

**UTILIZATION OF CARBON DIOXIDE FROM
COAL-FIRED POWER PLANT FOR THE
PRODUCTION OF VALUE-ADDED PRODUCTS**

*Yan Li
Brandie Markley
Arun Ram Mohan
Victor Rodriguez-Santiago
David Thompson
Daniel Van Niekerk*

Submitted in partial fulfillment of the requirements for the Design Engineering of Energy
and Geo-Environmental Systems Course (EGEE 580)

April 27, 2006

ABSTRACT

In this project we will discuss a few promising physical and chemical technologies for the utilization and conversion of CO₂ from a power plant into viable economic products. This task has been performed as part of a broader effort to appreciate the global concerns of increasing atmospheric concentrations of CO₂ and particularly the role of the recovery and utilization of CO₂ from industry. This project will be used in part towards development of a solution for optimal CO₂ utilization.

Various existing and future utilization technologies were explored in this project for optimum CO₂ utilization. The main areas of interest were microalgae biomass production (pond and bioreactor production), supercritical CO₂ extraction technology, fixation of CO₂ into organic compounds (production of various chemical products), and CO₂ reforming of methane. The feasibility of these processes was evaluated according to their thermodynamics, energetics, production rates and yields, product values and economics.

The value-added products that can be produced from these four main technologies are: biomass (high and low grade), biomass derived products (pharmaceutical, chemical or nutritional), synthesis gas (methanol, fuel and chemical production), specialty products (extracted using supercritical technology), organic carbonates (linear, cyclic or polycarbonates), carboxylates (formic acid, oxalic acid, etc), salicylic acid and urea.

It should be noted that the amounts of CO₂ consumed for making the chemical products are relatively small, but the advantages of the value-added products and the environment-friendly processing plus the CO₂ avoidance compared to the conventional energy-intensive or hazardous processes make CO₂ utilization an important option in CO₂ management.

In conclusion, there are various methods that can be employed to utilize the inherent value of CO₂. Any of the methods proposed in this project can make use of CO₂ to produce value-added products in environmentally friendly ways.

Table of Contents	<u>Page</u>
Abstract	2
Table of Contents	3
1 Introduction	5
2 Biological utilization	6
2.1 Algal mass culture pond systems	6
2.1.1 Introduction	6
2.1.2 Microalgae and seaweed selection for CO ₂ fixation	6
2.1.3 Pond location and climatic conditions	8
2.1.4 Technical aspects of pond design	8
2.1.5 Evaluation of different ponds	11
2.1.6 Pond design for mass culture <i>Spirulina</i>	12
2.1.7 Growth of microalgae and mass balance	16
2.1.8 Harvesting of biomass	18
2.1.9 Economics of algal biomass (<i>Spirulina</i>)	19
2.1.10 Conclusions	20
2.2 Biological utilization of CO ₂ via bioreactors	21
2.2.1 Introduction	21
2.2.2 Types of bioreactors	21
2.2.3 Selection of microalgae species	25
2.2.4 Biomass recovery	26
2.2.5 Value-added products	27
2.2.6 System design	29
2.2.7 Conclusions and recommendations	33
3. Utilization of supercritical carbon dioxide	35
3.1 Supercritical carbon dioxide	35
3.1.1 Introduction	35
3.1.2 Extraction of compounds from microalgae using scCO ₂	36
3.1.3 Other supercritical CO ₂ applications	41
3.1.4 Catalysis	46
3.1.5 Environmental remediation	47
3.1.6 Concluding remarks	50
4. Chemical utilization	51
4.1 Carbon dioxide fixation into organic compounds	51
4.1.1 Introduction	51
4.1.2 Principle industrial process of carbon dioxide utilization	51
4.1.3 Existing processes of carbon dioxide utilization	52
4.1.4 Prospective uses of carbon dioxide utilization	60
4.1.5 Conclusions	65
4.2 Electrochemical utilization of carbon dioxide	66

4.2.1 Introduction	66
4.2.2 Aqueous solution	66
4.2.3 Non-aqueous solution	68
4.2.4 Effect of electrode types and characteristics	68
4.2.5 Economic and energetic aspects	71
4.2.6 Advantages and disadvantages	72
4.2.7 Key issues	73
4.2.8 Electrochemical production summary	73
4.3 Carbon dioxide reforming of methane	75
4.3.1 Introduction	75
4.3.2 Carbon dioxide reforming of methane	75
4.3.3 Methanol from CO ₂	77
4.3.4 Dimethyl carbonate from methanol	77
4.3.5 Biodiesel production using methanol	78
4.3.6 Tri-reforming	79
4.3.7 Solid oxide fuel cell – GT combined cycle	82
4.3.8 Tri-reforming to produce chemicals	83
4.3.9 Conclusions and recommendations	85
5. Conclusions	86
6. References	87
7. Appendix	99

1. Introduction to project

1.1 Problem statement

Can value be added to current processes or emerging technologies to generate valuable products by the utilization of CO₂? Emphasis has been placed on value added products and processes and not in the amount of CO₂ utilized. The overall scheme for this project is shown in Figure 1.1.1.

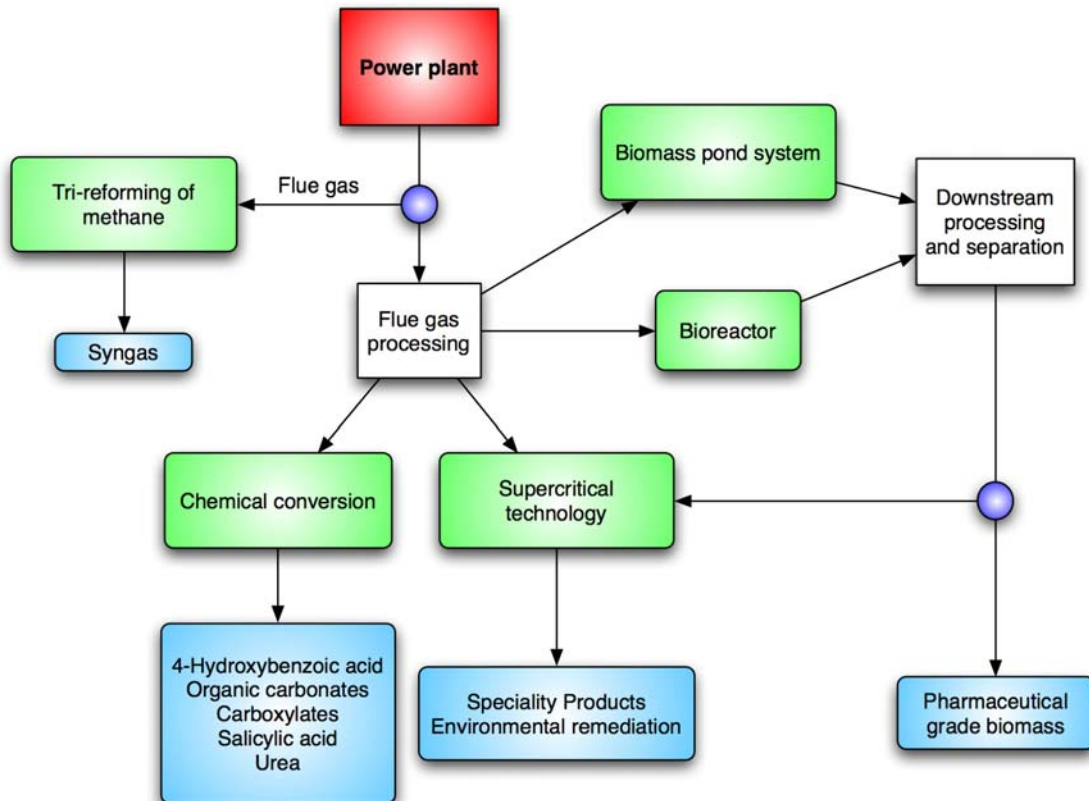


Figure 1.1.1: Overview of CO₂ utilization project.

1.2 Project assumptions

The amount of CO₂ emitted from a 500 MW coal-fired power plant is assumed to be 9.0×10^6 kg CO₂/day (9.0 ktons CO₂/day) or 3.3×10^9 kg CO₂/yr (3.3 Mtons CO₂/yr). It is also assumed that the power plant is operating 365 days/yr and the individual proposed CO₂ utilization methods (biological, supercritical, and chemical) are operating 365 days/yr unless otherwise stated. Each method incorporates reasonable assumptions where necessary to optimize process conditions and to predict present and future trends and values.

2. Biological utilization

2.1 Algal mass culture pond systems

2.1.1 Introduction

Carbon dioxide from various industrial sources (power plants, chemical industries, etc) can be converted to biomass using algal mass culture pond systems. The main advantage of using pond systems is that the technology is very well known and various commercial systems already exist.¹⁻⁴ Algal pond systems are currently the most economic method to produce biomass on a large scale.¹⁻⁴ For the effective conversion of CO₂ to biomass, studies have to be conducted to define growth characteristics of various organisms (microalgae and seaweed). The products obtained from algal mass culture can be of very high value (for example, pharmaceutical or food grade *Spirulina* or *Chlorella*).^{1, 4-7} Extraction technologies of algal biomass can provide very valuable bio-pharmaceuticals (antioxidants, carotenes, etc) and specialty products (toxins, coloring agents, etc).^{1, 4-7} To illustrate the design process for mass culture pond systems, the production and processing of *Spirulina platensis* will be discussed.

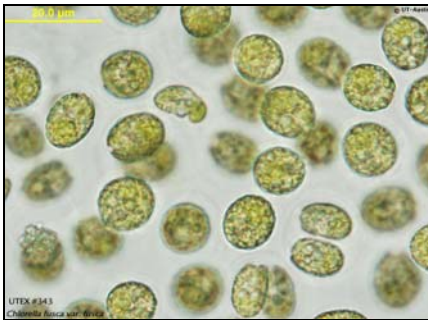
2.1.2 Microalgae and seaweed selection for CO₂ fixation

Microalgae can be isolated from various diverse sources, including rivers, lakes, ponds, springs, soil, seawater, basically anywhere in the world.^{1-4, 8, 9} Effective CO₂ fixing organisms must be selected from these samples using various selective growth conditions (CO₂ tolerance, temperature, etc).^{8, 10, 11} A few microalgae species that are commercially used are discussed in Table 2.1.1.

Microalgae and seaweed species must be selected that show optimum growth with CO₂ as the carbon source and that can be cultivated at moderate temperatures and pH. Some organisms have been isolated using flue gas, but studies to date have only been performed at a bench-scale (currently, no commercial ponds use flue gas).^{8, 10, 11} One of the major problems with using power plant flue gas, is the lowering of the pH of the pond due to NO_x and SO_x species present.^{8, 10, 11} The pH can be controlled in a pond system by the addition of CaCO₃.^{8, 10, 11} Two very promising organisms are *Chlorella sp.* (Figure 2.1.1) and *Spirulina platensis* (Figure 2.1.2).

Table 2.1.1: Various organisms used to produce biomass.

Microalgae	Description/growth parameters ^{3, 4, 9}
<i>Spirulina platensis</i>	<p>Spirulina is a multicellular, filamentous blue-green algae.³ Various commercial <i>Spirulina</i> production plants currently in operation.^{1-4, 12}</p> <p>Growth rate : 30 g/m²·day dry weight.</p> <p>Temperature : Optimum between 35 – 37 °C.</p> <p>pH : 8.3 - 11.^{3, 4} Very tolerable to pH change.</p>
<i>Chlorella sp.</i>	<p>Chlorella is a unicellular organism that can be found in almost any water environment (fresh water and marine).</p> <p>Growth rate : 26 g/m²·day dry weight.</p> <p>Temperature : 35 – 37 °C (depending on specie).</p> <p>pH : Depends on specie.</p>
<i>Enteromorpha clathrata</i>	<p><i>Enteromorpha</i> is a marine seaweed that can be grown in shallow ponds.⁹ Very little agitation is needed.</p> <p>Growth rate : 28 g/m²·day dry weight.</p> <p>Temperature : Optimum between 24 – 33 °C.</p> <p>pH : 7.5 - 8.0.⁹ Relative pH sensitive.</p>

Figure 2.1.1: *Chlorella fusca*.¹³Figure 2.1.2: *Spirulina platensis*.¹⁴

Seaweed, when compared to other biomass production, has a higher growth rate and yield.^{9, 15} The major advantage of seaweed biomass production is the amount of genera that are known and that are currently being commercially grown.¹⁵ Seaweed production has the advantage that cultivation can either take place in a pond system or directly in the sea.¹⁵ In this study, we will not be considering production directly in the sea due to environmental constraints and concerns. Most commercial seaweed farms cultivate seaweed in the ocean near the coast. Recently, studies have been conducted to determine the effect of this farming on the surrounding marine ecology.¹⁶ It was found that intensive seaweed farming could affect natural sea grass growth and this may disturb important ecosystem functions.¹⁶

2.1.3 Pond location and climatic conditions

Tropical or semi-tropical areas are the most practical locations for algal mass culture systems.³ The location chosen for construction has to consider the following:

- Evaporation
Evaporation is a significant problem in dry tropical areas (where the evaporation rate is higher than the precipitation rate).¹ A high evaporation rate increases salt concentration and pumping costs due to water loss.¹
- Precipitation
A high precipitation rate can cause dilution and a loss of nutrients and algal biomass.¹ In regions with high precipitation rates, overflow spillways and storage ponds have to be installed to prevent biomass loss.^{1,4}
- Humidity
With low relative humidity, high rates of evaporation occur that can have a cooling effect on the medium.^{1,4} With high relative humidity and no winds the medium may heat up (even up to 40 °C).^{1,4} The best humidity location is at an average humidity of 60%.^{1,4}
- Water
A location must be chosen where there is a constant and abundant supply of water for the mass culture pond systems.^{1,4}

2.1.4 Technical aspects of pond design

Types of ponds available

There are two major types of ponds for mass cultivation of microalgae: Horizontal ponds and sloped cultivation ponds.

Table 2.1.2: Various types of horizontal ponds for algal production.

Horizontal ponds	Comments
Raceway ponds	Most preferred pond system used in commercial plants. ^{1,3,4}
Circular ponds	Disadvantages are that it is expensive to construct due to reinforced concrete. ^{1,3,4} High-energy consumption and difficult to obtain turbulence in the center of pond. ^{1,3,4}
Closed ponds	Closed ponds are not exposed to the atmosphere but are covered with a transparent material. ^{1,3,4} Main advantage is the prevention of evaporation and constant temperatures. ^{1,3,4} The disadvantages are light reduction to the pond and the increase in capital layout per pond. ³

The second type of pond system is the slope cultivation pond.^{1,3,4} This type of system is designed to create a turbulent flow while the algal culture passes through a sloping enclosure.⁴ The main disadvantage of this method is the cost involved.⁴



Figure 2.1.3: Circular ponds (*Chlorella* production in Taiwan).¹⁷



Figure 2.1.4: Raceway pond (*Spirulina platensis* in California).¹⁷

Lining

The main factor that determines the lifespan and durability of an algal pond is the material used for the construction of the bottom and the walls (lining).^{1, 4} Presently commercial algal ponds are lined with either concrete or plastic.^{1, 4} Plastic is considered the most cost effective for pond lining, provided it is UV-resistant (polyvinylchloride).^{1, 4} Concrete linings require a much larger initial capital investment and are not recommended for large-scale operations.^{1, 4} The main requirement for a good lining is that it has to be resistant to chemicals, UV-resistant, non-toxic, easy to seam, able to prevent loss of media and be temperature resistant.^{1, 4}

Mixing and turbulence

Mixing of the pond is the most important parameter for consistent, high algal mass yield.⁴ The main reasons for constant mixing of the culture are the following:

- Prevent the microalgal cells from sinking to the bottom of the pond. If many cells sink to the bottom of the pond it will cause cell deterioration and anaerobic decomposition (cause “dead” areas in the pond).^{1, 3, 4}
- Mixing ensures that all the algal cells come in contact with nutrients, CO₂ and light for optimum growth.^{1, 3, 4}
- Ensure that produced oxygen is removed from the culture system. Oxygen causes inhibition of photosynthesis if present in high concentrations.^{1, 3, 4}

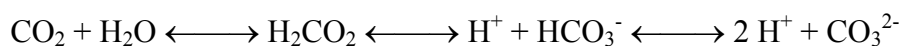
Various techniques can be employed for effective turbulent flow within the pond system and are illustrated in Table 2.1.3.

Table 2.1.3: Various types of mixing techniques for algal ponds.

Mixing method	Comments	Picture
Paddlewheel	Used in most commercial algal ponds. Mixing parameters very well known. Power demand is 600 W (100 m ² pond). ^{3,4}	
Free propeller	Only been tested in experimental ponds. Not suitable for filamentous algae. Power demand is 600 W (100 m ² pond). ^{3,4}	
Pumps and gravity flow	Used in large-scale slope cultivation plants. ⁴ Power demand is 200 W (100 m ² pond). ^{3,4}	
Injector	The algal suspension is injected through a nozzle and CO ₂ is added to obtain high turbulence and high CO ₂ transfer rates. ⁴ Not suitable for filamentous algae. ⁴ Power demand is 1000 - 2000 W (100 m ² pond). ⁴	
Airlift	Very simple installation. This system ensures high CO ₂ utilization efficiency and reduces over saturation of O ₂ . ^{3,4} Difficulties in large-scale cultivation. Power demand is 195 W (85 m ² pond). ⁴	
Low technology methods	Manual stirring is used. This method is labor intensive. ^{3,4}	

Supply of CO₂ to mass culture

The flue gas of the power plant will provide the carbon source for these organisms.^{8, 10, 11} It was assumed that flue gas consists of 20% (v/v) CO₂ and is the only source of carbon for the organisms (very little to no atmospheric CO₂ is utilized). It is also assumed that the flue gas has been processed to ensure that no particulates, arsenic, mercury or NO_x and SO_x are present. If SO_x and NO_x are present in the flue gas, the pH of the pond must be monitored to ensure that it does not fall below the optimum pH. When CO₂ dissolves in water it may appear as H₂CO₃, HCO₃⁻ and CO₃²⁻, depending on the pH.¹ Dissolution of CO₂ in water can be written as:



Microalgae use the CO₂ in its HCO₃⁻ form and excrete OH⁻ ions that elevate the pH of the pond.^{1, 4} Therefore, the pH of the pond can be used as a monitor to evaluate the state of the pond.^{1, 4} If the pH rises (due to OH⁻ ions) then it indicates that optimum growth is occurring. The pH levels are maintained at optimum (8.3 - 11 for *Spirulina*) by the addition of CO₂ to the pond.^{1, 4} Various methods can be employed to supply CO₂ to the pond system (Table 2.1.4).

Table 2.1.4: Supply methods of CO₂ to mass culture.

CO ₂ supply methods	Comments	CO ₂ utilization
Bubbling method (Figure 2.1.5)	Gas is supplied in the form of fine bubbles. Problematic in shallow ponds, residence time in pond is not sufficient to allow the CO ₂ to be dissolved. ¹ A lot of CO ₂ is lost to the atmosphere. ¹	13 - 20%
Floating gas exchanger	The gas exchanger consists of a plastic frame, which is covered by transparent sheeting and immersed in the suspension. ¹ CO ₂ is fed into the unit and the exchanger float on the surface. ¹ CO ₂ needs to be in a concentrated form. ¹	25 - 60%
Diffusion method	CO ₂ is let to diffuse through a porous metal or plastic pipe to form the smallest bubbles possible (not seen on surface). ¹	Unknown

The most effective method to use is the floating gas exchanger, but is only effective if a very concentrated and pure CO₂ feed is used.¹ In this method the CO₂ is trapped under the transparent plastic frame and very little CO₂ is lost to the atmosphere.¹ In the proposed pond design, flue gas is going to be used so this method will not be effective. The most effective method for the proposed pond is the diffusion method.¹ Figure 2.1.5 shows the various diffuse methods available for supplying CO₂ to shallow pond system. Very little information is available for the parameters required for optimum CO₂ delivery to the culture pond system (very little information published for mass and laboratory scale production).

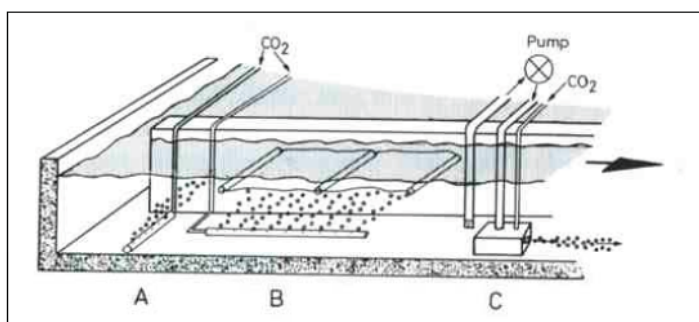


Figure 2.1.5 shows three methods to bubble CO₂ into ponds. A is a sintered stone, B is a porous pipe with a plastic sheet to trap CO₂ bubbles and C utilizes a high speed pressure pump for aeration and mixing. A diffuse method (not shown) was

selected as preferred method.

Figure 2.1.5: Various bubbling methods for ponds.¹

2.1.5 Evaluation of different ponds

The type of pond employed depends on the location of the pond. Three types of raceway ponds can be constructed: a freshwater pond, a marine pond and a closed pond.

Freshwater raceway pond

Fresh water raceway pond systems are used inland near the CO₂ source.^{1, 3, 4} To culture pharmaceutical or food grade microalgae, the water that is supplied must be as pure as possible (water from river must go to settling ponds and through filters before entering the pond system).^{1, 3, 4} If industrial water (water effluent from power plant, municipal water or sewage water) is utilized then the resulting biomass can be sold as low-grade biomass for energy generation.^{1, 3, 4} This biomass may contain various pathogens (from sewage water and municipal water) or various toxic heavy metals (from industrial water or flue gas from power plants).^{1, 3, 4}

Marine raceway pond

Marine water ponds can be used in coastal areas. Seawater can be pumped directly from the ocean into the ponds.^{1, 9} The main advantage is that adequate water is available, but the disadvantage is pumping costs and possible algal contamination from the seawater. Contamination may occur due to natural occurring marine algae present in the utilized seawater.⁹ Seawater has the advantage that very little to no nutrients have to be added to the water for optimum growth.^{9, 15}

Closed raceway pond

The closed raceway pond is a marine or freshwater pond that is covered with a transparent covering.^{1, 4, 18} The main disadvantage of using a closed pond is the initial capital cost per pond as well as lowering of the amount of light that will reach the culture.^{1, 4, 18} The advantages are that very high quality biomass can be produced (no leaves, insects or dust can fall in the water), less chance of contamination and less water loss due to evaporation.^{1, 4, 18} The main advantage is that there is more control in regards to the temperature of the ponds and there will be less seasonal effects on the growth of the biomass (growth rate will be more constant over the year).^{1, 4, 18}

2.1.6 Pond design for mass culture of *Spirulina*

The following diagram can summarize the design of the mass culture system:

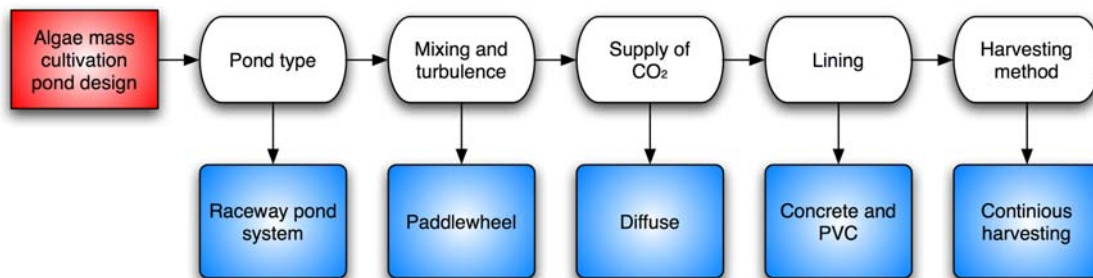


Figure 2.1.6: Scheme for the design for the mass culture pond system.

The design parameters for the pond are summarized in Table 2.1.5.

Table 2.1.5: Design parameters for mass culture pond

Parameter	Choice	Reason
<i>Pond type</i>	Raceway pond	Most preferred pond system used in commercial plants. ^{1,4}
<i>Mixing method</i>	Paddlewheel	Used in most commercial algal ponds. Mixing parameters very well known. ^{1, 4} Paddlewheel of 6 m x 1.8 m will be used in this project. ³ The proposed paddlewheel efficiency will be assumed to be 50%. ³
<i>CO₂ pond supply</i>	Diffuse CO₂ inlet	Most effective method for pond systems. Porous metal or plastic pipe will be used. ¹
<i>Lining</i>	Concrete and PVC	This lining will increase the capital costs, but will increase lifetime of pond. ^{1, 3, 4} This type of lining also provides less friction for mixing (Manning friction factor of 0.01). ^{1,3,4}
<i>Velocity of mixing</i>	30 cm/s	Experimentally obtained and used by various sources. ^{1,3,4}
<i>Depth of pond</i>	30 cm	Experimentally obtained and used by various sources. ^{1,3,4}
<i>Change in depth</i>	7.5 cm	Slight slope in pond will increase the efficiency of agitation in the pond. ^{1,3,4}
<i>Width of channel</i>	6 m	This value depends on the size of the paddlewheel that will be used. ^{1,3,4}
<i>Width of pond</i>	12 m	2 x 6 gives a pond width of 12 m.
<i>Length of pond</i>	500 m	This value was chosen to construct a pond of relative size (value not calculated)
<i>Area of pond</i>	5969 m²	Calculated.

Figure 2.1.7 shows the design of the mass culture pond (figure is not to scale). Table 2.1.5 summarizes all the required parameters of the proposed algal pond. As seen in Figure 2.1.7 the agitation system for this pond will be a paddlewheel (shown in blue) and the CO₂ inlet units (shown in yellow) will be diffuse inlets. The cross section shows the change in depth over the length of the pond (L). L in this case is the distance from A to B by way of channel.

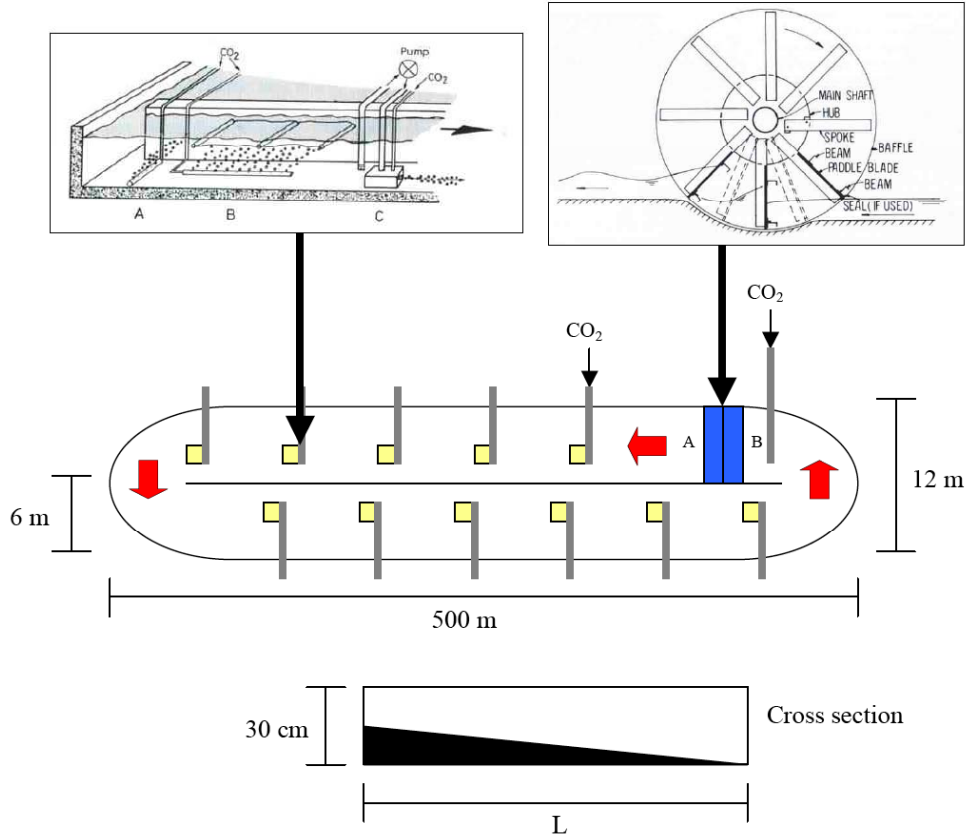


Figure 2.1.7: Design of mass culture pond (not to scale).

Calculating the permissible length of the proposed pond

For a pond that has a depth of 30 cm (d), a mixing velocity (V) of 30 cm/s, a change in depth (Δd) of 7.5 cm, a channel length (w) of 6 m, Manning friction factor (n) of 0.01 the optimum length of the pond (L) can be calculated (equation 2-1-1).

$$L = \frac{\Delta d(dw/(w + 2d))^{4/3}}{V^2 n^2} \tag{2-1-1}$$

$$L = \frac{0.075 m((0.30 m)(6 m)/(6 m + 2(0.30 m)))^{4/3}}{(0.30 m/s)^2 (0.01)^2}$$

$$L = 1,474 \text{ m}$$

The mixable area can be calculated by using Equation 2-1-2:

$$A = LW = (1,474 \text{ m})(6 \text{ m}) = 8,844 \text{ m}^2 \tag{2-1-2}$$

The proposed pond has an area of 5979 m² and the calculation shows that with the current parameters (depth, velocity, width, etc) the mixable area is 8,844 cm². Therefore the current pond design will facilitate adequate agetation (pond lenth can even be increased). The effect of depth and channel width in regards to the permissible mixable length were investigated and are shown in Figure 2.1.8 and 2.1.9.

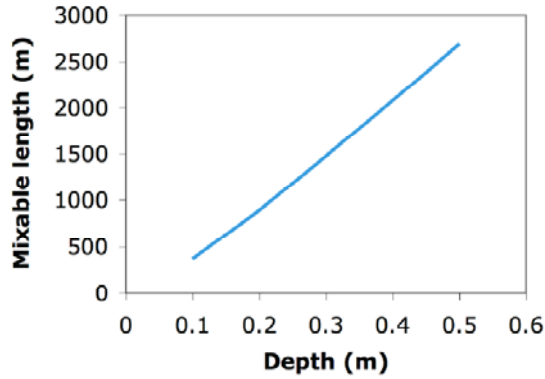


Figure 2.1.8: Mixable length in regards to the depth of the pond.

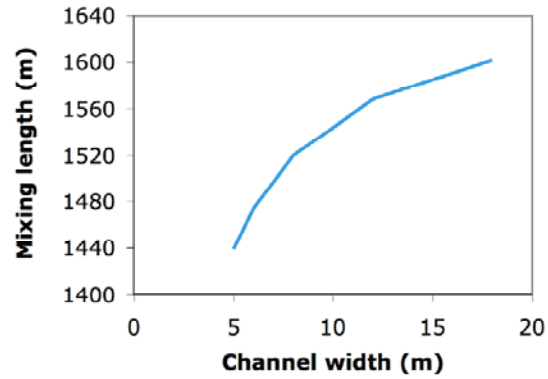


Figure 2.1.9: Mixable length in regard to the channel width of the pond

It is observed that if either the depth or width of the channels are increased the mixable length of the pond will increase.

The power requirements for mixing

The power requirement for mixing of the pond can be calculated by using equation 2-1-3:

$$P = \frac{QW\Delta d}{e} \quad (2-1-3)$$

where P is the power (kW), Q is the quantity of water in motion (m³/s), Δd is the change in depth, V is the mixing velocity, w is the width of the channel and e is the paddle wheel efficiency. We assume that the specific weight of water (W) is approximately 1000 kg/m³ and that the paddle wheel efficiency is 50%. Q can be dermined using equation 2-1-4:

$$Q = wdV \quad (2-1-4)$$

Therefore to determine the power requirement for the proposed pond equation 2-1-5 can be used:

$$P = \frac{w \times d \times V \times W \times \Delta d}{102 \times e} \quad (2-1-5)$$

$$P = \frac{(6)(0.3)(0.3)(1000)(0.075)}{(102)(0.51)}$$

$$P = 0.79 \text{ kW}$$

The effect of depth and channel width in regards to paddlewheel power consumption was investigated in Figure 2.1.10 and 2.1.11.

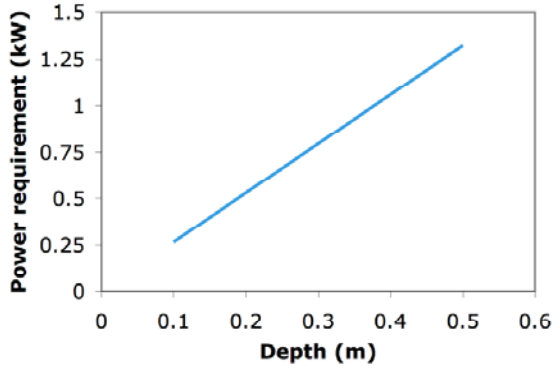


Figure 2.1.10: Power requirements in regards to pond depth.

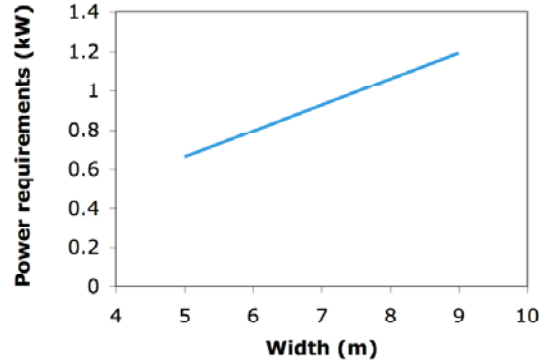


Figure 2.1.11: Power requirements in regards to channel width.

It is observed that the power requirements for the paddlewheel will increase if either the pond depth or channel width increase.

It can be concluded that the proposed pond (500 m in length, 30 cm deep, 12 m in width with a flow velocity of 30 cm/s) will be adequately mixed using a 6 x 1.8 m paddlewheel.

2.1.7 Growth of microalgae and mass balance

In the production of *Spirulina* it was found that at a cell concentration of 400 - 500 mg/L, a decline in the growth rate occurs.³ Therefore when this cell concentration is reached in the mass culture pond, harvesting should be done. If the algae concentration and culture depth are known then we can determine cell residence time for *Spirulina* using equation 2-1-6:

$$P_r = kdC_c/\theta \quad (2-1-6)$$

$$(30) = (1)(0.30)(400)/\theta$$

$$\theta = 4 \text{ days}$$

where P_r is the productivity (30 g/m²·day); the value of k is 1; d is the depth of the pond; C_c is the cell concentration (mg/L); and θ is the cell residence time (days between harvesting). It was determined that harvesting should be done every four days to obtain a cell concentration of 400 mg/L. There is a linear relationship between the cell concentration and the cell residence time (illustrated in Figure 2.1.12).

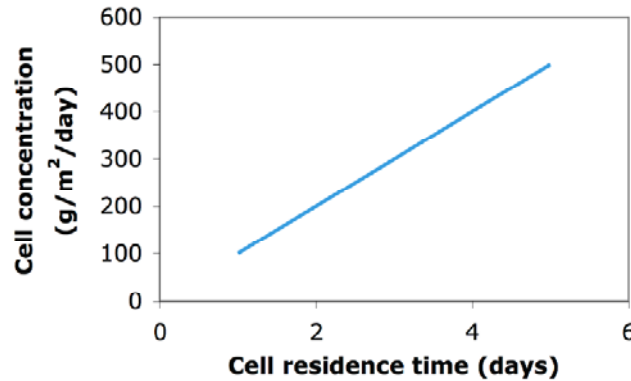
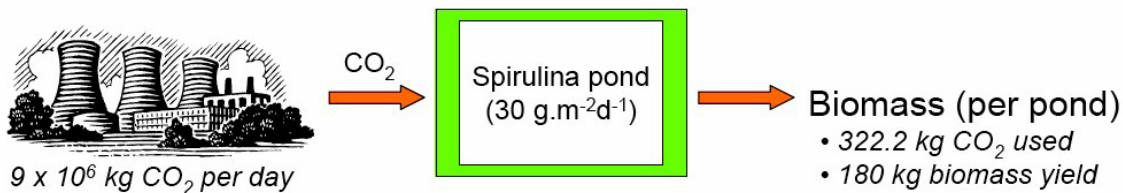


Figure 2.1.12: Linear relationship between cell concentration and residence time.

Mass balance of mass culture system

As mentioned, the algal growth rate for Spirulina is 30 g/m²-day (which is very conservative number). It has been experimentally determined that for every 1 g of algae biomass produced, 1.8 g of CO₂ was utilized (this is on the assumption that algae biomass consists of ~50% carbon).^{1, 3} Therefore, for a 5969 m² pond (single algal pond), a total amount of 180 kg algal biomass will be produced per day:



For 180 kg biomass to be produced per day, 322 kg CO₂ will be utilized per day. We assume that a 500 MW coal-fired power plant produces 9 x 10⁶ kg CO₂/day and the amount of biomass produced each day is 180 kg per pond. Therefore:

- Total amount of CO₂ used per day per pond: **322 kg/day (0.0036% of total CO₂)**.
- Total amount of CO₂ used per day for 12 ponds: **3866.4 kg/day (0.043% of total CO₂)**.

These values depend on the growth rate of the microalgae that are used in the pond system. The growth rate is dependant on the temperature and the season (high growth rate in the summer and low growth rate in the winter).^{1, 3, 6, 12} It must be concluded that although the amount of CO₂ utilized is very low, a very valuable product is obtained in high yields.

2.1.8 Harvesting of biomass

The economy of microalgae production depends on the technology employed for harvesting and the concentration of the algal suspension to obtain a product to sell or for further processing.^{1, 3, 6} The choice of harvesting methods depends on a few factors:

- Type of algae that has to be harvested (filamentous, unicellular, etc).^{1, 3, 6}

- Whether harvesting occurs continuously or discontinuously.^{1,3,6}
- What the energy demand is per cubic meter of algal suspension.^{1,3,6}
- What the investment costs are.^{1,3,6}

A few of the various methods that can be employed in harvesting of algal biomass are summarized in Table 2.1.6.

Table 2.1.6: Harvesting methods for algal biomass

Harvesting method	Comments
Centrifugation	Advantage is a high degree of algal removal. Applicable for filamentous and non-filamentous microalgae. <i>Spirulina</i> is a problem due to floating during centrifugation. ^{1,3,6}
Sedimentation	Very low cost method, but low efficiency. ^{1,3,6}
Filtration	Filtration from pond water usually clogs filters quickly. Regular backwashing necessary that can increase the costs for adequate algal removal. ^{1,3,6}
Screening & Straining	Filamentous organisms can be removed using screens of sieves. Very effective for <i>Spirulina</i> . ^{1,3,6} Not very effective for unicellular organisms (for example <i>Chlorella</i>). ^{1,3,6}
Flocculation	High yield, but introduction of chemicals can be costly and may reduce the quality of the biomass. ^{1,3,6}

The methods mentioned in Table 2.1.6 are only a few of the methods that can be employed in the harvesting of microalgae.^{1,3,6} The type of harvesting employed depends heavily on the type of organisms used in the mass culture. When *Spirulina* and *Chlorella* are compared it is observed in literature that due to the filamentous nature of *Spirulina* it is easier and cheaper to harvest. It is generally more expensive to harvest and concentrate *Chlorella* due its unicellular morphology. For harvesting *Spirulina*, filtration is most commonly used in commercial production.^{1,3,6} Gravity filtration is usually done using two filters. First, a 25-mesh filter is used to remove all the filamentous debris present in the water (leaves, insects, etc), secondly a 60-mesh filter is used to harvest the *Spirulina* biomass.^{1,6} Vibrating screens can be used to increase the filtration rate of the process (less clogging occurs with this method).^{1,6} The main problem with this method is that cell rupturing can occur due to cells rubbing against each other and the filter, therefore, increasing the organic load in the pond (this can increase the possibility of bacterial contamination in the pond).^{1,6}

There is currently no cost effective method of algal pond harvesting available. Even with the various problems associated with filtering, it is currently the best method available for optimum algal harvesting and concentration.^{1,3,6}

The last step in the production of algal biomass is drying. Various methods of drying exist and include spray-drying, sun-drying, freeze-drying and vacuum-drying, among others.^{1,4} To produce pharmaceutical grade biomass, the method that must be employed is spray-drying.^{1,3,4} This is the most utilized drying method used commercially to produce pharmaceutical and food grade *Spirulina* biomass.^{1,3,4} The disadvantage of this

method is the initial capital costs as well as the operational costs, but it has the advantage that a very pure and safe product is obtained that has a very high selling value.^{1,3,4}

2.1.9 Economics of algal biomass (*Spirulina*)

There has been a steady increase in the amount of *Spirulina* biomass produced each year due to increasing worldwide demand.^{2,5,6} Figure 2.1.15 shows a sharp increase in the amount of *Spirulina* produced from 1975 to 2000.^{2,5,6}

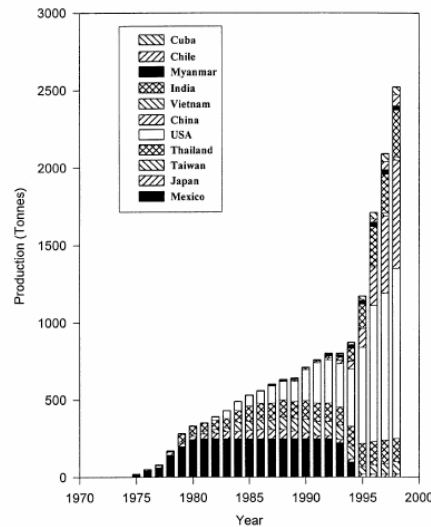


Figure 2.1.15: *Spirulina* production

The main drive for this increase in demand lies in the application of *Spirulina* and other microalgal biomass (for example *Chlorella*, *Dunaliella*, etc).^{5,6} High-grade algal biomass has a very high value as pharmaceutical, food and specialty products and, therefore, have a very high retail value.^{5,6}

Selling price for *Spirulina*

The cost of *Spirulina* in 1984 was \$10,000 per ton.³ If a very conservative estimation of a price increase of 5% per year is assumed, the current price for high-grade *Spirulina* is **\$32,000 per ton**. This is a very conservative estimation, and higher prices have been indicated.⁶

2.1.10 Conclusions

- A pond system 30 cm deep, 500 m in length, 12 m in width (6 m channel width) and a change in dept of 7.5 cm has been proposed. The pond system will be mixed using a 6 x 1.8 m paddlewheel at a velocity of 30 cm/s. Calculations showed that the current design would work very effectively.
- The organism that will be used in the mass culture pond system is *Spirulina*. The filamentous nature of *Spirulina* decreases the cost involved for harvesting. *Spirulina*

has a high growth rate and is very well known as an industrial organism. *Spirulina* has a very high market value (pharmaceutical or food grade).

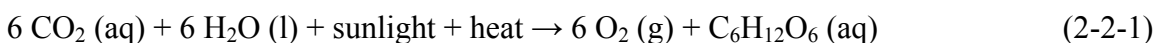
- The harvesting method that will be employed is filtering using a vibrating screen and spray-drying will be used to dry the product (this will ensure that a pharmaceutical grade product is obtained).
- Very little CO₂ is used during the production of biomass (0.043% of total flue gas CO₂ is used per day for 12 ponds). Although very little of the total CO₂ is fixated, a very valuable product is obtained in very high yield.
- *Spirulina* and other microalgae production and demand show a steady increase every year. Therefore, *Spirulina* production shows a bright future (pharmaceutical, food and specialty products).

2.2 Biological utilization of CO₂ via bioreactors

2.2.1 Introduction

Biological utilization of CO₂ using microalgae is an economically beneficial method to employ greenhouse gas emissions to generate value. Microalgae have a higher capacity for CO₂ utilization through photosynthesis than higher order plants, such as trees, shrubs and grasses.¹⁹ Harnessing this natural utilization through the production of biomass can be accomplished in fully contained photo-bioreactors or in open systems, such as open ponds and channels. Closed photo-bioreactors can be located inside a building or outdoors, the later of which is usually preferred to make use of natural sunlight.²⁰ Feed sources of CO₂ can be synthesized from gaseous mixtures containing captured CO₂ gas or flue gases directly from various combustion or gasification processes.

The main governing equation in a photo-bioreactor is photosynthesis (see Reaction 2-2-1), which is a reaction that removes electrons from H₂O via light energy.²¹ Carbon dioxide is reduced and organic materials are produced. This reaction occurs in two steps known as the “light reaction” and the “dark reaction”. During the very fast occurring light reaction, H₂O is oxidized and NADPH·H⁺ and ATP are synthesized using the energy found in light.²¹ The dark reaction is comprised of an anabolic reaction of CO₂ utilizing the NADPH·H⁺ and ATP produced during the light reaction.²¹ This step occurs much slower than the light reaction, and therefore, is the rate limiting step. Photosynthetic efficiency increases as the light period is shortened due to a saturation of energy produced during the fast-occurring light reaction.²¹



In this study, biomass is the desirable raw product produced from a bioreactor that can be treated downstream to produce a variety of fuels and specialty products. Carbon is the dominant nutrient in this organic product at around 45 - 50% of the dry weight. Accordingly, it is estimated that between 1.65 - 1.83 g CO₂ are needed for the synthesis of 1 g (dry) of algal biomass.^{22, 23}

2.2.2 Types of bioreactors

There are six main types of reactors that utilize solar light: air-lift, internal luminous stirrer-type, fountain-type, plain plate-type, liquid film-type, and algae immobilizing.²⁴ In the direct-sunlight utilizing area, there are three main types of reactors: tubular-type, floating ramp-type, and multi-stage culture-type.²⁴ Variations on these basic types have been successfully implemented in numerous bench and pilot-scale studies. Table 2.2.1 lists some pilot and full-scale photobioreactors that have been fabricated. For example, after conducting laboratory-scale experiments, Chae and co-authors²⁵ created a pilot-scale L-shaped photo-bioreactor that utilized sunlight as the energy source and flue gas (11% CO₂ vol/vol) as the feed emitted at 30 L/min from an industrial heater. The obvious

evaluation and comparison problem that presents itself is that there are many variables to consider for photobioreactors and the studies that have been performed thus far utilized different standards for evaluating performance.

Some major advantages of using a closed-system bioreactor are the production of biomass at high concentrations, less chance of contamination, and the prevention of water loss due to evaporation during routine operation; all of which make the process of recovering products easier and less costly.²³ Ultimately, the value of the microalgal products resulting from the photo-bioreactor will be a main factor in determining design feasibility.²³

Photobioreactors can be designed to be located indoors utilizing light collection systems or outdoors where natural sunlight is the light source for photosynthesis. Light collection and distribution systems are very complex and contribute a very significant portion of the capital cost in an indoor photobioreactor system.²⁶ Therefore, for most commercial processing, natural illumination is the only feasible option.^{26,27}

Table 2.2.1: Comparison of pilot and full scale photo-bioreactors.^{19, 22, 25, 28-30}

Scale	Type of bioreactor	Base area	Light source	CO ₂ feed	CO ₂ fixation	Productivity
Pilot	L-shaped glass plate	2.16 m ²	natural sunlight	flue gas (11% CO ₂)	74.0 g/m ³ /day	0.62×10 ⁶ cell/mL/day 113.8 gDW/day
Pilot	10 L cylindrical glass	0.95 m ²	12 fluorescent lamps (30 W)	air + CO ₂ (1%)	80 - 260 mg/L/hr	---
Pilot	Inclined outdoor tubular	0.5 m ²	natural sunlight	sparging air mixed with 5% CO ₂	10 times that of a tree	0.5 g/L/day
Pilot	Conical, helical, tubular	0.5 m ²	photo-redistribution	air + CO ₂ (10%)		1.01 g/L/day
Full	8 Open thin-layer	55 m ²	natural sunlight	flue gas (6-8% CO ₂)	92.4 kg/day	21 kgDW/day
Full	580 Glass, panel-type	3068 m ²	natural sunlight	1000 MW LNG power plant	50 g/m ² /day	3.05×10 ⁴ kg/yr 31 tons/yr

A literature survey by Sato and co-authors³¹ compared the performance of different types of photobioreactors and the microalgal species selected (i.e., a comparison of the amount of biomass produced per unit volume per day). This data is displayed in Table 2.2.2 along with the mass concentration of some systems. As it can be seen, tubular reactors generally had better performance than the other reactor types on a volume basis.

A key issue to consider with photobioreactors is the size requirements are extremely important on a capital and operational cost basis. In general, the larger and more complicated the design, the more cost intensive is the overall system. Early reactor designs were very shallow with a high surface-to-volume ratio (25 - 125 m⁻¹) allowing for

high volumetric costs.²³ Tubular reactors effectively fill this design requirement. Another key issue is in the scaling-up of photobioreactors. The high surface areas of most reactor types make complete back-mixing nearly impossible beyond a laboratory or experimental scale, due to these large systems exhibiting substantial plug flow characteristics.²³

Table 2.2.2: Performance of different photobioreactors.³¹

Type	Species	Performance (gDW/L/day)	Performance (gDW/m ² /day)	Mass concentration (gDW/L)
<i>Tubular reactors</i>				
indoor cone-shaped helical	<i>Chlorella</i> sp.	0.68	21.5	
outdoor horizontal	<i>Phaeodactylum tricornutum</i>	1.9	32	2.3
indoor nearly horizontal	<i>Arthrospira</i> sp.	1.2		
outdoor undulated	<i>Arthrospira platensis</i>	2.7		6
outdoor cylindrical-shaped helical	<i>P. tricornutum</i>	1.4		3
outdoor with horizontal solar receiver	<i>P. tricornutum</i>	1.48		
<i>Panel shaped reactors</i>				
flashing light effect	<i>Chlorella</i>	0.11		1.95
outdoor optimized light path length	<i>Nannochloropsis</i> sp.	0.24	12.1	
indoor photo-acclimation/ multi-compartment	<i>Synechocystis aquatilis</i>		67.7	
<i>Innovative design reactors</i>				
parabola	<i>Chlorococum littorale</i>	0.086	14.94	
dome	<i>Chlorococum littorale</i>	0.095	10.95	
pipe	<i>Chlorococum littorale</i>	0.146	20.5	
pipe	<i>Chaetoceros calcitrans</i>	0.266	37.3	2.5

The main disadvantages of most tubular-type photobioreactors are that they occupy vast land areas, are expensive to build, are difficult to maintain, and are limited in scalability.^{26, 32} The commercial horizontal tubular bioreactor facility depicted in Figure 2.2.1 is an example of a system that attempted large-scale production, but failed to perform to expectations and was abandoned.³² The facility was located in Cartagena, Spain and was owned by Photobioreactors Ltd. The productivity measured per unit area is low for conventional tubular bioreactors,³² which is a major concern with limited land available to build such large structures. A change in thinking to design a tubular reactor with low surface-to-volume ratios, such as air-lift and bubble column bioreactors seen in Figure 2.2.2, can overcome the downfalls of conventional systems.^{26, 27, 32} Due to simplicity of design and ease of scalability, bubble column photobioreactors were the type chosen for this project.

Bubble column photobioreactors incorporate CO₂ into their cultures via small bubbles created at the base of the column, which also effectively mix the culture. They are the only type of tubular-type bioreactors that are thought to be effective for large-scale operations.^{26, 27, 32} Bubble-column reactors provide a more homogeneous culture environment than conventional tubular reactors. They have a low surface-to-volume

ratio; therefore, there is much less temperature fluctuations compared to tubular reactors and less photo-inhibition is experienced during high light intensity periods.^{27, 32} The materials used in pilot-scale testing of bubble columns and airlift reactors that have proven most effective are 3.3 mm-thick transparent poly(methyl-methacrylate) tubes supported by the 0.25 m lower section composed of stainless steel.^{27, 32} The temperature of the unit, optimally held at 22 ± 1 °C, is controlled by circulating water through a jacket surrounding the lower steel portions of the columns.²⁶ Temperature and pH need continuous monitoring during operation as small fluctuations can cause large changes in the productivity of the facility; however, the incorporation of a bubble column or airlift reactor provides optimum control of these factors.

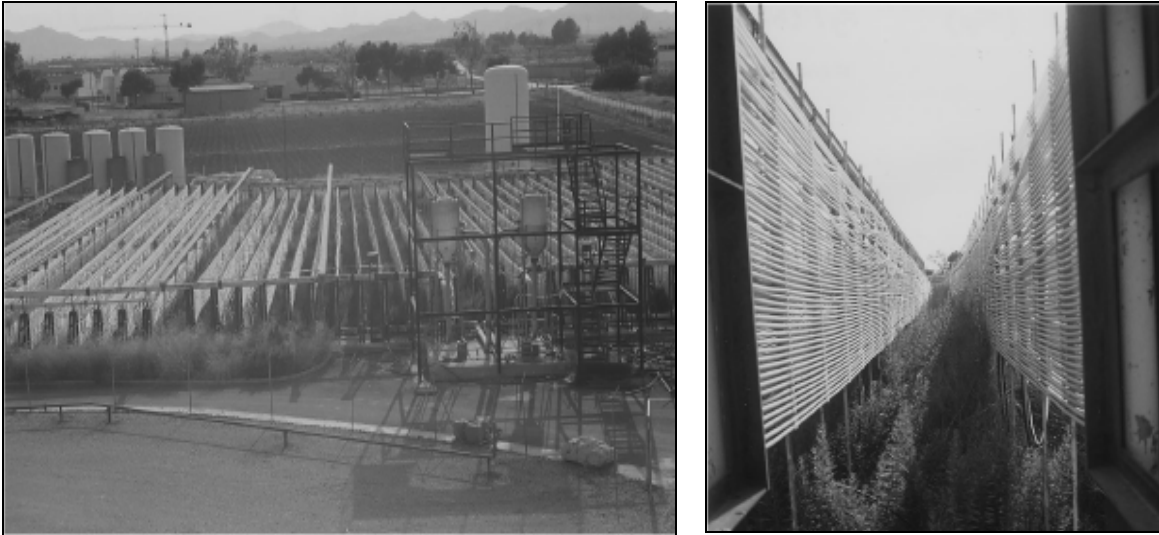


Figure 2.2.1: A commercial horizontal tubular bioreactor facility in Cartagena, Spain that failed to perform to expectations and was abandoned.³²

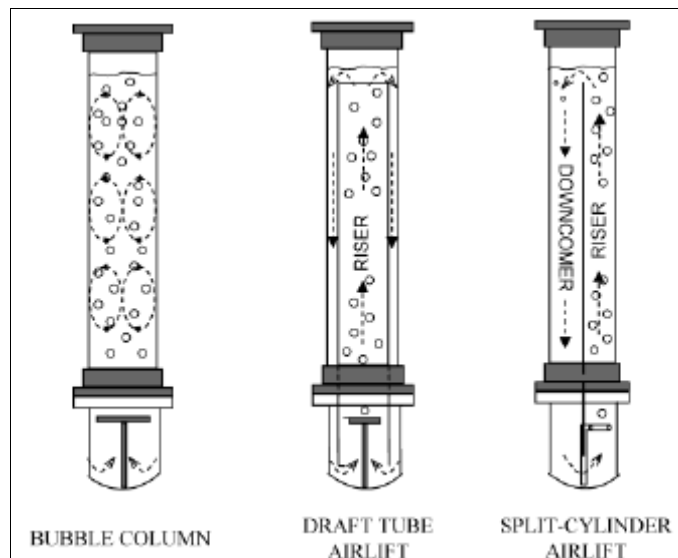


Figure 2.2.2: Configurations of bubble column and airlift photobioreactors.²⁶

Some other important advantages of using multiple vertical columns are: (i) a more uniform and better controlled pH than most other reactor types, (ii) improved culture homogeneity and, correspondingly, a relatively consistent metabolic cell rate, (iii) operational flexibility in that the number of columns in production at any given time can be easily adjusted, (iv) ability to culture several different algae at the same time in separate units, and (v) substantially reduced need for pumping the culture seen in other bioreactor types as there is no recirculation.³² Furthermore, rapid and automatic cleaning as well as sterilization of individual columns are feasible while part of the facility is still in operation.³²

2.2.3 Selection of microalgae species

Several thousands of species of microalgae exist. They can be grouped into four different categories: (i) Cyanobacteria, (ii) Rhodophytes, (iii) Chlorophytes, and (iv) Chromophytes (all others).³³ Many of these species have been successfully grown in photobioreactors to generate a variety of products. The most common species studied are *Chlorella* sp. and *Spirulina* sp., chosen for their resilience, productivity, and non-toxicity.^{22, 25, 28-31} A comparison of some microalgae species is displayed in Table 2.2.3. From the table, it can be determined that different microalgae species require different living conditions. Some species prefer more acidic cultures, like *Galderia* sp. and *Viridella* sp., while others grow best in neutral or slightly basic media, such as *Chlorococcum* and *Synechococcus lividus*. The species that survive best in acidic conditions are generally more tolerant to high CO₂ concentrations, since CO₂ lowers the pH of a solution. The microalgae with the shortest doubling times, like *Chlorella* and *Synechococcus lividus*, are the ones with a generally higher productivity, basically meaning they grow comparatively faster than other species.

Table 2.2.3: Comparison of some microalgal species.^{24, 25}

Species	Temp (°C)	pH	CO ₂ %	Doubling time, hr	Notes
<i>Chlorococcum</i> (marine green alga)	15 - 27	4 - 9	up to 70	8	High CO ₂ fixation rate Densely culturable
<i>Chlorella</i> (green alga)	15 - 45	3 - 7	up to 60	2.5 - 8	High growth ability High temp. tolerance Dispersible
<i>Euglena gracilis</i>	27 (optimum)	3.5 (optimum)			High amino acid content Good digestibility (effective fodder) Grows well under acidic conditions Not easily contaminated
<i>Galdieria</i> sp.	up to 50	1 - 4	up to 100	24	High CO ₂ tolerance
<i>Viridiella</i> sp	15 - 42	2 - 6	up to 100	13	Accumulates lipid granules inside the cell High temp. and CO ₂ tolerance
<i>Synechococcus lividus</i>	40 - 55	up to 8.2	up to 5	2.9	High pH tolerance

(cyanophyte)

Dispersible

Ultimately, the decision as to which microalgae species to choose depends on the product desired to be the end result of a photobioreactor system. *Phaeodactylum tricornerutum*, depicted in Figure 2.2.3, is a productive microalgal species that has a relatively high eicosapentaenoic acid (EPA) content.³² A comparison of various microalgae species and their demonstrated EPA productivities are listed in Figure 2.2.4.

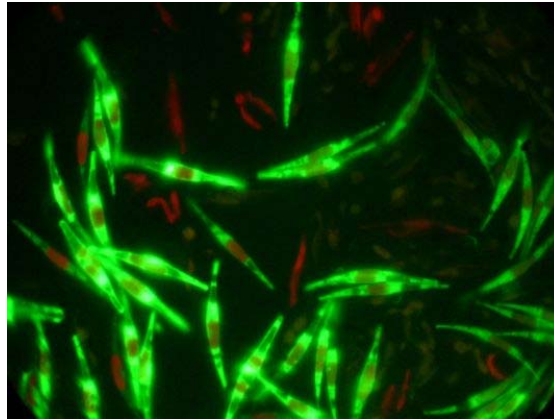


Figure 2.2.3: Enhanced photograph of *Phaeodactylum tricornerutum*.³⁴

Comparison of EPA yields of microalgae under various culture conditions			
Organisms	Culture mode	Growth mode	EPA yield (mg/l)
<i>Phaeodactylum tricornerutum</i>	Batch	Photoautotrophic	131.0
<i>Phaeodactylum tricornerutum</i>	Continuous	Photoautotrophic	100.9
<i>Monodus subterraneus</i>	Batch	Photoautotrophic	96.3
<i>Amphidinium carterae</i>	Batch	Heterotrophic	8.3
<i>Navicula saprophila</i>	Batch	Mixotrophic	34.6
<i>Phaeodactylum tricornerutum</i>	Batch	Mixotrophic	356.4
<i>Nitzschia laevis</i>	Perfusion	Heterotrophic	1112

Figure 2.2.4: A comparison of EPA yields from various microalgae species.³⁵

2.2.4 Biomass recovery

As with most microbial processes, the downstream treatment and recovery processes can be substantially more expensive than the culturing of the algae. Therefore, the selection of recovery methods used is very important.²⁰ Some of the current biomass recovery methods are evaluated in Table 2.2.4.

The recovery of biomass requires one or more solid-liquid separation steps. It can be harvested by centrifugation, filtration, or even gravity sedimentation; all of which may be preceded by a flocculation step.²⁰ The main problems with recovery lie in the small sizes of the algal cells. Also, when the culture is removed from the photo-bioreactor, it is

usually present in very dilute concentrations. The recovery and concentrating of this dilute broth is estimated to contribute 20 - 30% of the total cost of producing the biomass.²⁰ For the commercial recovery of high-value products, centrifugation is the most widely used method, which is feasible when the product selling price offsets the recovery costs.²⁰ Wherever possible, it is preferred to use moist biomass for recovery processes rather than a dried feed because a prior drying step can vastly increase costs.

Once the biomass is recovered from the photobioreactor or open pond system it can be further treated to extract valuable substances or processed as a fuel source depending on the type of microalgae cultivated.

*Table 2.2.4: Biomass recovery options.*²⁰

Method	Pros	Cons
Centrifugation	Feasible for high-value prods/large scale operations	Energy intensive
	Large volumes processed rapidly	Expensive
	Biomass fully contained during recovery	
	Can harvest most microalgae species	
Filtration	Effective for relatively large microalgae (such as Spirulina)	Relatively slow process
		Fails to recover bacterial-sized species
Gravity sedimentation	Good for low-value prods Enhanced by flocculation	Dilute biomass product
Flocculation/flotation (incr. effective particle size)	Flocculants can be inexpensive, non-toxic, and effective at a low conc. Only low level of mixing required May only need pH adjustment	
Dehydration/thermal drying	Preserves the biomass	Energy intensive
	Spray drying used for high-value prods	Expensive

2.2.5 Value-added products

The absence of support structures, such as roots and stems, allows for a larger fraction of the microalgae to be used to create desired products compared to other types of biomass.²³ There is a broad range of valuable products that can be harvested from the production of biomass. The type and quality of product obtained depends on the species of microalgae, growing conditions, and recovery methods implemented. The utilization areas of microalgae can be divided into three categories²⁴:

- Energy – production of substances such as hydrocarbons, hydrogen, methanol, etc.
- Foods and chemicals – e.g., proteins, oils and fats, sterols, carbohydrates, sugars, alcohols, etc.
- Other chemicals – e.g., dyes, perfumes, vitamins/supplements, etc.

Many researchers have demonstrated that biomass can be used as an effective feed substitute for animals. Furthermore, Chae and co-authors²⁵ determined the *E. gracilis* microalgae they produced was an especially effective feed source for broiler chickens as described previously. On average, one broiler chicken can consume approximately 114 g of dried microalgae each day.²⁵ The chicken would produce approximately 30 L (60 g) of CO₂/day due to respiration. This study concluded that the net CO₂ removal efficiency was approximately 19%.²⁵

One type of microalgae, cyanobacteria or blue-green algae, has been studied extensively because of its many valuable products.³³ The edible species include *Nostoc*, *Spirulina*, and *Aphanizomenon*, which can be used as a raw, unprocessed food as they are rich in carotenoid, chlorophyll, phycocyanin, amino acids, minerals, and bioactive compounds.³³ Besides their nutritional value, these compounds have immense medicinal value, such as immune-stimulating, metabolism increasing, cholesterol reducing, anti-inflammatory, and antioxidant properties.³³ Figure 2.2.5 shows the relative proportion of biological activity found in specifically marine cyanobacteria.

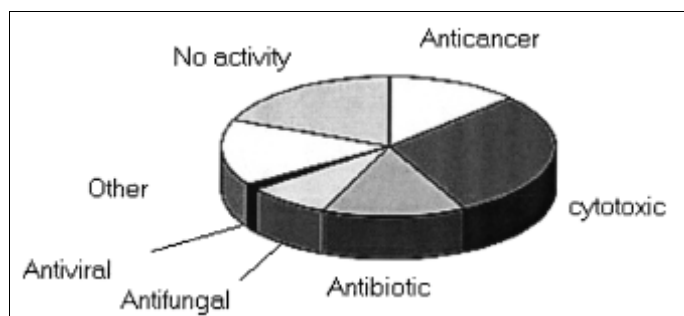


Figure 2.2.5: Relative biological activities of marine cyanobacterial compounds.³³

Currently, there is a substantial market for various products created from biomass. Table 2.2.5 shows some commercially sold microalgal products paired with the species of microalgae that produces the goods, as a result of the study by Walker and co-authors³⁶ in 2005.

Another important aspect of microalgae is that they are rich in omega-3 fatty acids including docosahexaenoic acid and EPA, which have significant therapeutic importance inherent in the ability to act as an anti-inflammatory to treat heart disease.³³ Furthermore, EPA has been shown to prevent and treat various medical conditions, such as coronary heart disease, blood platelet aggregation, abnormal cholesterol levels, several carcinomas, as well as arresting and minimizing tumor growth.³⁷ Eicosapentaenoic acid is also naturally found in fish oils; however, microalgal sources have important advantages, including the lack of fish-like flavor, enhanced purity, low cholesterol content, and a less-costly recovery process.^{33, 35} There are also important concerns regarding the contamination of fish oil with pesticides and heavy metals.³⁷ Microalgae are actually the primary producers of omega-3 polyunsaturated fatty acids and fish usually obtain EPA via bioaccumulation in the food chain.³⁵ The production of this compound is discussed in detail in the next section.

*Table 2.2.5: Companies selling microalgal-based products (2004).*³⁶

Company	Microalgae	Products
Cyanotech (www.cyanotech.com)	<i>Spirulina pacifica</i>	Spirulina extracts as nutritional supplements, immunological diagnostics, aquaculture feed/pigments and food colouring
Martek Biosciences Corporation (www.martekbio.com)	<i>Cryptocodinium cohnii</i>	Nutritional fatty acids
Mera Pharmaceuticals (www.aquasearch.com)	<i>Haematococcus pluvialis</i>	Natural astaxanthin as a nutraceutical
Earthrise Nutritionals (www.earthrise.com)	<i>Spirulina sp</i>	Nutritional supplement to inhibit replication and infectivity of viruses including HIV, CMV, HSV and influenza A
PharmaMar (www.pharmamar.com)	Various	Anticancer drugs derived from marine microorganisms
Nikken Sohonsa Corporation (www.chlostanin.co.jp)	<i>Chlorella sp. Dunaliella sp</i>	Dietary supplements: polysaccharide N,β-1.3 glucan (<i>Chlorella</i>) and β-carotene (<i>Dunaliella</i>)
Nature Beta Technologies	<i>Dunaliella bardowil</i>	β-carotene powder
Cognis (www.cognis.com)	<i>Dunaliella salina</i>	Mixed carotenoids
Subitec GmbH (www.subitec.com)	Undisclosed	Polyunsaturated fatty acids
Solazyme (www.solazyme.com)	Undisclosed	No products yet brought to market

2.2.6 System design

Bubble column tank farm design

The design of a bubble column tank farm that can produce 5 tons of EPA annually has been extrapolated down from the design of a system that produces 20 tons of EPA annually. Each individual bubble column is to be of uniform size and dimensions. The diameter is 0.2 m and the height is 2.1 m, which corresponds to a culture volume of 0.06 m³ and occupies 0.031 m² in surface area.³² To optimize the use of land area, the system will be comprised of rows of bubble columns with an east-west orientation. The rows will be 3.4 m apart and the spacing between the column centers within a row will be 0.35 m.³² To produce 5 tons of EPA annually with the system design as specified, a total production volume of 913.3 m³ is required. This will occupy a total surface area of 1.8 ha or 18,338 m².

To optimize land-use or minimize the surface area required for the system, the bubble column height can be increased to a maximum of 4 m.³² The efficiency of the entire system is shown to increase with column height and a reduction of nearly 60% in surface area requirements can be expected.³² This adjustment will, however, increase the amount of shading to which each column is exposed and ultimately, lower productivity of the biomass within the system. Figure 2.2.6 shows the incident angle the sun has on a bubble column. It is easy to see that when the sun is in the position of early morning or afternoon, there can be shading, or blocking of the sunlight by adjacent columns.

Seasonal variations in irradiance levels are inevitable. During the summer months, the Sun is highest on the horizon, indicating a lower average irradiance level experienced by the bubble columns compared to the winter months when direct radiation from the Sun affects a larger percentage of the reactor surface.³² Higher irradiance levels in the winter help to reduce any heating demands needed to stabilize the culture, whereas lower irradiance levels in the summer should reduce the need for any cooling of the columns.

Furthermore, the low surface-to-volume ratio helps to reduce heat losses during the night when solar radiation is absent.³² Productivity can be enhanced in bubble columns by adding artificial lighting systems to illuminate the system at night.³² Technology exists for placing a low-power, vertical light source at the axis of the column; however, this greatly adds to capital and operational costs of the system, as one would expect.³²

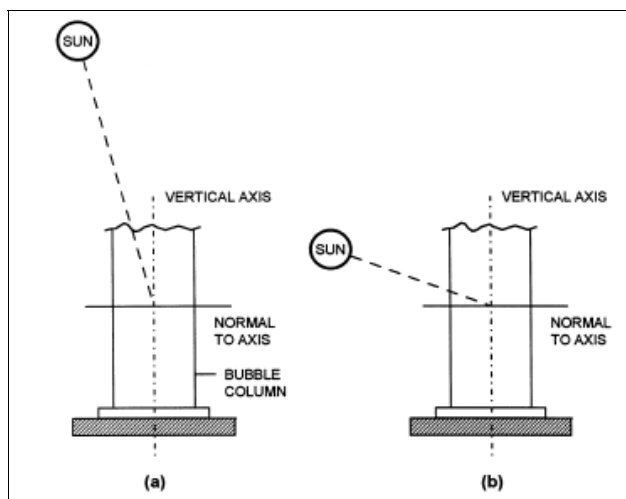


Figure 2.2.6: A representation of the sun's position with respect to the axes of the bubble column (in the northern hemisphere) (a) at solar noon, and (b) in the afternoon or early morning.³²

Mass balance

The mass balance for the system is shown in Figure 2.2.7. The input of air enhanced with 60% CO₂ by volume is required at 1,565.7 kg/day or 571,481 kg/yr (571.5 tons/yr) to achieve a utilization rate of 986.4 kg CO₂/day or 360,036 kg CO₂/yr (360 tons/yr), based on a CO₂ uptake efficiency of *P. tricornutum* at 63% of the CO₂ supplied.³⁸ The utilization rate of CO₂ by the microalgae is approximately 1.8 kg of CO₂ for every g of biomass as discussed previously. The productivity of the chosen microalgae species is assumed at 0.6 kg/m³·day as a conservative estimate. Calculated productivity levels have been measured as high as 0.729 kg/m³·day for the chosen microalgae.³² The outputs of the system will be 548.0 kg biomass/day or 200,020 kg biomass/yr (200 tons/yr) with an excess of 211,445 kg CO₂/yr. This unused CO₂ could be recirculated, concentrated, and reused as a feed to the system or sent to a sequestration process.

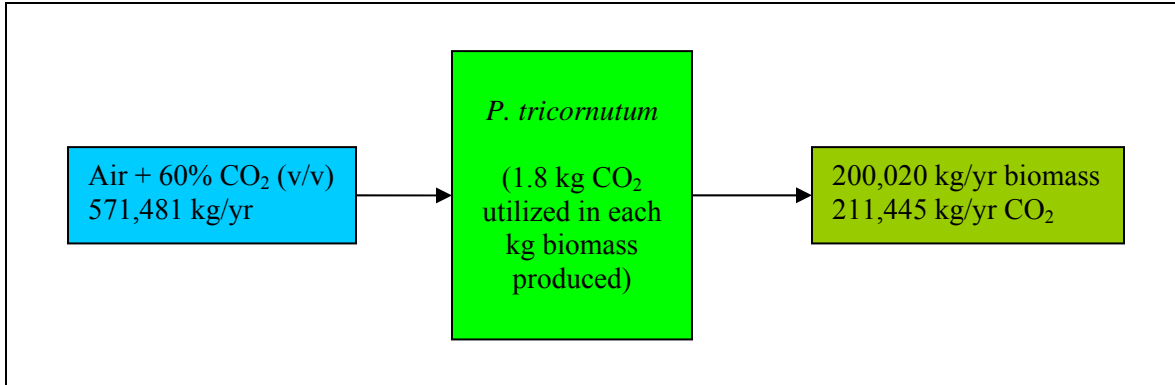


Figure 2.2.7: Mass balance for bubble column tank farm.

Power requirements

The main power input needed for the bubble column tank farm is aeration. Air plus CO₂ is sparged into each bubble column using a perforated pipe with 17 holes 1 mm in diameter, corresponding to a gas flow area approximately 0.05% of the total cross-sectional area of the column.³²

$$P_G/V_L = \rho_L g U_G, \quad (2-2-2)$$

where P_G is the power input for aeration (W), V_L is the volume of liquid in the reactor (m³), ρ_L is the density of the liquid (kg/m³), and U_G is the superficial gas velocity in the column (m/s).³² Equation 2-2-2 applies to the bubble flow regime, where U_G is less than approximately 0.05 m/s ($P_G/V_L \approx 500$ W/m³). The optimum superficial gas velocity for *P. tricornutum* is at 0.01 m/s, since the growth rate declines above this value due to hydrodynamic stresses.²⁷ For this particular system, the power input needed for aeration can be estimated at 98 W/m³. A facility producing 5 tons EPA/yr with a total production volume of 913.3 m³ would require 89.5 kW to aerate the system, which is a relatively moderate power requirement.

Eicosapentaenoic acid (EPA) recovery process

Eicosapentaenoic acid (EPA) is a substance that is incredibly rich in pharmaceutical and health industry benefits. It can be recovered in a highly pure form (>95% purity) from biomass using an established recovery process as shown in figure 2.2.8.³⁷

The recovery process requires many solvents and chemical inputs, summarized in Figure 2.2.9, that are neither human nor environmentally friendly. Improvements can be made here by incorporating supercritical CO₂ extraction to recover EPA in place of the current method. Supercritical CO₂ extraction is discussed in detail in chapter 3 of this report. This modification would also entail utilizing additional CO₂ in the proposed method, which enhances the goal of this study even further.

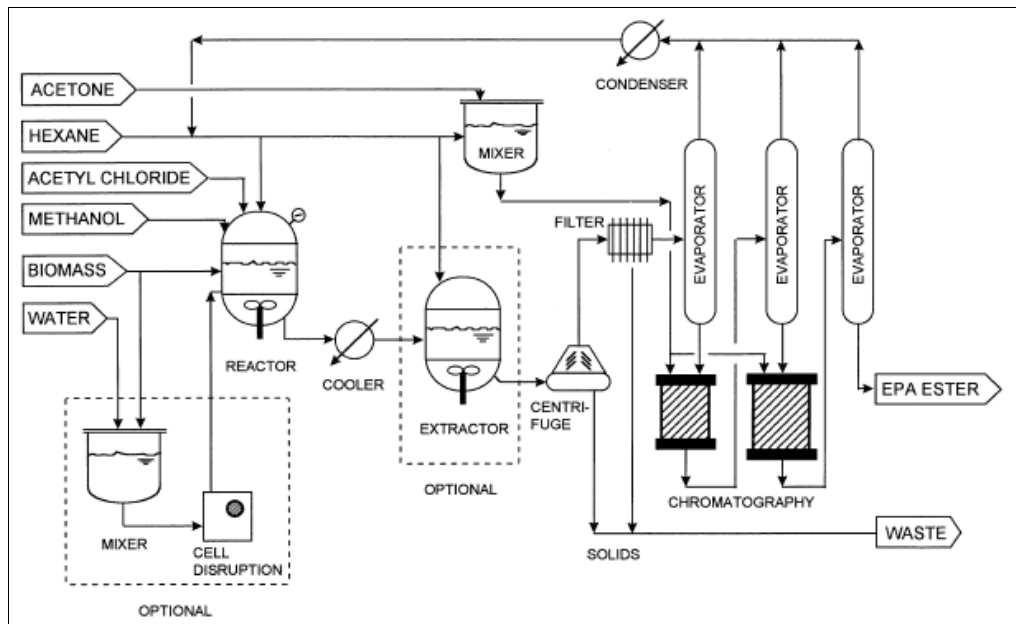


Figure 2.2.8: Flowsheet of EPA-from-microalgae process.³⁷

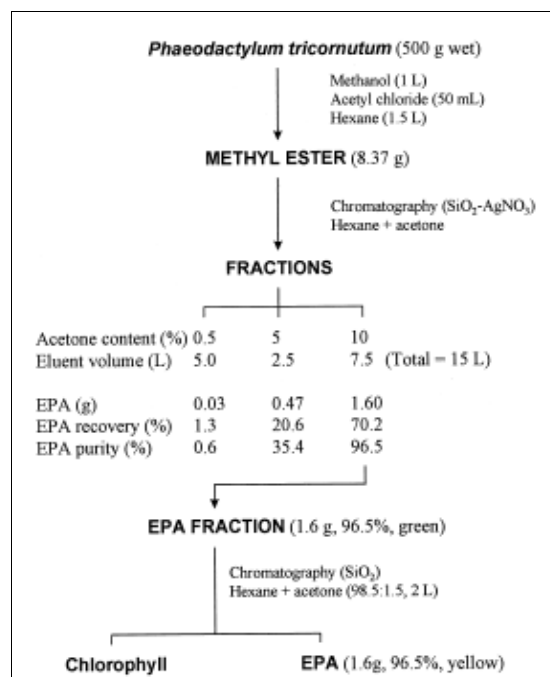


Figure 2.2.9: EPA recovery requirements from *P. tricornutum* paste.³⁷

Some factors that could improve the recovery of EPA from microalgae would be improving the yield. If the recoverable EPA concentration within the biomass is increased, the production facility size can be reduced by about 30%.³² One way to improve this is selective growth of specific microalgae species that demonstrate high yields of EPA; another is to utilize genetic manipulation to engineer a “new” microalgae with higher EPA concentrations.^{32, 35} It is estimated that the yield can be increased by approximately 44% in this way.³⁵

EPA market value

The market price of EPA (95% pure) in bulk quantities was approximately \$650/kg in 2000.³⁷ A sufficient demand on the order of 300 tons/year existed for this product on a global scale in 2000.^{33, 37} With new evidence of clinical effectiveness of EPA, as well as an indication that it may help to boost metabolism, overall energy, and mood, the demand is expected to increase greatly.³⁷ Ultimately, the market exists for a new source of EPA, especially one with numerous benefits over the current fish oil-derived sources.

To estimate the current market value of EPA, a moderate 25% increase in demand was assumed. This would bring the global demand up to 375 tons/yr. With an increase in demand and no new sources of EPA at present, the market value can be expected to increase. Again, to keep to a very conservative estimation and not to predict actual market value with the demand increase stated previously, a 25% increase in market price was assumed. This would raise the market price of EPA to approximately \$813/kg. When producing 5,000 kg EPA/yr (5 tons/yr), an annual revenue of \$4.06 million can be expected by selling the acid. If the facility is scaled-up to produce 10,000 kg EPA/yr (10 tons/yr), the annual revenue increases to about \$8.13 million.

Size design comparisons

A comparison between bubble tank farms that produce varied amounts of EPA is presented in Table 2.2.6. It can be seen from this table that an increase in EPA production results in an increase in required surface area for the system, as expected. A greater rate of CO₂ utilization is shown with an increase in biomass production as well.

Table 2.2.6: Comparison of different systems based on varied production levels.

EPA Production (kg/yr)	Total Volume (m ³)	Surface Area (m ²)	Aeration Power (kW)	Biomass Production (kg/yr, dry)	CO₂ utilized (kg CO ₂ /yr)	CO₂ required (kg CO ₂ /yr)
20,000	3,653	73,350	358	760,555	1,368,998	2,173,013
10,000	1,827	36,675	179	380,277	684,499	1,086,507
5,000	913	18,338	89	190,139	342,250	543,253

2.2.7 Conclusions and recommendations

A few comments on capital costs and feasibility would be that even if the initial investment of the entire production facility would be very large, for example \$5 million (or even \$10 million), the revenue that can be gained each year is significantly high to turn the expenses into profits after just a few years.

Overall, photobioreactors are an effective method for producing valuable products from microalgae. They have the potential to bring in high annual revenue from the products they generate. As far as being effective for CO₂ utilization, they are capable of using only a very small percentage of the total CO₂ generated by a 500 MW power plant, which was estimated at 9.0 x 10⁶ kg/day (9.0 x 10³) or 3.3 x 10³ ktons/yr, which was used as a basis

for comparison throughout this study. A facility producing even 20 tons EPA/yr will only fixate 0.041% of the total emissions from the plant. The larger the production capacity, the more CO₂ the system will be able to utilize; however, the larger the production, the larger the land requirements for the facility. Ultimately, photobioreactors are not effective for large-scale CO₂ utilization when the goal is to utilize as much CO₂ as possible from a 500 MW power plant.

3. Utilization of supercritical carbon dioxide

3.1 Supercritical carbon dioxide

3.1.1 Introduction

Supercritical carbon dioxide (scCO₂) is emerging as an alternative to environmentally harmful solvents and products. Besides the environmental factors, many solvents used today are expensive and require special handling conditions. Supercritical CO₂ is cheap, considered environmentally “benign”, and easy to handle. Some industries that are taking advantage of the properties of scCO₂ are the food and extraction industries. This section contains a review about the physico-chemical properties of scCO₂, its current and prospective uses, as well as the advantages and disadvantages of utilizing scCO₂ vs. some of the existing technologies.

Fundamentals of scCO₂

A substance is said to be in its supercritical state when it has exceeded its critical temperature and pressure. A pressure vs. temperature (P-T) diagram of CO₂ is presented in Figure 3.1.1.³⁹ For CO₂, the critical point is located at a temperature of 304.1 K and a pressure of 73.8 bar. Beyond its critical point a substance cannot be regarded as neither a gas nor a liquid; furthermore, there is no discernable phase, and the viscosity, dielectric constant, and heat capacity, among other properties, differ considerably from the vapor or liquid phases.⁴⁰ These changes give scCO₂ its solvent and extraction properties.

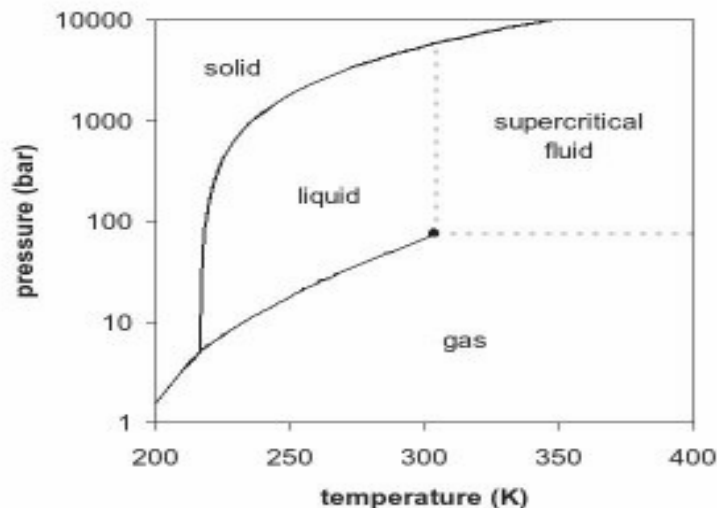


Figure 3.1.1: Phase diagram for CO₂.³⁹

Applications

There is a diverse range of applications for scCO₂. These applications vary between large or industrial scale to small or laboratory scale. Some minor applications include: (i) supercritical fluid fractionation (SFF)⁴¹, in which substances that have been already extracted are further processed to separate or fractionate them into their components. Examples include polymer and pharmaceuticals fractionation. (ii) Supercritical fluid impregnation (SFI) refers to the homogeneous distribution of active components into a solid matrix. This is done by taking advantage of the increased diffusivity of a supercritical fluid. Examples include preservatives delivery and textile dyeing. (iii) Supercritical fluid chromatography is a technique relegated as an analytical tool.^{41, 42} Some of the major applications are discussed in the following sections.

3.1.2 Extraction of compounds from microalgae using scCO₂

Introduction

Worldwide, the classic means for processing microalgae has been using organic solvents, the most favored of which are toxic to animals and humans. However, supercritical carbon dioxide (scCO₂) has some unique advantages over the organic solvents and is considered a good candidate for algae treatment because it is a nontoxic and fully “green” solvent.⁴³ Despite the advantages, using scCO₂ to extract valuable compounds from microalgae is not the prevailing technology in use today even though production costs are of the same order of magnitude as those related to classical processes. Following is a discussion of important factors to be considered in the extraction of compounds from microalgae using supercritical CO₂.

Microalgae products and types

Microalgae are a diverse group of organisms which yield a wide range of chemicals. The main commercial products from microalgae yield carotenoids, phycobilins, fatty acids, polysaccharides, vitamins, sterols and other biologically active compounds. Phycobilins for example, have found use as research tools. When they are exposed to strong light, they absorb the light energy, and release it by emitting light of very narrow wavelengths. The light produced is so distinctive and reliable, that phycobilins are used as chemical tags. The pigments chemically bond to antibodies and are put into a solution of cells. As the solution is sprayed past a laser and computer sensor, the cells in the droplets can be identified as being tagged by the antibodies. This is used extensively in cancer research, for tagging tumor cells.⁴⁴

Bench scale supercritical CO₂ experiments on microalgae have been performed on *Botryococcus*, *Chlorella*, *Dunaliella*, and *Arthrospira* to name a few.⁴³ The laboratory experiments are performed using bench-scale equipment which can be purchased from manufacturers specializing in the design, construction and operation of supercritical CO₂ extraction process equipment. Many such experiments have used the SEPAREX model

SFE 500.^{43, 45-47} These experiments produced numerous valuable products from the various microalgae types, a summary of which is listed below.

- Hydrocarbons (up to 85% mass of cell), *Botryococcus*.
- Pharmaceutical grade parafinic and natural waxes, *Botryococcus*, *Chlorella*.
- Strong Antioxidants (astaxanthin, canthaxanthin, β -carotene) *Chlorella*, *Dunaliella*.
- Linolenic acid (GLA), *Arthrospira*.

The moderate temperatures and inert nature of CO₂ have been shown to virtually eliminate the degradation of the product extracted. In addition to the extract quality, the ability to significantly vary the CO₂ solvation power by small changes in pressure and/or temperature adds operating flexibility to the scCO₂ extraction process that no other extraction method, including solvent extraction, can claim.⁴⁸ Carbon dioxide is the most used supercritical solvent because the toxic solvents are not needed. Industrialized countries are in the process of formulating legislative restrictions to eliminate the use of toxic solvents as good manufacturing procedure (GMP), especially in the manufacture of topical or ingestible pharmaceutical products.

CO₂ utilization for microalgae preparation

Industrial use of scCO₂ extraction processes have been hampered by a perception that the capital cost of the extraction plant is large, and the need for an efficient treatment of the biomass matrix prior to extraction does not exist. However, the high capital cost of the scCO₂ extraction process due to the cost of high-pressure equipment is balanced to some extent by lower operating costs if the process is carried out at optimal conditions and if the capacity of the extractor is sufficient.⁴⁸ Research indicates that preparation of the microalgae by thoroughly crushing the cells can significantly increase yield when compared to uncrushed, whole cells (Figure 3.1.2). The yield is further increased when the whole cells are first crushed and then ground with dry ice. When ethanol is added into the extraction processes, optimum yields have been reported (Figure 3.1.3).

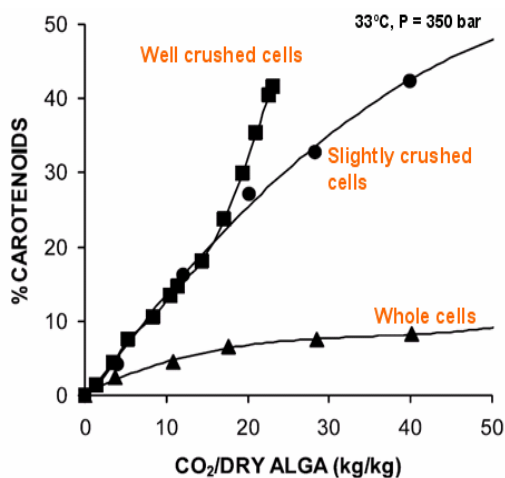


Figure 3.1.2: Extraction yield of carotenoids.⁴³

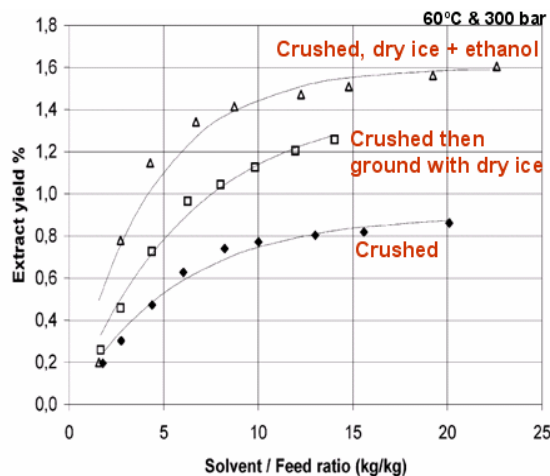


Figure 3.1.3: Extract yield of astaxanthine.⁴⁶

Supercritical CO₂ extraction process for microalgae

In the supercritical CO₂ extraction process (Figure 3.1.4) for microalgae the microalgae preparation is first loaded into the feedstock extraction vessel. Porous stainless steel disks at the top and bottom of the extraction vessel are used to prevent migration of biomass residue beyond the vessel. Bag filters are used to contain biomass and to aid the cleaning and recharging process of the extraction vessel. Pure (100%) CO₂ is added to the system from gas cylinders. Co-solvent, if desired, can be added before or after the condenser depending on the requirements of the extraction process. The condenser is used to cool the CO₂ which is passed to the inlet of the pump as liquid solvent. The compressed fluid is passed through a heater to optimize the solvent temperature prior to reaction with microalgae preparation. After percolating through the feedbed, the fluid is expanded into high performance separators where the extract is taken out by a precipitation process. Fluid leaving the last separator is recycled back to the condenser. On large-scale units, care must be taken to assure biomass residue is not passed through the expansion valve to reduce contamination of precipitated product and most importantly, avoid costly time loss due to stringent cleaning requirements.⁴⁶

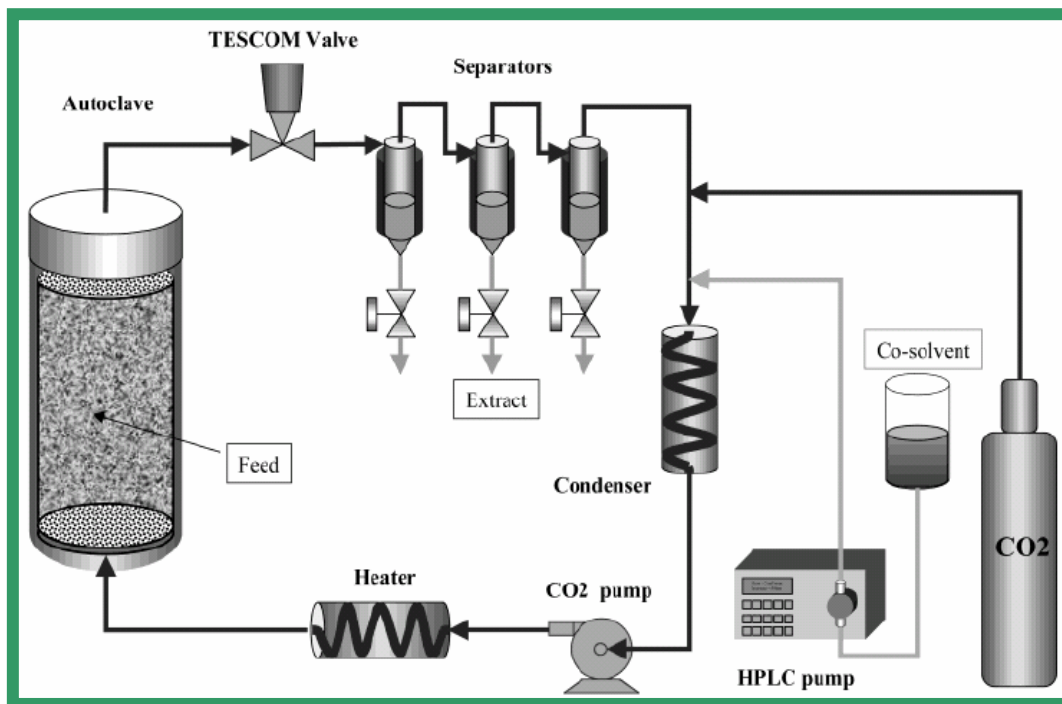


Figure 3.1.4: Schematic diagram of a bench-scale SFE-500 SEPAREx pilot plant.⁴⁶

Process scale

Very important research and development activities are presently dedicated to applications of scCO₂, and much has been published on results obtained using small scale equipment with a 10 mL precipitation chamber and a CO₂ flow rate of up to 0.5 kg/h.⁴⁵ However, until recently, little was known about the performance of equipment processing

batch sizes as required for industrial use. Emerging studies by equipment manufacturers indicate that equipment performance does not suffer as the extraction process is scaled-up. Published results also provide an indication of the amount of CO₂ utilized as the various equipment sizes are increased.⁴⁵

- Pilot Scale equipment: CO₂ flow rate: 5 kg/h
- Pilot Scale equipment (Pharmaceutical): CO₂ flow rate: 20 kg/h
- Industrial Scale equipment: CO₂ flow rate: 500 kg/h

Maintenance of industrial scale SFE pharmaceuticals (GMP)

Industrial operation of supercritical plants requires the high reliability and safety requirements associated with high pressure equipment. A thorough, preventative maintenance plan is required as many parts must be inspected and changed periodically. Additionally, a rigorous operation plan must be enforced to eliminate any risk of deterioration of the basic mechanical equipment, sensors, closure systems and gaskets in order to prevent solvent leakage. Maintenance is greatly reduced when great attention is paid to extract-solvent separation to avoid entrainment of some fraction of extract through the fluid recycle loop, and if an efficient cleaning process is strictly enforced.⁴⁹

The good manufacturing process (GMP) rules enforced in the pharmaceutical industry are those discussed below.

Between batches:

1. Rinse with adequate liquid solvent.
2. Dismantle and rinse again with liquid solvent.
3. Dry with gaseous nitrogen or CO₂ (to eliminate solvent vapor).
4. Rinse with liquid/supercritical CO₂ to eliminate extracted impurities (mainly liquid solvent).

Between different products:

1. Total or partly dismantle equipment & clean each part.
2. “Swab” the pressure vessels: scrub equipment wall with specific swab, extract, weigh and analyze dry residue.
3. Remove and replace fractionation equipment. Most parts of the supercritical fractionation equipment cannot be opened between each lot manufacture and the swab technique cannot be used.
4. Remove and replace most high pressure parts (like valves) which are not Clean-In-Place. This equipment is cleaned by special means which cannot be employed as installed.
5. Reassemble equipment – proceed as between batches.

It should be clear that simplification of the procedures can be used in the processing of foodstuffs and phyto-pharmaceuticals. For pharmaceutical products, manufacturer must prove no contamination has occurred by previously processed compounds, even if the

equipment used is dedicated to manufacturing a single product. The manufacturer must prove no cross contamination from one-lot to another has occurred.

Utilization of CO₂

Utilization rates of CO₂ for extraction of pharmaceuticals from microalgae are calculated and shown in Table 3.1.1. As a sidebar, one interesting use of CO₂ indicated is for sterilization purposes. When 100% CO₂ is used for sterilization to destroy *E.Coli*, the process can be carried out over 15 minutes at a pressure of 150 bar vs. 3000 bar without CO₂.⁴¹ This technique is gaining popularity in sterilization of equipment in health care application because it is safer, using lower pressure, and less costly, requiring less compressor energy. Liquid CO₂ used as a final rinse during cleaning operation is also indicated the on chart for completeness.

Table 3.1.1: Typical CO₂ utilization for extraction of pharmaceuticals from microalgae.

Process Description	Form	~ Rate (kg/hr)
Grow microalgae in an open pond system (as described under biological conversion)	Dilute	162
Crush and prepare microalgae for extraction 50-50 mix	Solid (100%) Dry Ice	90
Solvent for extraction. (includes swabbing procedure for GMP validation testing)	Super-critical	500
Sterilization of equipment	Pure (100% gas)	2
Washing of parts during cleaning operations	Liquid (100%)	1
	Total	755

The CO₂ utilization rate for extraction of pharmaceuticals from microalgae is computed in order to make a comparison with the amount of CO₂ emitted from a 500 MWe electric power plant. Accordingly, only 0.2% percent of the amount of CO₂ emitted by one power plant can be utilized by one industrial scale scCO₂ extraction vessel set-up to extract valuable products from microalgae.

$$755 \text{ kg CO}_2 \text{ per hour} \div 3.75 \times 10^5 \text{ kg CO}_2 \text{ per hour per power plant} \times 100 = 0.2\% \text{ (max)}$$

It is estimated that there are no more than 200 industrial scale scCO₂ extraction vessels in operation worldwide. If all of these are used to extract valuable products from microalgae, we would use only 40% of the CO₂ generating capacity of only one 500 MW electric power plant.

Estimated operating costs of industrial scale SFE units (including return-on-capital)

Food Ingredients:	\$1.2 to 12 per kg
Metallurgical/Mechanical Waste Recycling:	\$0.4 to 1.2 per kg
Polymer Paints and Powders:	\$1.2 to 6 per kg
Aerogels Drying:	\$2.4 to 12 per kg
Pharmaceutical Powder:	\$120 to 2400 per kg

Summary

Large capacity plants, with optimized design and operation, often lead to prices that are of the same order of magnitude as those related to classical processes but with improved benefits to environment and consumer protection.

3.1.3 Other supercritical CO₂ applicationsSupercritical Fluid Extraction (SFE)

Large-scale operations of SFE are mostly focused on tea and coffee decaffeination, hops and tobacco extraction⁴², and the removal of fats from food.⁴¹ The average industrial-scale extractor volume in the U.S. is around a 1000 L in volume.⁴² Smaller scale operations focus on specialty products manufacture such as aromas, colorants, pharmaceutical and cosmetic active ingredients.⁴¹

Supercritical CO₂ finds its advantage over other solvents (e.g., nitrous oxide, ethane, propane, *n*-pentane, ammonia, hexane, dichloromethane, etc.) in that it has low toxicity, inflammability and cost, as well as high purity.⁵⁰

Caffeine extraction has been traditionally done using hexane and dichloromethane as extracting agents. These agents, however, are considered harmful to humans and the environment.⁵¹ By utilizing scCO₂, the harmful factor is eliminated; however, scCO₂ can not extract caffeine by itself, so the utilization of a co-solvent is needed. Recent studies suggest that by mixing small amounts of ethanol (5%), methanol (10%), and isopropanol (5%), respectively, with scCO₂, the solubility of caffeine increases.⁵¹

Other specialty food products include spices. Catchpole and co-authors⁵² compared the extraction of chili, black pepper and ginger utilizing scCO₂ and the solvents commonly used in this kind of extraction, namely propane, acetone and dimethyl ester. Their results indicate that scCO₂ extracted comparable amounts of each of the spices; however, scCO₂ showed a higher selectivity for some of the other components in the spices such as aromas and other volatile components. Much of these trace components were not recoverable with the other solvents.

Another specialty product is the extraction of anti-oxidants. Carvalho and co-authors⁵³ reported the anti-oxidant extraction from rosemary; the substances associated with the anti-oxidant activity in Rosemary are phenolic diterpenes and phenolic acids. The authors

compared the extraction capability of scCO₂ vs. ethanol and hexane in terms of anti-oxidant activity, which is how much of the extract is active. Ethanol and hexane presented more yield than scCO₂, however the anti-oxidant activity of the products was much higher utilizing scCO₂. The utilization of scCO₂ for extracting specialty products has its advantage not in the amount but in the purity and “freshness” of the extracts; this can help to offset initial capital costs.

Supercritical CO₂ has also been used for the extraction of pesticides from food⁵⁴, and the extraction of BTEX (benzene, toluene, ethylbenzene, and xylene) and other hydrocarbons from gasoline spills.⁵⁵ Some of the advantages and disadvantages of SFE are summarized in Table 3.1.2.

There are several criteria to determine whether scCO₂ can compete with the existing extraction technology. Some aspects include the energy requirements, the effectiveness of extraction (i.e., quantity vs. quality), the value-added products, the amount of CO₂ utilized, and the operational costs. Several studies have been performed to assess these criteria, yielding mixed interpretations.

Table 3.1.2: Advantages and disadvantages of SFE.

Advantages	Disadvantages
Wide range of selectivity Good solvent properties Non-toxic and non-flammable Easy to remove Inexpensive	Poor solvent for polar analytes Immisible in water (limitation for aqueous and biological samples) Initial large investment

A study by Hawthorne and co-authors¹³ compared four different extraction methods, (i) Soxhlet extraction (organic solvents), (ii) pressurized liquid extraction (PLE), (iii) supercritical fluid extraction (SFE), and (iv) subcritical water extraction (SWE). The samples studied were soil specimens contaminated with polycyclic aromatic hydrocarbons (PAH). The parameters utilized for the different extraction methods are presented in Table 3.1.3. The comparison was made in terms of the selectivity and quality of the targeted extracts. For the selectivity criteria, it was analyzed how much of the original carbon and nitrogen compounds (belonging to the uncontaminated samples) were extracted. From Table 3.1.3 it can be seen that SFE requires a much higher operation pressure than the other methods, and it requires the second highest temperature. On the other hand, it requires considerably less operation time than the most commonly used Soxhlet method. In terms of selectivity, SFE and SWE were the most selective, and SFE left the least amount of residue after the extraction. Furthermore, SFE targeted the least amount of C and N matrix compounds (non-targeted compounds), as seen in Table 3.1.4.

Table 3.1.3: Parameters for the different extraction methods.¹³

	Soxhlet ^a	PLE ^b	SFE ^c	Subcritical water
Sample size (g)	2	2	2	2
Extraction solvent	CH ₂ Cl ₂ -acetone	CH ₂ Cl ₂ -acetone	Pure CO ₂	Water
Collection solvent	–	–	CH ₂ Cl ₂	Toluene
Pressure (bar)	ambient	70	400	50
Temperature (°C)	b.p. of solvent	100	150	300, 250
Flow-rate	15 ml/cycle	1 ml/min	1 ml/min	1 ml/min
Time	18 h	50 min	60 min	30, 60 min
Solvent volume (ml)	150	15	15 (60) ^c	10, 20 (30, 60) ^d

Table 3.1.4: Comparison of the soil extract characteristics.¹³

	Extract color	Extract turbidity	Residue ^a (mg/g soil)	% Removed by extraction ^b	
				C	N
Soxhlet	Black/brown	Heavy	107±24	32	34
PLE	Brown	Moderate	15±1	22	<5
SFE (pure CO ₂)	Light yellow	Clear	8±1	8	<5
Subcritical water:					
250°C	Orange	Moderate	8±1	34	79
300°C	Dark orange	Moderate	13±2	35	79

Despite the apparent advantage of SFE in terms of selectivity, SWE seems to be generally more effective. Supercritical CO₂ can only target non-polar analytes (its relative permittivity, ϵ_r , only varies between 1 and 2), whereas water (subcritical) can target a wide variety of components with different polarities. This property is attributed to the variation of the relative permittivity, which varies from 80 at 25 °C to 27 at 250 °C; at supercritical conditions the value of ϵ_r for water is around 1. This makes subcritical water extraction a more “tunable” extraction technique; this area, however, has not been extensively explored.

Particle synthesis

Particle synthesis utilizing scCO₂ is a promising area given the importance of nano-materials. Nano-materials are of great interest because their properties can vary significantly from those of the bulk material. A few applications of nano-materials include catalysts, paints, drug delivery systems, and abrasives among many others.⁴¹ There are several techniques for particle synthesis that vary according to their principle of operation.^{42, 56-59}

- Rapid Expansion of the Supercritical Solution (RESS)

In this method, the compound or substance of interest is dissolved in the scCO₂, and is allowed to expand through a nozzle or capillary into an expansion vessel. This rapid expansion leads to the precipitation of the solute into small particles. This method can create highly homogeneous particle size distributions, with the added benefit of tunable morphologies by varying the system parameters. A drawback of this technique is the limited range of solutes that can be used; the substances have to be soluble in scCO₂. In addition, large amounts of CO₂ are needed even to produce a small amount of product. This could make the technique unsuitable for large-scale development.

- *Supercritical Anti-Solvent Crystallization (SAS)*
This method utilizes a conventional solvent in which the solute is dissolved, next the solution is saturated with scCO₂ thus decreasing the solvating power of the solvent and causing the precipitation of the solute into particles. Several significant restrictions limit this technique, first of all, the solute is not soluble in scCO₂, and second, the solvent is immiscible in scCO₂. SAS has several modifications depending on the execution of the technique; these include Gas Anti-Solvent (GAS), Precipitation with Compressed fluid Anti-Solvent (PCA), Aerosol Solvent Extraction System (ASES), and Solution Enhanced Dispersion by Supercritical fluids (SEDS). Some details of these techniques are summarized in Table 3.1.5.⁵⁶ In general, SAS techniques are limited by poor control of particle morphologies, mainly due to the lack of a mechanistic understanding of the techniques. An advantage is that the techniques can be carried out in batches thus increasing the output of product.
- *Gas-Saturated Solutions (PGSS)*
This process consists of dissolving scCO₂ in a melt or liquid suspension of the substance or solute of interest after which the suspension is let to expand causing particle formation. The particle formation mechanism in this technique is due to a combination of a rapid decrease in temperature and the sharp increase of the volume of the matrix due to the expanding CO₂. One serious limitation for this technique is the poor control over particle size, and the possibility of not obtaining nano-particles at all.

*Table 3.1.5: Summary of particle synthesis techniques.*⁵⁶

Process	Solvent	Anti-solvent	Principle
RESS	scCO ₂	None	- Compound is dissolved in scCO ₂ - scCO ₂ solution is expanded over a nozzle
GAS	Conventional	scCO ₂	- Compound is dissolved in conventional solvent - scCO ₂ is fed into the solution
PCA	Conventional	scCO ₂	- Compound is dissolved in conventional solvent - Solution is discontinually sprayed into scCO ₂
ASES	Conventional	scCO ₂	- Compound is dissolved in conventional solvent - Solution is continually sprayed into scCO ₂
SEDS	Conventional	scCO ₂	- Compound is dissolved in conventional solvent - scCO ₂ and solution are sprayed simultaneously through a coaxial nozzle
PGSS	Compound	None	- scCO ₂ is dissolved in the melt of the compound - Solution is expanded over a nozzle

Energy Considerations

Besides the selectivity criteria for scCO₂, the energetic aspect is also important. Several authors have tried to model extraction processes to assess the viability of scale-up operations. In his study, Brunner⁶⁰ performed a thermodynamic analysis of a prototype

supercritical fluid extraction process using CO₂. According to his analysis, an extraction process utilizing a feed of 200 tons per year would require 17.5 kton per year of CO₂. Depending on the process pressure requirements, the amount of energy required will vary. A comparison of the energy requirements vs. process pressure is presented in Figure 3.1.5. Energy consumption may vary between 140 kJ/kg CO₂ with heat recovery systems to 350 kJ/kg CO₂ without heat recovery. These values were optimized with respect to flow rate, and extraction column dimensions and pressure.

Gani and co-authors⁶¹ developed a computer simulation program to analyze the energy requirements and costs of a fatty esters extraction facility. In their study, an average feed of 0.264 ton per year was used. Their energy consumption results yielded an estimate of 11.7 MJ/kg CO₂. This result is almost two orders of magnitude higher than Brunner's⁶⁰ estimate. It is difficult to compare these results without more details of their study. It is also possible that this inconsistency is due to the difference of the targeted extract in each process. If this is the case, analysis of the prospect of scCO₂ becomes extremely difficult, and extract dependent.

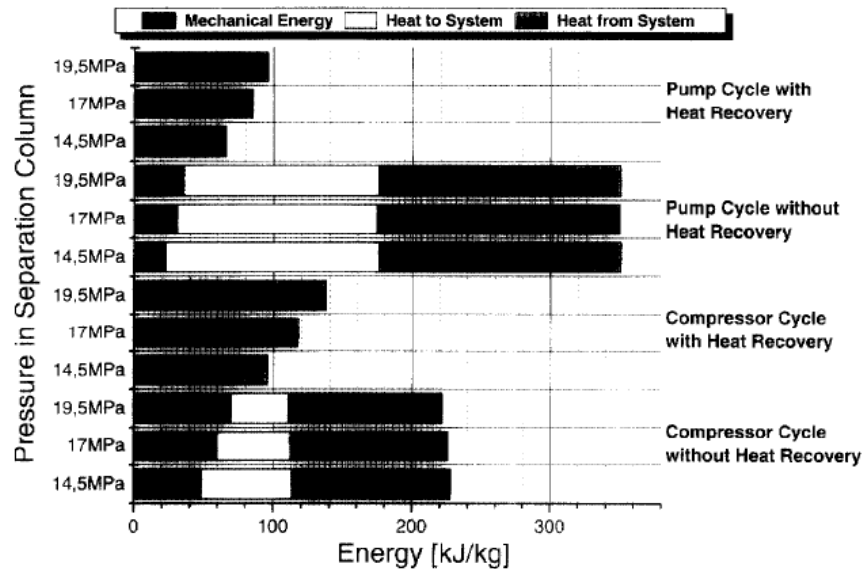


Figure 3.1.5: Energy requirement for a scCO₂ extraction process.⁶⁰

Another approach to determine the energy efficiency of scCO₂ extraction technologies is to perform a so-called exergy analysis. Smith and co-authors⁶² performed an exergy analysis to a naphthalene supercritical extraction process to determine the optimal conditions of operation. Their study suggested that the optimal pressure and temperature conditions for naphthalene extraction were 9.1 MPa and 40 °C. At these conditions, the exergy loss is around 6 kJ/kg CO₂.

3.1.4 Catalysis

Introduction

Carrying out catalytic reactions utilizing supercritical fluids as a reaction media offers significant advantages over organic solvents. Among these advantages we find increased diffusion, increased solubility of reagents, lower viscosity, enhanced mass transfer, tunable reaction environment, and the added benefit of using an environmentally benign solvent.⁶³⁻⁶⁵

Homogenous catalysis

Homogeneous catalytic reactions can particularly benefit from supercritical CO₂ as reaction media. A measure of the catalytic activity is the turnover frequency (TOF), which accounts for the amount of moles of product per mole of catalytic active sites or groups per hour. Figure 3.1.6 contains the data for the TOF of hydrogenation reaction in different media. When scCO₂ is combined with a co-solvent, the TOF more than doubles when compared to CH₃OH as a media. Other media yields products several orders of magnitude less than the scCO₂/co-solvent system.

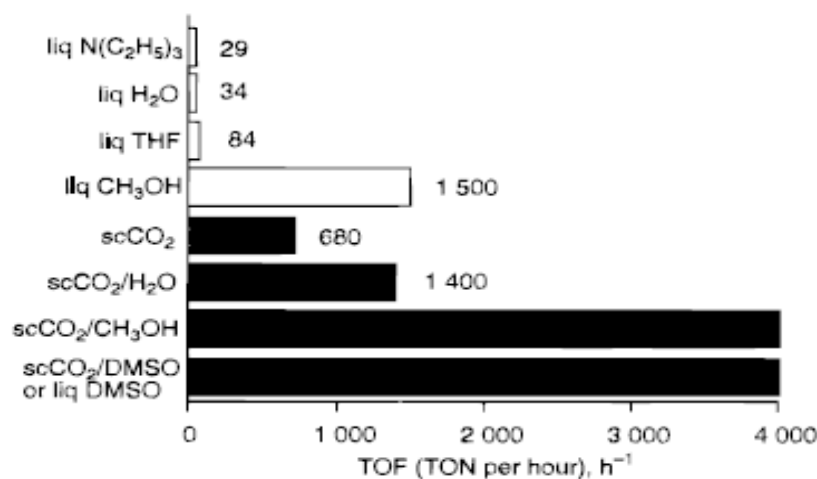


Figure 3.1.6: Turnover frequency for hydrogenation reactions in different media.⁶⁴

Heterogeneous catalysis

Supercritical CO₂ has also been used for heterogeneous catalytic reactions. Different parameters for heterogeneous catalytic reactions are presented in Table 3.1.6.⁶³ From the table it can be seen how each of the different reactions are affected by utilizing CO₂ as media. Most of the reactions experience an increase in reaction rate, *r*, some experience an increase in selectivity, *S*, while only in a few reactions the life of the catalyst was extended; all this with the added advantage of avoiding organic solvents.

This field encompasses too many reactions and reaction conditions, and research in this area will provide valuable results in the future and will probably replace most of the organic solvents currently used in the field.

Table 3.1.6: Heterogeneous catalytic reactions in CO₂.

reaction	catalyst	solvent	T, °C	P, Mpa	r ^a	S ^b	a ^c
Alkylation							
1-butane and isobutane	zeolite H-USY, sulfated zirconia	CO ₂	50-140	3.45-15.5			^
mesitylene 2-propanol	polysiloxane (DELOXAN) supported solid acid	CO ₂	200-300	15.0-20.0			
Esterification							
oleic acid and methanol	K2411 sulfonic macroporous ion exchange resin	CO ₂	40-68	0.95-1.3			^
Hydrogenation							
fats and oils	Pd or Pt on DELOXAN support	CO ₂	60-160	8.0-16.0	^	^	
acetophenone	5% Pd APII DELOXAN	CO ₂	90-300	12.0	^	^	
cyclohexene	5% Pd APII DELOXAN, 5% Pt APII DELOXAN	CO ₂ , propane	40-320	6.0-12.0			^
1,2-(methylenedioxy-4-nitrobenzene double bonds of unsaturated ketone	1% Pd DELOXAN	CO ₂	90	14.0			^
	Pd/Al ₂ O ₃	CO ₂	150-220	12.0-17.5			
Isomerization							
1-hexane	Pt/γ-Al ₂ O ₃	CO ₂ , n-pentane, n-hexane	250	18.0	^	^	^

^achange in reaction rate, ^bchange in selectivity, ^cchange in catalyst lifetime, ^increase

3.1.5 Environmental remediation

Introduction

Remediation of contaminated sites is a considerable task taking into account how expensive current cleanup processes are, and the amount of contaminated sites that exist. In 2003 the Environmental Protection Agency's (EPA) National Priority List (NPL) contained more than 1500 sites, at an estimated inclusion average of 28 sites per year.⁶⁶ Of these, approximately 142 sites are or will be designated mega sites. A mega site is determined to require more than 50 million dollars in total cleanup costs.⁶⁶

Polychlorinated Biphenyls (PCB)

Polychlorinated Biphenyls are synthetic, organic chemicals once widely used in electrical equipment, specialized hydraulic systems, heat transfer systems, and other industrial products. PCBs are highly toxic and a potent carcinogens, and concentrations of more than 50 parts per million of PCBs are subject to regulation under the Toxic Substances Control Act (TSCA).⁶⁷ PCBs and other toxic compounds are an environmental concern since millions of pounds have been spilled into the environment. In 2000, the EPA proposed a \$490 million cleanup of the Hudson River to remove less than 1% of the estimated 1.3 million pounds of PCBs.⁶⁸

The techniques currently used for remediation of contaminated sites are expensive or only can remove a fraction of the contaminants. Incineration is the most utilized technique for PCBs remediation. A comparison of the estimated cost of removal of PCBs for different techniques is given in Table 3.1.7. The cost estimates in Table 3.1.7 include equipment, utilities, employee wages, raw materials, excavation costs, and depreciation.⁶⁹ Incineration is by far the most expensive technique with the added disadvantage that the incineration flue gas may contain PCBs that were not destroyed. Furthermore, to thermally decompose PCBs in an incinerator would require approximately 4.1 MW_{th} which, utilizing methane, would release 1 kton of CO₂ a year. Bio-remediation is an environmentally benign and relatively inexpensive alternative but it is limited to the microorganisms reaching the PCBs contained in the pores of the contaminated soils. Supercritical CO₂ is proposed as a cheap technique for the removal of contaminants from soils.

*Table 3.1.7: Cost comparison for the removal of PCBs utilizing different techniques.*⁶⁹

Process	Cost (\$/m³)
SFE (CO ₂)	170-200
SCWO	250-733
Solvent Extraction	400-514
Bio-remediation	190-370
Incineration	~ 1600
SubCWE	150-220

Design considerations

A schematic of a supercritical CO₂ extraction process is presented in Figure 3.1.7. The product to be extracted is put to the extractor, and then CO₂, and a suitable co-solvent (optional), are introduced. At this stage, the targeted substances are dissolved into the supercritical/co-solvent mixture and fed to the separation system where the CO₂ and the co-solvent are let to expand and recycled back into the extractor. One of these co-solvents can be supercritical or subcritical water. As discussed in the previous sections, water has very selective and strong extraction capabilities. If the scCO₂ extraction process is coupled with supercritical or subcritical water extraction more substances can be targeted in the same extraction process.^{70, 71}

PCB extraction

The schematic presented in Figure 3.1.8 corresponds to a PCB-extraction process.⁶⁹ This process combines scCO₂ extraction, with co-solvent, and supercritical water oxidation (SCWO). The SCWO part is used to decompose the extracted PCBs. The process can handle 50 kton of contaminated soil a year, and would consume approximately 22 kton of CO₂ a year. This amount compares to the 26 kton of CO₂ a supercritical decaffeination process consumes a year.⁷² The process contains three extractors E1, E2, and E3 where the soil is processed. This process is designed to recycle CO₂ and co-solvents.

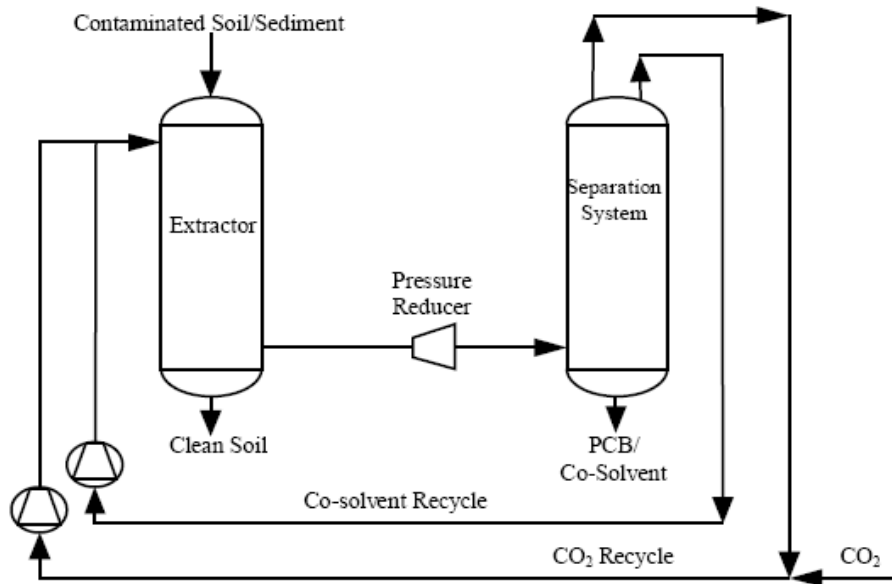


Figure 3.1.7: Schematic of a supercritical CO₂ extraction process.

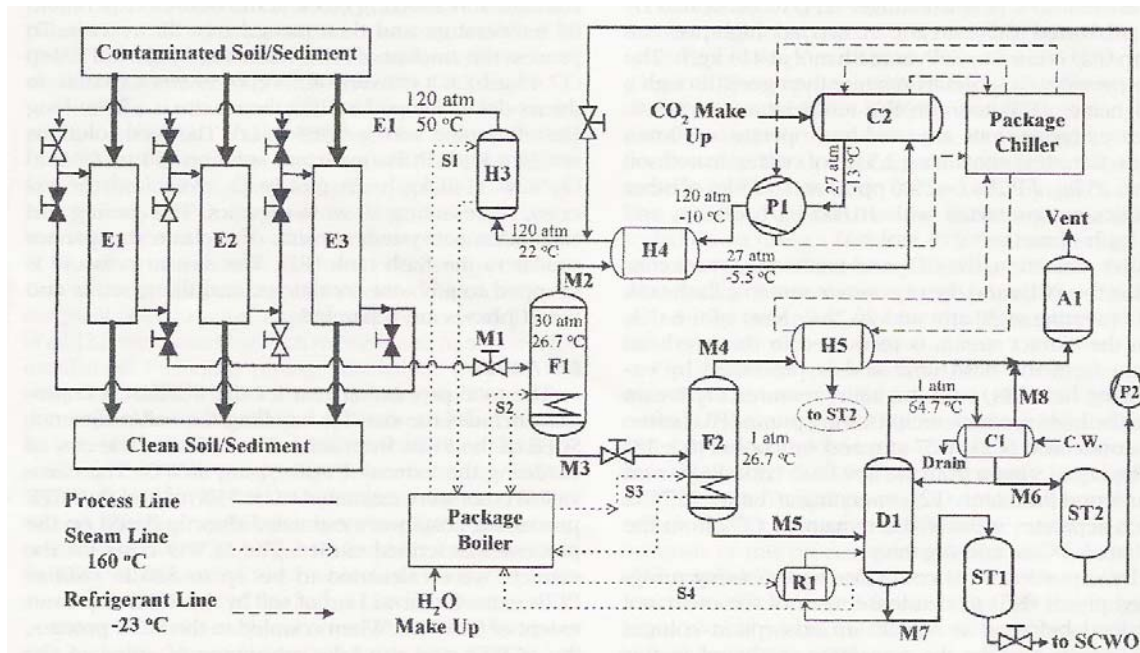


Table 3.1.8: Proposed scCO₂/SCWO combined PCB extraction process.⁶⁹

The capital cost of putting together such a process was estimated to be around \$3.7 million, and the energy consumption was estimated at around 2 MW.

3.1.6 Concluding remarks

Supercritical CO₂ is being utilized in other applications but it was not possible to explore them all. Certainly, a major application is in the homogeneous catalysis field, but its feasibility may be limited by the requirement of expensive catalysts.

Some constraints to the utilization of scCO₂ may include the high perceived initial investments, and the feasibility of scaled-up operations. Nonetheless, the value-added products generated may offset these constraints.

Much attention is paid to the energy efficiency of scCO₂ processes, and it is regarded as an essential part for a viable implementation. Nonetheless, this parameter by no means guarantees a successful implementation. For example, current industrial processes such as polyethylene polymerization runs continually at pressures of 2000 - 3000 bar (200 - 300 MPa) and temperatures around 520 K (247 °C).⁷³ As such, energy considerations are necessary but may not sufficient. Furthermore, future legislation may include regulations over the utilization and handling of CO₂, possibly making it an expensive material.

Supercritical CO₂ extraction constitutes a clean, selective and environmentally friendly process that eliminates or substantially decreases the utilization of organic solvents and toxic materials. It is particularly desirable to utilize scCO₂ extraction especially when dealing with pharmaceutical grade compounds.

Currently, most of the CO₂ utilized in industries, other than enhanced fuel recovery, comes from the output stream of ammonia synthesis by steam/air reforming.⁷³ Some estimates indicate the production of 148 Mton CO₂/yr by the ammonia synthesis industry.⁷⁴ Demand for CO₂ will determine if its utilization from a coal power plant is cost and energetically feasible.

4. Chemical utilization

4.1 Carbon dioxide fixation into organic compounds

4.1.1 Introduction

Synthesis of organic chemicals by utilization of CO₂ can effectively contribute to both develop clean synthetic processes and avoid CO₂ emissions. It can be seen as a great example of “carbon recycling”.⁷⁵ Carbon dioxide fixation into organic compounds refers to reactions that use the entire molecule. Therefore, the amount of excess energy, if required, is usually very low. The products are usually fine or commodity chemicals, which are molecules containing functionalities such as: -C(O)O-acids, esters, lactones; -O-C(O)O-organic carbonates; -N-C(O)O-carbamates; -N-C(O)-ureas, and amides. The world capacity of these chemicals is presently around 168 Mton/yr.^{76, 77} Only a few processes are presently on stream even though many ways of utilizing CO₂ are known today. However, if carbonates, especially dimethyl carbonate (DMC), will be used as gasoline additives, a large increase in its production is predictable. Also, if the method of carbonate synthesis based on CO₂ were to be incorporated, the amount of CO₂ used in chemical industry would be increased by several tens Mton/yr.⁷⁶ This analysis is consistent with the conclusion made in the early 1990’s of the potential of chemical utilization for CO₂ mitigation.⁷⁸ Recycling CO₂ was estimated to cut 7 - 10% of the excess amount of CO₂ in atmosphere.⁷⁶

4.1.2 Principal industrial processes of CO₂ utilization

Urea

Of the processes mentioned in Table 4.1.1, the synthesis of urea and the production of salicylic acid by Kolbe-Schmitt reaction have been exploited at the industrial level for more than one century. Urea, C(O)(NH₂)₂, synthesis currently utilizes the largest amount of CO₂ in organic synthesis. Urea is the most important nitrogen fertilizer in the world. It is also an intermediate in production of melamine and urea resins which are used as adhesives and bonding agents (Reaction 4-1-1). The production process is described by Figure 4.1.1.⁷⁹

Table 4.1.1: Use of CO₂ in the chemical industry for synthesis of organic compounds.

Industrial processes that utilize CO₂ as raw material	World capacity per year	Amount of fixed CO₂
Urea	143 Mton ⁷⁷	105 Mton ⁷⁷
Salicylic acid	70 kton ⁷⁶	25 kton ⁷⁶
Methanol	20 Mton ⁷⁶	2 Mton ⁷⁶
Cyclic carbonates	80 kton ⁷⁶	ca. 40 kton ⁷⁶
Poly(propylene carbonate)	70 kton ⁷⁶	ca. 30 kton ⁷⁶

Currently, urea is produced all over the world by the synthesis from CO₂ and ammonia and there is simply no need to replace this process. If urea could be used in the synthesis of carbonates according to Reaction (4-1-2), a market increase would be possible.

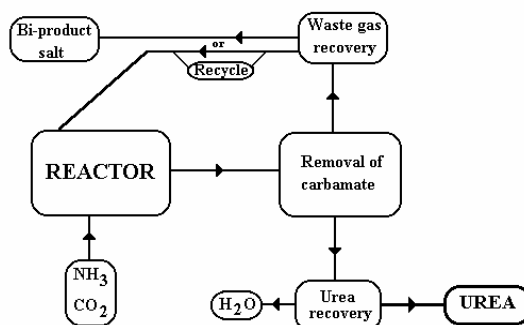
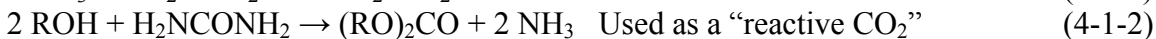
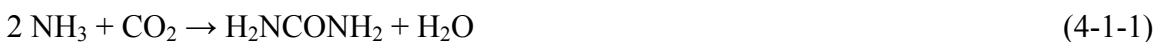
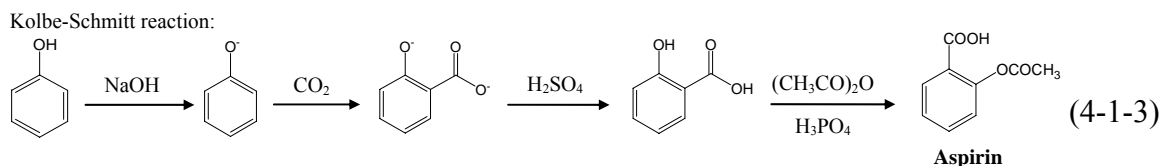


Figure 4.1.1: Simplified flow diagram of the production of urea.⁷⁹

Salicylic acid

For the salicylic acid synthesis, there are several different processes among which the Kolbe-Schmitt reaction (Reaction 4-1-3) is most widely used.

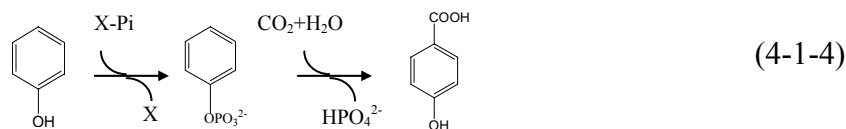


Salicylic acid is used to synthesize aspirin which is one of the world's safest and least expensive pain relievers and effective treatment for a variety of ailments. There are also no major changes to Kolbe-Schmitt reaction technologically. Radiation-induced salicylic acid formation from phenol and CO₂ is also under investigation, which is part of radiation-induced carboxylation technology related to CO₂ utilization.⁸⁰ Studies showed that the yield of salicylic acid depends on the absorbed dose, dose rate, and concentration of both reaction partners and pH of the solution.

4.1.3 Existing processes of CO₂ utilization

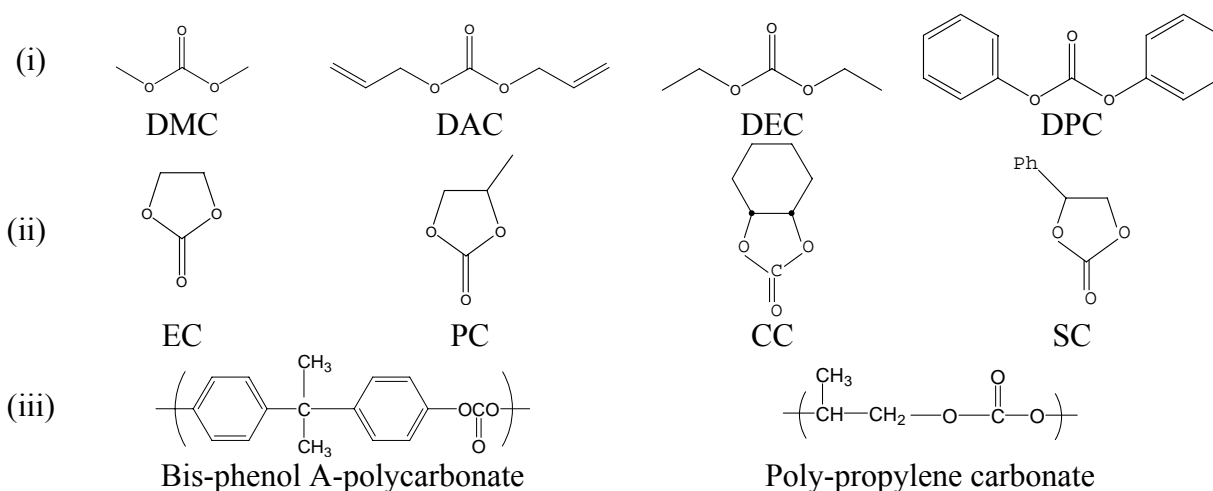
4-Hydroxybenzoic acid

4-Hydroxybenzoic acid is an intermediate in the manufacture of plastics, pharmaceuticals, pesticides and dyes. The enzymatic synthesis of 4-hydroxybenzoic acid (Reaction 4-1-4) has been reported by Aresta and co-authors.⁸¹ The selectivity could be as high as 100%.



Organic carbonates

Organic carbonates have broad application in the chemical industry as solvents, reagents, monomers for polymers and component of special materials. There are three categories of carbonates, (i) linear carbonates: dimethyl carbonate (DMC), diallyl carbonate (DAC), diethyl carbonate (DEC), diphenyl carbonate (DPC); (ii) cyclic carbonates: ethylene carbonate (EC), propylene carbonate (PC), cyclohexene carbonate (CC), and styrene carbonate (SC); (iii) polycarbonates: poly-(propylene carbonate) and bis-phenol A-polycarbonate (BPA-PC).



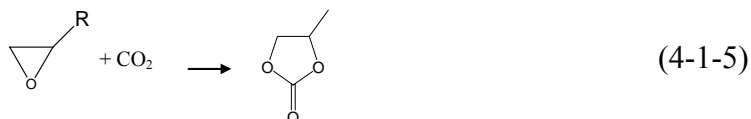
Bis-phenol A-polycarbonate is by far the carbonate that has the largest market (over 1.5 Mtons/yr)⁷⁶, and its potential is far from full exploitation.⁸² World demand is forecasted to grow at 9% annually through 2003.^{83, 84} BPA-PC is used in several industrial sectors, the most relevant being the electrical and electronic (38%), followed by the construction, automotive, optical and information storage systems, medical, and packaging.⁸⁵ It is a versatile plastic, second (27%) only to polyamides (35%) on the plastic market.⁸⁶ The largest manufacturers of BPA-PC are General Electric Plastics (0.6 Mton/yr), Bayer (0.5 Mton/yr), and Dow Chemicals (0.3 Mton/yr).⁷⁶ There is also the potential for a great expansion of the market for linear carbonates, especially for DMC that could be used as gasoline additive, thus demanding amounts that would be impossible to produce with existing synthetic technologies.⁸⁷ The current DMC production approaches 100 ktons/yr.⁷⁶ Increasing the use of DMC as non-toxic solvent and “green” reagent⁸⁸, and using DMC as gasoline additive would easily cause its market to reach the Mton/yr size.⁷⁶ DMC has a great advantage as a combustion promoter agent of gasoline compared to other additives used today due to its high oxygen content and low amount of CO₂ emissions. DMC is also an excellent substitute for dimethylsulphoxide in methylation reactions and is also active as methoxycarbonylation agent.⁸⁹

Cyclic carbonates are used in the production of polymers. They can also be used in lithium batteries, as extractants and reagents. The total production of cyclic carbonates is about 100 kton/yr, with Huntsman and BASF as leaders.⁷⁶ Aliphatic polycarbonates are mainly used in electronics industry as sacrificial binders for metals and ceramics due to their low ash content and decomposition temperature.⁹⁰

Ultimately, there is increasing interest in finding a clean synthetic method to produce DMC and other carbonates (possibly based on CO₂) given the fact that almost the total amount of carbonates are currently produced from phosgene, which is a major disadvantage.

Cyclic carbonates

There are two commercial routes to synthesize cyclic carbonates: phosgenation and carboxylation of epoxides using CO₂. The phosgenation of glycols, exploited by SNPE in 1970, has been the major technology for a long time.⁹¹ This technology has a negative environmental impact due to the use of phosgene and the production of halogenated waste (HCl). To date, no method has been discovered that is superior to the phosgene method in terms of reactivity. Currently, the carboxylation of epoxides (Reaction 4-1-5) is a fast developing process but research up to now is still a long way from practical application. IG Farben's discovery of the route based on ethylene oxide and CO₂ has led to the increased interest in the production of alkylene carbonates.⁹² Compared to phosgene, CO₂ is much less reactive, therefore this requires the development of a specific catalyst to overcome the kinetic barrier of the carboxylation reaction. Among the catalysts reported in literature^{93, 94}, alkyl ammonium-, phosphonium- and alkali metal halides are extremely effective in providing carbonates with 90 - 99% yields.⁷⁶ Main group metal halide salts⁹⁵ (M_nX_m: M-metal of III-V groups; X-Cl, Br, I) have also been found catalytically active but high concentration of catalyst is required. In general, these processes are carried out under high pressure CO₂, 5 MPa, and temperatures ranging from 97 to 127 °C.⁷⁶ High yields of cyclic carbonates at atmospheric CO₂ pressure by main group metal halide salts have also been reported.^{76, 96} Organometallic halides R_nMX_m^{76, 97}, where R-Me, Et, Bu, Ph; M-Sn, Te, Sb, Bi, Ge, Si; X-Cl, Br, I, are good catalysts. Classical Lewis acids, organometallic complexes, e.g., (Ph₃P)₂Ni, have also been used as catalysts.^{76, 98} Most recently, metal oxides (MgO^{76, 99}, MgO/Al₂O₃^{76, 100}, Nb₂O₅^{76, 101}, and others) have been used as heterogeneous catalysts. The latter have shown a considerable life-time and interesting turnover numbers (TON).⁷⁶



The Advanced Industrial Science and Technology (AIST) devised a two-phase system comprising supercritical CO₂ and ionic fluid as a new reaction system for selective and rapid cyclic carbonate synthesis with the potential for practical application.¹⁰² Most cyclic carbonate synthetic methods using conventional CO₂ fixation methods only produce a yield of around 50% at best, even at reaction temperatures of 150 - 200 °C and with reaction times of 4 - 24 hours. The supercritical CO₂ plus ionic fluid method, however,

produced 100% yield and 100% selectivity even at a reaction temperature of 100 °C and reaction time of only 5 minutes.¹⁰² This rivals the conventional phosgene method in terms of synthesis capabilities. This development is expected to significantly accelerate the production methods for more environmentally friendly engineering plastics, and should pave the way for practical application of this technique. Figure 4.1.2 shows the actual reactor system and the reaction diagram.

Cyclic carbonates can also be used to synthesize linear carbonates by transesterification reactions as shown in Reactions (4-1-6) and (4-1-7).

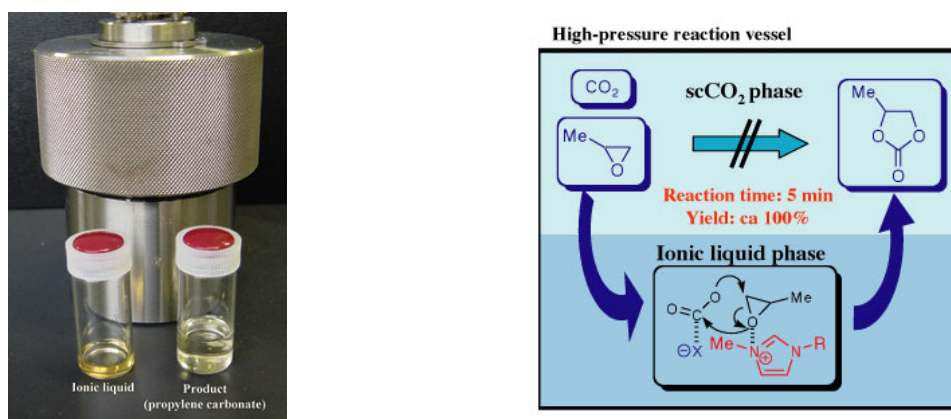
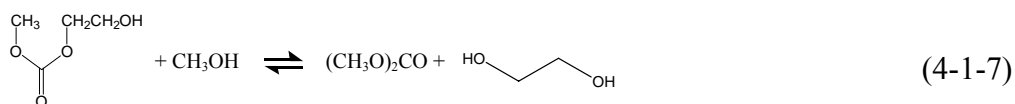
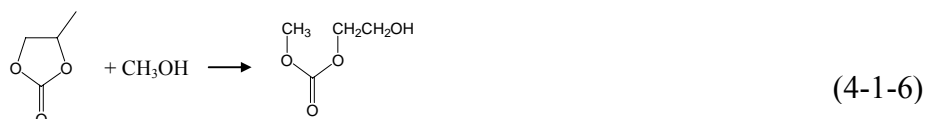


Figure 4.1.2: the rapid and selective synthesis of propylene carbonate by CO₂ fixation using scCO₂ + ionic liquid two-phase reaction system.¹⁰²

Bisphenol-A-polycarbonates

The conventional way to produce BPA-PC is by interfacial polymerization of BPA and phosgene which consists of three steps: (i) phosgenation of BPA to bis-chloroformate, (ii) carbonate oligomers from cyclization of bischloroformate, and (iii) ring condensation to get BPA-PC. The advantages of this process are high reactivity and high yield under mild conditions. The disadvantages of this process are the negative environmental impact due to the use of phosgene and the production of halogenated waste (HCl) which could erode the equipment. A new synthetic route was developed in order to respond to the environmental requirements and to the increasing demand of BPA-PC, which is melt transesterification of either DPC or DMC with BPA in a molten state without the solvent.¹⁰² The process includes three steps:

1. Prepolymerization of BPA with DPC or DMC,
2. Crystallization to produce oligomers,
3. Solid state polymerization.

This process is solvent-free and phosgene-free, and generally offers better quality polymers with higher molecular mass, no chlorine, more heat stability, and better handling.⁷⁶ As transesterification is reversible, phenol should be distilled continuously under vacuum conditions to facilitate the forward chain growth reaction.⁷⁶ Furthermore, sophisticated equipment is needed to control temperature and pressure.⁷⁶ The removal of volatiles and catalysts becomes difficult due to the melt polycarbonate viscosity⁷⁶, and high temperature induces undesirable chain branching reactions.⁷⁶

Bayer developed a solvent-free solid state polymerization process which produces BPA-PC with molecular mass in the range of 15 - 200 kDa.¹⁰³ In Europe, the technology was introduced by General Electric Plastics in the early 1990s.⁷⁶ Some of the disadvantages of this process can be reduced by catalyst optimization; therefore, developing a highly active catalyst is the critical point. Vladimir and co-authors^{104, 105} evaluated the activity of various catalysts in the reaction of melt transesterification of DPC and BPA (at 165 °C), and found that alkaline-earth and alkaline metals were the most active, and lanthanum acetylacetonate (La(acac)₃) was a very promising catalyst because of its low activity in PC thermal degradation and short reaction time. The current catalysts are lithium, sodium, potassium, tetraalkylammonium hydroxides and carbonates.⁷⁶

Aliphatic polycarbonates

Synthesis of aliphatic polycarbonates from ethylene oxide and CO₂ catalyzed by ZnEt₂/H₂O was first discovered in 1969.¹⁰⁶ It is the first polymer production involving the direct use of CO₂.¹⁰⁷ It is also a successful example of the exploitation of CO₂ in the chemical industry as a variety of catalysts were developed.^{108, 109} Insoluble zinc catalysts prepared by reaction of zinc hydroxide or zinc oxide with dicarboxylic acid proved to be the most active. Recently, soluble zinc complexes with high catalytic activity have also been discovered.¹¹⁰⁻¹¹³ Empower Materials (formerly PAC Polymers Inc.) produces aliphatic polycarbonates through ring-opening polymerization of terminal epoxides with CO₂ using its patented method (U.S. Patent 4,665,136). The method uses zinc adipionate as catalyst under operation conditions of 25 - 35 atm pressure and a temperature of 45 - 55 °C. The polymers are synthesized using corresponding alkyl epoxides and CO₂ at conditions mentioned above.¹¹⁴ The process is the property of Empower Materials and more details are not available. Thorat and co-authors¹¹⁴ investigated the physical properties of aliphatic polycarbonates based on the Empower Materials's method. Li and co-authors¹¹⁵ investigated the thermal properties and rheological behavior of a biodegradable aliphatic polycarbonate derived from CO₂ and propylene oxide by using zinc glutarate catalysts. The synthesis of polycarbonates using supercritical CO₂ has also been reported.¹¹⁶⁻¹¹⁹ Carbon dioxide-based technologies for the synthesis of polymers have a great importance because CO₂ could in this way eventually be fixed into long-lasting compounds that would represent a chemical sequestration of CO₂.^{76, 113}

Linear carbonates

Linear carbonates are still produced by the phosgene-based technology due to its high yield under mild conditions.¹²⁰ The two-step process is described by Reactions (4-1-8) and (4-1-9).



Anhydrous alcohols and COCl₂ are required to produce carbonates. Intermediate halogenated alcohols need post-treatment and the co-product, HCl, needs to be neutralized and disposed. The overall process is energy intensive and demands special equipment to avoid environmental and corrosion problems. Currently, more non-phosgene routes are being developed as illustrated in Figure 4.1.3, all of them being catalytic.

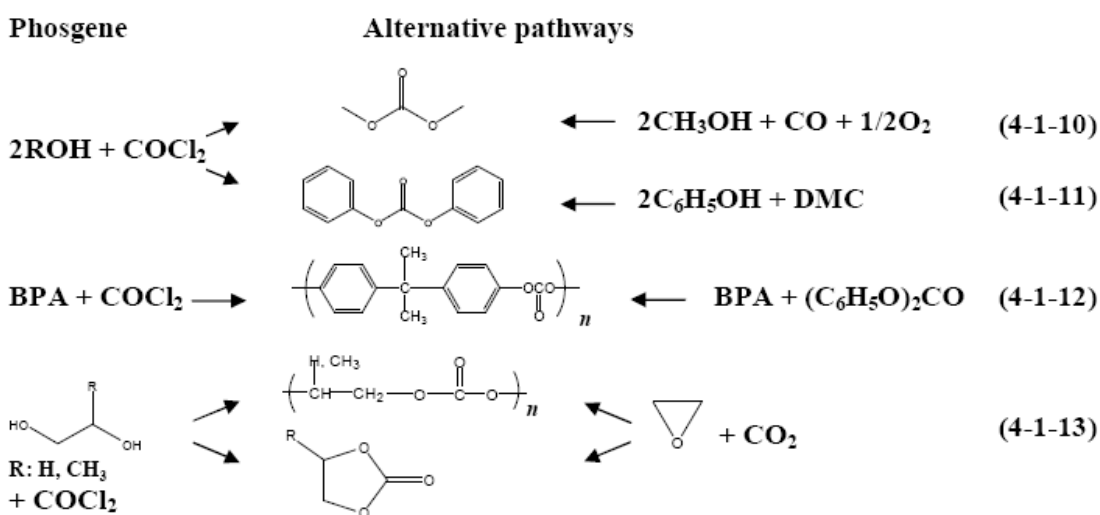


Figure 4.1.3: Phosgene-based, innovative methods for production of linear carbonates.⁷⁶

Dimethyl carbonate

Catalytic oxidative carbonylation of methanol, indicated in Equation (4-1-10), was introduced on an industrial scale in the early 1980's by EniChem in Italy.¹²¹ This is currently the state of the art commercial process for DMC production.⁷⁶ The reaction proceeds under reasonable conditions (100 - 130 °C, 2 - 3 MPa) with unsupported cuprous chloride catalyst suspended in a slurry reactor. DMC selectivity is higher than 95%, and the main by-products are methyl chloride, dimethyl ether, and CO₂. This process suffers from limited conversion per pass partly because of catalyst deactivation

by water, equipment corrosion due to the presence of chloride, and difficulties in product separation.

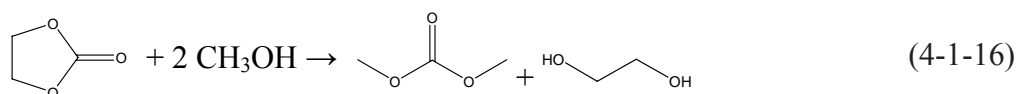
In principle, the use of solid catalysts should overcome corrosion problems and improve product recovery.⁷⁶ Drake and co-authors¹²² investigated the influence of catalyst synthesis method and Cu source on the activity and selectivity of SiO₂ supported catalysts for the gas-phase oxidative carbonylation of methanol to DMC and found that high DMC activity correlated with high Cu dispersion.

UBE successfully implemented a gas-phase technology in early 1990's.¹²³ The process also runs under reasonable conditions (110 -150 °C, 0.1- 2 MPa) with a heterogeneous PdCl₂-based catalyst supported on activated carbon according to Reaction (4-1-14).⁷⁶ The selectivity of DMC lies in the range of 90 - 95% based on CO and CH₃ONO consumptions.⁷⁶ Nitrogen monoxide (NO) can be recycled to regenerate CH₃ONO according to Reaction 4-1-15. Dimethyl oxalate, methyl formate and methylal are the main by-products.



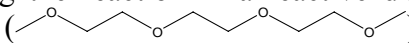
In this gas phase process, DMC synthesis and methyl nitrite regeneration are two separate reactions. Thus the formation of DMC is not accompanied by water, which enhances the activity and stability of catalyst. However, in both cases the catalysts contain chloride; leaching is observed for the heterogeneous system but corrosion seems less crucial than in the liquid-phase process.⁷⁶ The toxicity and handling of methyl nitrite and NO are still big concerns.

Transesterification of ethylene carbonate with methanol also produce DMC, co-producing ethylene glycol according to Reaction 4-1-16.



Homogeneous and heterogeneous acid and base catalysts have been tested at 60 - 150 °C. The base catalyst shows higher activity and selectivity.¹²⁴ Bhanage¹²⁵ gave a comprehensive report on a two-step synthesis of DMC from epoxides, CO₂ and methanol using various basic metal oxide catalysts. Among the catalysts examined, MgO is the most active and selective for both reactions. The selectivity is still low because of alcoholysis of the epoxide. The effect of numerous reaction variables on the activity and selectivity performance were also investigated.¹²⁶ The economic advantage of this method mainly relies on (i) reactants cost, (ii) enhancement of catalyst productivity, separation, recycling, and (iii) higher ceiling conversion by a drift in thermodynamic constraints.⁷⁶

The urea alcoholysis route to afford DMC has been known for decades.¹²⁷ In this case, urea and methanol, catalyzed by tin complexes, are reacted together to form DMC and

ammonia according to Reaction 4-1-2. The formation of several side products, which results in poor selectivity, is one of the major drawbacks of using this reaction.¹²⁸ The use of homogeneous catalysts also poses catalyst product separation and deactivation problems in some cases.^{87, 128} The yield and selectivity are drastically enhanced by running the reaction in a reactive distillation reactor with triethylene glycol dimethyl ether () as a high-boiling solvent. Furthermore, its integration with urea facility could optimize ammonia recycling. The overall process would allow production of DMC from methanol and CO₂.⁷⁶

Direct synthesis of DMC from CO₂ according to Reaction 4-1-17 has also been attempted.¹²⁹ It has been reported that organo-tin compounds^{88, 130}, such as Sn(IV) and Ti(IV) alkoxides and metal acetates¹³¹, can be used as catalysts. Tomishige and co-authors¹³² reported that DMC was synthesized from methanol and CO₂ with high selectivity using ZrO₂ catalysts and found the catalytic activity seemed to be related to acid-base pair sites of the ZrO₂ surface. Tomishige and co-authors¹³³ further developed even more effective CeO₂-ZrO₂ solid solution catalysts and found that the higher the calcination temperature, the higher the activity of the catalyst for DMC formation. The major drawback of this process is thermodynamic limitation but removal of water could be a solution to this problem. Trimethyl orthoformate, as described in Reaction 4-1-18, is used as dehydrated form of methanol to improve DMC production.¹³²



Using trimethyl orthoformate is not economical since this chemical is expensive. DMC synthesis from CO₂ and methanol was investigated at near supercritical conditions using nickel acetate as a catalyst. The yield was 12 times higher than that at non-supercritical conditions with 100% selectivity of DMC.¹³⁴ Wu and co-authors³⁰ investigated direct synthesis of DMC on H₃PO₄ modified V₂O₅. Under the optimum composition of H₃PO₄/V₂O₅ with P/V = 0.15 - 0.50, conversion of CH₃OH can reach about 2% and the selectivity of DMC can reach about 92%. The experimental results showed that the crystal phase of the catalyst influenced the reaction yield and selectivity of DMC greatly.³⁰ Kong and co-authors¹³⁵ investigated the photocatalytic reaction for the synthesis of DMC from CO₂ and CH₃OH over Cu/NiO-MoO₃/SiO₂ catalyst. The results showed that the addition of Cu and NiO greatly increased the dispersion of MoO₃ on SiO₂, and Cu and NiO could also disperse evenly on the support. Under the proper conditions, the CH₃OH conversion was up to 13.9% with DMC selectivity of 90.1%.¹³⁵ Cai and co-authors¹³⁶ investigated the synthesis of DMC from CH₃OH and CO₂ in the presence of CH₃OK and CH₃I under mild conditions; high yield (16.2%) and selectivity of 100% were achieved, which is the highest yield and selectivity among the results reported. Investigation results show that CH₃OK is an efficient catalyst and CH₃I is a promoter to the formation of DMC from CH₃OH and CO₂.¹³⁶ So far, the direct synthesis of DMC from methanol and CO₂ is still far from satisfactory and large-scale production of DMC is still challenging.

Diphenyl carbonate (DPC)

According to EniChem technology, DPC production involves two successive steps¹³⁷, the transesterification reaction between DMC and phenol to produce methylphenyl carbonate (MPC) (Reaction 4-1-19) and disproportionation of MPC to produce DPC and DMC (Reaction 4-1-20).

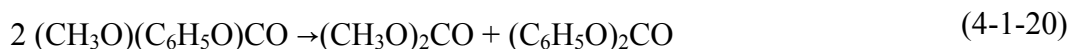


Table 4.1.2 gives a comparison between DMC and traditional phosgene or dimethylsulfate-based reaction. Using the DMC-based method, wastes and emissions generated are reduced from 1.69 to 0.39 (kg/kg), water usage is reduced from 0.02 (m³/kg) to virtually zero, and energy use is reduced from 0.04 (kWh/kg) to 0.01 (kWh/kg).

Table 4.1.2: Comparison between DMC and phosgene or dimethylsulfate-based reaction.^{138, 139}

	Phosgene or DMS	DMC
	Dangerous reagent	Harmless reagent
	Use of solvent	No solvent
	Waste water treatment	No waste water
	NaOH consumption	The base is catalytic
	By-products: NaCl, Na ₂ SO ₄	By-products: MeOH, CO ₂
	Exothermic	Slightly or not exothermic
Wastes & emissions	1.69 (kg/kg)	0.39 (kg/kg)
Water usage	0.02 (m ³ /kg)	virtually zero
Energy use	0.04 (kWh/kg).	0.01(kWh/kg)

4.1.4 Prospective uses of CO₂

Applications and current production processes of organic carboxylates

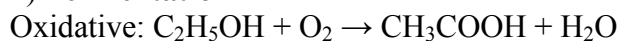
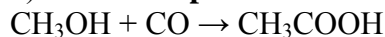
The synthesis method for organic carboxylates by the utilization of CO₂ has also been reported. Based on the actual market of these products, the expansion of CO₂ utilization is foreseeable if CO₂-based technologies will eventually be implemented. Table 4.1.3 lists the applications and markets of different carboxylates. Table 4.1.4 gives current carboxylate production processes and their drawbacks.

Table 4.1.3: Application and market of different carboxylate.

	Application	Market ⁷⁶
Formic acid	Leather and textile industries, Adjusting the pH in dyeing of natural and synthetic fibres, Coagulation of rubber latex, Manufacture of pharmaceuticals, Crop-protection agent, Silage agent, Additive for cleaning agents, Leonard Process in steel pickling (large potential market) Paper industry (large potential market)	400 kton/yr
Acetic acid	Manufacture of vinyl acetate, cellulose acetate, terephthalic acid, dimethyl terephthalate, esters of acetic acid, acetic anhydride.	6 Mton/yr
Oxalic acid	Recovery/separation of heavy metals, Textile treatment, Metal treatment, bleaching agent in leather tanning, agrochemical/pharmaceutical production	190 kton/yr
Long chain carboxylates	Surfactants (preferable to sulphonic acids due to environmental issues)	10 Mton/yr

Table 4.1.4: Current processes of carboxylate production and their drawbacks.

Current processes	Drawback
Formic acid 1) Oxidation of hydrocarbon C_4H_{10} (or naphtha) \rightarrow $CH_3COOH + HCOOH$ Less than 20% of the market ⁷⁶	By-product in manufacture of acetic acid, insufficient to meet the present demand
2) Hydrolysis of formamide $HCOOCH_3 + NH_3 \rightarrow HCONH_2 + H_2O$ $HCONH_2 + H_2O + 1/2 H_2SO_4 \rightarrow HCOOH + 1/2 (NH_4)_2SO_4$ Less than 6% of the market ⁷⁶	Disposing large amount of ammonium sulfate byproduct is not economically and environmentally desirable
3) Methylformate hydrolysis $CH_3OH + CO \rightarrow HCOOCH_3$ $HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH$ Ca. 50% of the market ⁷⁶	Methanol is produced from syngas. Syngas production is energy intensive.
4) Acid hydrolysis $NaOH + CO \rightarrow HCOONa$ $HCOONa + HX \rightarrow HCOOH + NaX$	NaOH and HX are highly corrosive, CO is toxic Ca. 24% of the market ⁷⁶

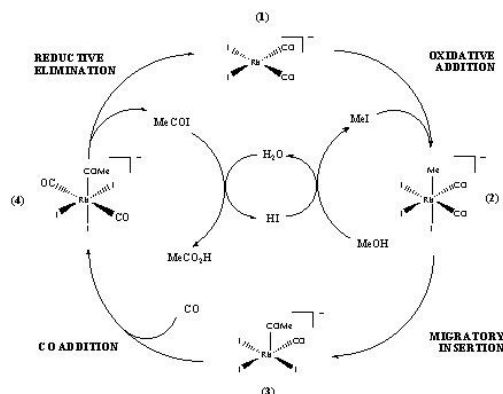
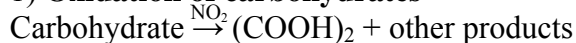
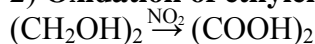
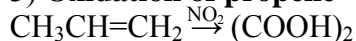
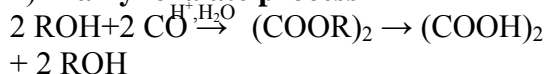
Acetic acid 1) **Fermentation**2) **Monsanto process**¹⁴⁰Ca. 80% of the market⁷⁹

Low yield,

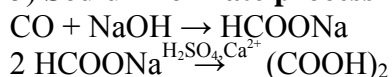
Long reaction time

Ca. 10% of the market⁷⁹

Catalysts usually contain noble metal (Rh, Ir) which is expensive, CO is toxic

The catalytic cycle of Monsanto process^{79, 140}Oxalic acid 1) **Oxidation of carbohydrates**NO₂ is toxic, Separation of products2) **Oxidation of ethylene glycol**NO₂ is toxic3) **Oxidation of propene**NO₂ is toxic4) **Dialkyl oxalate process**

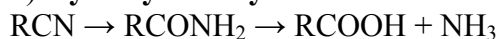
CO is toxic, Acid is corrosive to equipment, Separation of products

5) **Sodium formate process**

Energy intensive, Uses sulphuric acid, Calcium sulphate as byproduct

Long chain 1) **Oxidation of the corresponding alcohols**
carboxylates $\text{RCH}_2\text{OH} \rightarrow \text{RCOOH}$

Negative environmental impact

2) **Hydrolysis of cyano-derivatives**

Low atom efficiency

Synthesis of formic acid from CO₂

Formic acid can be synthesized directly from CO₂ and hydrogen according to Reaction (4-1-21) with 100% atom utilization. It was first discovered by Farlow and Adkins in

1935 by using Raney nickel as the catalyst.¹⁴¹ Different catalysts were also used such as zinc selenide and zinc telluride¹⁴², ruthenium and palladium complexes. BP Chemicals developed a process which includes multiple steps.¹⁴³ First, a nitrogen base (triethylamine) reacts with CO₂ and hydrogen in the presence of a ruthenium complex to yield the ammonium formate. The formate is then separated from the catalyst and the low-boiling constituent. The ammonium formate reacts with a high boiling base, for example 1-(n-butyl) imidazole, to yield a formate that can be thermally decomposed. The low-boiling base is liberated and distilled, and the high-boiling base recovered.⁷⁶



Hydrogenation of supercritical CO₂ for synthesis of formic acid is also being researched.¹⁴⁴ In presence of Ru catalysts, Ru(PMe₃)₄H₂ or Ru(PMe₃)₄Cl₂, CO₂ itself can be hydrogenated to produce formic acid or formic acid derivatives.¹⁴⁵ Using co-solvents such as water, methanol or dimethyl sulphoxide (DMSO) can lead to very high catalytic activity.¹⁴⁶ Table 4.1.5 compares different catalytic systems for the hydrogenation of CO₂ to formic acid.¹⁴⁷

Table 4.1.5: Different catalytic systems for the hydrogenation of CO₂ to formic acid.¹⁴⁷

Catalyst precursor	Solvent	Additives	p(H ₂ , CO ₂) ^a	T (°C)	t (h)	TON	TOF ^b (h ⁻¹)
Rhodium							
[RhCl(COD)] ₂ + dppb	DMSO	NEt ₃	20, 20	RT	22	1150	52
[RhCl(COD)] ₂ + dippe	DMSO	NEt ₃	40 total	24	18	205	11
[RhH(COD)] ₄ + dppb	DMSO	NEt ₃	40 total	RT	18	2200	122
[RhH(COD)] ₄ + dppb	DMSO	NEt ₃	40 total	RT	0.8	312	390
RhCl(PPh ₃) ₃	MeOH	PPh ₃ , NEt ₃	20, 40	25	20	2700	125
RhCl(PPh ₃) ₃	C ₆ H ₆	Na ₂ CO ₃	60, 55	100	3	173	58
RhCl(TPPTS) ₃	H ₂ O	NHMe ₂	20, 20	RT	12	3439	287
RhCl(TPPTS) ₃	H ₂ O	NHMe ₂	20, 20	81	0.5		7260
RhCl(TPPTS) ₃	H ₂ O	NHMe ₂	20, 20	23			1364
[RhCl(η ² -P-O) ₂] ₂ BPh ₄	MeOH	NEt ₃	25, 25	55	4.2	420	100
Rh(hfacac)(dcpb)	DMSO	NEt ₃	20, 20	25	–	–	1335
[Rh(nbd)(PMe ₂ Ph) ₃] ₂ BF ₄	THF	H ₂ O	48, 48	40	48	128	3
RhCl ₃ + PPh ₃	H ₂ O	NHMe ₂	10, 10	50	10	2150	215
Ruthenium							
Ru ₂ (CO) ₅ (dppm) ₂	Acetone	NEt ₃	38, 38	RT	1	207	207
Ru ₂ (CO) ₅ (dppm) ₂	Acetone	NEt ₃	38, 38	RT	21	2160	103
RuCl ₃ , PPh ₃	EtOH	NEt ₃ , H ₂ O	60, 60	60	5	200	40
RuH ₂ (PPh ₃) ₄	C ₆ H ₆	NEt ₃ , H ₂ O	25, 25	RT	20	87	4
RuH ₂ (PPh ₃) ₄	C ₆ H ₆	Na ₂ CO ₃	25, 25	100	4	169	42
RuH ₂ (PMe ₃) ₄	scCO ₂	NEt ₃ , H ₂ O	85, 120	50	1	1400	1400
RuCl ₂ (PMe ₃) ₄	scCO ₂	NEt ₃ , H ₂ O	80, 140	50	47	7200	153
RuCl(OAc)(PMe ₃) ₄	scCO ₂	NEt ₃ / C ₆ F ₅ OH	70, 120	50	0.3	31667	95000
TpRuH(PPh ₃)(CH ₃ CN)	THF	NEt ₃ , H ₂ O	25, 25	100	16	760	48

[Ru(Cl ₂ bpy) ₂ (H ₂ O) ₂][O ₃ SCF ₃] ₂	EtOH	NEt ₃	30, 30	150	8	5000	625
[(C ₅ H ₄ (CH ₂) ₃ NMe ₂)Ru(dppm)]BF ₄	THF	None	40, 40	80	16	8	0.5
[RuCl ₂ (CO) ₂] _n	H ₂ O, iPrOH	NEt ₃	81, 27	80	0.3	400	1300
K[RuCl(EDTA-H)]	H ₂ O	–	3, 17	40	0.5	na	250
[RuCl ₂ (TPPMS) ₂] ₂	H ₂ O	NaHCO ₃	60, 35	80	0.03	320	9600
[RuCl(C ₆ Me ₆)(DHphen)]Cl	H ₂ O	KOH	30, 30	120	24	15400	642
CpRu(CO)(μ-dppm)Mo(CO) ₂ Cp	C ₆ H ₆	NEt ₃	30, 30	120	45	43	1
Palladium							
Pd(dppe) ₂	C ₆ H ₆	NEt ₃ /H ₂ O	25, 25	110	20	62	3
Pd(dppe) ₂	C ₆ H ₆	NaOH	24, 24	RT	20	17	0.9
PdCl ₂	H ₂ O	KOH	110, na	160	3	1580	530
PdCl ₂ (PPh ₃) ₂	C ₆ H ₆	NEt ₃ , H ₂ O	50, 50	RT	na	15	Na
Other metals							
Ni(dppe) ₂	C ₆ H ₆	NEt ₃ , H ₂ O	25, 25	RT	20	7	0.4
NiCl ₂ (dcpe)	DMSO	DBU	40, 160	50	216	4400	20
[Cp*IrCl(DHphen)]Cl	H ₂ O	KOH	30, 30	120	10	21000	2100

^a Unit: atm. In some cases, the pressure of CO₂ was not given and was calculated from the total stated pressure minus the pressure of H₂.

^b The TOF values are not directly comparable to each other because some are at complete conversion and some are at partial conversion. They can, however, give an order of magnitude indication. Initial TOF values will be even higher.

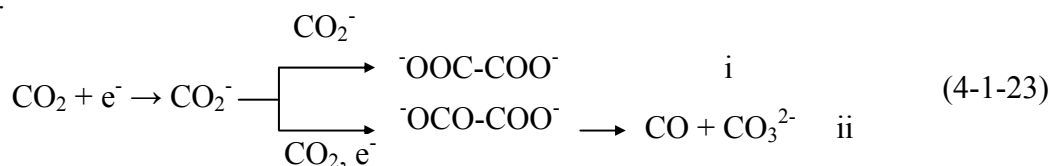
Synthesis of acetic acid from CO₂

In nature acetogenic bacteria can synthesize acetic acid from CO₂. This reaction has been mimicked using Ni-systems.^{148, 149} Another interesting reaction is the direct combination of methane and CO₂ to produce acetic acid as shown in Equation (4-1-22). Vanadium-based catalysts were used.¹⁵⁰ Activation of the C-H bond is the key step. Although the yield is still very low, this process is of great interest from an atom economy point of view.



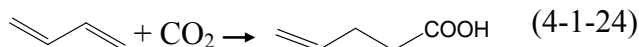
Synthesis of oxalic acid from CO₂

Oxalic acid can be synthesized electrochemically from CO₂ in non aqueous media.¹⁵¹ As shown in Reaction (4-1-23), after the formation of the radical anion CO₂^{•-}, two reactions compete for its use. One reaction leads to the oxalate dianion, the other leads to CO and CO₃²⁻. The yield and selectivity depend on the current density, solvent, and CO₂ pressure. A drawback is that the low conductivity of organic media only permits a low current density.⁷⁶



Synthesis of long chain carboxylates from CO₂

Long chain carboxylic acid synthesis by carboxylation of unsaturated hydrocarbons has been discovered using transition metal complexes as catalysts¹⁵², with Reaction (4-1-24) as an example. The formation of carboxylated products is often accompanied by homo-coupling by-products which can not be neglected. Therefore, to master the coupling issue is critical in order to develop possible industrial processes. One reaction that would be of industrial interest is acrylic acid synthesis from CO₂ and ethylene.¹⁵²⁻¹⁵⁵



Other possible processes of using CO₂ for organic synthesis

There are other possible processes of using CO₂ for organic synthesis. Some of them are listed below.

- Synthesis of carbamates.
- Synthesis of isocyanates.
- Synthesis of esters and other derivatives (lactones, amides).
- Insertion of CO₂ into C-C bonds.
- Electrochemical reactions that use CO₂.
- Electro-catalysis by metal complexes.
- Electrochemical reduction of CO₂.
- Radiation-induced syntheses of intermediates and fine chemicals.

All these processes require developing effective catalysts. Whether we can find alternative energy such as solar energy or nuclear energy is also a critical issue.

4.1.5 Conclusion

In conclusion, utilization of CO₂ in synthetic chemistry has long been considered by the prevalence of the economic over the environmental factor in decision making.⁷⁶ The new attitude towards environmental protection is now making economic and environmental issues equally important.⁷⁶ Carbon dioxide fixation into organic compounds requires no or very low amount of energy input. So in most cases, finding an effective catalyst, that may drive the reaction with low kinetic barriers, is the key issue. Among the processes discussed above, synthesis of organic carbonates from CO₂ is the most promising, which has the potential to be industrialized in the near future. Some other processes such as electrochemical conversion of CO₂ and radiation-induced carboxylation technology can find justification only when the energy used in the process originates from a source other than fossil fuel-fired power stations.

4.2 Electrochemical utilization of carbon dioxide

4.2.1 Introduction

A review has been conducted of electrochemical techniques that are proposed as pathways to industrial CO₂ utilization and is summarized in this report. No single case study has been identified whereby utilization of CO₂ is being performed by electrochemical means on a commercial or industrial scale. The central question regarding the possible future role of electrochemical methods for converting CO₂ into value-added chemicals remains open.

Electrochemical utilization of CO₂ has been studied for many years. Exploration of photosynthesis has occupied a large portion of the study up to the early 1980's. As the focus of man turned towards his impact on his own environment, CO₂ production by human activities has become an area of wide concern. Studies on electrochemical conversion of CO₂ in aqueous and non-aqueous solutions have emerged, indicating much promise for the conversion and reduction of CO₂.¹⁵⁶

An aqueous solution is any solution in which water is the solvent. A classic example of an aqueous solution of CO₂ is carbonated water made for human consumption. Organic solvents are usually flammable materials and may pose certain physical and chemical hazards. Consideration of aqueous and non-aqueous solutions is typically discussed in the context of liquid solutions. The use of porous electrodes can be employed in conjunction with both aqueous solutions and gaseous CO₂ mixtures. Beyond the type of solution employed, the appropriate selection of electrode type is an important aspect in all electrochemical processes.

4.2.2 Aqueous solutions

A primary reaction product in electrolyses of aqueous solution of CO₂ is formic acid. The formic acid reaction was reported for the first time in the year 1870 and competes with hydrogen evolution in the reduction of CO₂.¹⁵⁷ A formidable problem in the utilization of CO₂ in aqueous solution has to do with its low solubility in water at standard temperature and pressure. This means at the surface of the electrode there are very small amounts of CO₂ available for the reaction to proceed. For aqueous solutions, in order to speed the reaction process along, the pressure must be increased.¹⁵⁸

Manipulation of CO₂ solubility characteristics is a common theme throughout electrochemical studies on CO₂ utilization. The CO₂ phase diagram shown in Figure 4.2.1 shows the corresponding increase of CO₂ concentration (e.g. from 0.033 mol/L to 1.17 mol/L under 60 atm) when the pressure is increased. The point is that the mass transfer of reactant to the electrode is virtually unimpeded at the high concentration (or pressure) levels. Thus, the advantage in terms of productivity, associated with high pressure electrolysis of CO₂, may offset apparent energy inefficiencies for production of some high value products.¹⁵⁹

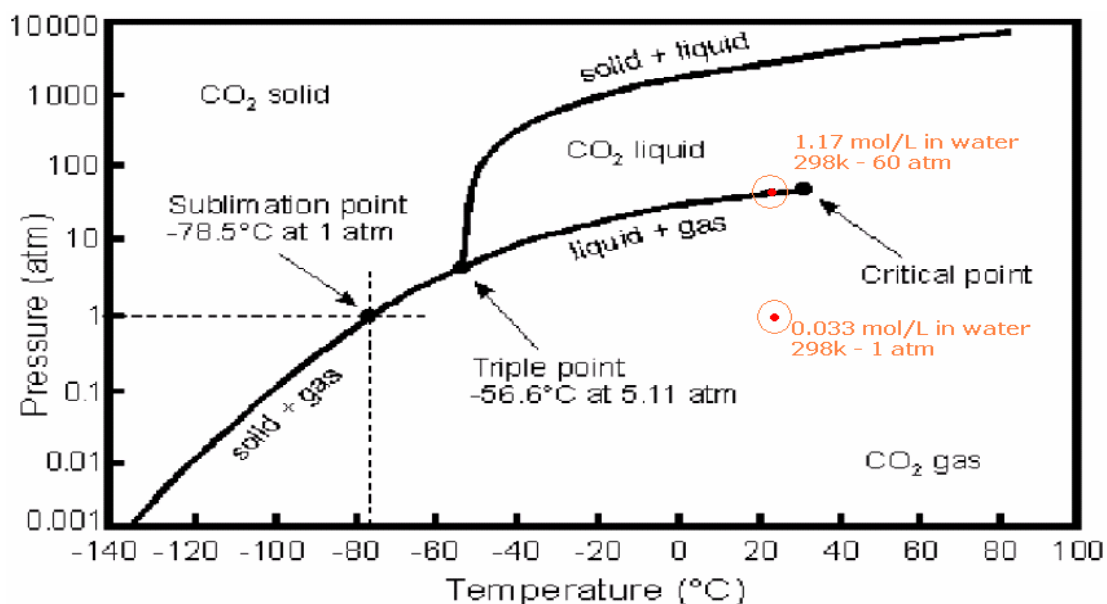


Figure 4.2.1: Pressure-temperature phase diagram for CO₂.¹⁵⁹

Numerous studies have been performed illustrating the effect of electrochemical reduction of CO₂ under high pressure on various electrodes in an aqueous electrolyte. Table 4.2.1 shows the faradaic efficiencies of CO₂ reduction on Group 8-10 metal electrodes, which have low overpotentials for hydrogen formation, increased substantially at 30 atm of CO₂ compared with that at 1 atm of CO₂. However, the total cathodic current barely increased with increasing CO₂ pressure.¹⁶⁰ It should be noted that the observed efficiencies were recorded for only limited period of times, on the order of minutes. For industrial-scale production, there is still much work required.

Table 4.2.1: The electrochemical reduction of CO₂ under 30 atm pressure.¹⁶⁰

Electrochemical reduction of CO ₂ under a pressure of 30 atm on various electrodes at 163 mA cm ⁻¹											
Group	Electrode	E°/V	Faradaic efficiency /%								PCD (CO ₂ red.)/mA cm ⁻²
			CH ₄	C ₂ H ₆	C ₂ H ₄	CO	HCOOH	H ₂	CO ₂ red.	Total	
8	Fe	-1.63	2.03	0.4	0.16	4.2	28.6	51.6	35.4	87	57.7
9	Cu	-1.54	3.09	0.17	0.38	15.6	21.9	40.9	41.5	88.4	7.6
	Rh	-1.41	0.26	0.03	0.01	51	19.5	13.1	80.8	93.9	131.7
	Ir	-1.55	0.62	0.05	0.05	17.5	22.3	48.3	40.5	88.8	66
10	Ni	-1.59	0.72	0.08	0.11	33.5	31.3	26	65.7	91.7	107.1
	Pd	-1.56	0.13	0.01	Trace	46.1	35.6	12.8	81.8	94.6	133.3
	Pd*	-1.76	0.21	0.01	0.02	35.1	44	33.8	79.4	93.2	397
	Pt	-1.48	0.22	0.02	Trace	6.1	50.4	33.6	56.7	90.3	92.4

Reaction temperature, 25°C; electrolyte, 0.1 mol dm⁻³ KHCO₃; charge passed, 300C

4.2.3 Non-aqueous solutions

Electrochemical synthesis involves the application of a voltage potential, in the presence of active electrode surfaces, and the resulting flow of electrons drives the oxidation or reduction and subsequent recombination reactants, as is the case in aqueous solutions.¹⁶¹ For non-aqueous solutions, it is still critical for the concentration of CO₂ close to the electrode surface to remain high. Alternative solvents are employed which exhibit high solubility of CO₂. Dimethyl-formamide can contain up to twenty times more CO₂ than corresponding amounts of aqueous solutions, such as KHCO₃, potassium formate and water. Carbon dioxide in propylene carbonate is eight times more soluble, and in methanol five times more soluble.¹⁶² This latter solution, in turn, supports CO₂ conversion into methane, ethylene and carbon monoxide.

Solubility of CO₂ in methanol is very high under increased pressure.¹⁶³ The methanol reaction is characterized by relatively high pressure and near critical concentrations of CO₂. High yields have been shown at very high current densities at the copper cathode with an electrolysis time of one minute.¹⁶⁴ However, the copper electrode became poisoned shortly thereafter. This dilemma is common with the use of organic solvents. Increased CO₂ solubility enables operation under large current densities, but low electrolytic conductivity leads to high ohmic losses.

A very promising means of utilizing CO₂ in electrochemistry for green chemical manufacturing is very close to reality for replacement of phosgene. This is a major industrial chemical used to synthesize plastics and pesticides. At room temperature, 70 °F (20 °C), phosgene is a poisonous gas. The replacement chemical for phosgene involves indirect synthesis of carbamides and electrochemically generated superoxide and CO₂ organic carbamates are valuable as synthetic intermediates for chemical and biochemical applications.^{165, 166}

4.2.4 Effect of electrode types and characteristics

Gas evolution in electrochemical cells

The evolution of gas in the electrochemical cell has a strong impact on its performance. This can be categorized in three ways. (i) gas bubbles reduce electrolyte conductivity and increase ohmic resistance, (ii) bubbles that adhere to an electrode block the surface and reduce the area available for reaction, (iii) convection, local heat and mass transfer are increased as the bubbles rise. The first two effects tend to reduce the performance of the cell; however the latter tends to increase its performance.¹⁶⁷ These factors are important when considering CO₂ reduction into hydrogen/carbon based fuels.

On the basis of work performed by the Kaneco group¹⁶⁸, a high efficiency electrochemical CO₂ to methane conversion method (Reaction 4-2-1) appears to be achieved. They report that methane can be obtained with high faradaic efficiency in aqueous solution at less than 0 °C using a copper electrode. The reduction potential at standard temperature, pressure, and equilibrium for CO₂ to methane is $E_{eq}^{\circ} = -0.25$ V.

of solar energy and production of intermediate material for the petrochemical industry. The development of industrial processes to this end must balance the relative importance of individual electrode effects with current density, cell geometry, hydrodynamics, and the degree of mass transport limitation.¹⁶⁷

Porosity of electrodes

Electrode porosity is another means of increasing the reaction rate per unit electrode area. By using an electrode with a large surface area per unit volume, the area on which the reaction can occur is increased. Surface areas of 10,000 cm² for each cubic centimeter of electrode volume are attainable.¹⁶⁷ The electrolyte supporting the reactants permeates the porous matrix structure, which is electronically conductive. The reactions proceed within the porous matrix structure. Fuel cells commonly employ porous electrodes in conjunction with gaseous reactants.

Nanotube composite electrodes were recently used to study the electrochemical reduction of CO₂ to methanol.¹⁷⁰ Current efficiencies up to 60.5% were reported (Table 4.2.2). In one study, a platinum electrode was mechanically polished, soaked in a slurry of Al₂O₃ and pretreated by electrolyzing in H₂SO₄ solution.¹⁷⁰ This electrode was then placed in a mixed solution containing TiO₂ nanotubes on which RuO₂ had been preloaded. The solvent was left alone to air dry resulting in a nanotube (NT) – nanoparticle (NP) film applied to the platinum electrode surface.

*Table 4.2.2: Faradaic efficiencies of the electrochemical reduction of CO₂ on various electrodes.*¹⁷⁰

Run time (h)	Electrode	Faradaic efficiency for CH ₃ OH (%)
2	RuO _x	30.5 [13]
2	RuO ₂ /TiO ₂ NPs composite	40.2
2	RuO ₂ /TiO ₂ NTs composite	60.5

Along this line, a more recent study shows that CO₂ can play an essential role during synthesis of carbon nanotubes from carbon monoxide.¹⁷¹ Here a clean wall reactor, made of ceramic tube, was mechanically cleaned and baked at 1200 °C to remove all catalyst material from the walls. A hot wire generator (HWG) method was used to produce CNTs. When pure carbon monoxide was used, no CNTs were produced. When 1000 ppm of CO₂ was injected into the clean reactor, CNT formation occurred. Variations on this base experiment suggest that CNT length can be increased up to 700 nm with a CO₂ increase of 1000 ppm over normal background levels.

Gas diffusion electrodes

Gas diffusion electrodes present a possible means to overcome mass transfer limitations during electrolysis. These are typically porous electrodes impregnated with electro-catalytically active metals. They are often deployed in hydrogen-oxygen fuel cells to

overcome the low solubility of gaseous reactants. Solid oxide fuel cells are the simplest fuel cells and are distinguished by their very high operating temperature (700 to 1000 °C). They can be operated in reverse to generate hydrogen from CO₂ and water; then, when there is a demand for electricity, they can reverse cycle to utilize the H₂ to produce electricity. Fuel cells produce significantly lower rates of CO₂ and sulfur dioxide emissions when compared to standard fuel burning power generating technologies (Figure 4.2.4).¹⁷²

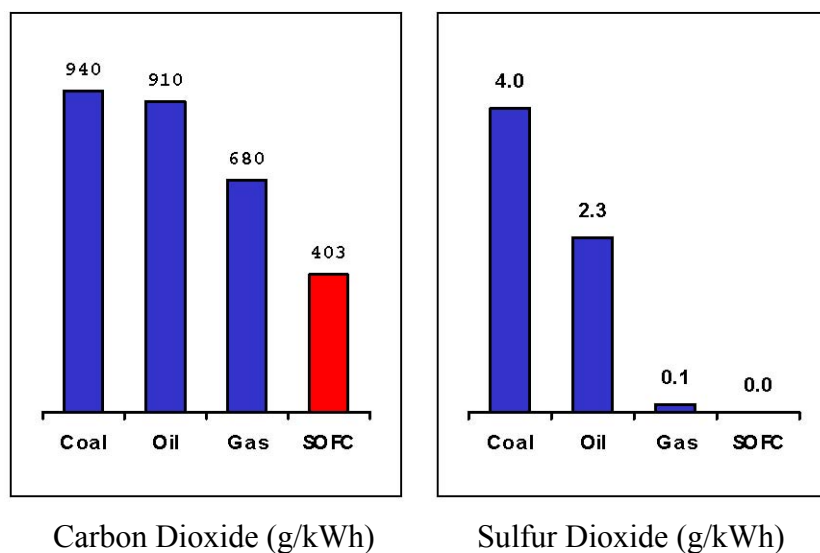


Figure 4.2.4: 5kW SOFC pollutant emission rates.¹⁷³

4.2.5 Economic and energetic aspects

From an economic and energetic aspect it appears the choice of electrochemical methods are justified only when the electrical energy in the process originates from a source other than fossil fuel fed power stations. Many indicate the storage of electrical energy produced by solar or nuclear power stations appears to be the most promising options, provided the electro-reduction of CO₂ will result in a selective formation of a liquid C₁ (or C₂) product such as formic acid, methanol or ethanol. For formic acid, low energy efficiency and high dilution of product, require at least 50% larger expenditure of electrical energy than that associated with the electrolysis of water to hydrogen directly. For methanol, the best current efficiency observed is 40%, which is too low for commercial feasibility. However, dense-phase CO₂ solvent is also raw material from the synthesis. This aspect eliminates the mass transfer limitations that plague electrochemistry in ordinary liquids.^{174, 175}

Direct electrochemical CO₂ reduction (ECR) methods can be justified only when the electrical energy used in the process originates from a source other than fossil fuel fed power stations. In the case that cheap and abundant electrical energy become available, electrochemical CO₂ reduction methods would still have to compete with the well established industrial process for electrolysis of water. This process demands less energy

than ECR, and from the point of view of investment costs, is more advantageous. However, the electric potential has fundamental superiority over high temperature and pressure conditions in enhancing the rates of reduction/oxidation reactions. Therefore, development of new electrochemical CO₂ reduction methods continues. Prospects for unique future applications are a driving force in this regards.

Products such as formic acid, methanol or ethanol have been generated in small quantities using ECR methods. These provide a means to store electrical energy produced by solar or nuclear power stations. Once generated, they are easier to store than hydrogen formed through the electrolysis of water.¹⁵⁸ However, the eventual use of these products as fuels, even in supporting development of the hydrogen economy, does not lead to an overall net reduction of CO₂ in the environment.

Comparing current electrochemical processes to current industrial processes is difficult because very few case studies exist on electrochemical processes being performed at an industrial scale. Trying to compete with traditional industrial methods (e.g. heterogeneous and homogeneous catalysis) will be very difficult in the short term due to heavy research and development costs. Presently, there is not much motivation to replace existing, profitable and proven technologies. Currently, the small-scale experiments of limited duration that have been performed seem to point to improved yields and higher product quality but are largely unrealized. However, some patents are beginning to appear which indicate electrochemical utilization methods may be starting to find favor with industry segments to the point of commercial deployment.¹⁵⁸

4.2.6 Advantages and disadvantages

There are apparent advantages for utilizing electrochemical conversion methods (Table 4.2.3).¹⁵⁸ Electrons flowing as current may be regarded as one of the reagents thereby simplifying requirements for commercial production. Reactions may take place in a low-temperature environment, reducing the local consumption of energy, and reducing the risk of corrosion, material failure, and accidental release. Also, reactions may occur on low volatility or no-volatility reaction media. Electrodes can be regarded as heterogeneous catalysts that are easily separated from the products. Supporting electrolyte and electrochemically active mediator species may be regenerated electrochemically and recovered.

Table 4.2.3: Formation of formic acid utilizing electrolyses.¹⁵⁸

Advantages	Disadvantages
1. On Amalgamated metals (indium, tin lead & mercury) faradaic yields can exceed 90%	1. Low energy efficiencies
2. Under increased CO ₂ pressure larger current densities reached are comparable to in. water electrolysis (to form H ₂ & O ₂)	2. High dilution of product
3. Formic acid can be relatively easily decomposed into H ₂ and CO ₂ making it a possible hydrogen storage agent.	3. Low solubility of CO ₂ in aqueous solutions
4. High CO ₂ concentrations can be reached at high pressures. This equates to high productivity at high pressures.	4. Paradigm shift required for use as an alternative energy source.

4.2.7 Key Issues

The use of electrochemical methods for CO₂ conversion would prove to be industrially viable if a paradigm shift toward alternative energy sources occurred. Many state governments are presently working to facilitate this change. Electrochemical syntheses provide a basis for environmentally friendly and sustainable methods for chemical production in conjunction with renewable energy development. The Commonwealth of Pennsylvania is working hard to develop the appropriate government policies to initiate the beginnings of such a paradigm shift. Other states and federal policy directives have moved significantly in this direction. In Pennsylvania, ACT 213 – The PA AEPS (Alternative Energy Portfolio Standards) Program was passed in December 2004.^{176, 177} Subsequently, a Final Order published by the PUC (Pennsylvania Utility Commission) was developed in October 2005. Presently a second Final Order dealing with “customer generation” and like topics is under final review, and expected to be issued early March 2006.¹⁷⁸ Overall, this demonstrates that we are headed in the right direction. Electrochemical methods for CO₂ utilization have the potential to be feasible in the future.

4.2.8 Electrochemical production summary

Carbon dioxide utilization

- Promising, but no commercial or industrial electrochemical processes identified as being used up to today.
- Non-electrochemical processes superior by today’s standards.
- Results to date show high-efficiency but of only limited duration.

Potential products and use

- Formic acid, methanol, ethanol – CO₂ reduction by alternative pathways.
- Ethylene – important feedstock – scCO₂ processes are favorable.
- Nanofibers¹⁷⁰ – uses only very minute quantities of CO₂.

- Synthetic replacement for phosgene¹⁶⁵ – better accomplished by chemical synthesis of organic carbonates.

A paradigm shift toward alternative energy sources would be the single most important factor to enhance electrochemical product development utilizing CO₂.

4.3 Carbon dioxide reforming of methane

4.3.1 Introduction

Carbon dioxide emissions are considered anthropogenic and are estimated at 2 Gton/yr.¹⁷⁹ The drastic changes in the annual temperature cycle of the northern hemisphere and the increasing volatility of the global weather patterns have been attributed to the increasing concentration of methane and CO₂ in the atmosphere originating from the refinery flares and the power plant stacks. It is therefore a consideration to prevent the emission of this green house gas into atmosphere. Carbon dioxide conversion involves both physical processes such as extraction and chemical synthesis. Carbon dioxide is a thermodynamically stable molecule¹⁸⁰ Therefore, to convert it into useful chemicals, a substantial input of energy, catalysts and appropriate reaction conditions are needed. If CO₂ is used as a co-reactant along with either methane or hydrogen which has a high Gibbs free energy, the formation of products is thermodynamically more favorable.

4.3.2 Carbon dioxide reforming of methane

Synthesis gas is a mixture of carbon monoxide and hydrogen. It is currently produced by gasification of coal and combusted in gas turbines to get power. Another method to produce synthesis gas is steam reforming, which is an endothermic reaction between steam and methane, accompanied by an exothermic water gas shift reaction. The synthesis gas produced is converted to organic hydrocarbons by Fischer-Tropsch synthesis. Instead of supplying heat to the steam reforming process, a partial oxidation reaction is also carried out to make it self-sustaining. The air-to-fuel ratio and the water-to-fuel ratio play an important role in the composition of the product gas. These ratios can be adjusted so that the autothermal reactor produces more hydrogen and less carbon monoxide needed for hydrogen economy or an appropriate amount of carbon monoxide and hydrogen needed for further Fischer-Tropsch synthesis. By maintaining an air-to-fuel ratio of 3.5 and water-to-fuel ratio of 2.5 to 4 with the reactor operating 820 – 871 K (547 - 598 °C) helps to produce more hydrogen and less carbon monoxide for direct use in Proton Exchange Membrane (PEM) fuel cells.¹⁸¹

Another possible method to produce carbon monoxide and hydrogen from methane is the dry reforming of CO₂. The dry CO₂ reforming of methane is 20% more endothermic than steam reforming of methane (see Reactions 4-3-1, 4-3-2).^{180, 182} Simultaneously, the reverse water gas shift reaction also takes place. Apart from these two reactions, the carbon deposit formation also takes place on the surface of the catalyst that prevents further reaction. Different authors have studied the heterogeneous catalysis of this reaction over catalyst like iridium, nickel, cobalt-nickel combination, ruthenium and rhodium with a combination of different supports like silica, magnesia, alumina, ultra-fine zirconia and lanthanum oxide.¹⁸⁰ Nickel catalyzes carbon formation by hydrocarbon decomposition and carbon monoxide disproportionation that deactivates the catalyst, but it is used in steam reforming reaction as a commercial catalyst. The probable solutions found were adding steam to the reactant mixture, reducing the concentration of Lewis

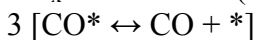
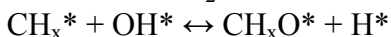
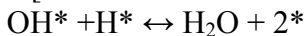
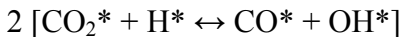
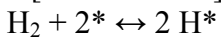
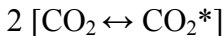
acid sites on the catalyst surface and reducing the size of the nickel metal particles. Adding cobalt to nickel increases the methane conversion. The conversion reaches a maximum for Co/Ni atomic ratio of 0.17.¹⁸³ This combination is promising for simultaneous CO₂ and steam reforming of methane to produce synthesis gas.

Molybdenum and tungsten carbide catalysis were prepared and tested.¹⁸⁴ They are not stable at atmospheric pressure and produced a lower H₂/CO ratio than a nickel based catalyst and noble metals at 650 °C and 750 °C. As far as ruthenium, the support played a vital role in methane conversion and H₂/CO yield.¹⁸⁵ Yittria support showed the highest methane and carbon dioxide conversion and H₂/CO ratio compared to all the other supports. Pretreatment of the catalyst with CO₂ showed a significant effect on the conversion and the ratios.

The reaction mechanism for Reaction 4-3-3 was proposed by Vannice and Bradford.¹⁸⁶ The asterisk (*) represents the active site on the surface of the nickel catalyst. Methane adsorbs on an active site where the tetravalency of the carbon atoms is satisfied. Carbon dioxide adsorbs and hydrogen undergoes dissociative adsorption on the active site of the metal. The associatively adsorbed CO₂ and hydrogen ion react to form carbon monoxide and a hydroxyl ion. The hydroxyl ion reacts with the dissociated hydrocarbon CH₂. The dissociation of methane and the dissociation of CH_xO intermediate are considered to be the rate limiting steps.



Reaction Mechanism: (4-3-3)



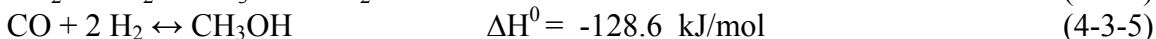
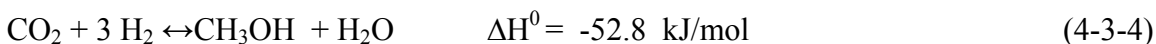
Interestingly, when using a nickel catalyst with Na-Y and Al₂O₃ as a support, the CO₂ and methane conversions decreased with increasing pressure.¹⁸⁷ The conversion of CO₂ was always higher than that of methane at all temperatures and pressures. At 8 wt % nickel loading, the conversion of methane and CO₂ reaches the maximum. The same trend was observed with 2.5 wt % rhodium catalyst with the same support materials.¹⁸⁸

It appears that to supply 20% more heat for the dry reforming of one mole of methane and to consume one mole of CO₂, either additional methane has to be partially oxidized or heat should be supplied externally. When it is scaled up to consuming tons of CO₂ produced from the power plant a day, the amount of heat to be supplied to the reactor would be of very large magnitude making the process uneconomical. The rate limiting

step is the breaking of the CO₂ double bonds, which occurs in order to make it more active to participate in chemical reactions, thereby making the process less energy consuming and economically viable.¹⁷⁹ This challenge has prevented the process from being commercialized to large-scale.

4.3.3 Methanol from CO₂

Currently, methanol is prepared from carbon monoxide and hydrogen (Reaction 4-3-4) with a feed ratio of 1:3 by three methods. (i) High pressure synthesis involved a pressure of 30 – 35 MPa with a temperature of 360 - 400 °C over ZnO-Cr₂O₃ catalyst. (ii) Low pressure synthesis occurs at 5 – 10 MPa pressure with a temperature of 220 - 350 °C over copper based catalyst. (iii) Fluidized bed which operates at pressure was 5 – 20 MPa with a temperature of 300 °C with Zn-B-Cu based catalyst. During the synthesis of methanol from CO₂ (Reaction 4-3-4), one of the two oxygen atom remains in the product. Four hydrogen atoms are added to form methanol; this process is called hydrogenation. This process is used in a test plant in Japan in pilot scale to produce 50 kg per day of methanol. Cu-ZnO based catalyst with ZrO₂ modified alumina support is used as a catalyst.¹⁸² The space time yield of methanol is several times higher compared to that obtained for synthesis gas conversion. Preparation of multifunctional catalyst Cu-Zn-Cr-Al through gelation method rather than the conventional precipitation method increased the catalytic activity by 50%. Palladium or gallium doped on the catalyst increases the activity of catalyst for methanol production.



Literature reveals that synthesis gas containing CO₂ rather than a mixture of CO₂ and H₂ can be converted to methanol with a copper oxide and manganese oxide catalyst at 230 °C and 1 MPa pressure.¹⁸⁹ Rather than alumina or silica support, zirconia support showed higher activity.

4.3.4 Dimethyl carbonate from methanol

Dimethyl carbonate is a methylating agent that has two chemically active carbon sites; one is the carbon atom in the carbonyl group and the other is the carbonyl atom in the methoxy group. Dimethyl carbonate is a biodegradable solvent with low toxicity. With two oxygen atoms present, it enhances the octane number of gasoline, thereby, acting as a substitute for methyl tertiary butyl ether.

Conventionally, DMC is prepared by reacting phosgene with methanol in concentrated sodium hydroxide (Reaction 4-3-6).¹⁸²



The second method is the oxidative carboxylation of methanol with carbon monoxide and oxygen in a slurry reaction system catalysed by cuprous chloride (Reaction 4-3-7).¹⁸²



The third method is the oxidative carboxylation of carbon monoxide with a palladium catalyst and methoxy nitride promoter (Reaction 4-3-8).



A non phosgene route to prepare dimethyl carbonate from methanol and carbon monoxide is (Reaction 4-3-9).¹⁹⁰



Phosphoric acid on zirconia has proven to be an effective catalyst¹⁸⁰. Oxides like alumina, titania, zeolite and mordenite used with the intention to produce dimethyl carbonate ended up producing dimethyl ether. Oxides like silica, tin oxide, yttria and gallium oxide did not catalyze the formation of dimethyl carbonate and dimethyl ether. Zirconia catalysed the above reaction (Reaction 4-3-9) at 673 K (400 °C).¹⁸² Zirconia modified with phosphoric acid works well with P/Zr = 0.05 exhibiting the highest performance at all temperatures compared to untreated zirconia and other catalysts¹⁸⁰. With an increase in calcination temperature, the amount of dimethyl carbonate produced increases but the BET surface area of the catalyst decreases.

4.3.5 Biodiesel production using methanol

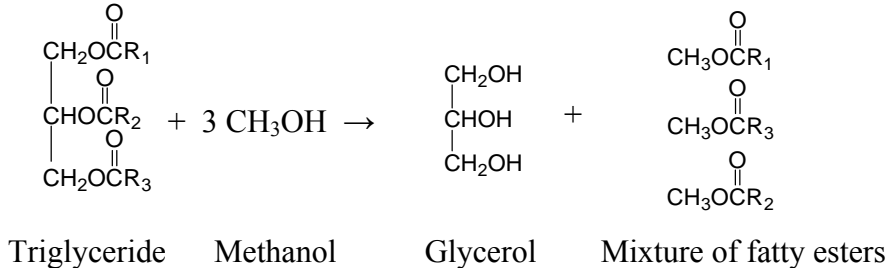
Annually, 33 billion gallons of diesel from the petroleum crude is consumed.¹⁹¹ Currently, 35.3 billion pounds of vegetable oil and animal fat are produced in the United States per year.¹⁹¹ If all the oil and fat are available, this could help meet 14% of the current demand for highway diesel.

The transesterification reaction involves (Reaction 4-3-10) the reaction of triglyceride with methanol to form glycerol and mixture of fatty acids. The long hydrocarbon chains R₁, R₂ and R₃ are alkyl hydrocarbon chains. There are only five chains that are common in soybean oil. It is better to have two conversion stages. In the first stage, part of the alcohol and catalyst are added at the beginning of each step. The solution is mixed in a continuous stirred tank reactor. The glycerol formed is removed and the extract is taken to the second stage. By doing so, the amount of methanol spent can be minimized. Water and free fatty acid inhibit the reaction.

The transesterification reaction can be either catalyzed by acid or by base depending upon the percentage of free fatty acids in the feedstock. Acid catalyzed transesterification is slower compared to base catalyzed transesterification. Acid catalysis is used if the percentage of free fatty acid is greater than 5% in the feed stock, and base catalysis if the percentage is lesser than 5%.¹⁹¹ The glycerol produced in this reaction is insoluble and can be removed by centrifugation. The methyl ester enters the neutralization step where acid is added to the biodiesel to neutralize any residual catalyst and to split up soap that

may have formed during the reaction. Soap reacts with the acid to form water soluble salts and free fatty acids. The soap that is formed in the reactor, if not removed, can create emulsion which causes difficulty in separating biodiesel from glycerol.

Transesterification Reaction (Reaction 4-3-10)

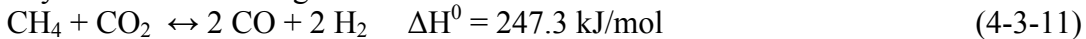


The water washing step eliminates the soap, salt and catalyst from the biodiesel. The base catalyzed transesterification takes place at 0.1 MPa and 60 °C with an alcohol-to-oil ratio of 6:1.¹⁹¹

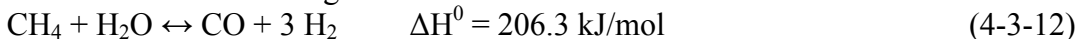
4.3.6 Tri-reforming

Tri-reforming is a novel concept proposed by Song co-authors¹⁹² to produce H₂/CO ratios of 1.5 - 2.0, depending upon the process conditions and catalyst. It is a combination of three reactions, (i) dry reforming of methane, (ii) steam reforming of methane and (iii) partial oxidation reactions. The synthesis gas obtained is a source of organic chemicals that are produced by Fischer-Tropsch synthesis. The three reactions involved in tri-reforming are given in Reactions (4-3-11), (4-3-12) and (4-3-13).

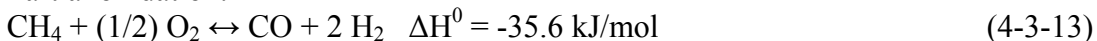
Dry methane reforming:



Steam methane reforming:



Partial oxidation:



Methane, carbon dioxide, steam and oxygen are the four reactants in tri-reforming. The last three reactants are present in the flue gas from the power plants. This shows that the flue gas coming out of the coal-fired and natural gas-fired power plant can be used in the process of tri-reforming to produce the synthesis gas. The composition of flue gas from natural gas-fired power plants demands the addition of methane, while that of coal-fired power plants demands the addition of methane, steam and oxygen to produce synthesis gas with H₂/CO ratio of 2:1.

Tri-reforming reactions are endothermic, but they consume the least amount of energy when compared to other processes like dry reforming of methane, and the currently

existing steam reforming of methane. To produce synthesis gas with H₂/CO ratio of 2, the energy requirement for the three processes, dry reforming of methane, steam reforming of methane and tri-reforming of methane is calculated and tabulated in Table 4.3.1. In the tables below the amount of energy consumed by absorption is also taken into account as it is supplied as a reactant to produce synthesis gas with desired ratio.

Thermodynamics

To produce one mole of hydrogen and two moles of carbon monoxide by CO₂ reforming, conventional steam reforming and modern tri-reforming, the energy consumptions are tabulated in Tables 4.3.1, 4.3.2, 4.3.3, and 4.3.4.

Table 4.3.1: CO₂ reforming H₂/CO ratio = 2.¹⁹²

Reactions	Energy (kJ/mol)
0.75 CH ₄ + 0.75 CO ₂ ↔ 1.5 CO + 1.5 H ₂	+182.5
0.5 CO + 0.5 H ₂ O ↔ 0.5 CO ₂ + 0.5 H ₂	---
CO ₂ from absorption (0.75 x 160)	+120
Total	305.25

Table 4.3.2: Steam reforming H₂/CO ratio = 2.¹⁹²

Reactions	Energy (kJ/mol)
0.75 CH ₄ + 0.75 H ₂ O ↔ 0.75 CO + 2.25 H ₂	+ 154.5
0.25 CO ₂ + 0.25 H ₂ ↔ 0.25 CO + 0.25 H ₂ O	+ 10.2
CO ₂ from absorption (0.25 x 160)	+ 40
Total	204.7

Table 4.3.3: Tri-reforming H₂/CO ratio = 2.¹⁹²

Reactions	Energy (kJ/mol)
0.22 CH ₄ + 0.22 CO ₂ ↔ 0.44 CO + 0.44 H ₂	+ 54.34
0.44 CH ₄ + 0.44 H ₂ O ↔ 0.44 CO + 1.32 H ₂	+ 90.64
0.12 CH ₄ + 0.06 O ₂ ↔ 0.12 CO + 0.24 H ₂	- 4.32
N ₂ heating from 150° C to 850 C	+ 25.5
Total	166.16

Table 4.3.4: Energy comparison for three reactions to produce H₂/CO = 2.¹⁹²

Process	Energy consumed (kJ/mol)	CH ₄ consumed (mol)	CO ₂ emission per (CO + 2 H ₂)
CO ₂ reforming	305.25	0.43	0.18
H ₂ O reforming	204.7	0.29	0.04
Tri-reforming	166.16	0.233	0.013

Kinetics of tri-reforming

From Figure 4.3.1, it is evident that the methane conversion increases with an increase in temperature for all catalysts. From Figure 4.3.1, it is observed that the ability to enhance the CO₂ conversion decreases in the order of Ni/MgO > Ni/MgO/CeZrO. This is because CO₂ interacts with MgO support much better than it does with other supports. Figure 4.3.2 indicates that at relatively low temperatures (around 700 °C), steam reforming is better compared to CO₂ reforming producing more H₂ and less CO. At higher temperatures (near 850 °C), CO₂ reforming is better compared to steam reforming producing more CO and less H₂. Relatively low temperatures are preferred to produce synthesis gas for chemicals and high temperatures are preferred to conduct tri-reforming for solid oxide fuel cells (SOFC) and gas turbine combined cycles.¹⁹²

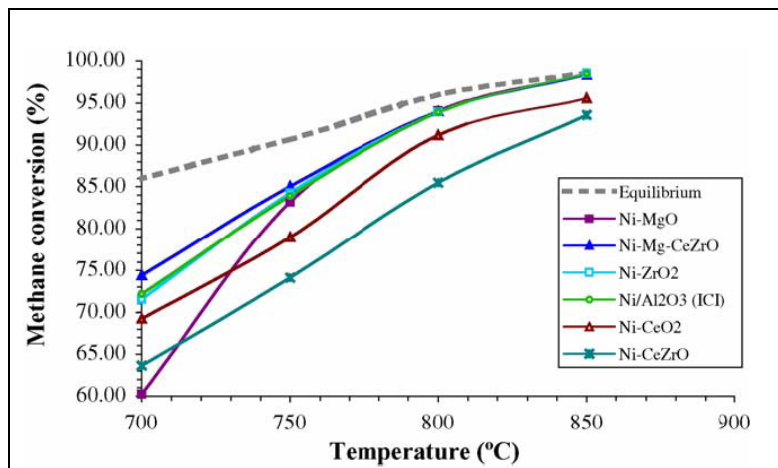


Fig 4.3.1: Methane conversion.¹⁹²

v

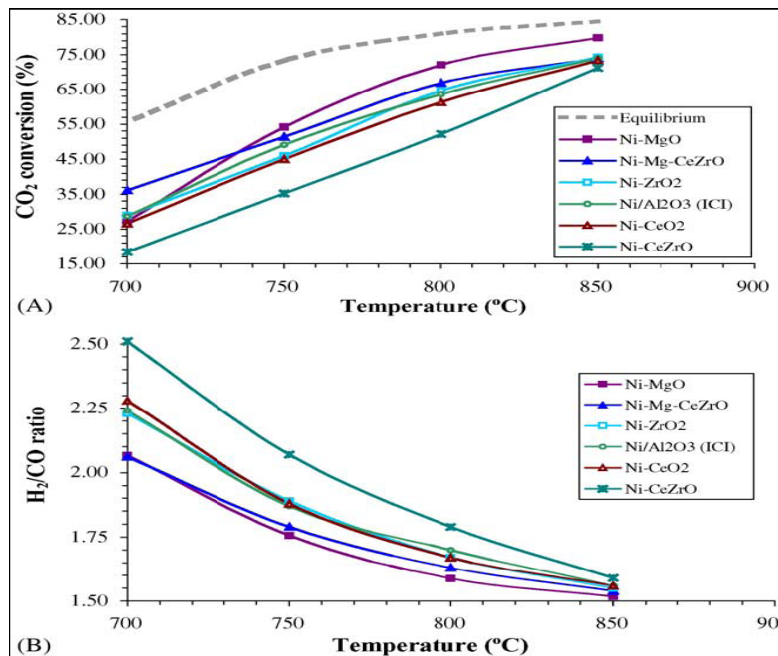


Figure 4.3.2: CO₂ conversion and H₂/CO ratios.¹⁹²

4.3.7 Solid oxide fuel cell – gas turbine combined cycle

The anode of the solid oxide fuel cells is a metal ceramic (cermet) made up of nickel on yttria stabilized zirconia. The electrolyte is yttria stabilized zirconia which transports oxygen anions at high rates and high temperatures. The cathode is a p-type semiconductor called lanthanum strontium manganite ($\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$).¹⁹³ The H₂/CO ratio for this solid oxide fuel cell (SOFC) is 1.5. Zirconia can also be doped with magnesia instead of yttria with some ceria on it. Ni/MgOCeZrO can be used as an anode in SOFC, and be operated at 0.3 MPa and 850 °C. The natural gas, air, and flue gas needed for tri-reforming and electrochemical oxidation are compressed to 0.3 MPa at the anode part of the SOFC. The heat produced by the electrochemical oxidation in the fuel cell will be utilized by the tri-reforming reaction. Air for electrochemical oxidation is fed at the same pressure to the cathode. The fuel utilization efficiency in the SOFC is 90%.¹⁹³ The unconverted fuel is fed to a gas burner. Oxygen is supplied in the burner to oxidize the unconverted carbon monoxide and hydrogen. The temperature in the exhaust of the burner is 900 °C. This hot gas at 0.3 MPa is expanded in a turbine to produce mechanical work (Table 4.3.5 and 4.3.6). The downstream pressure in the turbine is 0.12 MPa and temperature is 580 °C.¹⁹³ The heat in this gas is exchanged with the incoming feed gas (Figure 4.3.3).

Table 4.3.5: Mol % of gases in the inlet and outlet of a gas turbine.

Gas components	Inlet mol %	Outlet mol %
CO	1.75	---
H ₂	2.63	---
CH ₄	0.248	---
N ₂	42.19	47.3
CO ₂	17.68	17.8
H ₂ O	35.45	34.9

Table 4.3.6: Power input and output for SOFC-GT combined cycle.

Type	Input	Output
Flue gas compression	602 kW	---
Methane compression	100 kW	---
Air compression	514 kW	---
GT output	---	1205 kW
SOFC	---	2610 kW

$$\text{Net power output} = 2610 + 1205 - 504 - 100 - 602 = 2.59 \text{ MWe}$$

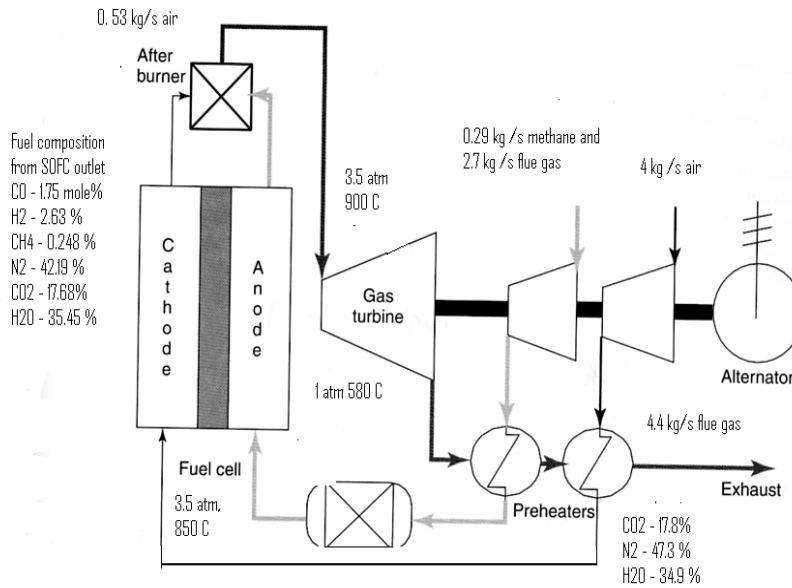


Figure 4.3.3: SOFC – GT combined cycle.¹⁹³

4.3.8 Tri-reforming to produce chemicals

Tri-reforming of methane with flue gas from coal-fired power plant

The amount of CO₂ emitted from a 500 MW coal-fired power plant is 3.29 Mton of CO₂ a year.¹⁹⁴ The four products used for the tri-reforming calculation are methanol, hydrogen, ammonia, and urea. The feed needed for the tri-reforming of natural gas (reaction 4-3-17) to produce H₂/CO ratio equal to 2 is specified in Table 4.3.7 at 0.1 MPa and 710 °C with the catalyst Ni/MgOCeZrO. From the stoichiometric coefficients of the reaction, the ratio of amount of synthesis gas produced per mole of CO₂ in the original flue gas is calculated (. Assuming 90% conversion in the water gas shift reaction, the amount of hydrogen produced per mole of carbon dioxide in the original flue gas is calculated. For 3.29 Mton of CO₂ in the original flue gas, the amount of methanol and hydrogen produced per year and the contribution to their world's capacity is specified in Table 4.3.8. Assuming 90% yield in ammonia synthesis and 100 % yield in urea synthesis, the annual production of ammonia and urea and their contribution to the world's capacity is specified in Table 4.3.8.

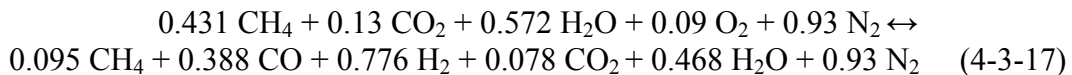


Table 4.3.7: Conditions for tri-reforming with flue gas to produce H₂/CO = 2.¹⁹²

Kinetic data		Feed	
Components	Conversion %	Components	moles
CO ₂	40	Methane	0.431
CH ₄	78	Flue Gas	1
O ₂	100	Steam	0.482
H ₂ O	18	Air	0.24

Currently, synthesis gas is produced by steam reforming of methane. Steam reforming of methane consumes large quantities of methane fuel and emits large amount of carbon dioxide to produce H₂/CO mole ratio 2. If the same synthesis gas is produced by tri-reforming of methane, large amount of carbon dioxide can be prevented from getting into atmosphere by consuming less amount of methane. By knowing the amount of methane consumed by steam reforming of methane and tri-reforming of methane to produce synthesis gas with H₂/CO ratio 2 and based on heat of combustion of methane, the amount of energy that can be saved tri-reforming is specified in Table 4.3.8. The cost of methane is \$6.73/MBTU.¹⁹⁴ The cost of each product based on tri-reforming of methane is tabulated in Table 4.3.9.

Table 4.3.8: Summary of advantages of tri-reforming.

Flue Gas Treatment	Product	% CO ₂ Emission Avoidance	% Fuel Saving	% World Capacity
<u>Coal</u>				
Tri-reforming	Methanol	59.8	30.5	4.95
	Hydrogen	22.8	72.6	0.29
	Ammonia	34.7	17	4.28
	Urea	65.6		9.75
<u>Natural Gas</u>				
Tri-reforming	Methanol	50	25.3	4.56
	Hydrogen	24.5	72.5	0.0825
	Ammonia	33.6	11	1.19
	Urea	38.6		2.72

Table 4.3.9: Economics of products obtained from tri-reforming.

Product	Cost based on conventional method ¹⁹⁴	Cost based on modern tri-reforming Process
Methanol	\$510 per ton	\$381 .5 per ton
Hydrogen	\$2.4 per kg	\$1.1 per kg
Ammonia	\$290 per ton	\$236 per ton

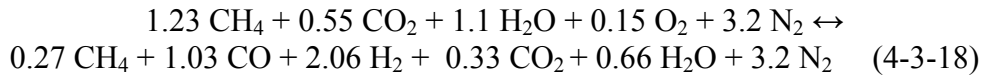
Tri-reforming of methane with flue gas from natural-gas fired power plant

The amount of carbon dioxide coming out of 400 MWe natural-fired power plant 1.47 Mton of CO₂ a year.¹⁹⁴ Under the conditions specified in Table 4.3.8, the flue gas from

the natural gas fired plant is reformed to produce synthesis gas (Reaction 4-3-18). As discussed above, the calculations were made and tabulated in Table 4.3.8, 4.3.9, and Table 4.3.10.

Table 4.3.10: Conditions for tri-reforming with flue gas to produce $H_2/CO = 2$ ¹⁹⁴

Kinetic data		Feed	
Components	Conversion %	Components	moles
CO ₂	40	Methane	1.23
CH ₄	78	Flue gas	5
O ₂	100		
H ₂ O	18		



4.3.9 Conclusion and recommendations

The objective for the utilization of CO₂ is to create value-added products and processes. Chemical utilization of the CO₂ captured from a power plant results in the formation of fuels and specialty chemicals. The precursor for these fuels is synthesis gas, which can be produced by tri-reforming, consuming at least 40% of the total CO₂ produced from the power plant. Based on the calculation, it is recommended to replace the existing steam reformers with tri-reformers. Mercury in the flue gas emitted from coal-fired power plants is of concern when the purity of the chemicals is of importance. Particulate removal is necessary when the synthesis gas from the tri-reformer is used in a combined cycle. Because of issues in the thermal management of solid oxide fuel cells, modeling efforts are required regarding the integration of SOFCs and gas turbine combined cycle systems. Presently, research is focusing on reducing mercury from the flue gas emitted by coal fired power plants. Developments in separating particles of size less than 5 microns from the hot gas are needed to feed the gas into tri-reformer. Tri-reforming is a very promising process and should be pursued by researches in the coming years.

5. Conclusions

Table 5.1 displays the amount of CO₂ that is utilized by the various proposed methods in this study.

Table 5.1: CO₂ utilization amounts for the methods in this project.

Utilization Method	Amount of CO₂ (kton/yr)
Algal pond system (12 ponds)	1.4 (0.04%)
Photobioreactor	0.6 (0.01%)
Supercritical CO ₂ extraction	0.7 (0.01%)
Environmental remediation	26 (0.65%)
Chemical conversion (urea production)	288 (7.20%)
Tri-reforming of CO ₂	1300 (32.8%)
TOTAL	1617

5.1 Team conclusions and recommendations

- In this study, it was determined that the most competing technologies are biological, supercritical, and chemical utilization of CO₂.
- Despite only a small percentage of CO₂ being utilized when compared to the total amount emitted by a 500 MW power plant, all the methods investigated in this project are recommended for the creation of value from CO₂.
- The choice of utilization method depends mainly on the desired product or process improvement.
- Carbon dioxide utilization is a newly-emerging field with substantial room to expand in the future.
- Due to the flue gas processing (e.g., mercury, arsenic, and particulate removal, etc.) that must be performed prior to exploitation; CO₂ utilization directly from a coal-fired power plant is not currently feasible with the available technologies. However, it may be viable in the future given the development of innovative flue gas cleaning methods.
- Carbon dioxide must be captured, purified and concentrated prior to employment in most utilization methods.

6. References

1. Becker, E. W., *Microalgae: Biotechnology and microbiology*, Cambridge University Press, 1994, USA.
2. Borowitzka, M. A., Commercial production of microalgae: ponds, tanks, tubes and fermenters. *Journal of Biotechnology* **1999**, 70, 313.
3. Borowitzka, M. A.; Borowitzka, L. J., *Micro-algae biotechnology*, Cambridge University Press, 1988, UK.
4. Richmond, A., *Handbook of microalgal mass culture*, 1986, CRC Press, USA.
5. Grima, E. M.; Belarbi, E. H.; Fernandez, F. G. A.; Medina, A. R.; Chisti, Y., Recovery of microalgal biomass and metabolites: process options and economics. *Biotechnology Advances* **2003**, 20, 491.
6. Pulz, O.; Gross, W., Valuable products from biotechnology of microalgae. *Appl. Microbiol. Biotechnol.* **2004**, 65, 635.
7. Sawraj, S.; Bhushan, K. N.; Banerjee, U. C., Bioactive compounds from Cyanobacteria and Microalgae: An Overview. *Critical Reviews in Biotechnology* **2005**, 25, 73.
8. Maeda, K.; Owada, M.; Kimura, N.; Omata, K.; Karube, I., CO₂ fixation from the flue gas on coal-fired thermal power plant by microalgae. *Energy Conversion and Management* **1995**, 36, 717.
9. Moll, B.; Deikman, J., Enteromorpha clathrata: A potential seawater-irrigated crop. *Bioresource Technology* **1995**, 52, 225.
10. Brown, L. M., Uptake of carbon dioxide from flue gas by microalgae. *Energy Conversion and Management* **1995**, 37, 1363.
11. Yue, L.; Chen, W., Isolation and determination of cultural characteristics of a new highly CO₂ tolerant fresh water microalgae. *Energy Conversion and Management* **2005**, 46, 1868.
12. Jimenez, C.; Cossio, B. R.; Niell, F. X., Relationship between physiochemical variables and productivity in open pond for the production of Spirulina: a predictive model of algal yield. *Aquaculture* **2003**, 221, 331.
13. Hawthorne, S. B.; Grabanski, C. B.; Martin, E.; Miller, D. J., Comparisons of Soxhlet Extraction, Pressurized Liquid Extraction, Supercritical Fluid Extraction and Subcritical Water Extraction for Environmental Solids: Recovery, Selectivity and Effects on Sample Matrix. *J. Chrom. A* **2000**, 892, 421-433.
14. Hartonen, K.; Inkala, K.; Kangas, M.; Riekkola, M. L., Extraction of Polychlorinated Biphenyls with Water under Subcritical Conditions. *J. Chrom. A* **1997**, 785, 219-226.
15. Guiry, M. D.; Blunden, G., *Seaweed resources an in Europe: Uses and potential*, John Wiley & Sons Ltd., 1991, UK.
16. Eklof, J. S.; Castro, M. d. I. T.; Adelskold, L.; Jiddawi, N. S.; Kautsky, N., Differences in macrofaunal and seagrass assemblages in seagrass beds with and without seaweed farms. *Estuarine, Coastal and Shelf Science* **2005**, 63, 385.
17. Available online at: <http://www.scieng.murdoch.edu.au/centres/algae/BEAM-Net/BEAM-App4a.htm> Last accessed April 21, 2006.

18. Hase, R.; Oikawa, H.; Sasao, C.; Morita, M.; Watanabe, Y., Photosynthetic production of microalgal biomass in a raceway system under greenhouse conditions in Sendai city. *Journal of Bioscience and Bioengineering* **2000**, 89, (2), 157.
19. Morita, M.; Watanabe, Y.; Saiki, H., Investigation of photobioreactor design for enhancing the photosynthetic productivity of microalgae. *Biotechnology and Bioengineering* **2000**, 69, (6), 693-699.
20. Grima, E. M.; Belarbi, E. H.; Fernandez, F. G. A.; Medina, A. R.; Chisti, Y., Recovery of microalgal biomass and metabolites: process options and economics. *Biotechnology Advances* **2003**, 20, 491-515.
21. Nishikawa, N.; Hirano, A.; Ikuta, Y.; Fukuda, Y.; Kaneko, M.; Kinoshita, T.; Ogushi, Y., Photosynthetic efficiency improvement by microalgae cultivation in tubular-type reactor. *Energy Conservation and Management* **1995**, 36, (6-9), 681-684.
22. Doucha, J.; Straka, F.; Livansky, K., Utilization of flue gas for cultivation of microalgae (*Chlorella* sp.) in an outdoor open thin-layer photobioreactor. *Journal of Applied Phycology* **2005**, 17, 403-412.
23. Weissman, J. C.; Goebel, R. P.; Benemann, J. R., Photobioreactor Design: Mixing, Carbon Utilization, and Oxygen Accumulation. *Biotechnology and Bioengineering* **1988**, 31, 336-344.
24. Michiki, H., Biological CO₂ Fixation and Utilization Project. *Energy Conversion and Management* **1995**, 36, (6-9), 701-705.
25. Chae, S. R.; Hwang, E. J.; Shin, H. S., Single cell protein production of *Euglena gracilis* and carbon dioxide fixation in an innovative photo-bioreactor. *Bioresource Technology* **2006**, 97, 322-329.
26. Sevilla, J. M. F.; Garcia, M. C. C.; Miron, A. S.; Belarbi, E. H.; Camacho, F. G.; Grima, E. M., Pilot-plant-scale outdoor mixotrophic cultures of *Phaeodactylum tricornutum* using glycerol in vertical column and airlift photobioreactors: studies in fed-batch mode. *Biotechnology Progress* **2004**, 20, 728-736.
27. Miron, A. S.; Camacho, F. G.; Gomez, A. C.; Grima, E. M.; Chisti, Y., Bubble-column and airlift photobioreactors for algal culture. *AIChE* **2000**, 46, (9), 1872-1887.
28. Cheng, L.; Zhang, L.; Chen, H.; Gao, C., Carbon dioxide removal from air by microalgae cultured in a membrane-photobioreactor. *Separation and Purification Technology* **2006** "in press".
29. Otsuki, T., A study for the biological CO₂ fixation and utilization system. *Science of the Total Environment* **2001**, 277, (1-3), 21-25.
30. Ugwu, C. U.; Ogbonna, J. C.; Tanaka, H., Characterization of light utilization and biomass yields of *Chlorella sorokiniana* in inclined outdoor tubular photobioreactors equipped with static mixers. *Process Biochemistry* **2005**, 40, 3406.
31. Sato, T.; Usui, S.; Tsuchiya, Y.; Kondo, Y., Invention of outdoor closed type photobioreactor for microalgae. *Energy Conservation and Management* **2006**, 47, 791-799.
32. Miron, A. S.; Gomez, A. C.; Camacho, F. G.; Grima, E. M.; Chisti, Y., Comparative evaluation of compact photobioreactors for large-scale monoculture of microalgae. *Journal of Biotechnology* **1999**, 70, 249-270.
33. Singh, S.; Kate, B. N.; Banerjee, U. C., Bioactive compounds from cyanobacteria and microalgae: an overview. *Critical Reviews in Biotechnology* **2005**, 25, 73-95.
34. MarineGenomicsEurope, Photograph of *P. tricornutum*. **2006**.

35. Wen, Z.-Y.; Chen, F., Heterotrophic production of eicosapentaenoic acid by microalgae. *Biotechnology Advances* **2003**, *21*, 273-294.
36. Walker, T. L.; Purton, S.; Becker, D. K.; Collet, C., Microalgae as bioreactors. *Plant Cell Rep* **2005**, *24*, 629-641.
37. Belarbi, E. H.; Molina, E.; Chisti, Y., A process for high yield and scaleable recovery of high purity eicosapentaenoic acid esters from microalgae and fish oil. *Enzyme and Microbial Technology* **2000**, *26*, 516-529.
38. Sobczuk, T. M.; Camacho, F. G.; Rubio, F. C.; Fernandez, F. G. A.; Grima, E. M., Carbon dioxide uptake efficiency by outdoor microalgal cultures in tubular airlift photobioreactors. *Biotechnology and Bioengineering* **2000**, *67*, (4), 465-475.
39. Reid, R. C.; Prausnitz, J. M.; Poling, B. E., *The properties of gases and liquids*. 4 ed.; McGraw-Hill: New York, 1987.
40. Kiran, E.; Debenedetti, P. G.; Peters, C. J., *Supercritical Fluids: Fundamentals and Applications*. Kluwer Academic Publishers: Dordrecht, 2000.
41. Perrut, M., Supercritical Fluid Applications: Industrial Developments and Economic Issues. *Ind. Eng. Chem. Res.* **2000**, *39*, 4531-4535.
42. Sihvonen, M.; Jarvenpaa, E.; Hietaniemi, V.; Huopalahti, R., Advances in Supercritical Carbon Dioxide Technologies. *Trends in Food Science and Technology* **1999**, *10*, 217-222.
43. Mendes, R. L.; Nobre, B. P.; Cardoso, M. T.; Pereira, A. P.; Palavra, A. F., Supercritical carbon dioxide extraction of compounds with pharmaceutical importance from microalgae. *Inorganica Chimica Acta* **2003**, *356*, 328-334.
44. Darling, D. The Encyclopedia of Astrobiology, Astronomy and Spaceflight. <http://www.daviddarling.info/encyclopedia/P/phyco bilin.html> (March 18, 2006),
45. Jung, J. In *Gram to Kilogram Scale-up of Supercritical Anti-Solvent Process*, 6th International Symposium on Supercritical Fluids, Versailles (France), 2003, 2003; Clavier, J.-Y., Ed. Versailles (France), 2003; pp 1683-1688.
46. Valderrama, J. O.; Perrut, M.; Majewski, W., Extraction of Astaxantine and phycocyanine from microalgae with supercritical carbon dioxide. *Journal of Chemical and Engineering Data* **2003**, *48*, (4), 827-830.
47. Macias-Sanchez, M. D.; Mantell, C.; Rodriguez, M.; Martinez De La Ossa, E.; Lubian, L. M.; Montero, O., Supercritical fluid extraction of carotenoids and chlorophyll a from *Nannochloropsis gaditana*. *Journal of Food Engineering* **2005**, *66*, (2), 245-251.
48. Gaspar, F., Comparison Between Compressed CO₂ Extracts and Hydrodistilled Essential Oil. In Leeke, G., Ed. 2004; p 7.
49. Jung, J. C., Jean-Yves; Perrut, Michel General Rules for Extrapolation from Pilot Plant to Industrial Scale SFE or SFF. www.separex.fe
50. Zougagh, M.; Varcacel, M.; Rios, A., Supercritical Fluid Extraction: A Critical Review of its Analytical Usefulness. *Trends in Analytical Chemistry* **2004**, *25*, 1-7.
51. Kopcak, U.; Sadeg Mohamed, R., Caffeine Solubility in Supercritical Carbon Dioxide/Co-Solvent Mixtures. *J. of Supercritical Fluids* **2005**, *34*, 209-214.
52. Catchpole, O. J.; Grey, J. B.; Perry, N. B.; Burgess, E. J.; Redmond, W. A.; Porter, N. G., Extraction of Chili, Black Pepper, and Ginger with Near-Critical CO₂, Propane, and Dimethyl Ester: Analysis of the Extracts by Quantitative Nuclear Magnetic Resonance. *J. Agric. Food Chem.* **2003**, *51*, 4853-4860.

53. Carvalho, R. N.; Moura, L. S.; Rosa, P. T. V.; Meireles, M. A. A., Supercritical Fluid Extraction from Rosemary (*Rosmarinus Officinalis*): Kinetic Data, Extract's Global Yield, Composition, and Antioxidant Activity. *J. of Supercritical Fluids* **2005**, 35, 197-204.
54. Aguilera, A.; Brotons, M.; Rodriguez, M.; Valverde, A., Supercritical Fluid Extraction of Pesticides from a Table-Ready Food Composite of Plant Origin (Gazpacho). *J. Agric. Food Chem.* **2003**, 51, 5616-5621.
55. Yang, Y.; Hawthorne, S. B.; Miller, D. J., Comparison of Sorbent and Solvent Trapping after Supercritical Fluid Extraction of Volatile Petroleum Hydrocarbons from Soil. *J. Chrom. A* **1995**, 699, 265-276.
56. Aresta, M., *Carbon Dioxide Recovery and Utilization*. Kluwer Academic Publishers: Dordrecht, 2003.
57. Cansell, F.; Aymonier, C.; Loppinet-Serani, A., Review on Materials Science and Supercritical Fluids. *Current Opinion in Solid State and Materials Science* **2003**, 7, 331-340.
58. Reverchon, E.; Adami, R., Nanomaterials and Supercritical Fluids. *J. of Supercritical Fluids* **2006**, 37, 1-22.
59. Yamaoka, S.; Shaji Kumar, M. D.; Kanda, H.; Akaishi, M., Crystallization of Diamond from CO₂ Fluid at High Pressure and High Temperature. *Journal of Crystal Growth* **2002**, 234, 5-8.
60. Brunner, G., Industrial Process Development Countercurrent Multistage Gas Extraction (SFE) Processes. *J. of Supercritical Fluids* **1998**, 13, 283-301.
61. Gani, R.; Hytoft, G.; Jaksland, C., Design and Analysis of Supercritical Extraction Processes. *Appl. Therm. Eng.* **1997**, 17, 889-899.
62. Smith, R. L.; Inomata, H.; Kanno, M.; Arai, K., Energy Analysis of Supercritical Carbon Dioxide Extraction Processes. *J. of Supercritical Fluids* **1999**, 15, 145-156.
63. Baiker, A., Supercritical Fluids in Heterogeneous Catalysis. *Chem. Rev.* **1999**, 99, 453-473.
64. Jessop, P. G., Homogeneous Catalysis in Supercritical Fluids. *Chem. Rev.* **1999**, 99, 475-493.
65. Licence, P.; Ke, J.; Sokolova, M.; Ross, S. K.; Poliakov, M., Chemical Reactions in Supercritical Carbon Dioxide: from Laboratory to Commercial Plant. *Green Chemistry* **2003**, 5, 99-104.
66. Loehr, R. *Final Report*; Superfund Subcommittee of the National Advisory Council for Environmental Policy and Technology: 2004; pp 1-264.
67. Toxic Substances Control Act. In United States Congress: 1976; Vol. 15 U.S.C. s/s 2601 et seq. (1976).
68. Johnson, K., U.S. to order \$490 million river cleanup by GE. *The New York Times* December 6, 2000.
69. Zhou, W.; Anitescu, G.; Rice, P. A.; Tavlarides, L. L., Supercritical Fluid Extraction-Oxidation Technology to Remediate PCB-Contaminated Soils/Sediments: An Economic Analysis. *Environ. Prog.* **2004**, 23, 222-231.
70. Field, J. A.; Monohan, K.; Reed, R., Coupling Supercritical CO₂ and Subcritical (Hot) Water for the determination of Dacthal and its Acid Metabolites in Soil. *Anal. Chem.* **1998**, 70, 1956-1962.

71. Heltai, G.; Feher, B.; Percsich, K.; Barabas, B.; Fekete, I., Application of Sequential Extraction with Supercritical CO₂, Subcritical H₂O, and an H₂O/CO₂ Mixture for Estimation of Environmentally Mobile Heavy Metal Fractions in Sediments. *Anal. Bioanal. Chem.* **2002**, 373, 863-866.
72. Schulmeyr, J., CO₂-Extraction Test Facility for Extraction Pressures up to 1000 bar: Experiments for the Traction/Decaffeination of Cocoa. In *10th European Meeting on Supercritical Fluids*, Colmer, France, 2005.
73. Beckman, E. J., Supercritical and Near-Critical CO₂ in Green Chemical Synthesis and Processing. *J. of Supercritical Fluids* **2004**, 28, 121-191.
74. EFMA *Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry*; European Fertilizer Manufacturers Association: Brussels, 2000; pp 1-44.
75. Song, C., CO₂ conversion and utilization: an overview. *ACS Symposium Series* **2002**, 809, (CO₂ Conversion and Utilization), 2-30.
76. Aresta, M.; Editor, *Carbon Dioxide Recovery and Utilization. (A summary report of the EU Project BRITE-EURAM 1998 BBRT-CT98-5089.)*. 2003; p 407 pp.
77. Strauss, L.,
http://www.grainsa.co.za/sagrain_article.asp?SAGrainId=373&IssId=164&SecId=5.
Magazine of Grain SA Accessed April 13, 2006.
78. Aresta, M.; Quaranta, E.; Tommasi, I., Utilization of carbon dioxide: a strategy for the control of its level in the atmosphere. The role of the photoconversion technology. *Photochem. Convers. Storage Sol. Energy, Proc. Int. Conf., 8th* **1991**, 517-50.
79. Industrial Production of Urea,
<http://www.keele.ac.uk/depts/ch/resources/urea/proddiag.html>. Accessed April 13, 2006.
80. Getoff, N., Control of greenhouse gases emission by radiation-induced formation of useful products. Utilization of CO₂. *Radiation Physics and Chemistry* **2006**, 75, (4), 514-523.
81. Aresta, M.; Quaranta, E.; Tommasi, I., Selective synthesis of 4-OH-benzoic acid from phenol and CO₂ under enzymic catalysis. *Book of Abstracts, 215th ACS National Meeting, Dallas, March 29-April 2* **1998**, COLL-240.
82. Chemical Economics handbook (CEH) Report (Abs) Polycarbonates resins.
<http://www.sriconsulting.com/CEH/Public/Reports/580.1100/> **1997**.
83. Solymosi, F.; Bugyi, L., Adsorption and dissociation of carbon dioxide on a potassium-promoted rhodium(111) surface. *Journal of the Chemical Society, Faraday Transactions I: Physical Chemistry in Condensed Phases* **1987**, 83, (7), 2015-33.
84. Solymosi, F.; Klivenyi, G., HREELS Study on the Formation of CO₂- on a K-Promoted Rh(111) Surface. *Surface Science* **1994**, 315, (3), 255-268.
85. Evans, T. L.; Brunelle, D. J.; Salem, A. J.; Stewart, K. R., Developments in the chemistry of oligocyclic carbonates for use in structural composites. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **1991**, 32, (2), 176-7.
86. Serini, V., Polycarbonates. *Industrial Polymers Handbook* **2001**, 1, 291-304.
87. Pacheco, M. A.; Marshall, C. L., Review of dimethyl carbonate (DMC) manufacture and its characteristics as a fuel additive. *Energy & Fuels* **1997**, 11, (1), 2-29.
88. Delledonne, D.; Rivetti, F.; Romano, U., Developments in the production and application of dimethylcarbonate. *Applied Catalysis a-General* **2001**, 221, (1-2), 241-251.

89. Aresta, M.; Dibenedetto, A., Mixed anhydrides: Key intermediates in carbamates forming processes of industrial interest. *Chemistry-a European Journal* **2002**, 8, (3), 685-690.
90. Aresta, M.; Quaranta, E.; Tommasi, I.; Giannoccaro, P.; Ciccacese, A., Enzymatic versus chemical carbon dioxide utilization .1. The role of metal centres in carboxylation reactions. *Gazzetta Chimica Italiana* **1995**, 125, (11), 509-538.
91. Buysch, H. J.; Groegler, G.; Schwindt, J.; Krimm, H. Aliphatic polycarbonates. 76-2605024
2605024, 19760210., 1977.
92. Aresta, M.; Forti, G.; Editors, *NATO ASI Series. Series C, Mathematical and Physical Sciences, Vol. 206: Carbon Dioxide as a Source of Carbon. Biochemical and Chemical Uses [Proceedings of the NATO Advanced Study Institute on Carbon Dioxide: Biochemical and Chemical Uses as a Source of Carbon, Pugnochiuso, Italy, June 22-July 3, 1986]*. 1987; p 441 pp.
93. Marquis, E. T.; Sanderson, J. R. Process for preparing high-purity alkylene carbonates from epoxides and carbon dioxide using metal phthalocyanine catalysts. 92-923760
5283356, 19920803., 1994.
94. Kuran, W.; Listos, T., Initiation and Propagation Reactions in the Copolymerization of Epoxide with Carbon-Dioxide by Catalysts Based on Diethylzinc and Polyhydric Phenol. *Macromolecular Chemistry and Physics* **1994**, 195, (3), 977-984.
95. Sakai, T.; Kihara, N.; Endo, T., Polymer Reaction of Epoxide and Carbon-Dioxide - Incorporation of Carbon-Dioxide into Epoxide Polymers. *Macromolecules* **1995**, 28, (13), 4701-4706.
96. Sone, M.; Sako, T.; Kamisawa, C. Organic carbonates and catalysts and production methods therefor. 98-142969
11335372, 19980525., 1999.
97. Darensbourg, D. J.; Holtcamp, M. W., Catalysts for the reactions of epoxides and carbon dioxide. *Coordination Chemistry Reviews* **1996**, 153, 155-174.
98. De Pasquale, R. J., Unusual catalysis with nickel(O) complexes. *Journal of the Chemical Society, Chemical Communications* **1973**, (5), 157-8.
99. Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yoshihara, M.; Maeshima, T., Magnesium oxide-catalyzed reaction of carbon dioxide with an epoxide with retention of stereochemistry. *Chemical Communications (Cambridge)* **1997**, (12), 1129-1130.
100. Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K., Mg-Al mixed oxides as highly active acid-base catalysts for cycloaddition of carbon dioxide to epoxides. *Journal of the American Chemical Society* **1999**, 121, (18), 4526-4527.
101. Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore, C., Nb(V) compounds as epoxides carboxylation catalysts: the role of the solvent. *Journal of Molecular Catalysis a-Chemical* **2003**, 204, 245-252.
102. AIST develops method for rapid synthesis of plastic raw materials: Research paves the way for manufacture of environmentally friendly plastics that use CO₂ as a raw material, http://www.aist.go.jp/aist_e/latest_research/2003/20030226/20030226.html. Accessed April. 13 2006.

103. Kuehling, S.; Pakull, R.; Grigo, U.; Tacke, P.; Freitag, D.; Alewelt, W. Preparation of solvent-free polycarbonates by solid-state polycondensation of oligomers. 91-116907 481296, 19911004., 1992.
104. Ignatov, V. N.; Tartari, V.; Carraro, C.; Pippa, R.; Nadali, G.; Berti, C.; Fiorini, M., New catalysts for bisphenol A polycarbonate melt polymerization, 2. Polymer synthesis and characterization. *Macromolecular Chemistry and Physics* **2001**, 202, (9), 1946-1949.
105. Ignatov, V. N.; Tartari, V.; Carraro, C.; Pippa, R.; Nadali, G.; Berti, C.; Fiorini, M., New catalysts for bisphenol A polycarbonate melt polymerization, 1. Kinetics of melt transesterification of diphenyl carbonate with bisphenol A. *Macromolecular Chemistry and Physics* **2001**, 202, (9), 1941-1945.
106. Inoue, S.; Koinuma, H.; Tsuruta, T., Copolymerization of carbon dioxide and epoxide. *Journal of Polymer Science, Polymer Letters Edition* **1969**, 7, (4), 287-92.
107. Inoue, S.; Koinuma, H.; Tsuruta, T., Copolymerization of carbon dioxide and epoxide with organometallic compounds. *Makromolekulare Chemie* **1969**, 130, 210-20.
108. Dinjus, E.; Fornika, R.; Pitter, S.; Zevaco, T., Carbon dioxide as a C1 building block. *Applied Homogeneous Catalysis with Organometallic Compounds (2nd Edition)* **2002**, 3, 1189-1213.
109. Aresta, M.; Quaranta, E., Carbon dioxide: A substitute for phosgene. *Chemtech* **1997**, 27, (3), 32-40.
110. Ishii, H.; Goyal, M.; Ueda, M.; Takeuchi, K.; Asai, M., Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd complex with 2,2'-bipyridyl ligands. *Applied Catalysis a-General* **2000**, 201, (1), 101-105.
111. Ishii, H.; Goyal, M.; Ueda, M.; Takeuchi, K.; Asai, M., Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd complex with diimine ligands. *Catalysis Letters* **2000**, 65, (1-3), 57-60.
112. Okuyama, K.; Sugiyama, J.; Nagahata, R.; Asai, M.; Ueda, M.; Takeuchi, K., Oxidative carbonylation of phenol to diphenyl carbonate catalyzed by Pd-carbene complexes. *Journal of Molecular Catalysis a-Chemical* **2003**, 203, (1-2), 21-27.
113. Wang, S. J.; Du, L. C.; Zhao, X. S.; Meng, Y. Z.; Tjong, S. C., Synthesis and characterization of alternating copolymer from carbon dioxide and propylene oxide. *Journal of Applied Polymer Science* **2002**, 85, (11), 2327-2334.
114. Thorat, S. D.; Phillips, P. J.; Semenov, V.; Gakh, A., Physical properties of aliphatic polycarbonates made from CO₂ and epoxides. *Journal of Applied Polymer Science* **2003**, 89, (5), 1163-1176.
115. Li, X. H.; Meng, Y. Z.; Chen, G. Q.; Li, R. K. Y., Thermal properties and rheological behavior of biodegradable aliphatic polycarbonate derived from carbon dioxide and propylene oxide. *Journal of Applied Polymer Science* **2004**, 94, (2), 711-716.
116. Lee, S.-J.; Kim, M.-S.; Chung, J. G., Preparation of porous polycarbonate membranes using supercritical CO₂ with enhanced solubility. *Journal of Industrial and Engineering Chemistry (Seoul, Republic of Korea)* **2004**, 10, (6), 877-882.
117. Rakhimov, T. V.; Said-Galiev, E. E.; Vinokur, R. A.; Nikitin, L. N.; Khokhlov, A. R.; Il'in, V. V.; Nysenko, Z. N.; Sakharov, A. M.; Schaumburg, K., Copolymerization of propylene oxide and carbon dioxide under supercritical conditions. *Vysokomolekulyarnye Soedineniya, Seriya A i Seriya B* **2004**, 46, (3), 521-526.

118. Khokhlov, A. R.; Rakhimov, T. V.; Said-Galiev, E. E.; Il'in, V. V.; Nysenko, Z. N.; Sakharov, A. M., Peculiarities of propylene oxide copolymerization with supercritical carbon dioxide. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **2004**, 45, (1), 514.
119. Nagaya, S.; Komura, K.; Watanabe, S.; Morita, H.; Hirai, S.; Nakamoto, T.; Tanaka, A. Preparation of polycarbonates by polymerization in supercritical or subcritical water. 2004-79058
2005263991, 20040318., 2005.
120. Malito, J., *Phosgene and related carbonyl halides* by T. A. Ryan, C. Ryan, E. A. Seddon and K. Seddon. 1997; p 524.
121. Romano, U.; Tesei, R.; Mauri, M. M.; Rebor, P., Synthesis of dimethyl carbonate from methanol, carbon monoxide, and oxygen catalyzed by copper compounds. *Industrial & Engineering Chemistry Product Research and Development* **1980**, 19, (3), 396-403.
122. Drake, I. J.; Furdala, K. L.; Bell, A. T.; Tilley, T. D., Dimethyl carbonate production via the oxidative carbonylation of methanol over Cu/SiO₂ catalysts prepared via molecular precursor grafting and chemical vapor deposition approaches. *Journal of Catalysis* **2005**, 230, (1), 14-27.
123. Uchiumi, S.; Ataka, K.; Matsuzaki, T., Oxidative reactions by a palladium-alkyl nitrite system. *Journal of Organometallic Chemistry* **1999**, 576, (1-2), 279-289.
124. Knifton, J. F.; Duranleau, R. G., Ethylene glycol-dimethyl carbonate cogeneration. *Journal of Molecular Catalysis* **1991**, 67, (3), 389-99.
125. Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M., Synthesis of dimethyl carbonate and glycols from carbon dioxide, epoxides, and methanol using heterogeneous basic metal oxide catalysts with high activity and selectivity. *Applied Catalysis a-General* **2001**, 219, (1-2), 259-266.
126. Aresta, M.; Caramuscio, P.; De Stefano, L.; Pastore, T., Solid state dehalogenation of PCBs in contaminated soil using NaBH₄. *Waste Management (Amsterdam, Netherlands)* **2003**, 23, (4), 315-319.
127. Suci, E. N.; Kuhlmann, B.; Knudsen, G. A.; Michaelson, R. C., Investigation of dialkyltin compounds as catalysts for the synthesis of dialkyl carbonates from alkyl carbamates. *Journal of Organometallic Chemistry* **1998**, 556, (1-2), 41-54.
128. Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M., Transesterification of urea and ethylene glycol to ethylene carbonate as an important step for urea based dimethyl carbonate synthesis. *Green Chemistry* **2003**, 5, (4), 429-432.
129. Peppel, W. J., Preparation and properties of the alkylene carbonates. *Journal of Industrial and Engineering Chemistry (Washington, D. C.)* **1958**, 50, 767-70.
130. Kizlink, J., Synthesis of Dimethyl Carbonate from Carbon-Dioxide and Methanol in the Presence of Organotin Compounds. *Collection of Czechoslovak Chemical Communications* **1993**, 58, (6), 1399-1402.
131. Kizlink, J.; Pastucha, I., Preparation of Dimethyl Carbonate from Methanol and Carbon-Dioxide in the Presence of Sn(IV) and Ti(IV) Alkoxides and Metal Acetates. *Collection of Czechoslovak Chemical Communications* **1995**, 60, (4), 687-692.
132. Tomishige, K.; Sakai, T.; Ikeda, Y.; Fujimoto, K., A novel method of direct synthesis of dimethyl carbonate from methanol and carbon dioxide catalyzed by zirconia. *Catalysis Letters* **1999**, 58, (4), 225-229.

133. Tomishige, K.; Furusawa, Y.; Ikeda, Y.; Asadullah, M.; Fujimoto, K., CeO₂-ZrO₂ solid solution catalyst for selective synthesis of dimethyl carbonate from methanol and carbon dioxide. *Catalysis Letters* **2001**, 76, (1-2), 71-74.
134. Zhao, T. S.; Han, Y. Z.; Sun, Y. H., Novel reaction route for dimethyl carbonate synthesis from CO₂ and methanol. *Fuel Processing Technology* **2000**, 62, (2-3), 187-194.
135. Kong, L. L.; Zhong, S. H.; Liu, Y., Photocatalytic reaction for synthesis of dimethyl carbonate from CO₂ and CH₃OH over Cu/NiO-MoO₃/SiO₂ catalyst. *Chinese Journal of Catalysis* **2005**, 26, (10), 917-922.
136. Cai, Q. H.; Jin, C.; Lu, B.; Tangbo, H. J.; Shan, Y. K., Synthesis of dimethyl carbonate from methanol and carbon dioxide using potassium methoxide as catalyst under mild conditions. *Catalysis Letters* **2005**, 103, (3-4), 225-228.
137. Rivetti, F., The role of dimethyl carbonate in the replacement of hazardous chemicals. *Comptes Rendus de l'Academie des Sciences, Serie IIc: Chimie* **2000**, 3, (6), 497-503.
138. Tundo, P., New developments in dimethyl carbonate chemistry. *Pure and Applied Chemistry* **2001**, 73, (7), 1117-1124.
139. Ciapponi, R., Production of Di Methyl Carbonate (DMC) from Carbon Monoxide and Methanol instead of the old method based on phosgene, http://www.emcentre.com/unepweb/tec_case/chemical_24/newtech/n4.htm Roberto. Accessed April 13 2006.
140. Paulik, F. E.; Roth, J. F., Catalysts for the low-pressure carbonylation of methanol to acetic acid. *Chemical Communications (London)* **1968**, (24), 1578.
141. Farlow, M. W.; Adkins, H., Hydrogenation of carbon dioxide and a correction of the reported synthesis of urethans. *Journal of the American Chemical Society* **1935**, 57, 2222-3.
142. Kirovskaya, I. A.; Pimenova, L. N.; Votyakova, I. A.; Sharangovich, N. N., Reaction of hydrogen with carbon dioxide on the surface of diamondlike semiconductors. *Zhurnal Fizicheskoi Khimii* **1978**, 52, (9), 2356-60.
143. Anderson, J. J.; Drury, D. J.; Hamlin, J. E.; Kent, A. G., Formic acid. *BP Chemicals Ltd., UK, PCT Int. Appl., WO 8602066, CAN 105:210757* **1984**, 15.
144. Jessop, P. G.; Leitner, W.; Editors, *Chemical Synthesis Using Supercritical Fluids*. 1999; p 480 pp.
145. Jessop, P. G.; Ikariya, T.; Noyori, R., Homogeneous Hydrogenation of Carbon-Dioxide. *Chemical Reviews* **1995**, 95, (2), 259-272.
146. Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R., Homogeneous catalysis in supercritical fluids: Hydrogenation of supercritical carbon dioxide to formic acid, alkyl formates, and formamides. *Journal of the American Chemical Society* **1996**, 118, (2), 344-355.
147. Jessop, P. G.; Joo, F.; Tai, C. C., Recent advances in the homogeneous hydrogenation of carbon dioxide. *Coordination Chemistry Reviews* **2004**, 248, (21-24), 2425-2442.
148. Aresta, M.; Quaranta, E.; Tommasi, I., The Role of Metal Centers in Reduction and Carboxylation Reactions Utilizing Carbon-Dioxide. *New Journal of Chemistry* **1994**, 18, (1), 133-142.
149. Tommasi, I.; Aresta, M.; Giannoccaro, P.; Quaranta, E.; Fragale, C., Bioinorganic chemistry of nickel and carbon dioxide: an Ni complex behaving as a model system for

- carbon monoxide dehydrogenase enzyme. *Inorganica Chimica Acta* **1998**, 272, (1-2), 38-42.
150. Taniguchi, Y.; Hayashida, T.; Kitamura, T.; Fujiwara, Y., Vanadium-catalyzed acetic acid synthesis from methane and carbon dioxide. *Advances in Chemical Conversions for Mitigating Carbon Dioxide* **1998**, 114, 439-442.
151. Gressin, J. C.; Michelet, D.; Nadjo, L.; Saveant, J. M., Electrochemical reduction of carbon dioxide in weakly protic medium. *Nouveau Journal de Chimie* **1979**, 3, (8-9), 545-54.
152. Hoberg, H.; Schaefer, D.; Oster, B. W., Diene carboxylic acids from 1,3-dienes and carbon dioxide by carbon-carbon bonding to nickel(0). *Journal of Organometallic Chemistry* **1984**, 266, (3), 313-20.
153. Derien, S.; Dunach, E.; Perichon, J., From Stoichiometry to Catalysis - Electroreductive Coupling of Alkynes and Carbon-Dioxide with Nickel Bipyridine Complexes - Magnesium-Ions as the Key for Catalysis. *Journal of the American Chemical Society* **1991**, 113, (22), 8447-8454.
154. Derien, S.; Clinet, J. C.; Dunach, E.; Perichon, J., Electrochemical Incorporation of Carbon-Dioxide into Alkenes by Nickel-Complexes. *Tetrahedron* **1992**, 48, (25), 5235-5248.
155. Derien, S.; Clinet, J. C.; Dunach, E.; Perichon, J., New C-C Bond Formation through the Nickel-Catalyzed Electrochemical Coupling of 1,3-Enynes and Carbon-Dioxide. *Journal of Organometallic Chemistry* **1992**, 424, (2), 213-224.
156. Jitaru, M.; Lowy, D. A.; Toma, M.; Toma, B. C.; Oniciu, L., Electrochemical reduction of carbon dioxide on flat metallic cathodes. *Journal of Applied Electrochemistry* **1997**, 27, (8), 875-889.
157. Royer, M. E., Reduction de l'acide carbonique en acid formique". In *Compt. Rend.*, 1870; pp 731-32.
158. Augustynski, J., Sartoretti, C.J., Kedzierzawski, P., , Carbon Dioxide Recovery and Utilization. **2003**, 407.
159. Shkhashiri, B. Carbon dioxide phase diagram. http://scifun.chem.wisc.edu/chemweek/CO2/CO2_phase_diagram.gif (2006),
160. Hara, K.; Kudo, A.; Sakata, T., Electrochemical reduction of carbon dioxide under high pressure on various electrodes in an aqueous electrolyte. *Journal of Electroanalytical Chemistry* **1995**, 391, (1-2), 141-147.
161. Matthews, M. A., Green Electrochemistry. Examples and Challenges. *Pure Appl. Chem.* **2001**, 73, (No. 8), 1305-1308.
162. Fischer, J., Lehmann, T., Heitz, E., The production of oxalic acid from carbon dioxide and water. *J. Appl. Electrochem.* **1981**, 11, 743-50.
163. Mizuno, T.; Naitoh, A.; Ohta, K., Electrochemical reduction of CO₂ in methanol at -30[deg]C. *Journal of Electroanalytical Chemistry* **1995**, 391, (1-2), 199-201.
164. Saeki, T., Hashimoto, K., Fujishima, A., Kimura, N., Omata, K., Electrochemical Reduction of CO₂ with High Current Density in a CO₂ - Methanol Medium. *J. Phys. Chem.* **1995**, 99, 8440-46.
165. Casadei, M. A.; Cesa, S.; Moracci, F. M.; Inesi, A.; Feroci, M., Activation of Carbon Dioxide by Electrogenenerated Superoxide Ion: A New Carboxylating Reagent. *J. Org. Chem.* **1996**, 61, (1), 380-383.

166. Casadei, M. A.; Moracci, F. M.; Zappia, G.; Inesi, A.; Rossi, L., Electrogenerated Superoxide-Activated Carbon Dioxide. A New Mild and Safe Approach to Organic Carbamates. *J. Org. Chem.* **1997**, 62, (20), 6754-6759.
167. Prentice, G., *Electrochemical Engineering Principles*. Prentice Hall, Englewood Cliffs, NJ: 1991; p 296.
168. Kaneco, S.; Hiei, N.-h.; Xing, Y.; Katsumata, H.; Ohnishi, H.; Suzuki, T.; Ohta, K., High-efficiency electrochemical CO₂-to-methane reduction method using aqueous KHCO₃ media at less than 273 K. *Journal of Solid State Electrochemistry* **2003**, 7, (3), 152-156.
169. Salimon, J., Kalaji, M., Electrochemical Reduction of CO₂ at Polycrystalline Copper in Aqueous Phosphate Buffered Solution: pH and Temperature Dependence. *malaysian Journal of Chemistry* **2003**, 5, (1), 023-029.
170. Qu, J.; Zhang, X.; Wang, Y.; Xie, C., Electrochemical reduction of CO₂ on RuO₂/TiO₂ nanotubes composite modified Pt electrode. *Electrochimica Acta* **2005**, 50, (16-17), 3576-3580.
171. Nasibulin, A. G.; Brown, D. P.; Queipo, P.; Gonzalez, D.; Jiang, H.; Kauppinen, E. I., An essential role of CO₂ and H₂O during single-walled CNT synthesis from carbon monoxide. *Chemical Physics Letters* **2006**, 417, (1-3), 179-184.
172. Technologies, P. F. C. Chlorine Production with Reduced Electric Power. <http://www.etek-inc.com>
173. Tuck, A., Manual for the Installation and Operation of a 5kW Solid Oxide Fuel Cell. In 2005; p 42.
174. Sanchez-Sanchez, C. M., Montiel, V., Tryk, D.A., Electrochemical approaches to alleviation of the problem of carbon dioxide accumulation. *Pure Appl. Chem.* **2001**, 73, (12), 1917-1927.
175. Sonoyama, N.; Kirii, M.; Sakata, T., Electrochemical reduction of CO₂ at metal-porphyrin supported gas diffusion electrodes under high pressure CO₂. *Electrochemistry Communications* **1999**, 1, (6), 213-216.
176. Alternative Fuels Incentive Act. In Session of 2003 ed.; 2004.
177. Charles, T. PUC Sets Standards for Demand Side Management, Energy Efficiency, Meets Major Commitment in Implementing Alternative Energy Portfolio Standards Act. www.puc.state.pa.us.
178. Commission, P. P. U., Portfolio Standards Act of 2004: Standards for the Participation of Demand Side Management resources. In 2005; Vol. 73 P.S. §§1648.1 – 1648.8, p 35.
179. Bradford, M. C. J., Vannice, M. A., CO₂ reforming of CH₄. *Catalysis Review, - Science, Engineering* **1999**, 41, (1), 1-41.
180. Song, C., Gaffney, A. M., Fujimoto, K., CO₂ Conversion and Utilization. *American Chemical Society Symposium Series 809* **2000**.
181. Chan, S. H., Wang, H. M., Thermodynamic Analysis of Natural Gas fuel processing for fuel cell applications. *International Journal of Hydrogen Energy* **2000**, 25, 441.
182. Chunshan Song, A. M. G., Kaoru Fujimoto, CO₂ Conversion and Utilization. *American Chemical Society Symposium Series 809* **2000**.
183. Choudhury V R, M. A. S., Uphade B S, Babcock R E, CO₂ Reforming and Simultaneous CO₂ and steam reforming of methane over Co_xNi_{1-x}O supported on

macroporous silica alumina precoated with MgO. *American Chemical Society Symposium Series 809* **2002**.

184. shamsi, A., Methane dry reforming over Carbide, Nickel based and Noble metal catalyst. *American Chemical Society Symposium Series 809* **2002**.

185. Kiyoharu Nakagawa, S. S., Noriyasu Akamatsu, Na-oka Matsui, Na-oki Ikenage, Toshimitsu Suzuki, CO₂ reforming of Methane over lanthanum Oxide catalyst. *American Chemical Society Symposium Series 809* **2002**.

186. Bradford M C J, V. M. A., CO₂ reforming of CH₄. *Catalysis Review,-Science, Engineering* **1999**, 41, (1), 1.

187. Chunshan Song, W. P., Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H₂/CO ratio. *Catalysis Today* **2004**, 98, 463-484.

188. Srinivas T Srimat, C. S., Effect of Pressure on CO₂ reforming of CH₄ over Rh/Na-Y and Rh/Al₂O₃ catalyst. *American Chemical Society Symposium Series 809* **2002**.

189. Omata K, I. G., Ushizuki K, Yamada M, Supported Copper and Manganese Catalyst for methanol synthesis from CO₂ containing syngas. *American Chemical Society Symposium Series 809* **2002**.

190. Ono, Y., Dimethyl Carbonate for environmentally benign reactions. *Pure & Applied Chemistry* **1996**, 68, (2), 367-375.

191. Gerpen, j. V., Biodiesel Processing & Production. *Fuel Processing Technology* **2005**, 86, (1), 1097.

192. Song, C., Pan, W., Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H₂/CO ratio. *Catalysis Today* **2004**, 98, 463-484.

193. Larminie, J., Dicks, A., Fuel Cell systems explained. **2003**, 223.

194. Halmann, M., Steinfeld, A., Thermoneutral Tri-reforming of flue gases from coal and gas fired power stations. *Catalysis Today* **2006**, xxx, xxx.

195. Stratanova, M., Siemens Westinghouse Power Corporation, Sacle Up of planar SOFC stack system for MW level combined cycle system. **2003**.

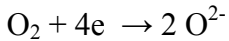
7. Appendix

The amount of methane needed to produce H₂/CO=1.5 is calculated. The amount of air needed for electrochemical oxidation of Carbon monoxide and hydrogen is calculated. The amount of flue gas needed for tri-reforming is calculated taking into account the kinetic information for Ni/MgOCeZrO.

Reaction in the anode



Reaction at the cathode



P_c = Power of SOFC = 2.61 MWe

V_c = Average cell voltage = 0.7 v

Air usage for electrochemical oxidation of CO = $7.15 \times 10^{-7} \times P_c / V_c$

Air usage for electrochemical oxidation of H₂ = $3.57 \times 10^{-7} \times P_c / V_c$

Total air needed for electrochemical oxidation = 28.97 gmoles / s

For synthesis gas with CO/H₂ = 1 : 1.5, oxygen needed for the electrochemical oxidation of Co and H₂ are 1 : 1.5 respectively

O₂ needed for electrochemical oxidation of CO = 11.588 gmoles /s

O₂ needed for electrochemical oxidation of H₂ = 17.382 gmoles /s

CO needed = 23.176 gmoles / s and H₂ needed = 34.764 gmoles / s

As the fuel utilization efficiency is 0.9,

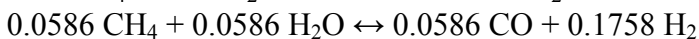
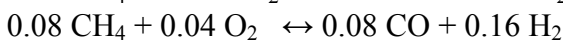
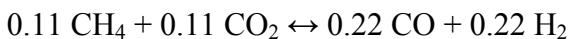
CO needed = 25.75 gmoles/s and H₂ = 38.63 gmoles/s

Amount of CO produced from the reactions DMR:SMR:POX = 15.75 :4.29:5.71

Amount of CO produced from the reactions DMR:SMR:POX = 15.18 :12.42:1.04

CH₄ Conversion = 98% and CO₂ Conversion = 74 %

The reactions involved are



Methane fed = 0.29 kg/s

Flue gas fed = 2.7 kg/s

GT Inlet:

CO = 2.575 gmoles/s, H₂ = 3.863 gmoles/s , N₂ = 61.92 gmoles/s, CH₄ = 0.365 gmoles/s

CO₂ = (0.9x 25.75) + (0.26 x 0.11 x 96.75) = 25.94 gmoles/s

H₂O = (0.9 x 38.63) + (0.22 x 96.75 x .813) = 52.07 gmoles/s

Power output from the gas turbine = **1205 kW**

Composition of the gas coming out of the gas turbine:

CO₂ = 17.8 % H₂O = 34.9% N₂ = 47.3%

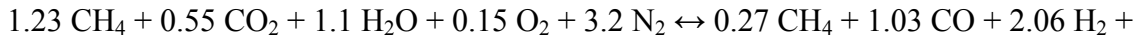
A 2.6 MWe SOFC with 26 mm diameter and 5 mm thick which has power density = 440 mW/cm² with average cell voltage = 0.7 V needs 14915 individual cells arranged in 12 arrays. (1 stack = 60 cells. 1 bundle = 3 stacks. 1 Array = 7 bundles)¹⁹⁵

Tri-reforming with flue gas from Natural Gas fired Power Plant¹⁹⁴H₂/CO ratio = 2 T = 710 °C P= 1 atmosphere Catalyst: Ni / MgOCeZrOCO₂ Conversion = 40 % O₂ Conversion = 100 %CH₄ Conversion = 78 % H₂O Conversion = 18%

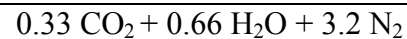
Feed:

1.23 moles of methane

5 moles of flue gas

Table 4.3.7 : Data for Conventional Process¹⁹⁴

Product	World capacity 10 ⁶ tons/yr	Fuel Spent GJ/mol	CO ₂ emitted per ton
Methanol	39	44.5	0.837
Hydrogen	440	602	9.21
Ammonia	155	39	2.2
Urea	143		0.517

Methanol ProductionProduction Capacity

CO₂ emission from a 49% efficient 400MWe natural gas power plant = 1.47 x 10⁶ tons/yr¹⁹⁴

CO₂ from the tri-reformer into the atmosphere = 60% of 1.47 x 10⁶ = 8.82 x 10⁶ tons/yr.

Mole ratio of CO/(CO₂ in the original flue gas) = 1.87

Overall yield in the conversion of CO to CH₃OH = 90 %

Annual methanol production if the CO₂ in the original flue gas is converted to methanol = 1.47 x 10⁶ x 1.87 x 0.9 x 32 / 44 = **1.8 x 10⁶ tons of methanol**

This contributes to 4.56 % of the total world capacity

Carbon dioxide avoidance:

Amount of CO₂ emitted by a conventional SMR plant for the production of methanol = 0.837 tons CO₂/ton methanol

Total CO₂ emission = [untreated flue gas from power plant] + [CO₂ from SMR]
= (1.5059 x 10⁶) + (1.47 x 10⁶) = 2.975 x 10⁶ tons/yr

CO₂ avoidance = (1.509 x 10⁶) x 100 / (2.975 x 10⁶) = **50%**

Fuels saving in methanol production:

1.23 moles of CH₄ yield 1.03 [CO + 2 H₂] which in turn yield 1.03 moles of methanol.

Heat of combustion for methane = 0.891 GJ/kmol Methane based on HHV¹⁹⁴

1.8 x 10⁹ kg of methanol consumes 1.07 x 10⁹ kg of methane which is equivalent to consuming 59.85 x 10⁶ GJ of energy.

Total energy consumed by conventional methanol synthesis = 80 x 10⁶ GJ
to produce 1.8 x 10⁹ kg of methanol

% Energy saved = $(1 - (59.85 \times 10^6)/(80.1 \times 10^6)) \times 100 = 25.3 \%$.

Economics:

For the annual production of 1.8 x 10⁹ kg of methanol the amount = 56.69 x 10⁶ MBTU of methane spent in terms of energy equivalent by tri-reforming

Price of natural gas = \$ 6.73 / MBTU¹⁹⁴

1 MBTU = 1.0556 GJ

Cost based on conventional process to Produce 1.8 x 10⁹ kg of methanol = $(80.1 \times 10^6 \times 6.73 / 1.0556) = \$ 510 \times 10^6$

Cost per ton by conventional process = \$ 510

Cost based on tri-reforming = $56.69 \times 10^6 \times 6.73 = \$ 381.52 \times 10^6$

Cost per ton by modern tri-reforming process = \$ 381.52

Hydrogen Production:

Production Capacity;

CO₂ emission from a 49% efficient 400MWe natural gas power plant = 1.47 x 10⁶ tons/yr¹⁹⁴

CO₂ from the tri-reformer into the atmosphere = 60% of 1.47 x 10⁶ = 8.82 x 10⁶ tons/yr.

Mole ratio of (2H₂ + CO)/(CO₂ in the original flue gas) = 5.62

Overall yield in the conversion of CO to H₂ in water gas shift reaction = 90 %

Mole ratio of (2H₂)/(CO₂ in the original flue gas) = 5.43

Annual hydrogen production if the CO₂ in the original flue gas is converted to hydrogen = $1.47 \times 10^6 \times 5.43 \times 0.9 \times 2 / 44 = 0.363 \times 10^6$ tons of methanol

This contributes to 0.0825 % of the total world capacity

Carbon dioxide avoidance:

Amount of CO₂ emitted by a conventional SMR plant = 9.21 tons CO₂/ton hydrogen for the production of hydrogen

Total CO₂ emission = [Untreated flue gas from power plant] + [CO₂ from SMR + WGS]
 $= (3.34 \times 10^6) + (1.47 \times 10^6) = 4.81 \times 10^6$ tons/yr

Mole ratio of (CO + CO₂)/(CO₂ in the original flue gas) = $(1.03 + 0.33) / 0.55 = 2.47$

Total CO₂ from tri-reforming and WGS = $2.47 \times 1.47 \times 10^6 = 3.63 \times 10^6$ tons/yr

CO₂ avoidance = $(1 - (3.63 \times 10^6) / (4.81 \times 10^6)) \times 100 = \mathbf{24.5\%}$

Fuels Saving in Hydrogen production:

1.23 moles of CH₄ yield 1.03 [CO + 2 H₂] which in turn yield 3.09 moles of hydrogen.

Heat of combustion for methane = 0.891 GJ/kmol Methane based on HHV¹⁹⁴

0.363 x 10⁹ kg of hydrogen consumes 1.07 x 10⁹ kg of methane which is equivalent to consuming 64.37 x 10⁶ GJ of energy.

Total energy consumed by conventional hydrogen synthesis = 218.5 x 10⁶ GJ to produce 0.363 x 10⁹ kg of hydrogen

% Energy saved = $(1 - (64.37 \times 10^6) / (218.5 \times 10^6)) \times 100 = \mathbf{72.5\%}$.

Economics:

For the annual production of 0.363 x 10⁹ kg of hydrogen amount of methane spent in terms of energy equivalent by tri-reforming = 60.97 x 10⁶ MBTU

Price of natural gas = \$ 6.73 / MBTU¹⁹⁴

1 MBTU = 1.0556 GJ

Cost based on conventional process to produce .1 kg of gaseous hydrogen = \$ 2.4/kg gaseous hydrogen

Cost per kg by conventional process = \$ 2.4

Cost based on tri-reforming = $60.97 \times 10^6 \times 6.73 / (0.363 \times 10^6) = \$ 1.1/\text{kg gaseous H}_2$

Cost per kg by modern tri-reforming process = \$ 1.1

Ammonia and urea Production:

Production capacity:

CO₂ emission from a 49% efficient 400MWe natural gas power plant = 1.47×10^6 tons/yr¹⁹⁴

CO₂ from the tri-reformer into the atmosphere = 60% of 1.47×10^6 = 8.82×10^6 tons/yr.

$N_2 + 3 H_2 \leftrightarrow 2 NH_3 \rightarrow 90\%$ yield

$2 NH_3 + CO_2 \leftrightarrow NH_4CO_2NH_4 \rightarrow NH_2CONH_2 + H_2O \rightarrow 100\%$ yield

Annual ammonia production from Hydrogen = $(0.363 \times 10^{12} / 2) \times 0.9 \times (2/3) \times 17$
= **1.85×10^6 tons of Ammonia**

This contributes to 1.19 % of the total world capacity

Annual urea Production rate = $(60 / 34) \times 1.85 \times 10^6 = 3.27 \times 10^6$ tons urea

This contributes to 2.72% of the total world capacity.

Carbon dioxide avoidance:

Amount of CO₂ emitted by a conventional SMR & WGS for the production of ammonia = 2.2 tons CO₂/ton ammonia

Total CO₂ emission = [untreated flue gas from power plant] + [CO₂ from SMR + WGS]
= $(4.07 \times 10^6) + (1.47 \times 10^6) = 5.54 \times 10^6$ tons/yr

Total CO₂ from tri-reforming and WGS = $2.47 \times 1.47 \times 10^6 = 3.63 \times 10^6$ tons/yr

CO₂ avoidance for NH₃ = $(1 - (3.63 \times 10^6) / (5.54 \times 10^6)) \times 100 = 33.6\%$

Amount of CO₂ emitted by a conventional SMR & WGS for the production of ammonia = 1.25 tons CO₂/ton urea

CO₂ consumed per ton urea = $-(44 / 60) \times 10^6 = -0.733$ tons CO₂/ton urea

Net amount of CO₂ emitted by a conventional SMR & WGS for the production of ammonia = 0.517 tons CO₂/ton urea

Total CO₂ emission = [untreated flue gas from power plant] + [CO₂ from urea process]
= $(1.69 \times 10^6) + (1.47 \times 10^6) = 3.161 \times 10^6$ tons/yr

Total CO₂ from modern process = CO₂ from tri-reforming and WGS - CO₂ consumed
= $(3.63 - 1.691) \times 10^6 = 1.939 \times 10^6$ tons/yr

CO₂ avoidance for Urea = $(1 - (1.939 \times 10^6) / (3.161 \times 10^6)) \times 100 = 38.6\%$

Fuels saving in ammonia & urea production:

1.23 moles of CH₄ yield 1.03 [CO + 2 H₂] which in turn yield 3.09 moles of hydrogen.

Heat of combustion for methane = 0.891 GJ/kmol Methane

0.363 x 10⁹ kg of hydrogen consumes 1.07 x 10⁹ kg of methane which is equivalent to consuming 64.37 x 10⁶ GJ of energy.

Total energy consumed by conventional synthesis = 39 GJ
to produce 1 ton of ammonia

$$\% \text{ Energy saved} = (1 - (64.37 \times 10^6) / (72.15 \times 10^6)) \times 100 = \mathbf{11 \%}.$$

Economics:

For the annual production of 1.85 x 10⁹ kg of ammonia amount = 60.97 x 10⁶ MBTU
of methane spent in terms of energy equivalent by tri-reforming

Price of natural gas = \$ 6.73/MBTU

1 MBTU = 1.0556 GJ

Cost per ton by conventional process = \$ 290

$$\begin{aligned} \text{Cost based on tri-reforming} &= (\text{fuel cost} + \text{conversion cost}) \text{ per ton ammonia} \\ &= (60.97 \times 10^6 \times 6.73 / (0.363 \times 10^6)) + 30^{194} \\ &= \$ 251.9 \end{aligned}$$

Cost per ton by modern tri-reforming process = \$ 251.9

Tri-reforming with flue gas from coal fired power plant:

H₂ / CO ratio = 2 T = 710 °C P = 1 atmosphere Catalyst : Ni / MgOCeZrO

CO₂ Conversion = 40 % O₂ Conversion = 100 %

CH₄ Conversion = 78 % H₂O Conversion = 18%

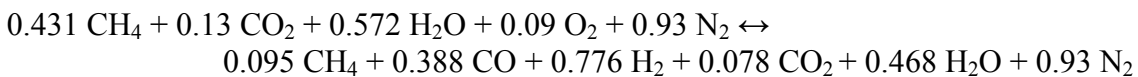
Feed:

0.431 moles of methane

1 moles of flue gas

0.482 moles of steam

0.24 moles of air

Methanol Production:

Production Capacity:

CO₂ emission from a 45% efficient 500MWe coal fired power plant = 3.29×10^6 tons/yr¹⁹⁴

CO₂ from the tri-reformer into the atmosphere = 60% of 1.47×10^6 = 1.974×10^6 tons/yr

Mole ratio of CO/(CO₂ in the original flue gas) = 0.9
Overall yield in the conversion of CO to CH₃OH = 90 %

Annual methanol production if the CO₂ in the original flue gas is converted to methanol = $3.29 \times 10^6 \times 0.9 \times 0.9 \times 32 / 44$
= **1.938×10^6 tons of methanol**

This contributes to 4.95 % of the total world capacity

Carbon dioxide avoidance:

Amount of CO₂ emitted by a conventional SMR plant for the production of methanol = 0.837 tons CO₂/ton methanol

Total CO₂ emission = [untreated flue gas from power plant] + [CO₂ from SMR]
= $(1.622 \times 10^6) + (3.29 \times 10^6) = 4.912 \times 10^6$ tons/yr

CO₂ avoidance = $(1.974 \times 10^6) \times 100 / (4.912 \times 10^6) = \mathbf{59.8\%}$

Fuels saving in methanol production:

0.431 moles of CH₄ yield 0.388 [CO + 2 H₂] which will yield 0.388 moles of methanol.

Heat of combustion for methane = 0.891 GJ/kmol Methane based on HHV¹⁹⁴

1.9388×10^9 kg of methanol consumes 1.076×10^9 kg of methane which is equivalent to consuming 59.94×10^6 GJ of energy.

Total energy consumed by conventional methanol synthesis to produce 1.938×10^9 kg of methanol = 86.2×10^6 GJ

% Energy saved = $(1 - (59.94 \times 10^6)/(86.24 \times 10^6)) \times 100 = \mathbf{30.5\%}$.

Economics:

For the annual production of 1.938×10^9 kg of methanol, amount of methane spent in terms of energy equivalent by tri-reforming = 81.75×10^6 MBTU

Price of natural gas = \$ 6.73/MBTU

1 MBTU = 1.0556 GJ

Cost per ton by conventional process = \$ 510

$$\begin{aligned} \text{Cost based on tri-reforming} &= (59.94 \times 10^6 \times 6.73) / (1.055 \times 1.938 \times 10^6) \\ &= \$ 227.3 \end{aligned}$$

Cost per ton by Modern tri-reforming process = \$ 227.3

Hydrogen production:

Production Capacity;

$$\text{CO}_2 \text{ emission from a 45\% efficient 500MWe coal fired power plant} = 3.29 \times 10^6 \text{ tons/yr}^{194}$$

$$\text{CO}_2 \text{ from the tri-reformer into the atmosphere} = 60\% \text{ of } 1.47 \times 10^6 = 1.978 \times 10^6 \text{ tons/yr.}$$

$$\text{Mole ratio of } (2\text{H}_2 + \text{CO}) / (\text{CO}_2 \text{ in the original flue gas}) = 8.9$$

$$\text{Overall yield in the conversion of CO to H}_2 \text{ in water gas shift reaction} = 90 \%$$

$$\text{Mole ratio of } (2\text{H}_2) / (\text{CO}_2 \text{ in the original flue gas}) = 8.7$$

$$\begin{aligned} \text{Annual hydrogen production if the CO}_2 \text{ in the original flue gas is converted to hydrogen} &= 3.29 \times 10^6 \times 8.7 \times 0.9 \times 2 / 44 \\ &= \mathbf{1.3 \times 10^6 \text{ tons of methanol}} \end{aligned}$$

This contributes to 0.29 % of the total world capacity

Carbon dioxide avoidance:

$$\text{Amount of CO}_2 \text{ emitted by a conventional SMR plant for the production of hydrogen} = 9.21 \text{ tons CO}_2 / \text{ton hydrogen}$$

$$\begin{aligned} \text{Total CO}_2 \text{ emission} &= [\text{Untreated flue gas from power plant}] + [\text{CO}_2 \text{ from SMR + WGS}] \\ &= (3.29 \times 10^6) + (11.97 \times 10^6) = 15.26 \times 10^6 \text{ tons/yr} \end{aligned}$$

$$\begin{aligned} \text{Mole ratio of } (\text{CO} + \text{CO}_2) / (\text{CO}_2 \text{ in the original flue gas}) &= (0.388 + 0.078) / 0.13 \\ &= 3.58 \end{aligned}$$

$$\text{Total CO}_2 \text{ from tri-reforming and WGS} = 3.58 \times 3.29 \times 10^6 = 11.78 \times 10^6 \text{ tons/yr}$$

$$\text{CO}_2 \text{ avoidance} = (1 - (11.78 \times 10^6) / (15.26 \times 10^6)) \times 100 = \mathbf{22.8\%}$$

Fuels saving in hydrogen production:

0.431 moles of CH₄ yield 0.388 moles [CO + 2 H₂]. which in turn yield 1.164 moles of hydrogen.

Heat of combustion for methane = 0.891 GJ/kmol Methane

1.3 x 10⁹ kg of hydrogen consumes 3.85 x 10⁹ kg of methane which is equivalent to consuming 214.5 x 10⁶ GJ of energy.

$$\text{Total energy consumed by conventional hydrogen synthesis} = 782.6 \times 10^6 \text{ GJ}$$

to produce 1.3×10^9 kg of hydrogen

$$\% \text{ Energy saved} = (1 - (214.5 \times 10^6)/(782.6 \times 10^6)) \times 100 = 72.6 \%$$

Economics:

For the annual production of 1.3×10^9 kg of hydrogen amount = 203.3×10^6 MBTU of methane spent in terms of energy equivalent by tri-reforming

Price of natural gas = \$ 6.73 / MBTU

1 MBTU = 1.0556 GJ

Cost based on conventional process to produce .1 kg of gaseous hydrogen = \$ 2.4/kg gaseous hydrogen

Cost per kg by conventional process = \$ 2.4

Cost based on tri-reforming = $214.5 \times 10^6 \times 6.73 / (1.3 \times 10^6) = \$ 1/\text{kg gaseous H}_2$

Cost per kg by modern tri-reforming process = \$ 1.0

Ammonia and Urea Production:

Production capacity:

CO₂ emission from a 45% efficient 500MWe natural gas power plant = 3.29×10^6 tons/yr¹⁹⁴

CO₂ from the tri-Reformer into the atmosphere = 60% of 1.47×10^6 = 1.974×10^6 tons/yr.

$\text{N}_2 + 3 \text{H}_2 \leftrightarrow 2 \text{NH}_3 \rightarrow 90\% \text{ yield}$

$2 \text{NH}_3 + \text{CO}_2 \leftrightarrow \text{NH}_4\text{CO}_2\text{NH}_4 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow 100\% \text{ yield}$

Annual ammonia production from hydrogen = $(1.3 \times 10^{12}/2) \times 0.9 \times (2/3) \times 17$
= **6.63×10^6 tons of Ammonia**

This contributes to 4.28 % of the total world capacity

Annual urea production rate = $(2/3) \times (1/2) \times 0.9 \times (1.3 \times 10^6 / 2) \times 60 = 11.7 \times 10^6$ tons urea

This contributes to 9.75% of the total world capacity.

Carbon dioxide avoidance:

Amount of CO₂ emitted by a conventional SMR & WGS for the production of ammonia = 2.2 tons CO₂/ton ammonia

$$\begin{aligned} \text{Total CO}_2 \text{ emission} &= [\text{Untreated flue gas from power plant}] + [\text{CO}_2 \text{ from SMR} + \text{WGS}] \\ &= (14.586 \times 10^6) + (3.29 \times 10^6) = 17.876 \times 10^6 \text{ tons/yr} \end{aligned}$$

$$\text{Total CO}_2 \text{ from tri-reforming and WGS} = 11.78 \times 10^6 \text{ tons/yr}$$

$$\text{CO}_2 \text{ avoidance for NH}_3 = (1 - (11.78 \times 10^6) / (17.88 \times 10^6)) \times 100 = \mathbf{34.1\%}$$

$$\begin{aligned} \text{Amount of CO}_2 \text{ emitted by a conventional SMR} &= 1.25 \text{ tons CO}_2/\text{ton urea} \\ \text{\& WGS for the production of ammonia} & \end{aligned}$$

$$\text{CO}_2 \text{ consumed per ton urea} = - (44 / 60) \times 10^6 = -0.733 \text{ tons CO}_2/\text{ton urea}$$

$$\begin{aligned} \text{Net Amount of CO}_2 \text{ emitted by a conventional SMR} &= 0.517 \text{ tons CO}_2/\text{ton urea} \\ \text{\& WGS for the production of Ammonia} & \end{aligned}$$

$$\begin{aligned} \text{Total CO}_2 \text{ emission} &= [\text{Untreated flue gas from power plant}] + [\text{CO}_2 \text{ from urea process}] \\ &= (6.049 \times 10^6) + (3.29 \times 10^6) = 9.339 \times 10^6 \text{ tons/yr} \end{aligned}$$

$$\begin{aligned} \text{Total CO}_2 \text{ from modern process} &= \text{CO}_2 \text{ from tri-reforming and WGS} - \text{CO}_2 \text{ consumed} \\ &= (11.78 - 8.5761) \times 10^6 = 3.203 \times 10^6 \text{ tons/yr} \end{aligned}$$

$$\text{CO}_2 \text{ avoidance for urea} = (1 - (3.203 \times 10^6) / (9.339 \times 10^6)) \times 100 = \mathbf{65.6\%}$$

Fuels saving in ammonia & urea production:

1.23 moles of CH₄ yield 1.03 [CO + 2 H₂] which in turn yield 3.09 moles of hydrogen.

Heat of combustion for methane = 0.891 GJ/kmol Methane

0.363 x 10⁹ kg of hydrogen consumes 1.07 x 10⁹ kg of methane which is equivalent to consuming 64.37 x 10⁶ GJ of energy.

$$\begin{aligned} \text{Total energy consumed by conventional synthesis} &= 39 \text{ GJ} \\ \text{to produce 1 ton of ammonia} & \end{aligned}$$

$$\% \text{ Energy saved} = (1 - (214.5 \times 10^6) / (258.5 \times 10^6)) \times 100 = \mathbf{17\%}$$

Economics:

For the annual production of 6.63 x 10⁹ kg of ammonia amount = 203.3 x 10⁶ MBTU of methane spent in terms of energy equivalent by tri-reforming

Price of natural gas = \$ 6.73/MBTU

1 MBTU = 1.0556 GJ

Cost per ton by conventional process = \$ 290

$$\begin{aligned} \text{Cost based on tri-reforming} &= (\text{fuel cost} + \text{conversion cost}) \text{ per ton ammonia} \\ &= (203.3 \times 10^6 \times 6.73 / (6.63 \times 10^6)) + 30 \\ &= \$ 233 \end{aligned}$$

Table 4.3.9: Summary of advantages of tri-reforming.

Flue Gas Treatment	Product	% CO₂ Emission avoidance	% Fuel Saving	% World Capacity
Coal				
Tri - Reforming	Methanol	59.8	30.5	4.95
	Hydrogen	22.8	72.6	0.29
	Ammonia	34.7	17	4.28
	Urea	65.6		9.75
Natural Gas				
Tri-Reforming	Methanol	50	25.3	4.56
	Hydrogen	24.5	72.5	0.0825
	Ammonia	33.6	11	1.19
	Urea	38.6		2.72

Cost per ton by Modern Tri-reforming process = \$ 251.9

Table 4.3.9: Economics of Products obtained from tri-reforming.

Product	Cost based on Conventional method	Cost based on Modern Tri-Reforming Process
Methanol	\$ 510 per ton	\$ 381 .5 per ton
Hydrogen	\$ 2.4 per kg	\$ 1.1 per kg
Ammonia	\$ 290 per ton	\$ 236 per ton