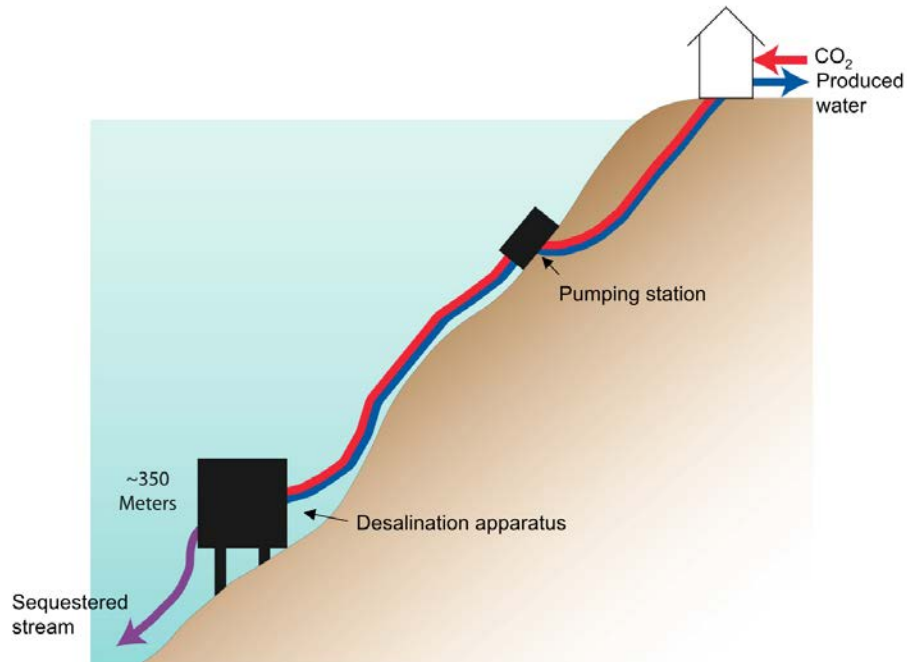


Figure 8. Conceptual application for CO<sub>2</sub> Hydrate Desalination with oceanic disposal of CO<sub>2</sub> (Source: MDS<sup>62,63</sup>).

This approach also represents an opportunity to use saline water that might be produced from sequestration. In order to avoid issues of either over-pressuring a formation or, more likely, to reduce the risk of trespass or the need to secure underground rights to a far greater area of impact (carbon dioxide plus displaced saline water), production of potable water could be a useful option. Because this approach has not been demonstrated as a continuous unit at a modest pilot-scale, potential applications must await further development as must assessments of the potential for applications either at coastal plants or in-land. Further calculations of the benefits of deploying some variant on this process to manage saline waters must await development of a commercially viable process.

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<sup>62</sup> Sheps, K., 2007. Seawater Desalination as a Factor of Oceanic CO<sub>2</sub> Disposal. Presented at CHEMRAWN XVII and ICCDU-IX Conference on Greenhouse Gases - Mitigation and Utilization, Kingston, Ontario, 8 – 12 July 2007. Available at: <http://www.chem.queensu.ca/Conferences/CHEMRAWN/Sheps.pdf> [Accessed October 26, 2010].

<sup>63</sup> Sheps, K. et al., 2009. A case for deep-ocean CO<sub>2</sub> sequestration. *Energy Procedia*, 1(1), pp.4961-4968.



The basic concept depicted, CO<sub>2</sub> Hydrate Desalination, is based on developing and applying oceanic in-situ industrial crystallization. In this approach, the hydrate growth rejects a number of contaminants found in the source water such as dissolved ions, chemicals and small particulates.

### 5.3.1 CO<sub>2</sub> Clathrate Desalination of Brackish/Saline Water Factsheet

<b>Estimated impact /Net CO<sub>2</sub> considered permanently sequestered (US)</b>	None, but would enable production of potable water in areas where only saline water is available with concurrent economic benefit.
<b>Gross current CO<sub>2</sub> consumption in this use (US), MT/year</b>	None
<b>Game-changing events/scenarios favorable for this process</b>	Regulations that either impact access to pore space or that restrict the use of cooling water or that facilitate use of treated saline waters.

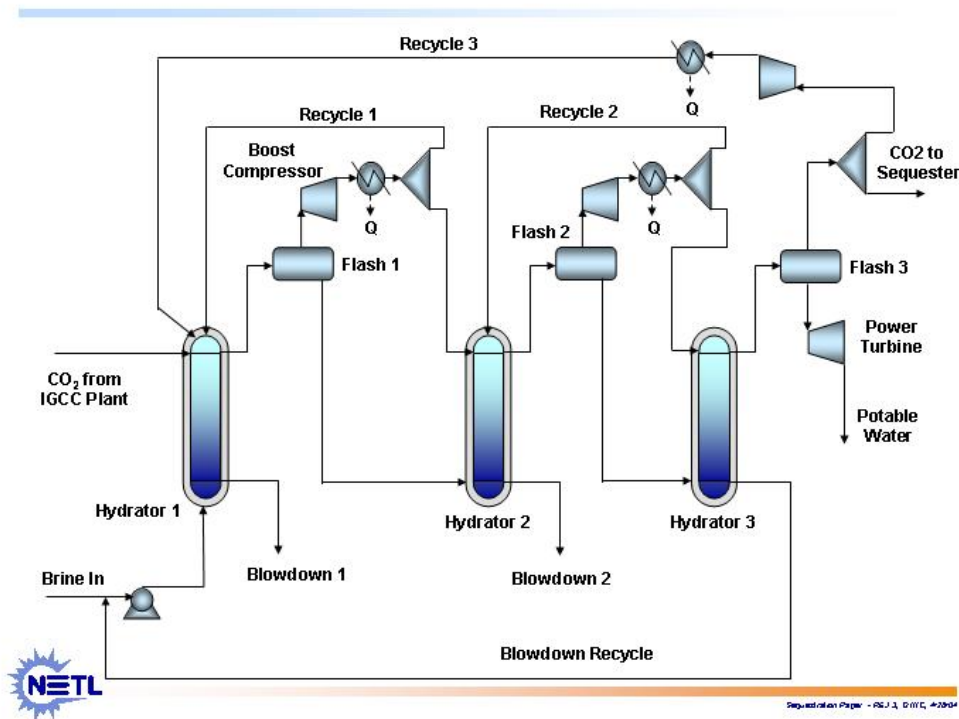


Figure 9. CO<sub>2</sub> hydrate-desalination process in an IGCC power plant systems perspective. Source: James and McGurl, 2004



*Draft*

<b>Gross/net CO<sub>2</sub> reduction per tonne of primary CO<sub>2</sub></b>	Does not directly reduce CO <sub>2</sub> via capture from an effluent stream that would be released to the atmosphere.
<b>Estimated scale of single application (i.e. plant size or field size)</b>	Economics of technology would determine minimum size of installation that would be feasible. Limited analysis focused on application at a 425 MW (nominal) IGCC unit.
<b>Estimated time to full deployment/ market saturation</b>	5 to 10 years depending upon whether an economic driver exists for this purpose.
<b>Estimated duration of significant impact</b>	Could be viable for the life of the facility to which it is attached.
<b>Special requirements on CO<sub>2</sub> (purity, etc.)</b>	Power plant, cement kiln flue gas
<b>Process/Technology Input Raw Materials and/or Energy</b>	Carbon dioxide, brine, seawater, electricity
<b>Process/Technology Outputs</b>	Potable water and a CO <sub>2</sub> sludge for disposal.
<b>Any concomitant advantages? (For example, Does this process eliminate the need for other pollution control equipment?)</b>	The process could produce plant process water and create potable water for sale at a lower cost compared to reverse osmosis systems.
<b>Value of carbon dioxide in this activity</b>	Carbon dioxide could have a value that approximates cost of materials (chemicals, etc.) used by competing treatment options.
<b>Legal/regulatory framework governing/impacting deployment of this option</b>	Water law could complicate distribution of produced water.

## 5.4 Carbon dioxide as a Working Fluid

### 5.4.1 Introduction

Aside from the potential consumptive uses for carbon dioxide and its potential for reuse in such applications as enhanced oil recovery, carbon dioxide can perform as a working fluid in a great number of applications:

- Coal cleaning<sup>64</sup> and injection of coal into gasifiers and combustors<sup>65</sup>
- Heat transfer fluid in power systems
  - Gen IV nuclear reactor studies<sup>66</sup>
  - Geothermal power studies<sup>67</sup>
  - More efficient heat transfer medium<sup>68</sup>
- Transport media in freight pipelines<sup>69</sup>
- Recovery of rare earth elements, treating hazardous waste via solvent extraction...see Actinide Separation Chemistry in Nuclear Waste Streams and Materials<sup>70</sup> and other similar (based on supercritical fluid properties) applications<sup>71</sup>.

In a few cases, the proposed use for carbon dioxide actually traps the CO<sub>2</sub> underground (see WO 2010/104599 A2) or may involve transforming some of the carbon dioxide into another form, perhaps as oxalates or carbonates (see the rare earth recovery patent).

These applications for carbon dioxide could form elements of a system that is designed to optimize the value derived from capturing large amounts of carbon dioxide. Ultimately, most of that captured CO<sub>2</sub> would be sequestered. However, on a region-by-region basis, many of the processes described in this summary could operate off a supply chain focused on a CO<sub>2</sub> pipeline network to produce value. How such economic benefits might be used to lessen the overall cost of capture and storage is not germane to the purpose of this document. If one sought to find useful things to do with carbon dioxide produced in energy conversion or other manufacturing processes to the greatest extent possible, constrained only by cost, energy consumption, and potential market size (see the section on metrics), these uses could be seen as bridges between sources and sinks or as opportunities that offset uses of other greenhouse gases with higher global warming potential (GWP). They would never justify capture nor increased use of a fossil fuel on their own. The concepts typically focus on the beneficial properties of supercritical carbon dioxide (scCO<sub>2</sub>).

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<sup>64</sup> See: Advanced Physical Coal Cleaning, CONF-940780, Vol. 1, Part 2 pages 67 – 74 (1994)

<sup>65</sup> J. Phillips, Program on Technology Innovation: Advanced Concepts in Slurry-Fed Low-Rank Coal Gasification – *Liquid CO<sub>2</sub>/Coal Slurries and Hot Water Drying*, Report #1014432, Technical Update, December 2006

<sup>66</sup> Chang H. Oh, Thomas Lillo, William Windes, Terry Totemeier, Bradley Ward, Richard Moore and Robert Barner, Development Of A Supercritical Carbon Dioxide Brayton Cycle: Improving VHTR Efficiency And Testing Material Compatibility - Final Report, INL/EXT-06-01271(March 2006) Idaho National Laboratory

<sup>67</sup> See, for example, WO 2010/104599 A2, International Patent Application PCT/US 2010/000756 (March 2010)

<sup>68</sup> See, for instance, (a) US Patent 3,971,211 (July 1976), (b) <http://www.echogen.com/products>

<sup>69</sup> See, for instance (a) US Patent 4,721, 420 (Jan 1988)

<sup>70</sup> NEA Nuclear Science Committee, Actinide Separation Chemistry in Nuclear Waste Streams and Materials, NEA/NSC/DOC(97)19

<sup>71</sup> Eric J. Beckman, Supercritical and near-critical CO<sub>2</sub> in green chemical synthesis and processing, J. of Supercritical Fluids 28 (2004) 121–191

To address this disparate collection of concepts, this section will start with coal cleaning and coal transport (including injection into combustion devices or gasifiers) then proceed through power cycles based on carbon dioxide, to long-distance freight pipelines based on scCO<sub>2</sub> as the carrier fluid to a host of smaller commercial applications such as solvent extraction.

#### 5.4.2 Coal Cleaning and Coal Transport

Among a number of proposed uses for carbon dioxide in coal cleaning, the liquid carbon dioxide (LICADO) process<sup>72</sup> has been the subject of significant R&D. The process was originally conceived as a separation technique when seeking deep levels of cleaning for finely-ground bituminous coals. The process relies on the relative “wettability” of clean coal and mineral matter to liquid carbon dioxide and water, respectively. Process development included conducting tests in a small-scale continuous unit that recycled the carbon dioxide. The CO<sub>2</sub> was flashed off of the coal and back to a gas then returned to the liquid state for reuse.

EPRI<sup>73</sup> issued a report in 2006: *Program on Technology Innovation: Advanced Concepts in Slurry-Fed Low-Rank Coal Gasification - Liquid CO<sub>2</sub>/Coal Slurries and Hot Water Drying (#1014432)*. In summarizing the work supported by EPRI and others, the author states:

“...to our knowledge, no other organization is currently looking at liquid CO<sub>2</sub>/coal slurries. During the 1980s EPRI sponsored several projects related to the concept of using liquid CO<sub>2</sub> as a slurring medium for pulverized coal. The most relevant of the earlier EPRI projects on liquid CO<sub>2</sub>/coal slurry was documented in EPRI AP-4849 in 1986. That project, conducted by Arthur D. Little, Inc., carried out laboratory and pilot plant scale tests on liquid CO<sub>2</sub> slurries...with up to 88wt% solids...

The results of AP-4849 were used in a subsequent engineering-economic study on the use of lignite in an IGCC [power cycle]. The study was documented in EPRI AP-4509, also published in 1986. The results indicated that the cold gas efficiency of the gasification process could be increased by 13 percentage points by using liquid CO<sub>2</sub>/lignite slurry...contemporary concerns about greenhouse gas emissions and their link to climate change has increased interest in capturing and storing CO<sub>2</sub> from future coal-based power plants. If CO<sub>2</sub> is going to be captured and compressed to greater than 2000 psi (14 MPa) for storage, then the incremental cost of producing liquid CO<sub>2</sub> for a coal slurry will be quite small... While the present analysis has cast doubts on the ability to actually achieve slurry solids contents as high as 88 wt%, the analysis does indicate there is sufficient promise in the concept to justify additional work...”

#### 5.4.3 Power Cycles

There is a rich history of papers and patents dealing with uses of carbon dioxide as a working fluid (heat transfer fluid). In particular, there have been numerous power cycles or power cycle improvements put forward using supercritical carbon dioxide. For instance, a power cycle was developed and patented by Ernest G. Feher (US patent 3,237,403 entitled “Supercritical Cycle Heat Engine”). Subsequent patents improving on the concept include US Patent 3,971,211 (issued in 1976) entitled Thermodynamic Cycles with Supercritical CO<sub>2</sub> Cycle Topping.

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<sup>72</sup> See (a) earlier citation #64...Klinzing, Chang, Morsi, etc. and (b) Advanced Coal Cleaning session

<sup>73</sup> EPRI

As part of the program to develop the Very High Temperature Gas Reactor (HTGR), a Gen IV nuclear system designed for high efficiency electricity generation and high temperature process heat applications, INL<sup>74</sup>, ANL<sup>75</sup>, and MIT<sup>76</sup> all explored the role that supercritical CO<sub>2</sub>-based Brayton cycles might play in this system. The HTGR and other Gen IV concepts included an indirect heat exchange between the internal heat exchanger within the reactor and an external cooling system. The working fluid for the external portion of the indirect heat exchanger was a subject of study and one of the options was to replace the standard steam Rankine cycle with a supercritical CO<sub>2</sub> Brayton cycle.

Multiple gases have been evaluated during the Gen IV program but several of the papers found an advantage when using supercritical carbon dioxide. The INL study found that the reduced volumetric flow rate of carbon dioxide due to higher density compared to helium will reduce compression work, which lowers turbine work losses, enhancing the plant net efficiency. Over a range of simulations, varying outlet temperatures and pressures, the CO<sub>2</sub> Brayton cycle typically showed the highest efficiency amongst the gases tested in the indirect configuration, reaching ~50.7%. This was two to four percentage points higher than with other gases in similar configurations. The supercritical CO<sub>2</sub> approach also suggested other simplifications and the use of smaller components representing a savings in capital cost. A number of other applications for supercritical carbon dioxide in heat transfer applications have been developed.

#### 5.4.3.1 Use of CO<sub>2</sub> in Enhanced Geothermal Energy Recovery Systems

Conventional geothermal energy systems require water as a working fluid. Heat is recovered using a steam turbine, which requires geothermal source temperatures above 185 °C. The drawbacks of this system include water losses, and the inability to use low-temperature geothermal sources. The use of CO<sub>2</sub> to overcome such limitations was first proposed in 2000. CO<sub>2</sub> sequestration and concomitant geothermal energy recovery are the twin features of this process. The U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) is currently funding multiple field- and laboratory-scale research and modeling studies aimed at better understanding of the behavior and impacts of CO<sub>2</sub> injection in geothermal reservoirs. These projects are addressed under the ‘*enhanced geothermal systems*’ and ‘*low-temperature and co-produced resources*’ program portfolios. Two field studies in Arizona and Texas are focused on CO<sub>2</sub>-enhanced geothermal electric power generation. GreenFire Energy’s CO<sub>2</sub>E<sup>TM</sup> suite of technologies will be field-tested at St. John’s Dome in eastern Arizona. Heat is recovered from CO<sub>2</sub> in a binary power generation cycle<sup>77</sup> (Figure 10A). Lawrence Berkeley National Laboratory (LBNL) and Echogen Power Systems plan to design, build and test a geothermal system with CO<sub>2</sub> as the working fluid operating on a high-efficiency supercritical CO<sub>2</sub> turboexpansion cycle<sup>78</sup> (Figure 10B). The magnitude of CO<sub>2</sub> use in this process depends on reservoir and wellbore flow properties, and CO<sub>2</sub> stored within the reservoir by mineralization, dissolution, or out-of-zone migration.

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<sup>74</sup> Chang, Oh, Ibid., page 33

<sup>75</sup> Anton M. and James J. Sienicki, Argonne National Laboratory, Supercritical CO<sub>2</sub> Brayton cycle control strategy for autonomous liquid metal-cooled reactors, presented at The Americas Nuclear Energy Symposium, Miami Beach, Florida, October 3-6, 2004

<sup>76</sup> Hejzlar et al., Assessment of gas cooled fast reactor with indirect supercritical CO<sub>2</sub> cycle, Nuclear Engineering and Technology, v.38(2), Special Issue on ICAPP '05.

<sup>77</sup> EERE, 2011, Department of Energy Announces \$20 Million to Boost Development of Innovative Geothermal Technologies, Available at: [http://apps1.eere.energy.gov/news/progress\\_alerts.cfm/pa\\_id=401](http://apps1.eere.energy.gov/news/progress_alerts.cfm/pa_id=401), Accessed 9/28/2011.

<sup>78</sup> Krotz, D., 2011, Store CO<sub>2</sub> Underground and Extract Electricity? A Berkeley Lab-led Team is Working on it, Available at: <http://newscenter.lbl.gov/feature-stories/2011/08/08/geothermal-co2/>, Accessed 9/28/2011.

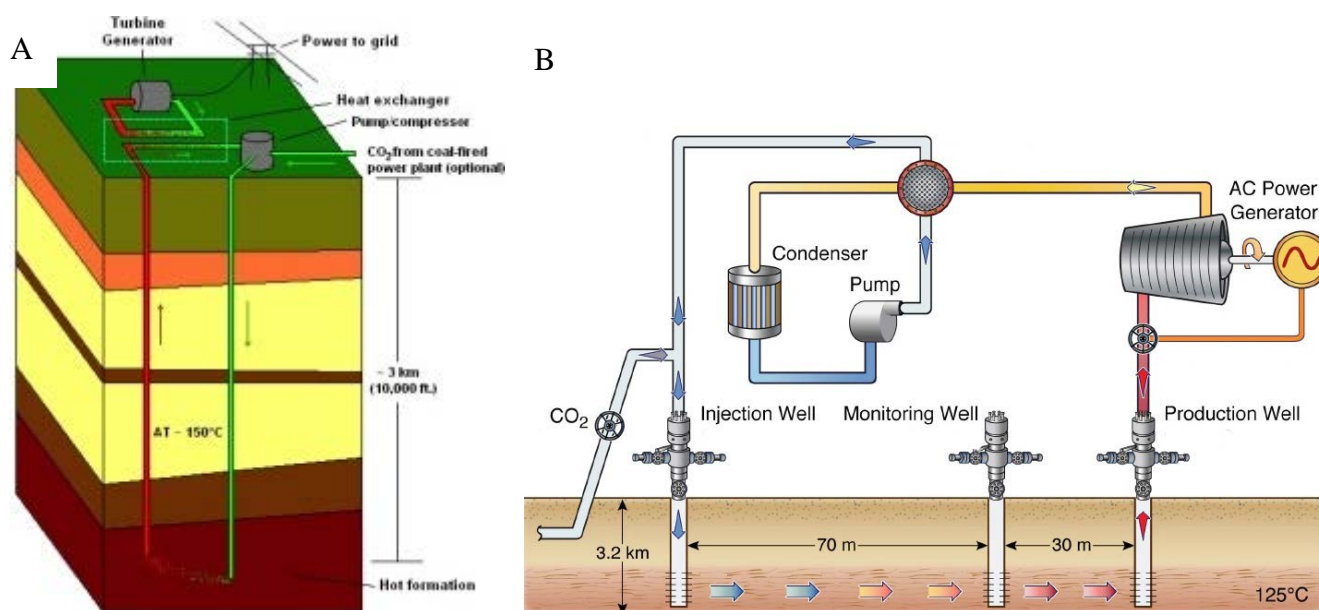


Figure 10(A): Schematic of the GreenFire geothermal system, (B): Illustration of the proposed LBNL/Cranfield field-scale geothermal power system test.

#### 5.4.4 Freight Pipelines

A significant body of literature exists on the concept of freight pipelines. The term captures a broad range of technologies including pipelines with automated rail systems based on electromagnetic/linear induction, slurry pipelines, and pneumatic (or gas-driven) systems. The Texas Transportation Institute at Texas A&M completed a study in 2003<sup>79</sup> that looked at freight pipeline systems for Texas. The report examined a number of options for freight pipeline systems hauling a variety of goods and commodities across the state. The benefits result directly from lower costs per ton-mile, lower energy consumption (and lower greenhouse gas emissions) and indirectly from reduced congestion on road that would otherwise bear increasing numbers of heavy trucks. The report favored pneumatic systems driven by high pressure gases (inert or air). The concept of using carbon dioxide in some form as a transport media in pipelines<sup>80</sup> has also been explored for bulk solids.

#### 5.4.5 Solvent Extraction

Supercritical carbon dioxide has been proposed as a sustainable solvent by a number of researchers and process developers. Beckman (2004)<sup>81</sup> reviewed the use of supercritical or near-critical carbon dioxide in chemical synthesis and processing. The focus of the article was to “uses of CO<sub>2</sub> that are relatively new and appear to provide ‘green’ advantages. It should be noted that there are examples provided in this paper where a CO<sub>2</sub>-

<sup>79</sup> Stephen S. Roop, et al., Texas Transportation Institute, Year 4 report on the technical and economic feasibility of a freight pipeline system in Texas, Report 9-1519-4, Sponsored by the Texas Department of Transportation In Cooperation with the U.S. Department of Transportation Federal Highway Administration October 2003

<sup>80</sup> See reference 6: US Patent 4,721, 420 (Jan 1988)

<sup>81</sup> Beckman, Ibid, page 121-122

based process is not particularly ‘green’, yet is generating interest because it produces better quality product than conventional alternatives.”

One area in which a substantial body of literature exists focuses on recovery of rare earth elements from various materials including nuclear wastes<sup>82</sup>. Current methodologies used for fuel reprocessing generate large amounts of low level waste. The use of scCO<sub>2</sub> would facilitate separation leaving concentrated residues that could then be more easily stored. The NEA Nuclear Science Committee published a report, Actinide Separation Chemistry in Nuclear Waste Streams and Materials<sup>83</sup>, a report of the NEA Nuclear Science Committee (NEA/NSC/DOC(97)19) which discussed the recovery of uranium, thorium, and various lanthanides through the use of scCO<sub>2</sub> in supercritical fluid extraction (SFE). Small amounts of chelating agents needed to be added to achieve satisfactory results. No specific tonnages were cited but stored waste from the nuclear industry is a significant issue even if quantities are modest (100,000’s of tons) compared to other applications. Mineral processing for lanthanides could also be a high-value use, because of the current market situation<sup>84</sup> is creating incentives for domestic development and recycling.

## 5.5 Fuels and Organic Chemicals from CO<sub>2</sub>

Fuels and organic chemicals are discussed together because the processes used to produce fuels and organic chemicals generally differ only slightly, if at all. This is also true for their production from CO<sub>2</sub>. The products form two categories; those that we burn are called fuels and those we use for other purposes are called chemicals.

To produce hydrocarbon fuels and organic chemicals from CO<sub>2</sub> requires that the combustion process be reversed and that oxidized carbon, in the form of CO<sub>2</sub>, be chemically reduced. This reduction is energy intensive and while the complete process is thermodynamically unfavorable, it does have merit. The value of the concept is that the products used for fuel are then carbon neutral, provided that the energy source for conversion is carbon neutral, e.g., hydrogen generated from nuclear, solar or other renewable energy sources. The net result is that non-fossil energy sources can be made portable by converting their energy to hydrocarbon fuels which use existing technologies and infrastructure. The conversion of CO<sub>2</sub> to organic chemicals results in a net-carbon emission reduction which is dependent on the lifetime of the products. For example, polymers would keep carbon in the reduced state longer than volatile compounds. It should be noted that any eventual oxidation of chemicals produced in this way would be carbon neutral. The net-benefits from converting CO<sub>2</sub> to fuels or chemicals strongly depend on the cost of hydrogen. Various studies indicate that hydrogen produced from steam methane reforming (SMR) or coal gasification is cheaper than that produced using renewable energy technologies such as solar photovoltaics, concentrated solar power (CSP), wind energy and biomass. Studies also indicate that CO<sub>2</sub> emissions from the production of hydrogen from coal or natural gas can be mitigated by geologic CCS, at costs of ~2.5 \$/kg for H<sub>2</sub> from SMR and 1.8 \$/kg for H<sub>2</sub> (2007 \$) from coal

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<sup>82</sup> Quintus Fernando, et al. , Formation of Rare Earth Carbonates Using Supercritical Carbon Dioxide, US Patent 5,045,289 (September 1991)

<sup>83</sup> NEA Nuclear Science Committee, Actinide Separation Chemistry in Nuclear Waste Streams and Materials, NEA/NSC/DOC(97)19

<sup>84</sup> Lee, J., 2009. China’s Ring of Power. Foreign Policy. Available at: [http://www.foreignpolicy.com/articles/2009/09/09/going\\_green](http://www.foreignpolicy.com/articles/2009/09/09/going_green) [Accessed September 29, 2011].



gasification (Bartels et al., 2010<sup>85</sup>). Bartels et al. also report that the near-term cost of hydrogen production using wind energy would be \$4 to \$5.5/kg H<sub>2</sub>. The higher value is consistent with electrolyzer power consumption of ~52 kWh/kg H<sub>2</sub> and levelized electricity costs of ~\$100/MWh. The EIA's annual energy outlook (AEO, 2011) projects that wind electricity, currently considered to be the most cost-effective among renewable energy technologies (excluding hydroelectric power) would have a levelized cost of ~97 \$/MWh (2009\$, by 2016)<sup>86</sup>. In comparison, the U.S. DOE goal for hydrogen cost is 2 to 3 \$/gge (ca. 2 to 3 \$/kg H<sub>2</sub> delivered, untaxed, 2005 \$, by 2015)<sup>87</sup>. This goal is independent of the pathway used to produce hydrogen. We used \$3.5/kg H<sub>2</sub> as the reference hydrogen price in this report. The costs of hydrogen vary with the scale of production and also vary geographically. For example, small-scale (100 kg/d) electrolysis production costs in the U.K. were estimated to be \$6 to \$16/kg H<sub>2</sub><sup>88</sup>.

Producing hydrocarbons from CO<sub>2</sub> also conserves petroleum while permitting continued use of the existing petroleum based infrastructure. This latter is important when considering the "hydrogen economy." If the hydrogen, as an energy carrier, is distributed as molecular hydrogen, replacement of the petroleum-based transportation infrastructure is estimated to be on the order of trillions of dollars with a complex transition phase. Chemically reducing CO<sub>2</sub> to hydrocarbons with hydrogen would use the carbon as a hydrogen shuttle and avoid the expense of infrastructure replacement while providing the high energy densities and ease of handling only afforded by liquid hydrocarbons. The technologies addressed by this section could be readily applied, in the future, to CO<sub>2</sub> captured from the atmosphere and recycled indefinitely as a hydrogen carrier in the form of hydrocarbon fuels.

There are many pathways to chemically reduce CO<sub>2</sub> to hydrocarbons by a chemical reducing agent, such as hydrogen or methane, by electrons in an electrochemical cell, or by photons in photocatalytic processes, such as photosynthesis in biological organisms. In all cases, the carbon would be reused at least once and the process would be carbon neutral, provided that the reductant was produced using non-fossil resources. Although full scale production would use non-fossil resources to reduce CO<sub>2</sub> to hydrocarbons, many of the experimental and developmental projects will use available materials and power for convenience.

### 5.5.1 Metrics: Conversion of CO<sub>2</sub> to fuels and organic chemicals

Nominal-net benefit analysis indicates that the conversion of CO<sub>2</sub> to fuels such as diesel, gasoline and methanol (~200 \$/T) is less 'beneficial' than CO<sub>2</sub> to chemicals (formic acid, acrylic acid, plastics: ~750 to 2000 \$/T). However, the quantity of CO<sub>2</sub> which could be used to produce chemicals is small compared to amounts of CO<sub>2</sub> which could be used to make fuels. Both of these applications recycle carbon from fossil fuels.

Table 7 provides an overview of results for the options identified.

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<sup>85</sup> Bartels, Jeffrey R., Michael B. Pate, and Norman K. Olson. 2010, An economic survey of hydrogen production from conventional and alternative energy sources, *International Journal of Hydrogen Energy*, v.35 (16) (August), pp.8371-8384.

<sup>86</sup> [http://205.254.135.24/oiaf/aeo/electricity\\_generation.html](http://205.254.135.24/oiaf/aeo/electricity_generation.html)

<sup>87</sup> [http://www1.eere.energy.gov/hydrogenandfuelcells/news\\_cost\\_goal.html](http://www1.eere.energy.gov/hydrogenandfuelcells/news_cost_goal.html)

<sup>88</sup> <http://www.renewableenergyfocus.com/view/22045/itm-power-says-hfuel-hydrogen-costs-already-below-european-2015-target/>

Table 7. Fuels and Organic Chemicals from CO<sub>2</sub>

	CO <sub>2</sub> Mitigation			Benefits
	(A) CO <sub>2</sub> Reduced (total)	(B) Amount of CO <sub>2</sub> consumed (MT/y)	(C) CO <sub>2</sub> Capture in-built?	(D) Cost of CO <sub>2</sub> reduction (\$/T)
<b>Gasoline</b>	See (B)	1,229* (100%) See Appendix	No	247 \$/T CO <sub>2</sub> * See Appendix
<b>Distillate Fuel (diesel)</b>		416* (100%) See Appendix		237 \$/T CO <sub>2</sub> * See Appendix
<b>Methanol</b>		11* (100%) See Appendix		190 \$/T CO <sub>2</sub> * See Appendix
<b>Acrylic acid</b>		0.73* (100%) See Appendix		-1,988 \$/T* See Appendix
<b>Polyethylene carbonate (Plastics)</b>		2.5* See Appendix		-760 \$/T CO <sub>2</sub> * See Appendix
<b>Urea production</b>		101* (see Urea write-up for details)		-183 \$/T CO <sub>2</sub> See writeup
<b>Formic acid</b>		0.5 (globally, see writeup)		-1075 \$/T CO <sub>2</sub> * See Appendix
<b>Algal fuels</b>		2 T CO <sub>2</sub> /T dry algal biomass, 14 to 47 kg CO <sub>2</sub> /gal algal oil/biodiesel		May use pure CO <sub>2</sub> or flue gas (dilute CO <sub>2</sub> )

Values preceding asterisks are specific to the U.S.A

Market potential: A fraction of the value in (1.2) in the preceding table could be realistically supplied using CO<sub>2</sub> for each of the processes where CO<sub>2</sub> is converted to fuels and organic chemicals. CO<sub>2</sub> conversion to urea does not remove CO<sub>2</sub> from atmosphere, because urea is decomposed back to CO<sub>2</sub> when used as a fertilizer or a source of ammonia. Asterisks in table indicate U.S.-specific estimates. Life cycle analyses would be required to estimate energy consumption, energy penalty and CO<sub>2</sub> emissions from processes converting CO<sub>2</sub> to fuels and organic chemicals.



## 5.5.2 Fuels and Organic Chemicals by Chemical Process

### Introduction

The reduction of CO<sub>2</sub> in two electron increments produces first formic acid, then formaldehyde, then methanol, and finally methane. Methanol synthesis is a common industrial process that uses CO and hydrogen:



but the process can be run using the same catalyst with CO<sub>2</sub> as a feedstock



The synthesis of methanol from CO<sub>2</sub> may also involve indirect reduction. For example, the catalytic hydrogenation of organic carbonates, carbamates and formates under mild-temperature and pressure conditions to methanol has been recently demonstrated<sup>89</sup>. Such routes may be more cost-effective compared to direct hydrogenation of CO<sub>2</sub>. The production of organic carbonates from methanol and CO<sub>2</sub> and their subsequent hydrogenation results in net-methanol production. Other applications include the synthesis of organic carbonates from CO<sub>2</sub> and methanol under mild conditions, e.g. the Novomer process. The advantage of producing methanol is that the capital expenses are relatively low, the economy of scale does not handicap distributed production, and methanol is an important chemical commodity that can be used as a fuel in a high-compression internal combustion engine. The downside to methanol is that while it is a liquid fuel, it lacks the energy density of hydrocarbon fuels, has lower fuel economy than gasoline, and requires modifications to infrastructure and vehicular fuel and engine systems. Fortunately, methanol is readily converted to gasoline with high specificity by the ExxonMobil methanol-to-gasoline (MTG) process. Methanol can also be converted to diesel by the oligomerization and isomerization of ethylene, an important chemical intermediate produced by modifying the MTG process.

Alternatively, CO<sub>2</sub> can be reduced to CO and, with additional hydrogen, all reactions of synthesis gas (a mixture of carbon monoxide and hydrogen also known as syngas) become available including the Fischer-Tropsch (F-T) synthesis. This process is the most proven of the synthetic hydrocarbons processes and has a long history of development in South Africa by Sasol. Additionally, a broad suite of chemicals is available through syngas chemistry (Wender, 1996).

### 5.5.2.1 Algae-Based Fuels

Microalgae are photosynthetic microorganisms which convert CO<sub>2</sub>, water and light energy to algal biomass, typically at significantly higher productivities as compared to terrestrial plants<sup>90</sup>. Under certain conditions, genetically unmodified microalgae can store as much as 50% of their biomass in the form of oils such as lipids or triacylglycerols (TAGs) (Pienkos and Darzins, 2009; Wijffels and Barbosa, 2010). These oils are one of the precursors for fuels such as biodiesel, jet fuel and gasoline. Microalgae can be grown using non-arable lands and a wide variety of water sources which could lessen perceived food-fuel conflicts. This section is intended to be a review of the main features of algal biofuels and not a comprehensive, detailed review. The reader is

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<sup>89</sup> Balaraman, E. et al., 2011. Efficient hydrogenation of organic carbonates, carbamates and formates indicates alternative routes to methanol based on CO<sub>2</sub> and CO. *Nature Chemistry*, 3(8), pp.609-614.

<sup>90</sup> This discussion includes cyanobacteria (informally known as blue-green algae), which lack cell nuclei (prokaryotes) are therefore not formally classified with algae (eukaryotes). The term 'algae' refers to microalgae, as compared with macroalgae (sea weeds).

referred to pertinent scientific studies and systems analyses on algal biofuels (such as Pienkos and Darzins, 2009; Chisti, 2008; Beer et al., 2010; Greenwell et al., 2009, Lundquist et al., 2010) for further details.

The general steps involved in producing liquid fuels from algae are: species selection, culture and growth, nutrient and waste-stream management, oil extraction and processing to produce the desired fuel. The algal oil can be extracted from the microalgae and converted into biodiesel using alcohols (similar to soy biodiesel) or it may be used to produce linear hydrocarbons. Algae can also make hydrogen, ethanol and hydrocarbons resembling crude oil (Wijffels and Barbosa, 2010). The spent algal biomass could be used as animal feed, or converted to synthesis gas (syngas), the feedstock for a wide variety of chemicals and fuels via synthetic processes (Wender, 1996). Spent algal biomass may also be fermented in the absence of air to produce biogas with a high methane content, which could be readily upgraded to pipeline-quality natural gas. Other routes include integrated processing of algal biomass in a biorefinery producing a slate of valuable by-products and fuels, and the production of hydrocarbons and other fuels directly from genetically modified microorganisms such as cyanobacteria (e.g. Reppas and Ridley, 2010).

Microalgae may be cultivated in shallow open ponds, closed photobioreactor (PBR) systems, or hybrid designs. Open shallow ponds or raceway systems are less expensive and have lower algal biomass yields compared to engineered PBR systems. High-algal biomass and high-lipid content may be mutually exclusive (with genetically unmodified algae) (Sheehan et al., 1998). Two-stage, or hybrid designs aim to overcome this limitation. In hybrid designs, microbes are initially grown in closed photobioreactor systems under controlled conditions favoring cell growth, and minimal contamination before being transferred to open ponds or raceway systems (Huntley and Redalje, 2006). Such hybrid approaches may lead to reduced costs compared to photobioreactors alone. At least two algal biofuel companies (HR BioPetroleum, Sapphire Energy) currently adopt the hybrid approach to cultivate and harvest algae.

The extent to which algal biofuels may displace fossil-derived petroleum fuels and the amount of CO<sub>2</sub> recycled is shown in Table 8. Pienkos and Darzins (2002) note that the theoretical maximum algal productivity cannot exceed 100 grams.m<sup>-2</sup>.d<sup>-1</sup> (22,340 gal/acre/yr, assuming 50% w/w oil). The current U.S. EPA renewable fuels standard (RFS2) calls for 0.8 billion gallons/year of biodiesel in 2011<sup>91</sup>. Systems analyses indicate that at the current state of development, algal biofuels cannot supply this volume for the next 10 to 15 years (see Bartis and Van Bibber, 2011 and references therein). If algal biofuels could be successfully commercialized, these preliminary calculations indicate that 10 to 40 million tonnes of CO<sub>2</sub> could be utilized by the producing 0.8 billion gallons of biodiesel (2.2 million gallons/day) using microalgae. Analysis of life-cycle CO<sub>2</sub> emissions from fuel produced from algae fixation of CO<sub>2</sub> and solar reduction of CO<sub>2</sub> indicates that such processes are could have significantly lower lifecycle CO<sub>2</sub> emissions, resulting in a significant climate benefit (i.e. reduction in CO<sub>2</sub> emissions) compared to petroleum (Kreutz, 2010; Vasudevan et al., 2012)<sup>92,93</sup>.

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<sup>91</sup> <http://www.epa.gov/otaq/fuels/renewablefuels/420f10056.htm>

<sup>92</sup> Kreutz, T., 2011. Prospects for producing low carbon transportation fuels from captured CO<sub>2</sub> in a climate constrained world. *Energy Procedia*, 4(0), pp.2121-2128.

<sup>93</sup> Vasudevan, V. et al., 2012. Environmental performance of algal biofuel technology options. *Environ. Sci. Technol.*, 46(4), pp.2451–2459. Low-impact, nominal, and high-impact algal oil productivity values used in this article are 19.2 g oil/m<sup>2</sup>/d, 5 g oil/m<sup>2</sup>/d, and 2.25 g oil/m<sup>2</sup>/d, which are close to those used in Table 8 (multiplication of first two rows results in 25, 6.25, and 1.5 g TEG/m<sup>2</sup>/d for the high-, medium-, and low-biofuel productivity cases, respectively).

The most practical approach to integrate algal fuels with the existing infrastructure would be to subject the algal oils to the same refining steps as petroleum, either alone or as a mixture with petroleum. This would produce a fuel identical to petroleum derived fuels and eliminate separate processes and logistics chains for raw and transesterified oils. Further, by allowing a ready fit of the new fuel into existing infrastructure and eliminating the need for biofuel-specific engine modifications, the economics of use and marketability would be greatly enhanced.

The production of algal biofuels is limited by the availability of suitable land resource, access to CO<sub>2</sub> and water. Estimates of future algal biofuel production vary significantly. Lundquist et al. (2010) note that land, water and CO<sub>2</sub> limitations may restrict algal biofuel production to less than a couple of billion gallons per year<sup>94</sup>. A report from Pike Research notes that 60 million gallons of algal biofuels may be produced worldwide (~20 million gallons in North America, mainly in the U.S.A.) annually by 2020<sup>95</sup>. More optimistic assessments from the Algal Biomass Organization (ABO) indicate 6,000 million (6 billion) gallons of algal biofuels per year by 2022<sup>96</sup>. A recent summary of US efforts on algal biofuels is provided by Morello and Pate (2010)<sup>97</sup>. The amount of land area and CO<sub>2</sub> needed to meet the current RFS2 advanced biofuel requirement (considering only algal biodiesel) under various scenarios of algae productivity is shown in Table 8.

Table 8: Estimates of algal biofuel production and CO<sub>2</sub> utilization to meet a RFS biodiesel mandate of 0.8 billion gallons of biodiesel per year (<http://www.epa.gov/otaq/fuels/renewablefuels/420f10056.htm>)

Scenario	Low Biofuel Productivity	Medium Biofuel Productivity	High Biofuel Productivity
<b>Productivity, g biomass/(m<sup>2</sup>.d)</b> See <sup>98</sup>	10	25	50
<b>% TAG</b>	15%	25%	50%
<b>gal/acre</b> See	633	2,637	10,549
<b>Million acres needed to produce 0.8 billion gallons/year*</b>	1.26*	0.30*	0.076*
<b>CO<sub>2</sub> used, MT/y</b> (@ 2 g CO <sub>2</sub> /g algal biomass)	37*	22*	11*

Values preceding asterisks are specific to the United States.

<sup>94</sup> Lundquist, T.J. et al., 2010. A realistic technology and engineering assessment of algae biofuel production, Energy Biosciences Institute. Available at: [http://digitalcommons.calpoly.edu/cenv\\_fac/188](http://digitalcommons.calpoly.edu/cenv_fac/188) [Accessed February 2, 2011].

<sup>95</sup> Lawrence, M. & Wheelock, C., 2010. Algae-Based Biofuels - Demand Drivers, Policy Issues, Emerging Technologies, Key Industry Players, and Global Market Forecasts. Executive summary available at: <http://www.pikeresearch.com/research/algae-based-biofuels> [Accessed February 2, 2011].

<sup>96</sup> Algal Biomass Organization, 2011. Algae biofuels edge closer to commercialization. Available at: <http://www.algalbiomass.org/news/2064/algae-biofuels-edge-closer-to-commercialisation/> [Accessed February 2, 2011].

<sup>97</sup> Morello, J. & Pate, R., 2010. The promise and challenge of algae as renewable source of biofuels. Available at: [www1.eere.energy.gov/biomass/pdfs/algae\\_webinar.pdf](http://www1.eere.energy.gov/biomass/pdfs/algae_webinar.pdf) [Accessed February 3, 2011].

<sup>98</sup> Data from Pienkos and Darzins (2009).

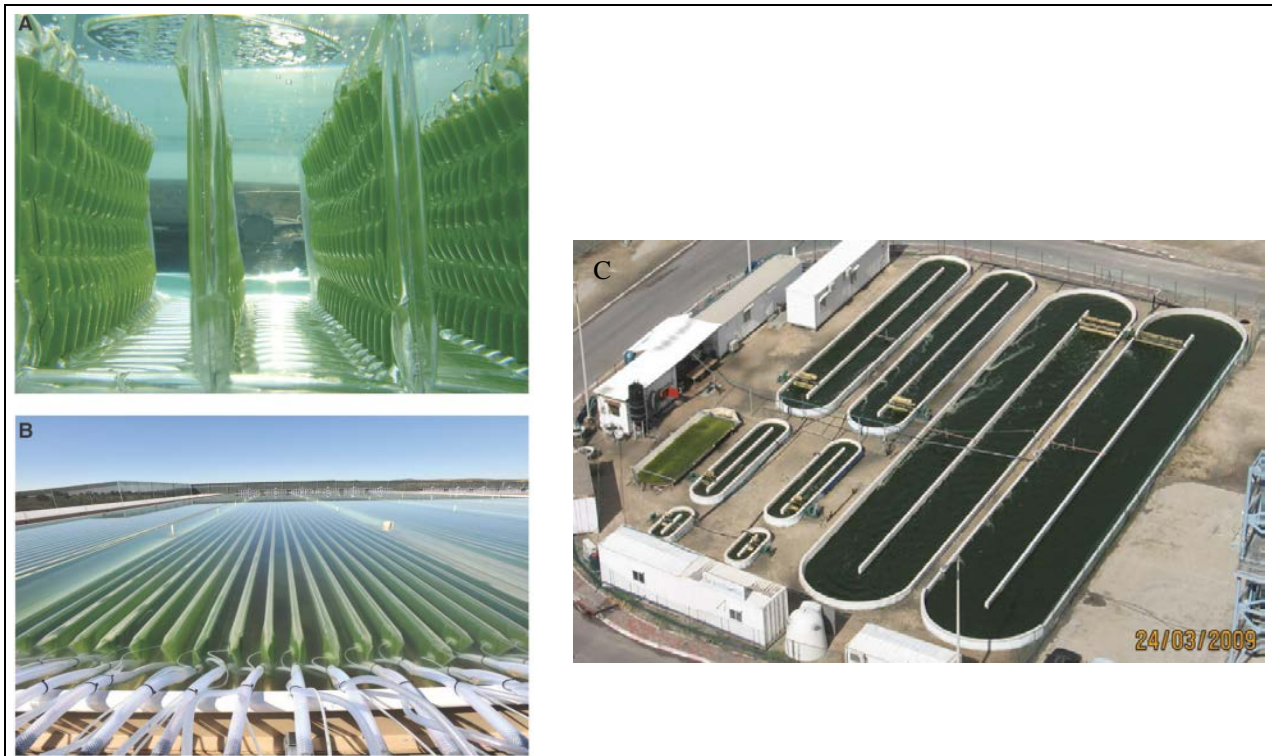


Figure 11: Photobioreactors and raceway systems for microalgae cultivation. (A, B): Flat-panel photobioreactors from Proviron, Belgium and Solix Biofuels, USA.(C): Open large-scale algae culture ponds, Nature Beta Technologies Ltd., Eilat, Israel.  
Source: Greenwell et al., 2009; Wijffels and Barbosa, 2010.

5.5.2.2 Algal Biofuels Process Factsheet

<b>Estimated impact /Net CO<sub>2</sub> considered permanently sequestered (US, MT CO<sub>2</sub>/yr)</b>	Replacement of 0.8* billion gal/yr of biodiesel results in the use of 11* to 40* MT CO <sub>2</sub> /yr (gross), depending on algal productivity
<b>Gross current (equivalent) CO<sub>2</sub> consumption in this use (US), million MT/year</b>	Zero
<b>Projected growth in future CO<sub>2</sub> demand for this application</b>	TBD
<b>Game-changing events/scenarios favorable for this process</b>	Less expensive algal biomass growth and processing, addressing contamination issues with genetically modified strains, higher algal productivity, better use of by-products

Values preceding asterisks are specific to the U.S.A

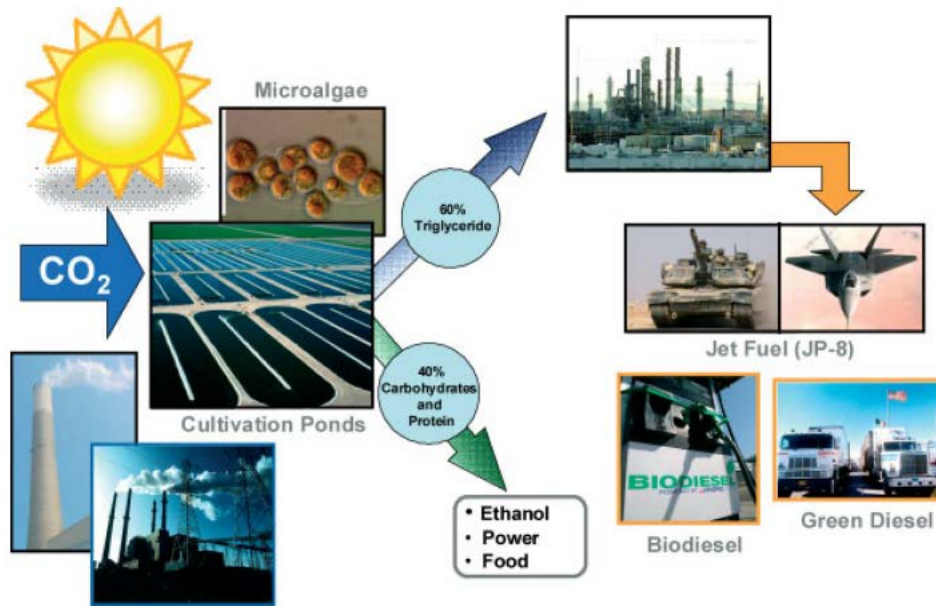


Figure 12. Algal biomass product streams. Source: Pienkos and Darzins, 2009.

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<b>Gross/net CO<sub>2</sub> reduction per tonne of primary CO<sub>2</sub> (<i>mention basis</i>)</b>	Estimates of CO <sub>2</sub> mitigation require a full life cycle analysis
<b>Indirect carbon dioxide impacts (tonnes per tonne)</b>	The fossil energy ratio ( $E^{\text{algal biofuel produced}}/E^{\text{fossil fuel spent}}$ ) of algal biofuels is claimed to be between 3.3 and 7.5 (Chisti, 2009)
<b>Estimated scale of single application (i.e. plant size or field size)</b>	TBD. Depends on light, water, land, CO <sub>2</sub> availability, and temperature. A 100 ha facility may require up to 50 TPD (100%) CO <sub>2</sub> , or equivalent amount of flue gas
<b>Number of deployments at maturity</b>	TBD
<b>Estimated time to full deployment/market saturation</b>	Analyses estimate a time period of 10 to 15 years for full commercialization
<b>Estimated duration of significant impact</b>	Can have a significant impact through the lifetime of the facility because the demand for high energy density liquid fuels would only increase in the future
<b>Cumulative reduction through 2050</b>	TBD. A life cycle analysis would determine CO <sub>2</sub> , and other GHG emissions avoided.
<b>Special requirements on CO<sub>2</sub> (purity, etc.)</b>	Flue gas streams may be used for algal biofuel production after SO <sub>x</sub> removal
<b>Process/Technology Input Raw Materials and/or Energy</b>	CO <sub>2</sub> stream, electrical energy required for operation, nutrients (nitrogen, phosphorus fertilizers), water, sunlight and the availability of land area
<b>Process/Technology Outputs</b>	Algal fuel, spent biomass/methane, water
<b>Any concomitant advantages?</b>	Generates biofuels
<b>Typical costs to deploy (state basis)</b>	TBD. Cost estimates vary by region, algae strain and the exact cultivation methods used. A 100 ha high-rate pond facility which also treats wastewater may cost from 35 to 50 million \$ (Lundquist et al., 2010).
<b>Value of carbon dioxide in this activity</b>	TBD. Site- and algal strain-specific life cycle analyses are required to estimate the net benefits. The costs of algal biofuels vary significantly among various analyses.
<b>Legal/regulatory framework governing use of this option</b>	Any future algal biofuel tax credit (currently none). EPA includes algal biofuels as ‘advanced biofuels’ in the renewable fuels standard



### 5.5.2.3 Chemicals

CO<sub>2</sub> can be used to produce chemicals such as urea, polycarbonates and acrylic acid-derivatives.

#### *Acrylates*

Acrylates are the salts and esters of acrylic acid. Polymers produced from acrylates are called polyacrylates. The various uses of acrylic acid and its derivatives include<sup>99</sup>:

1. Water-based acrylics: Used in decorative, masonry and industrial coatings.
2. Polyacrylates: Used as thickeners, dispersants and for rheology control applications.
3. Superabsorbent polymers (SAP): Superabsorbent polymers (SAP) are cross-linked polyacrylates with the ability to absorb and retain more than 100 times their own weight in liquid. SAPs are used in baby diapers and as soaker pads for packaging poultry, meat, fish and vegetables.
4. Detergent polymers (homopolymer polyacrylates and copolymers of acrylic acid and maleic anhydride): Used with both zeolites and phosphates in washing powder formulations.

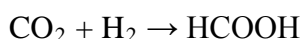
#### *Polycarbonates*

Polycarbonates are polymers containing organic carbonate (-O-(C=O)-O-) groups. One example of the use of CO<sub>2</sub> to produce plastics is the production of polyethylene carbonate (PEC) from ethylene oxide (EtO) and CO<sub>2</sub>. PEC is used as an oxygen barrier layer for food applications. The key innovations here include the development of catalysts which make the production of organic carbonates feasible under mild-temperature and pressure conditions. For example, Novomer is currently commercializing a process to produce PEC from CO<sub>2</sub> and ethylene oxide. Additionally, Bayer has been operating operating a kilogram-scale pilot plant since 2011, at Chempark Leverkusen, Germany, which uses CO<sub>2</sub> from a RWE lignite-fired power plant in Niederaußem, near Cologne, to produce polyether polycarbonate-polyols (PPP) used for the production of the high-grade plastic polyurethane. Industrial production is scheduled to begin in 2015<sup>100</sup>.

The benefits of using PEC instead of conventional barrier resins include a lower environmental footprint, and the capability to recycle CO<sub>2</sub>. PEC barrier layers can be integrated into traditional packaging plastics to enhance food storage and shelf life characteristics.

#### *Formic acid*

The synthesis of formic acid may be represented as:



As with all the CO<sub>2</sub>-to-chemicals applications, the source of hydrogen is assumed to be carbon neutral or renewable energy. The synthesis of formic acid may involve direct-CO<sub>2</sub> reduction by hydrogen gas, or indirect electrochemical reduction of aqueous carbonates or dissolved CO<sub>2</sub>. Processes such as the Mantra electrochemical reduction of carbon dioxide (ERC) belong to the latter category<sup>101</sup>. The nominal-net benefit of

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<sup>99</sup> <http://www.icis.com/v2/chemicals/9074870/acrylic-acid/uses.html>

<sup>100</sup> <http://www.press.bayer.com/baynews/baynews.nsf/ID/2012-0060-e>

<sup>101</sup> Oloman, C. & Li, H., 2007. Continuous Co-current Electrochemical Reduction of Carbon Dioxide. WO 2007/041872 A1. Available at: <http://www.wipo.int/patentscope/search/en/WO2007041872> [Accessed July 27, 2011].

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formic acid production from CO<sub>2</sub> and H<sub>2</sub> is calculated to be approximately \$1075/T CO<sub>2</sub>\*<sup>102</sup>. Det Norske Veritas (DNV) recently demonstrated the small-scale electrochemical reduction of CO<sub>2</sub> to formic acid and formate salts<sup>103</sup>, which adopts a different methodology to estimate CO<sub>2</sub> costs. The cost of CO<sub>2</sub> (\$ 220/T in the DNV study) is listed as a benefit, and the energy cost in the DNV analysis is estimated to be ~420 \$/T formic acid, compared to ~166 \$/T formic acid in the current analysis. With these estimates, the DNV analysis estimates a net nominal benefit of ~\$ 980/T HCOOH, or ~\$937/T CO<sub>2</sub>.

Global production of formic acid was 498,000 T in 2007, with 25,000 T produced in the USA<sup>104</sup>. This represents a CO<sub>2</sub> market of 476350 T/yr or ~0.5 MT/yr CO<sub>2</sub> globally and 0.024 MT/yr CO<sub>2</sub> in the USA. New applications such as hydrogen storage, fuel cells, oil-well completion and airport runway deicing, could increase the demand for formic acid.

### Urea production

The synthesis of urea from ammonia and carbon dioxide is a mature process compared to PEC, acrylate and biofuel production. Ammonia and CO<sub>2</sub> are reacted to form ammonium carbamate which is further dehydrated to form carbamide (urea) H<sub>2</sub>N-(C=O)-NH<sub>2</sub>. Note that ammonia itself is produced by the Haber process from hydrogen (produced by steam reforming of natural gas, or by water gas shift reactions of syngas derived from coal/petcoke gasification) and nitrogen (from cryogenic air separation). Global urea production in 2009 was 147.3 MT, leading to a CO<sub>2</sub> consumption of 109 MT<sup>105</sup>. Urea production in East Asia (including China) was 65.4 MT in 2009. North American urea production in 2009 was 9.7 MT. The annual rate of global growth (averaged for the past seven years) in urea production was 3.3%, compared to -2.3% decline in North American urea production. Global urea production in 2010 was estimated to be 149 MT (Heffer and Prud'homme, 2010)<sup>106</sup>.



Nominal-net benefit: 183\* \$/T CO<sub>2</sub><sup>107</sup>

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<sup>102</sup> 44 T CO<sub>2</sub> requires 2 T H<sub>2</sub> and produces 46 T formic acid. 1 T CO<sub>2</sub> = 1/22 T H<sub>2</sub> = 1/22\*3500 \$ H<sub>2</sub> cost = \$159/T CO<sub>2</sub>. 1 T CO<sub>2</sub> = 46/44 T HCOOH. Formic acid costs are ~1220 \$/T (see Sridhar and Hill, 2011) = 1275 \$/T CO<sub>2</sub>. Net benefit = 1275 – 159 – 40 ~ 1075 \$/T CO<sub>2</sub>.

<sup>103</sup> Sridhar, N. & Hill, D., 2011. Carbon Dioxide Utilization, Electrochemical Conversion of CO<sub>2</sub> – Opportunities and Challenges, Research and Innovation position paper, 07-2011, Available at: [http://www.dnv.com/binaries/DNV-position\\_paper\\_CO2\\_Utilization\\_tcm4-445820.pdf](http://www.dnv.com/binaries/DNV-position_paper_CO2_Utilization_tcm4-445820.pdf). [Accessed 31 March, 2011]

<sup>104</sup> Dunia Frontier Consultants, 2008. Dunia formic acid survey, <http://www.dfcinternational.com/files/DuniaFormicAcidSurvey15June2008.pdf>, [Accessed 31 March, 2011]

<sup>105</sup> [http://www.fertilizer.org/ifa/content/download/7858/122024/version/5/file/2009\\_urea\\_public.xls](http://www.fertilizer.org/ifa/content/download/7858/122024/version/5/file/2009_urea_public.xls)

<sup>106</sup> [http://www.fertilizer.org/ifacontent/download/48774/709486/version/1/file/2010\\_council\\_newdelhi\\_ifa\\_outlook.pdf](http://www.fertilizer.org/ifacontent/download/48774/709486/version/1/file/2010_council_newdelhi_ifa_outlook.pdf)

<sup>107</sup> 44 T CO<sub>2</sub> requires 34 T NH<sub>3</sub> and produces 60 T urea and 18 T water. Ammonia and urea U.S. CFR prices: [470 \\$/T](#) and [430 \\$/T](#) from ICIS. CO<sub>2</sub> price: 40 \$/T. 1 T CO<sub>2</sub> = 34/44 T NH<sub>3</sub> = 60/44 T urea. Raw material costs: 40 + 34/44x470 = 403 \$/T CO<sub>2</sub>. Urea cost: 430x60/44 = 586 \$/T CO<sub>2</sub>. Nominal-net benefit = 586-403 = 183 \$/T CO<sub>2</sub> (negative cost).



*Co-utilization of CO<sub>2</sub> and CH<sub>4</sub> to produce chemicals*

1. The source of hydrogen for the CO<sub>2</sub>-to-chemicals conversion processes discussed is natural gas, or some form of renewable energy. The co-utilization of CO<sub>2</sub> and CH<sub>4</sub> offers the prospect of using methane directly to produce valuable chemicals. Recent developments in shale gas plays have added production and gas reserves to the U.S. natural gas market. In its 'reference case' scenario, the EIA Annual Energy Outlook, 2011 (AEO2011) projects that shale gas would account for 47% of the U.S. natural gas production by 2035. The co-utilization of CO<sub>2</sub> and methane enables the use of two relatively inert gases and produces synthesis gas which can be used to produce chemicals such as methanol. The various routes to use CO<sub>2</sub> and CH<sub>4</sub> are: Tri-reforming of flue gas CO<sub>2</sub> with CH<sub>4</sub> and steam to produce syngas for F-T synthesis (Minutillo & Perna, 2009, 2010)<sup>108,109</sup>.
2. Use of methane as an anode fuel in fuel cells (e.g., FuelCell Energy's direct fuel cell [DFC]<sup>110</sup>) to convert flue gas and fuel to hydrogen and power.
3. Dry reforming of methane with CO<sub>2</sub> and processing the resultant syngas to obtain a CO:H<sub>2</sub> ratio favorable for chemical synthesis (1:2 for methanol) using the reverse water-gas shift reaction. A startup company, Carbon Sciences, Inc. plans to use dry reforming of methane using CO<sub>2</sub> to produce syngas for making fuels<sup>111</sup>. It is claimed that the overall process is close to carbon-neutral and has a low-steam usage, indicating a possible advantage of this process over conventional Fischer-Tropsch synthesis using steam methane reforming.
4. Stepwise production of ethylene (C<sub>2</sub>H<sub>4</sub>) using oxidative coupling of methane (e.g., Siluria process<sup>112</sup>) and subsequent production of plastics (polyethylene carbonates) and other chemicals (acrylic acid) using pure (i.e. separated) CO<sub>2</sub>.

The quantities of CO<sub>2</sub> and natural gas that could be used in the above processes is subject to further technology development.

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<sup>108</sup> Minutillo, M. & Perna, A., 2009. A novel approach for treatment of CO<sub>2</sub> from fossil fired power plants, Part A: The integrated systems ITRPP. *International Journal of Hydrogen Energy*, 34(9), pp.4014-4020.

<sup>109</sup> Minutillo, M. & Perna, A., 2010. A novel approach for treatment of CO<sub>2</sub> from fossil fired power plants. Part B: The energy suitability of integrated tri-reforming power plants (ITRPPs) for methanol production. *International Journal of Hydrogen Energy*, 35(13), pp.7012-7020.

<sup>110</sup> NETL, 2004, Combining power generation and carbon sequestration using a Direct FuelCell®, Available at: [www.netl.doe.gov/publications/factsheets/project/Proj319.pdf](http://www.netl.doe.gov/publications/factsheets/project/Proj319.pdf), [Accessed 10/31/2011].

<sup>111</sup> <http://www.carbonsciences.com/technology.html>, [Accessed: 10/31/2011].

<sup>112</sup> <http://siluria.com/Technology/Process>, [Accessed: 10/31/2011].

## 6 Consumptive Options

These applications involve the formation of minerals, or long-lived compounds from CO<sub>2</sub> leading to net-carbon sequestration by ‘locking-up’ carbon.

### 6.1 Consumptive Uses (Carbonation): Introduction

The conversion of CO<sub>2</sub> to mineral carbonates occurs naturally in the environment, but is exceedingly slow, and does not comprise an effective mitigation or a beneficial use of CO<sub>2</sub>. On the other hand, reactions leading to the formation of mineral carbonates are well understood. For the purposes of this document, the term carbonation refers to the conversion of CO<sub>2</sub> to mineral carbonates. This process requires “alkalinity” (i.e. base capacity) and water. Because magnesium and calcium form more stable carbonates, abundant magnesium- and calcium-silicate minerals (such as serpentine and olivine) have been a focus of previous research on aqueous/non-aqueous carbonation<sup>113,114</sup>. Such processes are energy-intensive, require additional alkalinity (i.e. sodium carbonate or sodium hydroxide addition) and require considerable investment in new plant infrastructure, resulting in high costs per ton of CO<sub>2</sub> converted to carbonate.

Whereas previous research into mineral carbonation assumed the use of high-purity CO<sub>2</sub>, current research efforts also include the use of flue gas CO<sub>2</sub> (10-15%). The use of enzymes such as carbonic anhydrase, which catalyze the hydration of CO<sub>2</sub>, may enhance carbonation rates. As an example, the use of such enzymes to improve the rates of carbonation of waste metal oxides from bauxite ore processing is being studied by Alcoa. The use of additional alkalinity generated by electrolysis of brines or saltwater to form alkali and alkaline-earth metal carbonates is being investigated by Skyonic and Calera. A process to cure precast concrete products in the presence of humid CO<sub>2</sub> is being developed by McGill University using the solvent technology of 3H Company to capture CO<sub>2</sub>. Finally, a process for carbonation of slag from steelmaking and the production of magnesium-based supplementary cementitious materials (Novacem) are also discussed. The primary benefits from the consumptive uses are comprised of avoided-CO<sub>2</sub> emissions (use of mineral carbonates, and various by-products such as hydrogen, chlorine and aggregate), and the sale of the mineral carbonates and by-products. These process-specific factsheets are included in the Appendix. A summary of various carbonation processes is presented in Table 12.

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<sup>113</sup> Metz, B. et al. eds., 2005. IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage, Chapter 7. Prepared by Working Group III of the Intergovernmental Panel on Climate Change, Cambridge University Press, 442pp and references therein.

<sup>114</sup> O’Connor, W.K., D.C. Dahlin, G.E. Rush, S.J. Gledermann, L.R. Penner, D.N. Nilsen, 2005. Aqueous mineral carbonation, Final Report, DOE/ARC-TR-04-002.

## 6.2 Metrics

Table 11. Consumptive Uses, Carbonation

Carbonation Process	CO <sub>2</sub> Mitigation		Benefits	Energy Consumption			Market Potential		Benefit * Market Size, billion \$/y
	(A) Amount of Captured CO <sub>2</sub> utilized	(B) CO <sub>2</sub> Capture in-built?		(C) Value of by-products (\$/T CO <sub>2</sub> )	(D) Energy required for capture and disposal	(E) Energy penalty/gain for by-product process	(F) CO <sub>2</sub> emissions avoided	(G) Market Size	
<b>Skyonic</b>	Cl <sub>2</sub> : 14* MT/y Na <sub>2</sub> CO <sub>3</sub> : 20 MT/y H <sub>2</sub> : 836* MT/y <sup>115</sup> Algal biofuels: 578* MT/y, 4842 MT/yr (global -direct) <sup>[ Total Available Markets ]</sup>	Yes	Na <sub>2</sub> CO <sub>3</sub> : ~\$300/T, H <sub>2</sub> : ~\$10/T Cl <sub>2</sub> : ~\$240/T	1.456 MWh/T <sup>(NG-fired gen)</sup>	20%	2.91 T CO <sub>2</sub> /T CO <sub>2</sub>	See (A). A fraction of this could be supplied	Direct: Displaces natural Na <sub>2</sub> CO <sub>3</sub> or CaCO <sub>3</sub> used in Solvay process	3.4* to 9* <sup>116</sup>
<b>Alcoa</b>	2* to 23* MT/y	Yes	\$10 to \$300/T	NA	NA	NA		NA	~500* <sup>117</sup>
<b>Calera</b>	1500 MT/y sand and aggregate market: 3 billion T U.S. cement (20% share): 24 MT/y (of SCM w/ 50% w/w CO <sub>2</sub> )	Yes	Aggregate: \$7/T (i.e. \$14/T CO <sub>2</sub> overall) \$100/T cement	0.08 to 0.28 T CO <sub>2</sub> emitted/T CO <sub>2</sub> captured	8 to 28%	0.5 T CO <sub>2</sub> /T CO <sub>2</sub>		Displaces CaCO <sub>3</sub> for cement, replaces aggregate	21* <sup>118</sup>
<b>Concrete Carbonation</b>	2 to 8 million T/y*	No		0.2 T CO <sub>2</sub> emitted/T CO <sub>2</sub> converted	See (D)	NA		NA	NA

<sup>115</sup> Large quantities of hydrogen and algal biofuels would require tremendous infrastructure investments on top of the investment in CO<sub>2</sub> infrastructure.

<sup>116</sup> U.S. Cl<sub>2</sub>: [240x14] 3.4 billion \$/yr. Global Na<sub>2</sub>CO<sub>3</sub>: (20x300) 6 billion \$/yr. U.S. H<sub>2</sub> (replacing NG): 836x10 ~8.4 billion \$/yr

<sup>117</sup> Potentially in the 10s of MT CO<sub>2</sub>/yr x 50 \$/T CO<sub>2</sub> range

<sup>118</sup> U.S. aggregate market: 1.5x14 = 21 billion \$/yr, U.S. Portland cement market: 24/0.5x100 = ~5 billion \$/yr

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Carbonation Process	CO <sub>2</sub> Mitigation		Benefits	Energy Consumption			Market Potential		Benefit * Market Size, billion \$/y
	(A) Amount of Captured CO <sub>2</sub> utilized	(B) CO <sub>2</sub> Capture in-built?	(C) Value of by-products (\$/T CO <sub>2</sub> )	(D) Energy required for capture and disposal	(E) Energy penalty/gain for by-product process	(F) CO <sub>2</sub> emissions avoided	(G) Market Size	(F) CO <sub>2</sub> subjected to capture & storage	
<b>Slag Carbonation</b>	7 to 18 MT/y, 0.5* to 1.3* MT/y	Currently no, possible	NA	0.14 T CO <sub>2</sub> w/ gridding slag/T CO <sub>2</sub> captured	NA		See (A). A fraction of this could be supplied	NA	TBD
<b>Novacem</b>	2130 MT/y <sup>(100% market share)</sup> , 54* MT/y	No	Cement: \$100/T cement blended	TBD					
<b>Cambridge Carbon Capture</b>	50 to ~1000 MT/y	Yes	NA						
<b>Calix</b>	2* to 23* MT/y	Yes	Cement fertilizer		Claimed 17% for syngas and ~7% for natural gas				

Various consumptive uses, or applications where CO<sub>2</sub> is converted into products with a long-life, form the basis for the third category of CO<sub>2</sub> uses. Several processes currently being developed to convert CO<sub>2</sub> to sodium or calcium/magnesium carbonates/bicarbonates were evaluated. In general, consumptive uses may have the potential to use or mitigate large quantities (billions of tonnes per year globally) of CO<sub>2</sub>. However, larger scale demonstration pilots are needed to evaluate their feasibility. In addition to mineral carbonates, other by-products from consumptive-use processes include chlorine, hydrogen, soil amendments, fertilizers, and building materials. Nominal-net benefits from consumptive uses vary from \$10 to \$300/T CO<sub>2</sub> depending on the product.

Table 12: An Overview of Various Carbonation Processes

	<b>Processes converting CO<sub>2</sub> to sodium carbonates (Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>)</b>	<b>Processes converting CO<sub>2</sub> to calcium and magnesium carbonates</b>		
<b>Source of base capacity</b>	NaOH produced by electrolysis of brine	Brine electrolysis, fly ash, alkaline waste, metal silicates, calcinations of dolomite	Calcium silicate hydrolysis producing lime	Fly ash, bauxite processing waste (red mud)
<b>Inputs</b>	Brine, CO <sub>2</sub> from flue gas	Brine, alkaline waste, dolomite, fly ash, metal silicates, CO <sub>2</sub> from flue gas, hydrocarbons	Pure, high-pressure CO <sub>2</sub> , concrete, water	CO <sub>2</sub> in flue gas, alkaline waste, fly ash, water
<b>Products</b>	Baking soda, soda ash, hydrogen, chlorine	Mixture of hydrated calcium and magnesium carbonates, calcium and magnesium oxides; carbonated silicate mineral, silica, electrical energy, fresh water	‘Cured’ concrete blocks (surface layer of calcium carbonate)	Mixture of sodium, calcium and magnesium carbonates, and other minerals including silica
<b>Primary product use</b>	Glass manufacture, source of CO <sub>2</sub> for microalgae cultivation, bleach, fuel	Cementitious material to blend with Portland cement, or for use as a custom binder material, or as aggregate, or a soil amendment	Precast concrete industry	Soil amendment, fertilizer
<b>Projected growth in future CO<sub>2</sub> demand</b>	Soda ash global demand: 1.5 to 2%, hydrogen demand growth may exceed that of soda ash	U.S. cement/aggregate: 1.1% to 1.6% World cement demand: 5% to 6%		Aluminum production grew at 5% per year historically (U.S.)
<b>Value of product</b>	\$10* to \$300* /T CO <sub>2</sub>	10 to 300 \$/T product	TBD	TBD, soil remediation products are priced similar to limestone
<b>Time duration of significant impact</b>	5 to 20 years depending on the economic incentives for each particular application			

## 7 Conclusions

This summary presents a survey of an emerging area of practical interest – the reuse and consumption of carbon dioxide. Although this has long been viewed as an attractive concept, most assessments have not found beneficial uses for carbon dioxide anywhere close to the scale of anthropogenic emissions of this greenhouse gas and therefore have suggested maintaining primary focus on large-scale capture and geologic storage. However, careful review of the full range of beneficial uses suggests that the contribution of these approaches might serve to both jump-start development of the infrastructure needed to manage large amounts of captured carbon dioxide (the chicken-and-egg problem) and to lessen the total social cost from this activity. Some of the beneficial use processes may fall under the purview of different environmental regulations compared to geologic CO<sub>2</sub> storage because they avoid the need for subsurface disposal (e.g., Calera or Skyonic processes). Comprehensive environmental assessments of all beneficial use processes are required to evaluate impacts on site permitting, operator liabilities, and facility operations.

Development of this document started with a review of previous work and an attempt to establish metrics that bridged across the wide range of uses for carbon dioxide – some that consume the carbon dioxide forming new chemical compounds, some that simply raise the useful energy extracted from the carbon-containing fuel that was reacted to form carbon dioxide, while leaving the CO<sub>2</sub> molecule in its original form (before being stored via sequestration), and another collection of ideas that would both tie the pieces of a carbon dioxide infrastructure together and perhaps improve the overall energetic efficiency of the carbon-based energy system. Primary considerations in establishing these metrics were:

- Total amount of CO<sub>2</sub> permanently sequestered
- Unit value (benefit) or cost of application
- Energy consumed by the application (or net-CO<sub>2</sub> savings from the technology)
- Market Potential of primary CO<sub>2</sub> use and any by-products

This summary has sought to discuss general categories of each of these aspects and to provide more significant detail on individual processes or pathways under the major headings. Where available, data on the potential market size and benchmark numbers for the value of any by-products or the energy benefits of a process are reported on a basis to allow comparisons. In the course of this study, certain technologies claimed to be competitive with geologic CCS. Some of the factors contributing to uncertainties in the costs and efficiencies of beneficial-use processes include:

1. Lack of operational experience with some technologies, and technology scalability issues, impacting capital and operational cost estimates,
2. Uncertain market incentives or costs for the end products,
3. The need for infrastructure and/or raw materials to capture or transport CO<sub>2</sub> on a large scale,

Several major conclusions become apparent:

1. No single application is capable of consuming major fractions of current or projected CO<sub>2</sub> emissions. This conclusion is certainly not new and has been stated by others in past assessments. Over the next several decades, large potential beneficial impacts (\$/T CO<sub>2</sub>eq) could be realized by the use of CO<sub>2</sub> to produce sources of raw material, fuels or chemicals. Hydrocarbon resource extraction (specifically, EOR) using advanced technologies could potentially result in a considerable demand for CO<sub>2</sub>.

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2. Use of carbon dioxide for hydrocarbon resource recovery presents the largest opportunity in terms of the amount that might be used annually but this sink has a finite lifetime. Estimates both the potential amount of carbon dioxide that could be utilized (then stored) and the economic value are considerable. Depending upon the scenario, the U.S. CO<sub>2</sub>-EOR potential demand could be 16 to 22.3 billion metric tonnes of carbon dioxide between now and 2050 with an average annual value in oil recovered of between \$4 and \$10 billion dollars. The global potential is larger, but was not quantified in this work.
3. The use of carbon dioxide to produce fuels is limited by the cost of hydrogen, or the relatively high cost of producing fuels from photosynthetic microorganisms. On the other hand, the production of chemicals is relatively more 'beneficial', although the amount of CO<sub>2</sub> used in these processes can be considerably lower than the CO<sub>2</sub>-to-fuels applications.
4. The use of CO<sub>2</sub> to produce chemicals, which have a slightly higher value compared to fuels is constrained by the difference in the cost of energy (hydrogen, electricity) required to produce the chemical and the price of the chemical. A DNV report notes that formic acid and carbon monoxide have a higher value from the energy required for their synthesis than conventional fuels such as methanol, ethylene and methane.
5. Other consumptive uses hold potential to provide a sustainable sink for carbon but the market size for these applications is far more limited, based on current markets, than resource recovery options and important aspects of the various relevant process chemistries need to be proven at scale. For instance, a series of carbonation processes claim benefits ranging between \$10 to \$300 per ton of carbon dioxide used, depending upon the products produced, but may consume as little as 20 million metric tonnes or up to 1.5 billion metric tonnes of carbon dioxide in a year if they saturate their target markets.
6. Carbonation approaches, which produce building materials or aggregates, still need to be demonstrated at a scale sufficient to prove their commercial viability. This sector of the economy consumes substantial quantities of these raw materials (concrete, aggregates, etc.) surpassing billion ton quantities globally. On the other hand, processes producing carbonates which cannot be used as building materials or aggregate (soda ash, baking soda) may mitigate CO<sub>2</sub> to a lesser extent. In the latter processes, the highest value, or quantity by-products, for instance hydrogen, present their own difficulties in developing the necessary infrastructure.
7. A number of other uses for carbon dioxide might offer indirect benefits through improved energy efficiency, through production of potable water from produced, saline waters, or simply by raising the efficiency of power cycles. These applications could improve overall efficiency from a system point of view.
8. In general, the resource recovery options are better understood, and closer to practical application. For many of the other opportunities, more work remains before they are technologically mature in applications that would use large amounts of carbon dioxide or yield substantial economic benefits.

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Novel approaches to reuse CO<sub>2</sub> continue to draw the attention of researchers. A recent publication<sup>119</sup> presents a summary of various efforts to use carbon dioxide in chemical synthesis, and notes that synthesis could account for up to 7% of global CO<sub>2</sub> emissions. Similarly, Rice University recently announced an initiative to explore uses of carbon dioxide<sup>120</sup>. Investors are also taking interest in CO<sub>2</sub> reuse. Biological, chemical and catalytic, and mineralization approaches to re-use CO<sub>2</sub> are described in a report by Prize Capital LLC<sup>121</sup>. One of the focus areas of the Joint Center for Artificial Photosynthesis (JCAP), a U.S. DOE Energy Innovation Hub, is the production of solar fuels from CO<sub>2</sub><sup>122</sup>. Therefore, this compendium of options is a snapshot in time which could be updated in the future as new advancements occur.

Finally, it is essential to apply sound analytic methodologies to assess the potential for use of any concept and to estimate the full range of benefits. Typical benefits include the amount of net-carbon dioxide removed from the atmosphere, the duration of such storage (if it is not consumed), the potential market value of a use, and the net-energetic impact. In the metrics tables, we refer to the need to apply sound life cycle assessment methodologies to appreciate the benefits (if any) of a candidate beneficial use. Some of the options discussed in this report involve incremental improvements to existing CO<sub>2</sub>-use processes, whereas others are ‘grey swans’, i.e. predictable high-risk, high-reward developments.

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<sup>119</sup> Aresta, M. ed., 2010. Carbon Dioxide as Chemical Feedstock, Wiley-VCH.

<sup>120</sup> Tour, J.M., Kittrell, C. & Colvin, V.L., 2010. Green carbon as a bridge to renewable energy. Nature Materials, 9(11), pp.871-874.

<sup>121</sup> Prize Capital LLC, 2011. Carbon capture and recycling industry overview.  
[http://www.prizecapital.net/Prize\\_Capital/CCR\\_Industry\\_Overview\\_Report.html](http://www.prizecapital.net/Prize_Capital/CCR_Industry_Overview_Report.html)

<sup>122</sup> <http://solarfuelshub.org/home>



## 8 Appendix

### Supporting documentation: Conversion of CO<sub>2</sub> to fuels and organic chemicals

#### CO<sub>2</sub> to Gasoline

44 T CO<sub>2</sub> = 14 T gasoline = 4939 gal gasoline. 138 billion gal/yr gasoline = 1229 million T CO<sub>2</sub>/yr. Synthetic hydrogen cost from Graves et al., 2010: 6 c/kWh, 53.5 kWh/kg H<sub>2</sub>. H<sub>2</sub> cost: 3.5 \$/kg H<sub>2</sub>. Gasoline cost: 2.4 \$/gal ([EIA](#), accessed 1/6/11). Gasoline demand: 138 billion gal/yr (<sup>378E6 gal/d</sup>, [EIA](#), accessed 1/6/11) = 391 million T/yr. 44 T CO<sub>2</sub> = 6 T H<sub>2</sub>. 1 T CO<sub>2</sub> = 6/44 T H<sub>2</sub> = 0.136 T H<sub>2</sub> = 0.136\*3500. Value of H<sub>2</sub> is 477.3 \$/T CO<sub>2</sub>. Sales value of gasoline is 378 million gal/d \* 2.4 \$/gal /3.233 million T CO<sub>2</sub>/d = 270 \$/T CO<sub>2</sub>. Net cost = -270 + 40 + 477.3 ≈ 247 \$/T CO<sub>2</sub>, or ca. 2200 \$/gal gasoline.

#### CO<sub>2</sub> to Diesel

44 T CO<sub>2</sub> = 14 T diesel = 4448 gal diesel. Diesel volume: 42x10<sup>9</sup> gal/yr = 416 million T CO<sub>2</sub>/yr. Diesel cost: 2.5 \$/gal ([EIA](#), accessed 1/6/11) = 105E9 \$/yr. This consumes 414E6 T CO<sub>2</sub>/yr. Gross benefits = -281 \$/T CO<sub>2</sub>. H<sub>2</sub> and CO<sub>2</sub> used in diesel cost the same as that used for gasoline. So net costs = -280 + 40 + 477 \$/T CO<sub>2</sub> = -237 \$/T CO<sub>2</sub>

#### CO<sub>2</sub> to Methanol

44 T CO<sub>2</sub> = 32 T methanol. Methanol market: 8 million T MeOH/yr ([Methanex](#), accessed 1/6/11) = 11 million T CO<sub>2</sub>/yr. Methanol cost: 449 \$/T ([Methanex](#), accessed 1/6/11). Gross benefit: 449 \$/T MeOH\*8 million T MeOH/yr/11 million T CO<sub>2</sub>/yr = 327 \$/T CO<sub>2</sub>. H<sub>2</sub> and CO<sub>2</sub> costs the same as in diesel and gasoline production, 477 \$/T CO<sub>2</sub> and 40 \$/T CO<sub>2</sub>. Net cost = -327 \$/T CO<sub>2</sub> + 40 \$/T CO<sub>2</sub> cost + 477 \$/T CO<sub>2</sub> (hydrogen cost) = 190 \$/T CO<sub>2</sub>

#### CO<sub>2</sub> to Acrylic acid

U.S. acrylic acid capacity is ~1.2 million T/yr ([ICIS](#), accessed 1/6/11). 44 T CO<sub>2</sub> = 72 T acrylic acid (CH<sub>2</sub>=CH-COOH). Ethylene price from [ICIS](#) (accessed 1/6/11): 1135 to 1180 \$/T ethylene. 1 T CO<sub>2</sub> = 28/44 T ethylene = 28/44x1180 = 751 \$/T CO<sub>2</sub>. 44 T CO<sub>2</sub> = 72 T acrylic acid. Acrylic acid price from [PUDaily](#) (accessed 1/6/11): 1698 \$/T GAA. 1 T CO<sub>2</sub> = 72/44 T GAA = 72/44\*1698 = 2779 \$/T CO<sub>2</sub>. Net cost = -2779 (GAA cost)+ 40 (CO<sub>2</sub> cost)+ 751 (ethylene cost) = -1988 \$/T CO<sub>2</sub>. Net benefit = 1988 \$/T CO<sub>2</sub>

#### CO<sub>2</sub> to Polyethylene carbonate (PEC)

Polyethylene carbonate (PEC) market size in the U.S.: 5 million tonnes/year. CO<sub>2</sub> consumption: 5/2 = 2.5 million tonnes/year. Ethylene oxide (EtO) cost: 1200 \$/T, CO<sub>2</sub> cost: 40 \$/T, PEC cost: 1000 \$/T. Costs per ton of CO<sub>2</sub> are: 1200+40 = 1240 \$/T CO<sub>2</sub>. Value/T CO<sub>2</sub>: 1000x2 = 2000 \$/T CO<sub>2</sub>. Gross costs = -760 \$/T CO<sub>2</sub>. Gross benefits (negative costs): 2000 - 1240 = 760 \$/T CO<sub>2</sub>.

## Algae Fuels

Table A-1: Summary of various algae technologies producing value-added fuels, chemicals and raw materials from photosynthetic microorganisms

	Biofuel Production from Algae		Multiple-purpose Algae Technologies
	Raceway Systems/ Hybrid Systems	Closed Systems/Photobioreactors (PBR)	
<b>Yield, gallons of 'oil'/acre/year</b>	Hybrid systems may achieve 10,000 gal/acre/yr <sup>123</sup> , raceway ponds ~3,000-5,000	Up to 15,000	NA
<b>Yields, g dry, ash-free biomass/m<sup>2</sup>/d</b>	10 to 50	Higher than 10 to 50	NA
<b>CO<sub>2</sub> Re-used, T/acre/year (2 g CO<sub>2</sub>/g biomass)</b>	30 to 150	Higher than 30 to 150	NA
<b>Type of algae/microorganisms</b>	Cultured strains, genetically engineered microalgae, cyanobacteria and other microbes		Wild/cultured strains of microalgae and other photosynthetic microorganisms
<b>Current State of Development</b>	Four companies received U.S. DOE funding for pilot-scale biorefineries processing algae in 2010.		
<b>Inputs</b>	Salt/brackish water, nutrients, CO <sub>2</sub> , algal cultures, biomass/sunlight		Municipal wastewater, marine/brackish water (little additional nutrients)
<b>Cell Harvesting and Dewatering</b>	Processes include centrifugation, vacuum filtration	Some may not require separation, others may use mechanical/chemical processes	Fish feeding on microalgae, wild algae harvesting/processing/refining
<b>Product Recovery &amp; Refining</b>	Solvent extraction, in vivo/ex vivo fermentation, transesterification, biocrude processing at refineries (hydrogenation, cracking/thermal pyrolysis, decarboxylation), gasification and anaerobic digestion of spent biomass		Fish processing, biocrude processing/refining operations similar to the open/closed systems
<b>Products</b>	Ethanol, liquid hydrocarbons, biodiesel, petroleum		Omega-3 fatty acids, fish feed, fish protein, algal protein, biopolymer

<sup>123</sup> See Huntley and Redalje, 2006 for an estimate of the potential performance of a coupled system of photobioreactors and open-pond batch cultures.

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	diesel, methane, dry process fuels, and electricity	precursors, treated waste water, petroleum fractions, specialty solvents, surfactants	
<b>Representative Examples</b>	PetroAlgae, Sapphire Energy, HR BioPetroleum	Solix, Joule Unlimited, Algenol, Solazyme	Aurora Algae, Aquaflow/UOP, Live Fuels

In a recent conceptual study of biofuel-focused algae production using wastewater, Lundquist et al. estimated production costs of 240 to 330 \$/bbl (of biodiesel) for a site located in California. In comparison, cases where algae production was considered as a part of wastewater treatment, the production costs were considerably lower, at 28 \$/bbl of biodiesel. The use of spent algal biomass as animal feed, or for the production of high-value products such as carotenoids and pigments could improve the economics of algal biofuel production.

However, Lundquist et al. (2010) note that the market demand for high-value products such as pigments, is somewhat limited (order of tons) and would be easily overcome by large-scale algal biofuel production. The use of algal biomass to produce animal feed would require additional processing steps, including the removal of heavy metals, which would increase capital and operating costs. Reducing the costs of algae cultivation, harvesting, oil extraction and further processing are required to commercialize large-scale algal biofuel production and the beneficial use of CO<sub>2</sub>. In Table A-1, the technologies are arbitrarily classified based on algae productivity, as: (1) raceway systems/hybrid systems, (2) closed systems/photobioreactors for producing algal biofuels and, (3) multi-purpose algae technologies whose end products include biofuels, fine chemicals, protein, wastewater treatment and other uses.

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