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CO₂ Sources for Microalgae-Based Liquid Fuel Production

D. Feinberg M. Karpuk

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Solar Energy Research Institute A Division of Midwest Research Institute

1617 Cole Boulevard Golden, Colorado 80401-3393

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SUMMARY

The Solar Energy Research Institute's (SERI) Aquatic Species Program is developing microalgal species and culture technologies that result in microalgal cells with a high percentage of lipids. The lipids can be extracted and converted to a diesel fuel substitute. Optimal microalgae growth occurs in carbon dioxide (CO_2) saturated solutions. If these research efforts are successful, large quantities of low-cost CO_2 will be needed. The purpose of this study is to identify possible CO_2 sources for microalgaebased fuel production and to quantify the amounts available and possible costs. Because of the early stage of development of the fuel synthesis technology, and the current plentiful supplies of gaseous and liquid fossil fuels, we chose the year 2010 as the earliest date that CO_2 for fuel synthesis would be needed.

We analyzed four sources of CO₂:

<u>Natural Reservoirs</u>. Large natural reservoirs of CO_2 in the southwestern United States are currently being utilized for enhanced oil recovery (EOR). These reservoirs are expected to be depleted by the year 2010 and consequently unavailable for microalgae production. However, the CO_2 used for EOR will remain in the depleted oil fields, and could be recovered for microalgae production. Some natural gas fields contain significant quantities of CO_2 , which are not currently being produced because of high separation costs. If the economics of these fields improve, this CO_2 could become available.

<u>Fossil Fuel Combustion</u>. The United States has very large coal reserves, and coal is expected to remain a primary energy source in 2010 and beyond. Coal combustion in power, synthetic fuels, and chemical process plants will produce large quantities of CO_2 . Clean coal technologies under investigation by the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE) have the potential to produce large quantities of CO_2 at low cost. Concern about possible regulation of global warming caused by the release of CO_2 into the atmosphere may make CO_2 available from these sources at low or even negative costs.

<u>Air Separation</u>. It is conceivable that CO_2 could be recovered directly from the atmosphere, where it is the fourth-largest constituent. However, because the atmospheric CO_2 concentration is very low (330 ppm), significant technical breakthroughs are required to make the process viable.

<u>Anaerobic Digestion</u>. Anaerobic digestion of biomass and wastes is currently being investigated as a source of methane. Methane and CO_2 are coproduced in approximately equal molar volumes and are easily separated. Large quantities of CO_2 could be available from fuel-scale anaerobic digestion plants.

The results of this study indicate that there are several large sources of CO_2 that could support microalgae-based fuel production.

We also evaluated the costs of transporting CO_2 . Supercritical pipelines are the most economical method of transporting CO_2 for the flow rates required for fuel synthesis. Transportation costs are typically \$0.008/kg per 100 miles for a pipeline capacity of approximately 2.6 x 10⁶ kg/d. Therefore, transportation of CO_2 is feasible only from large concentrated sources over relatively short distances. This implies that microalgae production facilities should be sited near CO_2 sources.

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1.0 INTRODUCTION

This study, funded by the Solar Energy Research Institute's (SERI) Aquatic Species Program, examines sources of carbon dioxide (CO_2) for microalgae-based fuel production in the year 2010 and beyond.

1.1 Purpose of Study

Under the auspices of the U.S. Department of Energy (DOE), the SERI Aquatic Species Program is developing microalgal species and culture technologies that result in microalgal cells with a high percentage of lipids. Lipids can be extracted and converted to a diesel fuel substitute. Optimal microalgae growth occurs in a CO_2 saturated solution.

If these research efforts are successful, large quantities of low-cost CO_2 will be needed. The purpose of this study is to identify possible CO_2 sources for microalgae-based fuel production and quantify the amounts available and possible costs. Because large quantities of CO_2 will be needed over the next 25-50 years for enhanced oil recovery (EOR), we have made extensive use of many studies and projections developed by those involved in EOR; we acknowledge the value and usefulness of their efforts. Because of the early stage of development of the microalgae-based fuel production technology, and the current plentiful supplies of gaseous and liquid fossil fuels, 2010 was chosen as the earliest date that CO_2 for microalgae-based fuel production would be needed.

1.2 System Overview

1.2.1 Energy Sources

Microalgae-based liquid fuel production using CO_2 may be important in the future when petroleum and natural gas supplies have largely been depleted. Microalgae production facilities will be located in sunny areas with moderate climates. Consequently, we have emphasized CO_2 sources in the southern and southwestern United States where solar radiation is the greatest. We have analyzed CO_2 sources in the ten sunniest states in the United States: Alabama, Arizona, California, Florida, Georgia, Louisiana, Mississippi, New Mexico, Oklahoma, and Texas.

1.2.2 Microalgae Conversion Technology

SERI is pursuing research on the production of liquid fuels through photosynthetic organisms such as microalgae. Microscopic algae have demonstrated the ability to accumulate cell mass in the form of high-energy products, or lipids, while achieving high rates of growth (Neenan et al. 1986). The lipids produced are chemically similar to hydrocarbons, having long chains of 12-24 carbon atoms, with 0-5 double bonds (Tornabene et al. 1983). However, increases in lipid content are mainly achieved at the expense of higher growth rates, and vice versa. Neenan et al. (1986) concluded that further species improvement in productivity, lipid content, and environmental tolerance was critical in establishing the economic viability of fuels from microalgae technology.

1.2.3 Quantities of CO₂ Needed

1.2.3.1 Fuel Synthesis. The quantity of CO_2 required to support the synthesis of a given amount of fuel product depends on which product is considered. For the synthesis of carbohydrate, the generalized reaction is

$$CO_2 + H_2O ----> C(H_2O) + O_2.$$

Based on a heat of combustion for the typical carbohydrate of 7500 Btu/lb (17.4 MJ/kg), the CO_2 requirement is 90 x 10⁹ kg/quad (1.7 TSCF/quad).



For lipid fuel products, two sets of values were calculated, each based on "typical" microalgal lipids as being triglycerides of a saturated 12-carbon fatty acid or a polyunsaturated 18-carbon fatty acid. For the latter, the generalized reaction would be

57
$$CO_2$$
 + 31 H_2O ----> $C_{57}H_{62}O_6$ + 69.5 O_2 .

Based on a triglyceride heat of combustion of 17,000 Btu/lb (39.5 MJ/kg), the CO₂ requirement is 80 x 10° kg/quad (1.5 TSCF/quad). For the 12-carbon triglyceride ($C_{39}H_{74}O_6$), the CO₂ requirement is 72 x 10° kg/quad (1.4 TSCF/quad).

The above calculations for lipids are based on recycle of all nonlipid cell mass by anaerobic digestion, with resulting production of methane and more CO_2 . If the nonlipid constituents are not recycled, then more CO_2 is required per quad of stored energy. Table 1-1 summarizes the quantities of CO_2 required for microalgae-based fuel production via the various routes discussed.

Product	Fuel Synthesis' g CO ₂ /g product	Energy Storage 10 ⁹ kg/quad ^b	
CH ₂ O	1.5	89	
Lipids ^c (with cell recycle)	2.7-3.0	72-80	
Lipids (without cell recycle)	3.6-4.0	96-107	

Table 1-1. CO₂ Quantities Required for Microalgae-Based Fuel Production

a 100% utilization efficiency

b To convert kg to SCF, divide by 0.0522

c 60% lipid content

1.2.3.2 Enhanced Oil Recovery. We will review CO_2 demand for EOR uses because it has many similarities to the CO_2 needs for microalgae-based fuel production. Hare et al. (1978) estimates the ultimate quantities of oil that could potentially be recovered through the use of CO_2 at 4-8 x 10° bbl. The CO_2 requirement to recover 1 bbl of oil can vary between 5 and 15 MSCF/bbl (260-780 kg/bbl), with a more likely range of 5-10 MSCF/bbl after recycling. Multiplying these two quantities together could yield a range of anywhere from 20 to 80 TSCF (1-4 x 10¹² kg). To arrive at an annual demand, we arbitrarily assume an depletion period of 25 yr, which is consistent with derived estimates of 0.6-1.2 x 10⁶ bbl/d (based on 80% production) from the work of Hare et al. (1978). This depletion period yields annual demand figures of 40-160 x 10° kg CO_2/yr . Because a barrel of domestic crude oil represents, on average, 5.8 MMBtu (31 MJ/m³), between 45 and 135 x 10° kg of CO_2 would be required to produce one quad of crude oil, which is in the same order of magnitude as the estimates for microalgae-based fuel production of Table 1-1.

1.2.4 Conversion Factors

Because CO_2 quantities are expressed in units of weight and volume with nearly equal frequency, we will clarify here the conversion factors that we will use throughout this report. The abbreviation "SCF" will refer to the standard cubic foot as used by the gas industry, which is at 68°F and 14.7 psia (1 atm). The weight of 1 SCF of CO_2 is 0.115 lb, so

 $1 \text{ SCF} = 0.115 \text{ lb} (68^{\circ}\text{F}, 1 \text{ atm}).$

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The convention for English (not SI units) of "M" to indicate thousands, "MM" to indicate millions, and "B" and "T" to indicate billions and trillions enables us to make the following conversion:

1 ton = 17,400 SCF = 17.4 MSCF.

Based on the fact that 1 kg = 2.204 lb:

$$1 \text{ SCF} = 52.2 \text{ g} \\ 1 \text{ MSCF} = 52.2 \text{ kg} \\ 1 \text{ MMSCF} = 52.2 \text{ Mg or } 52.2 \text{ x } 10^3 \text{ kg} \\ 1 \text{ BSCF} = 52.2 \text{ x } 10^6 \text{ kg, etc.} \\ \end{cases}$$

In addition, a note about annualized figures presented in this report is in order. In much of the gas processing industry, it is convenient to express daily quantities, e.g., one billion standard cubic feet per day is represented by 1 BSCFD. What annualized quantity does this represent? Many of the sources we rely on assume a capacity factor of 80%, or roughly 300 operating days per year. Others ensure a capacity factor of 90% or 330 days per year. Still others are less clear; where this occurs we opt for the rigorous approach, which is to cite the daily and annualized numbers separately and, where applicable, to cite the capacity factor explicitly.

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2.0 CURRENT SOURCES AND USES OF CO₂

2.1 Merchant Market

Although the merchant market accounts for only a tiny fraction of the total annual CO_2 production, its components are reliably estimated and reported. The two primary sources of carbon dioxide for the merchant market are the production of ammonia from natural gas and ethanol from the fermentation of sugars (*Chemical and Engineering News*, 1984, 1986). The key factor that makes the CO_2 from these processes (as well as the others detailed below) available to the merchant market is that it must be separated from the main product during the purification of that product. Thus, no extra costs are required for CO_2 recovery. Table 2-1 summarizes recent annual domestic production of CO_2 for the merchant market.

	Production (10 ⁹ kg/yr)		
State	1986	1985	
Solid	0.44	0.41	
Liquid	4.00	4.13	
Gas	3.76	3.50	
Total	8.20	8.04	

Table 2-1. Annual Production of CO2 for
the Merchant Market

Source: U.S. Department of Commerce, 1987

2.1.1 Sources of CO₂ for the Merchant Market

2.1.1.1 Ammonia plants. The production of ammonia from natural gas is a multiple-step process, primarily consisting of (1) steam reforming of the natural gas into synthesis gas (carbon monoxide and hydrogen), (2) water-gas shift reaction of carbon monoxide and water into hydrogen and CO₂, and (3) reaction of the hydrogen with nitrogen to form ammonia. In typical plants, 1.1-1.2 kg of CO₂ are produced per kilogram of ammonia, a portion of which is often used captively for the production of urea (Stern 1986). The majority (up to two-thirds) of the CO₂ coproduced with ammonia is actually vented, as adequate CO₂ sources exist to meet current demand. The total CO₂ coproduction is 15-19 x 10⁹ kg/yr; of this, one-fourth is used for urea production, and only about 40% actually enters the merchant market (*Chemical and Engineering News*, 1987).

2.1.1.2 Ethanol plants. The production of ethanol by the fermentation of organic substances such as corn, molasses, and potatoes has grown significantly throughout this decade. The increased use of ethanol as a blending agent in automotive gasoline, the result of tax incentives as well as mandated reductions in tetraethyl lead, has opened up the market considerably. In the fermentation process, ethanol and CO_2 are produced in approximately equal weights. Based on current fermentation ethanol production of 700 million gallons per year (Alcohol Outlook, July 1987), more than 2.1 x 10⁹ kg of CO_2 are coproduced. Again, much of this gas is vented, leaving a merchant production of about 1 x 10⁹ kg/yr.

2.1.1.3 Hydrogen plants. Refineries produce hydrogen for operations such as hydrocracking and isomerization, using the first two major steps in the production of ammonia described above. The CO_2 must be removed to produce a high-purity hydrogen product. The volumetric ratio of CO_2 to hydrogen produced by this process is 1 to 4 (Stem 1986). Only about 5%-10% of the nearly 9 x 10⁹ kg/yr of CO_2 produced in this way enters the merchant market.



2.1.1.4 Other sources. These include CO_2 coproduction with ethylene oxide, as well as those sources that produce CO_2 as a dilute component of a product or waste stream; e.g., electric power plants, cement plants, and industrial boilers and furnaces. None of these sources currently contributes significant quantities of CO_2 to the merchant market, although all of them have the potential to do so if the economics and the technology improve. We will discuss these considerations in Section 3.

Figure 2-1 summarizes the discrepancy between the quantity of by-product CO_2 produced and the quantity that would actually be required for future demands such as EOR or microalgae-based fuel production. It also compares the current production and sales to that which would be needed for EOR.

2.1.2 Uses of CO₂ in the Merchant Market

2.1.2.1 Refrigeration. Liquid carbon dioxide provides a readily available method of rapid refrigeration and is used for quick chilling of loaded trucks and rail cars before shipment. For example, a 4-min injection of liquid CO_2 into a loaded ice cream truck can decrease the temperature as much as 70°C, flushing the warm air from the truck and leaving a layer of CO_2 snow. This process greatly reduces the load on the truck's mechanical refrigeration system and minimizes the time required to cool the truck's contents to a safe storage temperature. Solid carbon dioxide (dry ice) is also an important refrigerant in many laboratories and hospitals, as well as for molded rubber products, aluminum rivets, and food products such as meats and ice cream (Ballou 1978). Production of liquid and solid carbon dioxide from the gaseous state is summarized in Section 2.1.3.

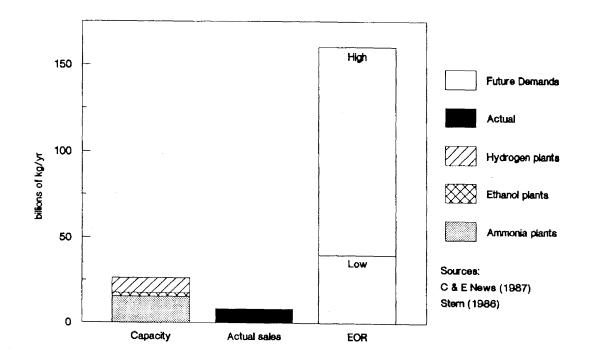


Figure 2-1. CO₂ merchant market: capacity, production, and future demand

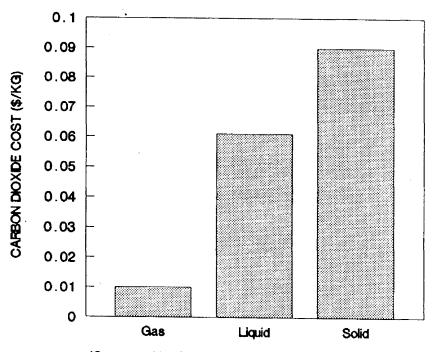
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2.1.2.2 Beverage manufacture. Gaseous CO_2 under pressure is introduced into beverage mixes; on pressure release, the foaming beverage product is produced. Both soft drinks and so-called "light" beers are made in this way (Ballou 1978).

2.1.2.3 Miscellaneous. There is a wide variety of other uses for carbon dioxide. The gas is used for shielded arc welding, where speed has been increased tenfold with semiautomatic microwave welding equipment. The gas is also used in foundries (to harden sand cores and molds) and slaughterhouses (to immobilize the animals prior to slaughter). Liquid CO_2 is used as a fire extinguisher in chemical plants, warehouses, and airplanes; it is also used in the coal mining industry. It also finds applications as a chemical reagent in the manufacture of sodium, potassium, and ammonium carbonates and bicarbonates (Ballou 1978).

2.1.3 Value of CO₂ in the Merchant Market

The value of carbon dioxide in the merchant market depends on its state. These values, summarized in Figure 2-2, are based on 1985 data from the U.S. Department of Commerce. The price differences are essentially functions of the costs associated with phase-change. Liquefaction is accomplished by two common processes; the first involves compression at 32° C to 75 atm followed by condensation. The second involves compression to 16-24 atm, followed by cooling to the range of -12° to -23° C, and condensation. Filtration and drying are included in both processes to remove any oil and water. Dry ice is produced in blocks by hydraulic presses. The liquid CO₂ is fed to the press chamber at 7 atm and -46° C. The feed is then expanded to atmospheric pressure, thus passing the triple point (5 atm) and solidifying to form carbon dioxide snow. The hydraulic rams then press the snow into a solid block of dry ice, which is usually stored in insulated bins or trucks (Ballou 1978).



(Source: U. S. Department of Commerce, 1987)

Figure 2-2. Merchant market CO₂ cost

2.2 Enhanced Oil Recovery

Carbon dioxide is used in EOR in a procedure known as miscible flooding. CO_2 is injected into a reservoir to modify the viscosity-temperature-pressure profile of the oil, making the oil flow more easily. EOR may be conducted early in the life of a reservoir, or at any time during its producing life. It is most likely to occur after primary recovery (normal depletion without the addition of injected fluids), and secondary recovery (the injection of immiscible fluids, e.g., water as an energy source), have been completed. Estimates of the ultimate potential for CO_2 -based EOR are speculative, but, as discussed in Section 1.2.3, could be as high as 2-8 x 10⁹ bbl (Hare et al. 1978), or somewhere between 10%-30% of the 1986 proven crude oil reserves (U.S. Department of Energy 1987a).

As discussed in Section 1.2.3, the annual CO_2 demand for EOR is estimated to fall in the range of 40-160 x 10⁹ kg, or between 150% and 500% of the current merchant market production capacity of 27 x 10⁹ kg/yr.

2.2.1 Sources of CO₂ for Enhanced Oil Recovery

2.2.1.1 Natural sources. Carbon dioxide exists underground in significant quantities, in reservoirs of essentially pure CO_2 or CO_2 mixed with natural gas. When these reservoirs are located near crude oil reservoirs, they become the source of choice for EOR projects, since CO_2 from natural reserves can be produced at low costs and transportation costs increase significantly with distance. Hare et al. (1978) collected data on the major natural CO_2 sources in the Rocky Mountain region (Colorado, Utah), Southwest (Texas, New Mexico), and Appalachian states (West Virginia) and were able to formulate estimates of the quantities of reserves available. However, they could not estimate CO_2 costs from such sources because of uncertainties in critical factors such as well reserve size, flowing wellhead pressure, and actual drilling costs. In fact, these uncertainties are not always fully resolved by the time a venture becomes commercial. Arco Oil and Gas Company is currently operating a 400-mile CO_2 pipeline from Huerfano County, Colorado, to Gaines County, Texas, whose design was based on erroneous reservoir performance data (Watson and Siekkinen 1986), causing many of the components to be larger or more expensive than necessary. The details of natural CO_2 sources will be discussed further in Section 3.1.

2.2.1.2 Electric power plants. There are so many power plants spread throughout the country that, in the aggregate, they represent a huge potential source of CO_2 . However, their current use is limited because of two factors: (1) the CO_2 content of the typical flue gas is only about 14%, and (2) the power plants are rarely located in close proximity to either the EOR project itself or a pipeline that can deliver the CO_2 to the project. The first factor can be overcome by suitable CO_2 separation techniques (Section 5.0); the second factor must be overcome by constructing either new power plants or pipelines (Section 4.0).

2.2.2 Value of CO₂ in Enhanced Oil Recovery

Because EOR may compete with microalgae production for CO_2 , we have examined possible prices in this application. Based on a 10% annual rate of return, and for CO_2 flooding efficiency of 520 kg/bbl (10 MSCF/bbl), the maximum allowable CO_2 cost was estimated at \$0.015/kg (\$0.80/MSCF) for a wellhead oil value of \$20/bbl. If the price of oil were to double to \$40/bbl in constant dollars, the allowable CO_2 cost would increase to \$0.040/kg (\$2.00/MSCF). More efficient utilization of CO_2 in the miscible floods would increase the allowable CO_2 costs (Stern 1986): at a flooding efficiency of 260 kg/bbl (5 MSCF/bbl), the allowable CO_2 cost would range from \$0.040/kg (\$2.10/MSCF) to \$0.080/kg (\$4.20/MSCF).

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3.0 POTENTIAL CO₂ SOURCES FOR MICROALGAE-BASED LIQUID FUEL PRODUCTION

To be considered a suitable source for microalgae-based fuel production in 2010 and beyond, a CO_2 source must be able to supply sufficient quantities at sufficiently low cost to those regions of the country where fuel production facilities would most likely be located. For microalgae production, warm sunny climates are needed. This means that the CO_2 must either be produced or be cheaply deliverable to the southern or southwestern United States.

3.1 Natural CO₂ Reservoirs

3.1.1 Estimated Reserves

Hare et al. (1978) examined all the natural CO_2 sources in the United States. Nearly 90% of the total domestic supply is located within the borders of four states: Colorado, New Mexico, Utah, and Wyoming (Figure 3-1). Table 3-1 summarizes the major domestic natural CO_2 sources.

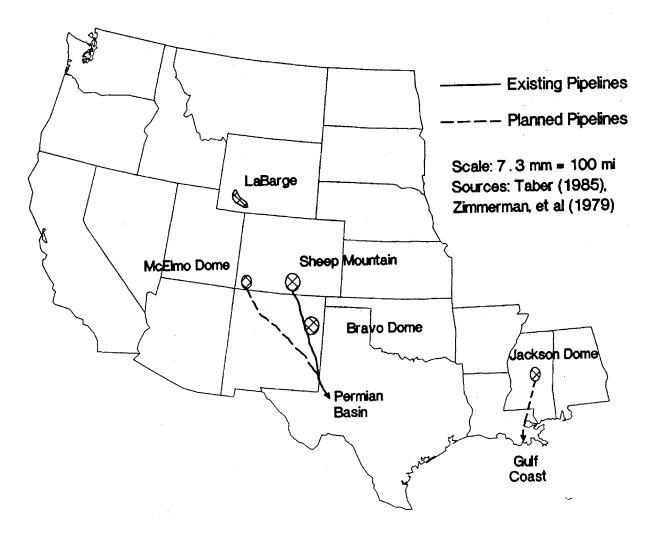


Figure 3-1. Major natural CO₂ reserves

	Reserves 10 ⁹ kg	Capacity, Current	10 ⁹ kg/yr ^a Planned
Sheep Mountain, CO	52	5.0	
McElmo Dome, CO	438	5.3	9.9
Bravo Dome, NM	313	5.2	6.1
LaBarge, WY	1044		
Jackson Dome, MS	52-157		
Total	1900-2000	15.5	16.0

Table 3-1. Major Natural CO₂ Reserves

a Based on 80% production

Source: Stern 1986

3.1.2 Depletion

As can be seen from Table 3-1, the major natural CO_2 reservoirs would be insufficient to meet the projected daily EOR demand of 360-440 x 10⁶ kg/d, even though they would appear to satisfy the ultimate projected demand of 1-4 x 10¹² kg (Anada et al. 1982, 1983; Hare et al. 1978). This is primarily due to regional mismatches, e.g., essentially all the CO_2 demand is in the west Texas oilfields, but the supply is spread over several nonadjoining states. We can conclude, then, that the highest purity and closest proximity CO_2 sources will be the first developed for EOR, with the more dilute and more distant sources utilized later. As the demand for CO_2 continues to increase, natural CO_2 sources are likely to be drastically depleted; the lack of development of a given CO_2 reserve would indicate only an uncertain geology or some other factor making it uneconomic. But because natural CO_2 supplies are insufficient to meet projected EOR demands, those in the EOR business have examined potential future sources of CO_2 . The majority of studies reviewed for this report were produced from the perspective of EOR supply and demand. The potential annual fuel synthesis requirements considered here require an even harder look at potential sources of CO_2 .

3.1.3 EOR CO₂ Reuse

One possible source of CO_2 in the years beyond 2010 is from depleted oilfields that have been produced using CO_2 flooding. The areas where EOR has been most extensive will become new underground CO_2 reservoirs. Much of the CO_2 will remain trapped underground in these reservoirs. Normally, estimates of both daily and ultimate CO_2 demand for EOR projects are based on the ability of significant portions of the CO_2 injected (typically 35%-50%) to be recycled and reused. Assuming that 20% of the annual projected CO_2 used for EOR (40-160 x 10⁹ kg/yr) could be recovered and reused after the petroleum reserves were depleted, 8-32 x 10⁹ kg/yr could be recovered. We could not reliably estimate the cost of recovering this CO_2 ; it would likely be at high concentration (<90%) and low to intermediate pressure, and thus cost roughly the same as CO_2 coproduced with ethanol (Section 3.3.1).

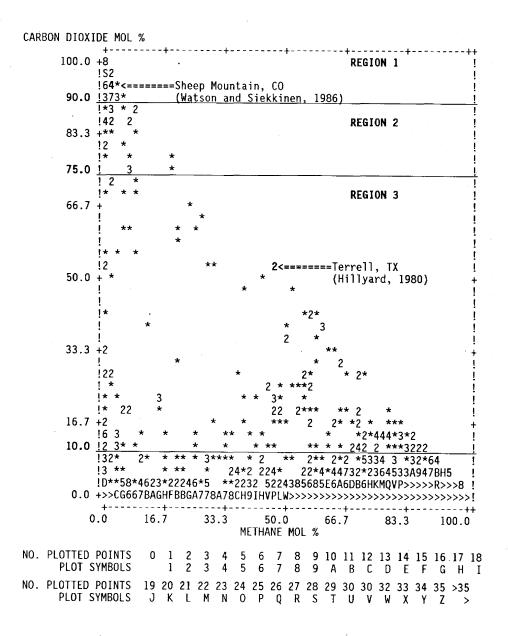
3.2 Noncommercial Quality Natural Gas

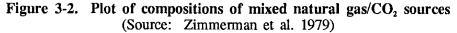
Although most natural gas deposits contain less than 10% CO_2 , there are significant deposits with much higher CO_2 content. Some deposits contain greater than 50% CO_2 , which could be too high for economical development. Reevaluation of these resources would lead to the conclusion that, if the demand for CO_2 and methane (and hence the price) were sufficiently high, then both could be developed. The mixed gas would have to be treated with one of the conventional processes to separate the CO_2 from the natural gas.



3.2.1 Estimated Reservoirs

Zimmerman et al. (1979), utilizing data published by the U.S. Bureau of Mines, constructed a data base of more than 11,000 analyses of gas samples from oil and gas wells. The analyses were performed using the Orsat apparatus, a mass spectrometer, and other devices. Using this extensive data base, the researchers were able to develop plots such as that shown in Figure 3-2. This plot was constructed on a printer-plot module in such a way that the module indicates the number of data points falling in one point location; e.g., at the top left corner the number 8 indicates 8 data points with CO_2 composition of 100%. One is struck by the huge numbers of data points with >80% methane, and relatively few points with >80% CO₂. The authors attempted to estimate the additional quantities of CO_2 that might be available in reservoirs containing dilute CO_2 , methane, or both. The plot was





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divided into three regions as follows: region 1 contains samples with CO_2 content >90%, which includes those discussed in section 3.1; region 2 contain samples with CO_2 content between 75% and 90%; and region 3 contains samples with CO_2 content between 10% and 75%. Samples with CO_2 content below 10% were not considered, because these samples would already be commercially attractive.

For all four regions, the number of samples and the weighted average CO_2 composition were calculated. Based on these quantities and from Stern's (1986) estimates in Table 3-1, the total naturally occurring CO_2 was estimated using two different assumptions:

(1) Low-range estimate: known natural CO₂ reserves (2.1- 10^{12} kg) assumed to fill regions 1 and 2 (2) High-range estimate: known national CO₂ reserves assumed to fill region 1 only.

Figure 3-3 summarizes the estimated CO_2 reserves from these calculations. The total natural CO_2 in noncommercial reservoirs could range as high as 1.3-2.5 x 10^{12} kg. With depletion in 25 yr, 52-100 x 10^9 kg/yr of CO_2 could be recovered from noncommercial natural gas sources. This CO_2 could also be used for EOR.

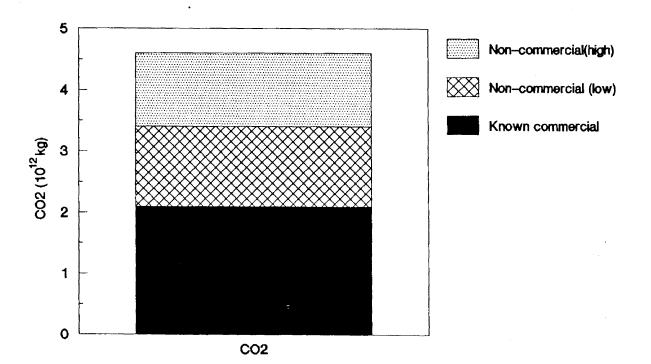


Figure 3-3. Commercial and noncommercial CO₂ reserves

3.2.2 Separation Cost

Anada et al. (1982, 1983) present detailed technical and economic analyses of purification of CO_2 from a variety of sources. Two chemical absorption processes are compared: one using alkanolamines, usually monoethanolamine (MEA); and one using a potassium carbonate (K₂CO₃). The MEA process is the most widely used for natural gas purification in this country; however, there are indications that the K₂CO₃ process may have particular advantages when SO₂ is present. Because this would be especially important when treating stack gases from coal-fired power plants and cement plants, we will discuss it in more detail below.

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Of the three regions of CO_2 shown in Figure 3-2, regions 1 and 2 require essentially no treatment because of their high purity; only compression and drying would be required to upgrade it (as with all CO_2) to pipeline quality. Region 3 requires an entire purification system to upgrade the dilute CO_2 to 98+%.

In estimating the recovery and drying costs of this CO_2 , we used a capacity factor of 80% (300 d/yr), for a facility size of 35 MMSCFD (1.8 x 10⁶ kg/d). Anada et al. (1982) determined that CO_2 recovery cost was quite sensitive to plant capacity, but not so sensitive to recovery efficiency: the price of CO_2 when 60% was recovered was typically only 5% more than when 90% was recovered. Nonetheless, only one facility size was chosen, in order to concentrate on direct comparison between CO_2 sources of differing concentrations. The recovery and drying costs estimated are summarized in Table 3-2. The recovery cost for CO_2 in region 1 and 2, at concentrations between 75% and 90%, could not be reliably estimated from the data of Anada et al. (1982). They considered all CO_2 above 90% to have zero recovery costs, but did not examine any gas streams with compositions in the 75%-90% range. Region 3 has lower compression and drying costs because its system is designed to use steam-driven compressors, using excess steam produced in the recovery system. Regions 1 and 2, with no recovery system, must purchase electric power for their compressors.

Table 3-2.	CO ₂ Recov	ery and Dryi	ng Costs from
Nonco	mmercial N	atural Gas (1	986 \$/kg)

Region	Recovery Costs ^b	Compression and Drying Costs	Total
1	0	0.011	0.011
2	0	0.011	0.011
3	0.049	0.004	0.053

a Refer to Figure 3-2

b Treatment by K_2CO_3 in recovery step

c Based on 1.8 x 10⁶ kg/d (35 MMSCFD) capacity

Source: Anada et al. (1982, 1983)

3.3 Fossil Fuel Combustion

The vast majority of carbon dioxide produced during the next 50 years, a quantity sufficient to meet not only all projected EOR demands but also all demands for microalgae-based fuel production, will be derived from various conversions of fossil fuels. These conversions are either direct combustion (i.e., in the generation of electric power) or production of a commodity chemical (e.g., ammonia). Most but not all of these conversions represent processes that are currently in commercial use. Other processes are likely to be commercially developed, with one objective being the actual enhancement of CO_2 coproduction. We will consider the process plants first, then the electric power plants.

3.3.1 Process Plants

3.3.1.1 Ammonia. The major steps used in the manufacture of ammonia from natural gas were summarized in Section 2.1.1. For further details, consult references such as Shreve (1977). The important facts to note are the typical feedstock requirement of 21,000 SCF of natural gas per ton of ammonia produced, and CO₂ coproduction of about 21,000 SCF per ton (1.2 kg/kg) of ammonia. This means that essentially 100% of the natural gas feedstock volume actually ends up as CO₂ coproduct. Also note the requirement that CO₂ be removed before the hydrogen-nitrogen reaction, to prevent it from poisoning the nickel catalyst. As a result, a CO₂ stream of typically 97.5% purity is produced, which requires a very minimal treatment system consisting of only compression and drying to upgrade it to pipeline quality.

However, even though ammonia is an important commodity chemical, it would not contribute significantly to the CO₂ demand for microalgae-based liquid fuel production. Recent ammonia production has ranged from 13 to 16 x 10⁹ kg/yr (*Chemical & Engineering News* 1987). This means that, even if all the domestic ammonia-derived CO₂ could be captured, it would amount to just under 20 x 10⁹ kg/yr. Further, urea production averages 5-7 x 10⁹ kg/yr, representing the utilization of roughly 25% of the annual ammonia and CO₂ coproduction (*Chemical & Engineering News* 1987). Urea also represents a substantial value added to both the ammonia and CO₂, and so would not likely be displaced by a fuel substance. The greatest amount of CO₂ that could ever be available for microalgae-based fuel production is thus 75% of the annual coproduction with ammonia, or 10-12 x 10⁹ kg/yr. The amount that is actually produced near potential new microalgae-based fuel synthesis, in the 10 states on the United States' southern border (i.e., Alabama, Arizona, California, Florida, Georgia, Louisiana, Mississippi, New Mexico, Oklahoma, and Texas), amounts to 8.6 x 10⁹ kg/yr. Fully half this potential is in one state, Louisiana.

3.3.1.2 Hydrogen. It is convenient to consider all the refinery operations where CO_2 is produced in this section. Anada et al. (1982) contacted Exxon representatives in Baytown, Texas, who identified the fluid catalytic cracking regeneration unit and the hydrogen production unit as the sources of economically recoverable CO_2 . The hydrogen production unit was discussed briefly in Section 2.1.1. The similarities between this process and the production of ammonia should again be emphasized, especially the high purity of the CO_2 stream (estimated at 97.5%).

The fluid catalytic cracking unit (FCCU) is much more prevalent in refineries than the hydrogen unit. Nearly every refinery has an FCCU, while usually only those refineries treating sour crudes require a separate hydrogen unit. The FCCU uses high temperatures and low pressures to crack heavier, highboiling petroleum fractions into lighter, more reactive materials. Because of the severity of the cracking process, the catalyst must be continuously regenerated to remove coke formed on its surface. In the regenerator the coke is burned off to form a mixture of CO and CO₂; this mixture is then fed to a CO boiler where the remaining CO is burned to CO₂. The outlet of the CO boiler has roughly 15% CO₂ content. CO₂ coproduction in the typical FCCU is reported by Anada et al. (1982) as 205 SCF/bbl (10.7 kg/bbl) fed to the FCCU.

The CO₂ that could reasonably be contributed by refineries (FCCUs and H₂ plants) in the 10-state area of interest is about 50% greater than that available from ammonia plants, totaling 13 x 10⁹ kg/yr. As is the case with ammonia plants, the potential capacity is fairly well concentrated by state: Texas would supply nearly half of the total refinery-derived CO₂, and California and Louisiana 20%-25% each.

3.3.1.3 Cement. Portland cement is produced in approximately equal amounts by one of two processes: a dry process and a wet process. In the dry process, limestone and sand are crushed, blended, and fed to a kiln to produce clinkers. The clinkers are produced by heating the raw materials to drive off CO_2 from the CaCO₃ leaving CaO in a process known as calcination. Gypsum is then added to the clinkers to form cement. The wet process is similar except that water is added to the raw materials before grinding and the resulting slurry is then fed to the kiln. The fuel for the kiln is either coal or natural gas. The combustion products from the kiln mix with CO_2 from calcining, and the resulting exhaust gas is cleaned of particulates before being vented at 300° - 400° F.

The primary difference between the wet and dry processes as they apply to CO_2 generation is that in the wet process the water content of the exhaust gas is much higher than in the dry process, over 30% compared to under 12%. CO_2 from the wet process plant will thus require slightly higher drying costs than that from the dry plant. CO_2 content is generally in the range of 21%-29% for either type of plant, using either fuel source. One other factor of note is the increased energy efficiency in newer plants versus older ones: Anada et al. (1982) found that plants built after 1963 (i.e., which were 10 years old or less in 1973) could cut their fuel consumption and their CO_2 output below that of plants built earlier. CO_2 production, CO_2 content, and H_2O content for the various configurations of cement plants are summarized in Table 3-3. Only the post-1963 cement plants have been included, because only they are likely to be operating by the year 2010.

The CO₂ quantities that might be recovered from cement plants are greater than from refineries and ammonia plants combined. In the 10-state area of interest, over 26×10^9 kg/yr of CO₂ could be recovered from cement plants. About half the CO₂ potential is from wet-cement plants, where recovery costs might be somewhat higher because of the high water content in the flue gas. California and Texas have the largest cement plant CO₂ capacity; about two-thirds of the plants in Texas are wet-cement plants, while those in California are divided about evenly between the wet and dry process.

Type of plant	103 kg CO ₂ /d*	wt.% CO ₂	wt.% H ₂ O
Wet coal	883	25.8	35.2
Dry coal	883	29.3	6.3
Wet gas/oil ^b	801	23.6	37.3
Dry gas/oil	801	28.6	10.1

Table	3-3.	CO ₂ Production and Concentration from	n
	Cem	ent Plants (Constructed after 1963)	

a Based on 910 x 10³ kg/d (~1000 ton/d) plant

b Gas- and oil-fired plants of similar age assumed to perform equivalently

Source: Anada et al. (1982, 1983)

3.3.1.4 Ethanol. Fermentation ethanol represents another potential source of high-purity CO_2 , but not in significant quantities. To supply CO_2 to support one quad of microalgae, it would take more than 26 x 10⁹ gal/yr of ethanol production. Ethanol production could grow that drastically only if ethanol were to become a major transportation fuel. Ethanol from lignocellulosic biomass and agricultural waste is, however, the subject of continuing research efforts; if significant technological breakthroughs were to occur, ethanol production could become a significant source of coproduct CO_2 .

3.3.1.5 Recovery Costs. Recovery costs for CO₂ from various process plants were examined by Anada et al. (1982, 1983). As Figure 3-4 shows, the CO₂ from ammonia and ethanol plants is much less expensive to recover, requiring only compression and drying costs of \$0.009-\$0.016/kg (\$0.44-\$0.84/MSCF), based on plant capacity, while cement plants and refinery effluents require the recovery step of treatment with MEA or K₂CO₃. Total costs for these plants range from \$0.054-\$0.096/kg (\$2.82-\$5.00/MSCF), with about 85% going for recovery and the rest for compression and drying. The lowest recovery cost from an ammonia plant is at a flow rate of 3.2 x 10⁶ kg/d, which represents the largest ammonia plant in the United States, a 4400 ton/d (4 x 10⁶ kg/d) plant in Donaldsville, Louisiana.

3.3.2 Conventional Power Plants

Recovery from power plant stack gases clearly represents a major potential source of CO_2 . As Stern notes (1986), the supply is stable, reliable, and widely dispersed to minimize transportation costs. The amount of CO_2 varies with type of fuel burned, and even among different samples of the same type of fuel. Table 3-4 summarizes the typical quantities of CO_2 generated per unit of energy input (Btu) and output (MW_e), as well as annual estimated CO_2 production. The major potential source of CO_2 is from coal-fired power plants, because of their greater number as well as their higher CO_2 production per Btu.

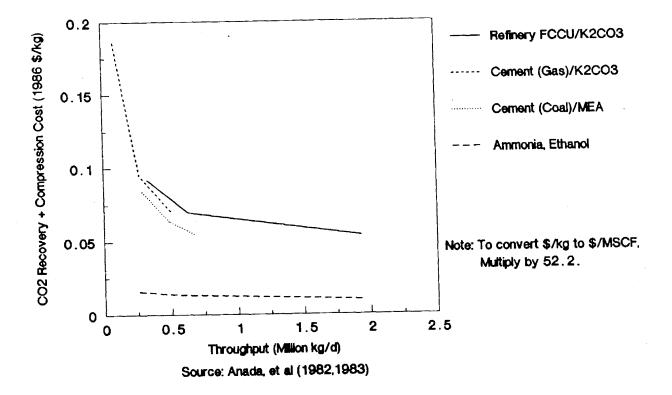


Figure 3-4. CO₂ recovery + compression costs from process plants

(Conventional Fower Flams)			
Fuel	Coal	Oil	Natural Gas
Heating value (Btu/lb)	12,700	19,600	24,000
(common units)	25 MMBtu/ton	6.4 MMBtu/bbl	1000 Btu/SCF
Liquid/gas density		7.8 lb/gal	0.042 lb/SCF
CO_2 concentration (wt %)	14-15	12	9
CO_2 produced (lb CO_2 /lb fuel)	2.5	3.7	3.0
lb CO ₂ /MMBtu	200	160	130
SCF CO ₂ /MMBtu [*]	1740	1390	1100
SCF CO ₂ /bbl		8900	
kg CO ₂ /MMBtu	90.8	72.6	57.4
kg CO ₂ /MWh ^b	935	748	591
1986 electric generation			
(10^6 MWh_{e})	1386	137	249
$CO_2 (10^{12} \text{ kg/yr})$	1.30	0.10	0.15

Table 3-4.	Coproduction of CO ₂ with Electricity from Fossil Fuels
	(Conventional Power Plants)

^a Gas density = 0.115 lb/SCF for CO₂ at 68°F and 1 atm ^b Power plant efficiency = 33% (10,300 Btu in/kwh_e out)

Sources: Steinberg et al. (1984); Stern (1986); Anada et al. (1982, 1983); U.S. Department of Energy (1987)

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Data from the work of Anada et al. (1982, 1983) on CO_2 recovery costs for power plants are shown in Figure 3-5. The cost difference between the recovery costs for coal and those for natural gas is primarily due to cost differences in purchased fuel, since heat is required to operate the separation processes. Low- sulfur coal plants have lower recovery costs than high-sulfur coal plants. The MEA process appears to be more economical for low-sulfur coal plants, while the K₂CO₃ process is less expensive in the other cases examined. The costs of compression and drying also vary with plant capacity and contribute 10%-15% to the total recovery/compression/drying costs.

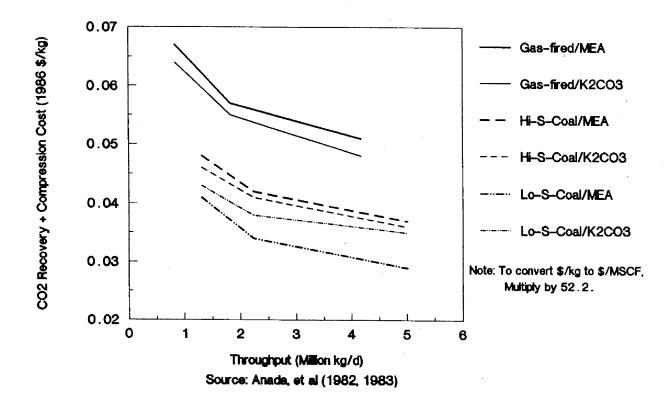


Figure 3-5. CO₂ recovery and compression costs for power plants

There was a recent commercial attempt at recovering CO_2 from flue gas (Wiggins and Bixler 1983; *Chemical and Engineering News* 1982). Flue gas from twin 50-MW natural gas units at Lubbock, Texas, was treated with an alkanolamine in a solvent extraction process licensed by Dow Chemical. The 1100 ton/d (1 x 10⁶ kg/d) CO₂ plant is no longer in operation, primarily for economic reasons. According to a representative of Carbon Dioxide Technology Corp., former operator of the plant, CO₂ recovery cost was at least \$0.038/kg (\$2.00/MSCF), so the process was not economically viable after the oil price drop of the mid-1980s. There were other problems at the facility, but they were not directly associated with the CO₂ recovery process (Mohun 1988).

3.3.2.1 Domestic Coal Resources. It is reasonable to expect that coal will continue to supply larger and larger fractions of this country's primary energy, especially in the area of electric power generation. Figure 3-6 shows the 1985 Demonstrated Coal Reserve Base (DRB), the total tonnage that is commercially minable (U.S. Department of Energy 1986a). The DRB totals 478 x 10⁹ ton, which, at 25 MMBtu/ton is nearly 12,000 quads. This would be enough to meet the total primary energy needs of the United States for 160 yr. Montana alone contains 25% of the DRB, with Illinois and Wyoming containing another 15% each.

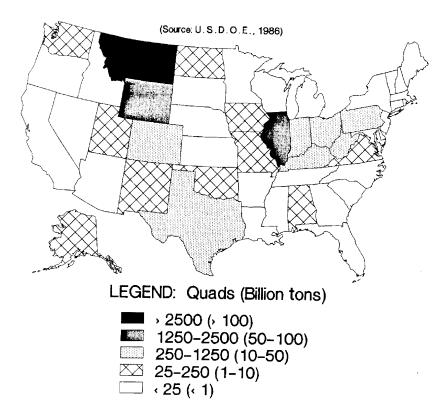


Figure 3-6. U.S. demonstrated coal reserves

3.3.2.2 Year 2010 Projected Electric Generation. The official projections of DOE's Office of Policy, Planning and Analysis (1983) have been used to estimate the quantity of CO_2 that might be produced from coal-fired power plants in the year 2010. First, state-by-state data for fossil-fired steam-electric production were tabulated for 1985, the same year as the above DRB data (U.S. Department of Energy 1986b). A total of 18.3 quads of fossil fuels was used by utilities for steam-power generation. The 2010 projection was then developed by taking DOE's mid-range projection of 27.8 quads (total fossil fuel input) and scaling it down to account for slower than expected growth before 1985 (actual 1985 fossil fuel input was 18.8 quads, compared to DOE's estimate of 20.5 quads). Total projected fossil fuel input to power production in 2010 was thus estimated at 25.5 quads, of which 24.8 quads represent steam-power production. Individual state projections were then developed based on their proportions in 1985 (Figure 3-7).

The total of 24.8 quads of fossil fuel input to electric production is sufficient to supply 2.25 x 10^{12} kg/yr of CO₂ every year. With respect to the areas most likely to be suitable for microalgae production, the 10 states mentioned in the discussion of ammonia, the projected electric generation amounts to 8.7 quads, enough to produce 790 x 10^9 kg/yr of CO₂.

3.3.3 Clean Coal Technologies

3.3.3.1 Concentrated CO_2 Combustion. Scientists at Argonne National Laboratory (ANL) have suggested one novel approach to the problem of CO_2 recovery from coal-fired power plants. They have proposed to circumvent the problem of dilute CO_2 concentration in the stack gas by separating the combustion air into oxygen and nitrogen before it is fed to the furnace (Wolsky 1985; Barry et al. 1986). The coal is then combusted with a mixture of pure oxygen plus CO_2 and H_2O recycled from the stack. The stack gas, after drying, would contain 95% CO_2 or more, with small amounts of SO_x and NO_x . It would probably be suitable for EOR because of the enormous capacity of petroleum reservoirs to neutralize and remove SO_x and NO_x (Taber 1985). The effects of these acids on

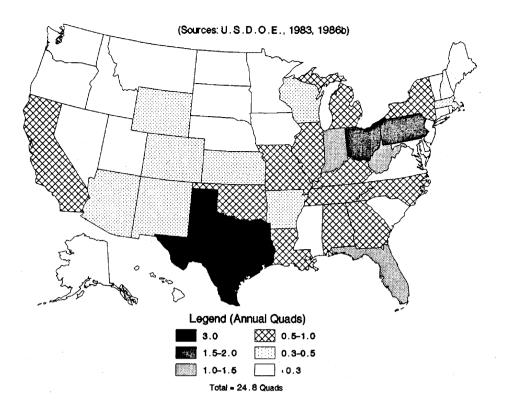


Figure 3-7. Projected year-2010 combustion of fossil fuels for electricity

microalgae production are unknown, but the large amounts of electrolytes required in solution by algae could mitigate their harmful effects by buffering action.

The proposed ANL combustion scheme, shown in Figure 3-8, attempts to operate the existing furnace on some mixture of O_2 and CO_2 exactly as it would run on air. Evaluation of various CO_2/O_2 ratios was based on such considerations as flame stability, heat transfer rates, and excess O_2 requirement. Early results of their experimental work indicates that a CO_2/O_2 molar ratio of 2.23 performed most similarly to typical combustion in air atmosphere. It is interesting to compare this ratio with that of air: 3.76 mol N_2 per mol O_2 . Even though the amount of "carrier gas" CO_2 is much less than for air, the overall combustion characteristics are reasonably similar.

Although researchers at ANL feel it is too soon for definitive estimates of the costs associated with this type of approach, they do raise some of the critical related issues. First, they feel that the CO_2 cost is likely to depend primarily on the cost of separating O_2 from the air. This is commonly done through a cryogenic liquefaction/rectification process (Shreve 1977), taking advantage of the normal boiling point difference between O_2 (90 K) and N_2 (77 K). Between 10-12 kWh would be required per SCF of CO_2 (0.52-0.63 kWh/kg CO_2), which is close to 20% of the gross power output of a typical power plant. To a utility with excess generating capacity, this might look attractive. The utility could charge itself the incremental operating cost, including an electricity cost substantially below wholesale.

Another option would be to provide storage so that O_2 production could be interrupted during peak hours, when all the power produced would be needed to meet demand. Still another possibility would involve running the power plant on air instead of CO_2 and O_2 during peaks; this would obviate the need for O_2 storage. O_2 production is estimated to contribute \$0.30-\$0.50/MSCF (\$0.016-\$0.026/kg) to the cost of CO_2 . A further advantage of this process is that, because the CO_2 produced is essentially pipeline quality, there are no emissions; the cost of SO, and NO, removal is avoided. The utility

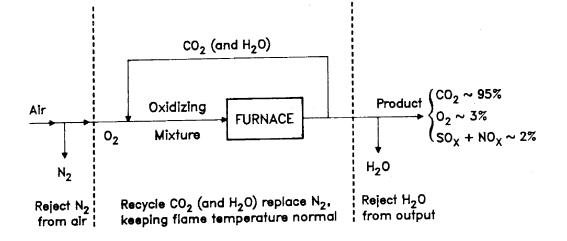


Figure 3-8. ANL scheme for concentrated CO₂ combustion

could credit itself the avoided cost of SO_x and NO_x removal. Based on analysis of two potential versions of federal air pollution legislation, ANL estimated the cost of SO_x and NO_x removal to vary from 0-1.50/MSCF CO₂ (0-0.78/kg) (Wolsky 1985), with the majority of plants falling in the range of 0.30-0.60/MSCF (0.016-0.031/kg). If this process could be successfully developed, the avoided costs of NO_x removal might outweigh the costs of installing the additional equipment, resulting in net positive cash flow.

3.3.3.2 Fluidized-Bed Combustion. In their review of environmental issues affecting the use of coal, Yeager and Baruch (1987) stress the importance of developing a variety of technological improvements for the next generation of coal-fired power plants. Fluidized-bed combustion (FBC), in particular, can drastically reduce SO_x and NO_x emissions. FBC power plants can be designed to operate at either atmospheric or increased pressure; the latter type has the advantage of requiring smaller sized components, allowing for modular in-shop fabrication. The SO_x and NO_x are captured right in the boiler by calcined limestone, forming calcium sulfate, which can be easily separated and disposed. The Electric Power Research Institute (EPRI) is currently sponsoring three FBC demonstration projects of 100-160 MW, one of which involves conversion of an existing boiler and the others addition of new boilers to existing turbine-generators (Yeager and Baruch 1987). No data are available on CO_2 production or recovery costs from these units, but the atmospheric design is likely to be similar to conventional power plants, while the pressurized design may allow lower recovery costs because of the high partial pressures of stack CO_2 .

3.3.3.3 Gasification Based Cycles. Coal gasification represents another viable alternative to the standard coal combustion practice. Turbine generators can be run on coal-derived gas (either medium-Btu gas or synthetic methane); sulfur removal and CO_2 recovery are aided by the high partial pressures of the gasifier effluent. EPRI has sponsored research on coal gasification for many years, and is one of the principals in the Cool Water Coal Gasification Combined-Cycle Power Plant, near San Bernardino, California. This 100-MW_e unit, which began operation in 1984, is the world's first integrated, commercial-scale coal gasification combined-cycle (GCC) power plant (Yeager and Baruch 1987). Based on a large-scale (500-MW_e) design of the Cool Water plant, an EPRI-funded study by Fluor proposed that with only minor design changes significant quantities of CO_2 could be coproduced.

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Figure 3-9 shows the original (the so-called electricity-only) design, and the modified (CO₂ coproduction) designs (Snyder and Depew 1986). The only difference in the two is the CO₂ removal (plus subsequent drying and compression) step from the gas before it is fed to the turbine generator. This process is identified as the minimum CO₂ production process. A further modification quenches the gasifier outlet with water, then produces much larger quantities of CO₂ with the water-gas shift reaction. More than five times as much CO₂ is produced in this so-called maximum CO₂ production system.

Capital and energy requirements of the coproduction plants were compared to the electricity-only plant. Because CO_2 coproduction reduces the net power output, these plants were scaled up so that their power production matched that of the electricity-only plant (all these designs were for nominal 500-MW_o capacity). This enabled all the capital and operating costs for CO_2 coproduction in both processes to be broken out, and the incremental CO_2 costs calculated independently of power production. Based on initial commercial operation in 1991, 6% annual inflation, and rates of return typical for a regulated utility, Fluor calculated the following levelized costs (mid-1985 dollars):

\$0.016/kg (\$0.85/MSCF) for Minimum CO_2 (41.8 MMSCFD or 2.18 x 10⁶ kg/d); \$0.012/kg (\$0.64/MSCF) for Maximum CO_2 (263.0 MMSCFD or 13.7 x 10⁶ kg/d).

These calculations were for a utility-owned, GCC power plant with a required selling price for electricity of 0.0395/kWh. The CO₂ market price at the time of the study was 0.024/kg (1.25/MSCF). Other scenarios were examined for their effects on power or CO₂ selling price. For example, sale of CO₂ at the market price would lower the required electricity selling price to (0.0285/kWh), with no loss to rate payers. If the electricity price remained constant, and CO₂ was sold for the market price, return on common equity could increase from 8.5%/yr to 16.6%/yr (constant dollars). If the drying and compression steps were performed by others, the utility's decreased capital and operating costs would enable it to sell the CO₂ for 0.007/kg (0.38/MSCF) versus 0.012/kg for pipeline quality CO₂. Finally, if a nonutility company owned and operated the entire electricity-CO₂ complex and sold its power to a utility at an avoided cost of 0.06/kWh and its CO₂ at the market price of 0.024/kg (1.25/MSCF), it would achieve constant dollar returns of 11.9%/yr on 100% common equity.

3.3.3.4 Projected Impact of Synthetic Fuels. DOE has developed projections for synthetic fuels production through the year 2010. Synthetic liquid and gaseous fuel production from coal in 2010 is estimated to amount to 5.9 quads, with 2.5 quads for synthetic liquid fuels and 3.4 quads for synthetic methane (U.S. Department of Energy 1983). The potential CO_2 coproduction can be estimated using portions of the Fluor designs discussed above. In the minimum CO_2 production case, the Texaco gasifier produces a fuel gas consisting of 54 (mol) % CO, 42% H₂, and 1.4% CO₂, along with Ar and N₂. Instead of being burned, such a gas would be directly usable for hydrocarbon synthesis, with a suitable C:H ratio (1:1.6) for production of olefins, the most reactive type of hydrocarbon. The projected 2.5 quads would require a coal input of 111 MM ton/yr. The resulting CO_2 coproduction would be 40×10^9 kg/yr. For gaseous methane synthesis, a shift reaction would be required to obtain the proper 1:4 carbon:hydrogen ratio to make methane. By converting water molecules to hydrogen, the shift reaction also causes greater CO_2 quantities to be produced, normally in the range of 3.1 SCF CO_2 per SCF CH₄ (Nelson 1983). For the projected 3.4 quads of synthetic methane, a total of 220 x 10⁹ kg CO₂ would be co-produced. It will also be recalled that gasification produces CO₂ of both high concentration (99+%) and high pressure (2000 psi), which therefore enables it to be fed directly to pipelines in significant quantities with minimal recovery costs.

3.3.3.5 Advanced Coal Refinery. Given the large domestic coal reserves, and the continuing technological improvements in coal utilization processes, Yeager and Baruch (1987) introduce the concept of the advanced coal refinery (Figure 3-10). They suggest that in the 21st century, the conventional coal-fired power plant will evolve from resource-inefficient, mechanical combustion units into fully integrated refineries, where power generation is only one element of a much broader resource processing capability. Such a refinery would produce products serving all sectors of the economy:

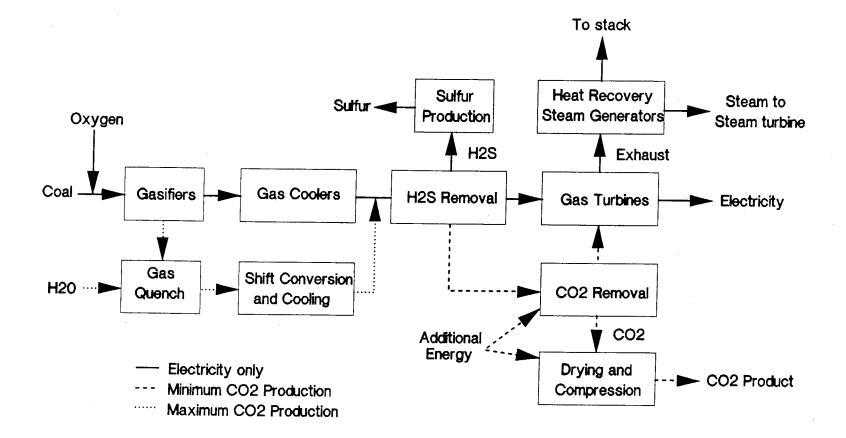


Figure 3-9. EPRI/Fluor coal gasification with and without CO₂ coproduction

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residential, commercial (liquid and gaseous fuels and electricity), and industrial (heat plus CO_2 , building materials, and other useful substances). In addition, process development improvements should enable cost-competitive recovery of valuable byproducts from the ash.

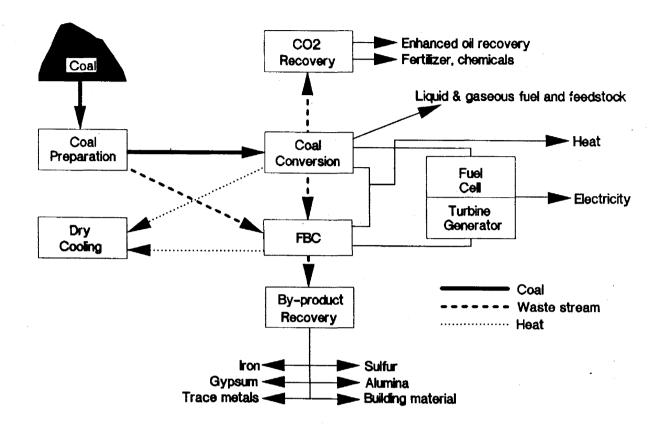


Figure 3-10. The advanced coal refinery

3.3.4 CO₂ Emissions Controls

The potential for climatic change brought about by the buildup of CO_2 in the atmosphere (the socalled "greenhouse effect") has been well documented, but it has so far proven impossible to develop a consensus among the scientific community regarding many aspects of this problem (Laurmann 1985). In particular, the time frame during which harmful effects might occur depends heavily on future rates of economic and energy growth; the fraction of CO_2 emissions that can be biologically reabsorbed; and the quantities and effects of other trace gases, e.g., CH_4 , NO_2 , and chlorofluorocarbons (CFC).

Based on laborious studies of the problem, Laurmann (1986) has suggested a range of scenarios where the doubling of atmospheric CO₂ content from its pre-industrial level of about 280 ppm to 560-600 ppm could occur as early as 2025, and with increasing probability at any time throughout the following century. The effects of the resulting temperature increase of $2^{\circ}-5^{\circ}C$ are also debatable, possibly including longer growing seasons and other effects that might actually be welcomed in some regions of the world, at least initially. But the long-term effects are likely to include some melting of the polar ice caps with subsequent severe disruption of weather and, hence, agricultural patterns (Ember et al. 1986). Laurmann makes the point that, by the time the global warming trend becomes a problem, its solution could be extremely disruptive to the world's economy, as well as very expensive to implement. Another study found that, regardless of the longer term effects, a mean temperature rise of 1° C by 2000 would increase the generating capacity requirements of electric utilities (Linder and Gibbs 1987). Those in southern regions that already have large peak summer loads, primarily air-conditioning, would be most seriously affected. It was estimated that climate-induced capacity increases for such utilities could reach 10%-20% of base case (no climate change) increases by 2016. Another significant effect could be that of stream flow changes on hydroelectric production in those regions that rely heavily on hydropower (e.g., New York).

One possible result of the major contribution of CO_2 emissions to global warming is that the policymakers would step in and mandate a reduction (or elimination) of CO_2 emissions, either by reductions in fossil fuel combustion or by utilization of CO_2 recovery processes. Examination of the potential policy impact has progressed to the point where some are considering disposal of CO_2 by pumping to the deep ocean, salt caverns, or spent oil and gas wells (Steinberg et al. 1984). Power requirements for such endeavors would approach 15% of total generating capacity. Further, at 1986 CO_2 costs of \$0.035/kg (\$1.80/MSCF), the across-the-board mandate of this scenario would increase electricity-generating costs an average of 75%. Although this estimate was based on liquid pipelines, which are not the most economical option (see Section 4.0), the CO_2 costs are somewhat lower than those calculated by Anada et al. (1982; see Figure 3-5). Clearly, using CO_2 for microalgae-based fuel production would be preferable to mandated disposal schemes, having a positive economic impact with minimal disruption of existing conventions.

3.4 Atmospheric Recovery

As the CO₂ quantities potentially available from the combustion of fossil fuels dwarf those present in natural reservoirs, so the quantities present in the atmosphere dwarf even those produced by fossil fuel combustion. The *Handbook of Chemistry and Physics* (1979) published an estimate for the mass of the atmosphere at 5.14 x 10^{18} kg. Given a CO₂ concentration of 510 ppm by weight (330 ppm by volume), the total CO₂ in the atmosphere would be 2.6 x 10^{15} kg. The likelihood of recovering this amount is negligible, but the point is that the atmospheric quantities of CO₂ are large compared even to power plants.

The primary obstacle to recovery of CO_2 from the atmosphere is its low partial pressure, roughly 0.25 mm Hg at atmospheric pressure. The same principles used in commercial CO_2 purification from natural gas and ammonia could be employed for atmospheric recovery. It is known that CO_2 will dissolve in a dilute K_2CO_3 solution to roughly 10 times the concentration that it will in pure water; in fact, the CO_2 reacts chemically with the K_2CO_3 to form KHCO₃, which is the most easily metabolized form of CO_2 for many species of microalgae. The type of system designed by Anada et al. (1982) would have to be significantly modified. Preliminary consideration has yielded two approaches. The first approach involves changing the absorption tower into something resembling a cooling tower, where large quantities of air could be contacted with the K_2CO_3 solution, which would concentrate the CO_2 . Another approach involves a spray pond with a series of nozzles spraying the K_2CO_3 solution out where it contacts the air. The advantage of this approach is that large horsepower motors are not required for air movement; an average wind velocity of 2 mph would cause sufficient air circulation for CO_2 absorption into the water. Such a pond would probably require a control system that closely monitored wind direction and velocity to prevent carbonate losses by shutting down nozzles whose spray would be blown offsite.

3.5 Anaerobic Digestion

Anaerobic digestion is the biological reduction of biomass or waste material to methane and CO_2 under anoxic conditions. The process is generally considered to consist of two stages: the breakdown of the carbohydrate, protein, and lipid into volatile acids; and the conversion of the volatile acids, primarily via acetate, into methane. The generalized reaction for the anaerobic digestion of carbohydrate follows (Klass 1980):

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n C₆H₁₂O₆ ---> 3n CH₃COOH ---> 3n CH₄ + 3n CO₂.

If these reactions were the only ones proceeding in a digester, 1 mole of CO_2 would be produced for each mole of methane produced. In actual practice, however, many other substances exist in digesters because of incomplete conversion; roughly 2 moles of CO_2 are produced for each 3 moles of methane, yielding a product gas with heating values of 500-750 Btu/SCF. Anaerobic digestion of biomass and wastes represents a substantial potential methane source, and incidentally a substantial CO_2 source as well.

It is possible that higher energy costs will improve the competitive economics of anaerobic digestion to the point that large-scale industrial digesters will be built. The resulting biogas could be burned directly as a medium-Btu fuel or it could be purified to pipeline-quality by MEA or K_2CO_3 separation processes. The former alternative might occur first, providing no additional CO_2 for microalgae-based fuel production, but when the latter occurs, significant quantities of CO_2 would be introduced to the marketplace. Klass (1980) estimated that 1 quad of methane would require 13.8 x 10⁶ acre, or 0.6% of the total U.S. surface area, based on biomass yields of 25 metric ton/ha-yr (11 ton/acre-yr) and an overall thermal efficiency of 50% in digestion. Coproduced with this would be 35 x 10⁹ kg/yr of CO_2 .

The DOE-sponsored SERI Anerobic Digestion Program is projected to produce 6.6 quads by anaerobic digestion of methane from biomass and wastes in the year 2010, as shown in Table 3-5 (Goodman 1988). If this methane contained the typical 40% CO_2 , an additional 130-230 x 10⁹ kg/yr of CO_2 could become available for conversion to microalgal lipids.

The lowest cost estimated for biogas, equal to the lowest ethanol cost of \$0.011/kg (\$0.57/MSCF), would occur only when high demand forced natural gas pipeline companies to bear the separation costs themselves. If this did not occur, then the recovery costs for biogas would approach those of, e.g., cement plants, up to \$0.084/kg (\$4.40/MSCF).

Energy Source	Methane from Anaerobic Digestion (quad/yr)	CO ₂ for Fuel Synthesis (10 ⁹ kg/yr) ^a
Biomass	3.7	130
Wastes	2.9	100
Total	6.6	230

Table 3-5. Energy Potential of Fuel Synthesis Using CO2from Anaerobic Digestion

^aBased on 60% methane/40% CO₂ product composition.

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4.0 TRANSPORTATION COSTS

Recovery, drying, and compression costs are not the only costs that must be considered in the evaluation of CO_2 sources for microalgae production. The costs of transporting CO_2 from the source (e.g., power plants) to the microalgae production facility must also be considered. Hare et al. (1978) and Anada et al. (1982) estimated costs for a range of transportation options, based on potential future demands of EOR. Hare et al. (1978) evaluated pipelines only, for three designs: supercritical (1400-2000 psi), subcritical (<1070 psi), and liquid pipelines. The cases considered by Anada et al. were supercritical pipelines, trucks carrying liquified CO_2 (300 psia at 0°F), trucks carrying saturated vapor CO_2 (1000 psia at 67°F), rail transport, and barge transport.

Both Hare et al. (1978) and Anada et al. (1982) calculated pipeline costs in the same way: they estimated capital and operating costs, and computed levelized gas costs from a discounted cash flow economic model. A variety of discount rates were considered, but because 15% was used by both groups, the data for that discount rate are presented here. Because both groups analyzed a supercritical pipeline system, their results can be compared directly. Table 4-1 presents a comparison of the line sizes the two groups used in their studies. Because the investment cost differences (and much of the annual operating costs) are essentially caused by line size differences, the costs estimated by Hare et al. (1978) would be expected to be much lower than those of Anada et al. However, the effect of line size differences is mitigated because of the years in which the cost estimates were performed. The costs developed by Hare et al. (in fourth-quarter 1978 dollars: Marshall and Swift (M&S) Index of 545.3) were required to be inflated by an additional 32% relative to those of Anada et al. (costs in first-quarter 1981 dollars: M & S Index of 721.3). All costs presented here have been inflated to 1986 dollars, with a M & S Index of 797.6. Capital cost estimates for the largest size pipeline vary from \$57 MM by Hare et al. (1978) to \$79 MM for Anada et al. (1982).

CO ₂ Flow rate	Pipeline Size (in.)		
(10 ⁶ kg/d)	Hare (1978)	Anada (1982)	
0.5		5	
2.6	8	10	
6.5	10	16	
13.0	14	22	
26.1	18	30	

Table 4-1. Comparison of Assumed Line Sizes for Supercritical Pipelines

Tractor-trailers are commonly used to haul liquid CO_2 ; their insulated steel containers have a maximum pressure of 300 psi. The cost of liquefaction could be avoided by transporting the vapor form under high pressure (1000 psi). According to Anada et al. (1982), a 1000 psi trailer could be constructed using current technology, but none is available. Based on the current design, trailer capacity in either case is 20,000 kg. The 1000 psi trailer was assumed to cost twice that of the 300 psi trailer. Truck transport is highly sensitive to labor costs, representing up to half of annual operating costs. Another 40% is accounted for by fuel and maintenance costs. It will be seen that a substantial portion of the transportation cost of liquid CO_2 is accounted for by the liquefaction costs.

Rail transport has the advantage of avoiding an initial capital investment, but it is complicated by other factors. Among these are the complexity of rail freight rates, the need to lease standard Department of Transportation (DOT) approved tank cars, the need to locate the microalgae-based fuel production plant near an existing rail line (if possible), and the greater rail mileage required to connect source with destination. The latter can be anywhere from 20% to 200% greater than the straight line distance

between the two. In their evaluation, Anada et al. (1982) found that no potential EOR sites were located within 20 miles of existing rail lines; this distance would most likely need to be covered by truck. A fuel production facility may or may not have more flexibility in location. The tank cars (DOT class 105A500W) have a capacity of about 75,000 kg; a typical 1000-ha microalgae facility would require 9-10 carloads daily (Neenan et al. 1986). Another potential advantage is the possibility of cheaper rail rates for large, steady volumes of traffic, such as after construction of a new facility. Rail transport might be suitable as a short-term option or for pilot-scale facilities, before a decision on large capital expenditures has been made.

Barge transport is feasible only for regions adjacent to navigable waterways, i.e., the Jackson Dome region of central Mississippi (Figure 3-1), and was not further considered by Anada et al. (1982), since they focused on the Permian Basin area of western Texas and the Williston Basin area of the Dakotas.

Figure 4-1 presents all the transportation cost estimates developed by Hare et al. (1978) and Anada et al. (1982), inflated to 1986 dollars as described above. All costs are based on a transport distance of 100 miles; additional estimates that were developed for longer distances are not included here in order to better focus on the primary cost factors for each mode of transportation. It is easily seen that the supercritical pipeline is most economical over a wide range of flow rates from 2.6-26 x 10^6 kg/d (50-500 MMSCFD). The costs estimated by Hare et al. (1978) are within 10% of those estimated by Anada et al. (1982) at all flow rates except the highest, where there is a difference of 20%. The subcritical pipeline design was estimated to be between 50%-100% more expensive than the supercritical pipeline, over the limited range of flow rates examined; these flow rates were the ones that Hare et al. (1978) felt to be the most economical based on a preliminary screening. The liquid pipeline option is clearly uneconomic, because of the costs of the liquefaction plant, which contributed up to 50% of the capital costs and 50%-75% of the operating costs to the total CO₂ transportation costs.

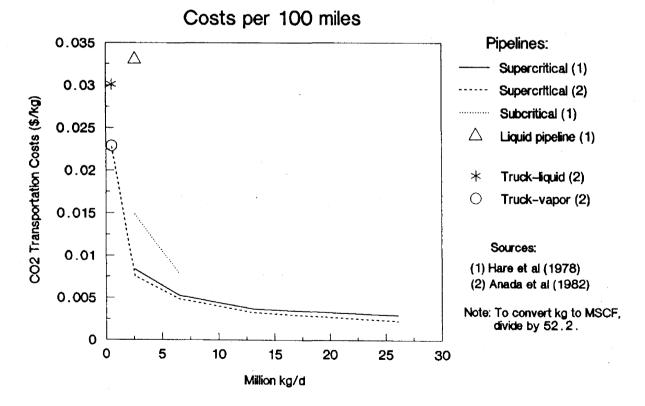


Figure 4-1. Transportation costs for various transportation options

At low flow rates such as 0.5×10^6 kg/d (10 MMSCFD), a tractor-trailer system carrying 1000 psi vapor might be economically competitive, especially for start-up or pilot-plant capacity. Although no other flow rates were examined by Anada et al. (1982), it would be very difficult to predict the same economies of scale for truck transport as are realized by the supercritical pipeline. The economics of transport of the liquid CO₂ are similarly uncompetitive to the liquid pipeline. Using Anada et al.'s (1982) estimate of \$0.009/kg for liquefaction costs (which seems to be based on the market price differential between vapor and liquid CO₂), liquefaction accounts for a full third of the transportation cost of the liquid, and makes it 25% more expensive than that of the high-pressure vapor trucks. Although tractor-trailer transport of liquid CO₂ will continue to be widely used in the food and chemical industries, the need to minimize transportation costs will probably render this option infeasible for energy-related industries such as EOR and microalgae-based fuel production.

Now that transportation costs have been estimated for a variety of options, they can be coupled with the recovery costs discussed in Section 3.0. Then, using the maximum allowable CO_2 cost for microalgae-based fuel production of \$0.032-0.054/kg (\$1.67-\$2.82/MSCF, based on data from Neenan et al. 1986), we can calculate the longest allowable distance that a given source of CO_2 can be economically transported. These data are plotted in Figure 4-2. For each CO_2 source, transportation costs for supercritical pipelines are calculated, based on the flow rates shown in Figures 3-4 and 3-5.

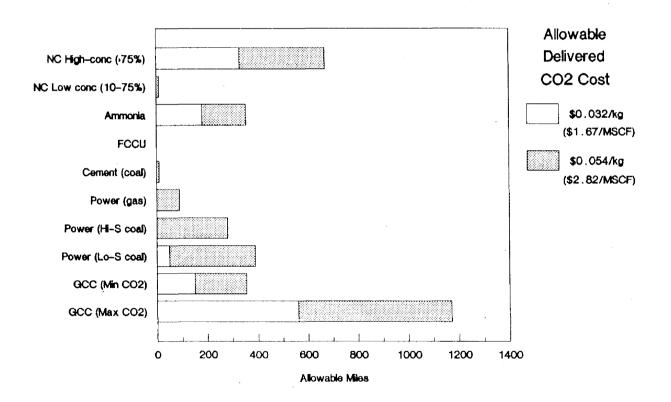


Figure 4-2. Allowable transportation distance based on CO₂ source (Source: Zimmerman et al. 1979)

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At the higher allowable CO_2 cost, various sources could be transported a distance of several hundred miles. Natural sources of CO_2 that can be recovered at a concentration of >75% and CO_2 from GCC power plants of the maximum CO_2 production design are clearly the best sources from the standpoint of allowable distance. The reasons for this are obvious: the high initial concentrations minimize recovery costs, and the high flow rates minimize per-mile transportation costs, especially for the GCC case. This case in fact has an estimated economic transportation distance of nearly 1200 miles, which is sufficient to reach the Permian Basin in Texas from Wyoming.

At the lower allowable cost, the situation is not so promising, nor are there the variety of possible economic CO_2 sources. Only the natural high-concentration and maximum CO_2 production GCC sources could be transported over 200 miles, and only two others, ammonia plants and minimum CO_2 production GCC power plants, could be transported over 100 miles. At this lower allowable CO_2 cost, some sources drop out altogether, including gas-fired and high-sulfur coal power plants, cement plants, and dilute noncommercial natural sources. Note that no methane credits are taken in the latter case, and that the conventional gas and coal-fired power plant calculations are highly dependent on the fuel cost, as discussed in Section 3.0.

5.0 ANALYSIS OF SEPARATION TECHNIQUES

The recovery of CO_2 from dilute streams (e.g., flue gas from cement and power plants) was discussed in some detail in Section 3.0. We placed particular emphasis on chemical absorption processes using alkanolamines and potassium carbonate. Separation costs are the major cost of recovering CO_2 from these sources. It is worthwhile to consider the entire range of CO_2 separation techniques, both commercial and noncommercial, to identify the potential improvements that could be achieved with further research. Thus an examination of the advantages and disadvantages of each process will be useful.

5.1 Physical Solvents

Physical solvents perform separations by selectively dissolving one gas over all others, then desorbing the gas in a low-pressure area. Physical solvents are only economical where the CO₂ partial pressure in the source is relatively high, at least 100 psi (Anada et al. 1982, 1983). Compare this with the flue gas from a coal-fired power plant: at atmospheric pressure and containing 15% CO₂, the CO₂ partial pressure is 15% x 14.7 = 2.2 psi, well below the 100 psi minimum. Physical solvents are used commercially only in the purification of natural gas (Ballou 1978). The major processes used are the Sulfinol process (using a mixture of alkanolamine, water, and sulfolane, this is actually a combination physical-chemical solvent process); the Rectisol process (typically using methanol at low temperatures, e.g., 0°C); the Purisol process (using N-methyl-2-pyrrolidinone at 570-1000 psi); and the Fluor process (using propylene carbonate). These processes could be used commercially for dilute CO₂ sources, but the cost of compression would make them uneconomical.

5.2 Chemical Solvents

As discussed in Section 3.0, the two most commonly used chemical solvents utilized for CO_2 separation are amines, e.g., MEA or diglycolamine (DGA), or potassium carbonate. Chemical solvents actually react with the CO_2 chemically to form another chemical species (e.g., KHCO₃); they are well suited to CO_2 partial pressures as low as 6.89 kPa (1 psia). These processes can also be operated at elevated pressures; the increased absorption of CO_2 into the solvent and decreased steam consumption can partially offset the higher costs of compression. Alkanolamine processes usually require some sort of corrosion inhibitors as well. This is especially true as solvent concentrations are increased in pursuit of higher CO_2 loading rates per unit mass of solvent. Schendel (1985) discussed the need for further improvements in corrosion, loading rates, and energy utilization in chemical solvent processes.

5.3 <u>Membranes</u>

The use of membrane filtration processes for CO_2 recovery has to this point been restricted to the processing of associated gas from oil wells (Stookey and Pope 1985). As with physical solvent processes, the effectiveness of CO_2 recovery depends strongly on CO_2 partial pressure. Another consideration is the trade-off between membrane selectivity and permeability. Selectivity is the ratio of permeation rates; e.g., of CO_2 versus N₂. Higher selectivities inevitably lead to lower overall permeation rates, which in turn require larger and more expensive membrane installations. For flue gases, two-stage processes would probably be required: the first stage would produce a permeate of 30%-35% CO_2 , and would be followed by interstage compression. The second stage could then produce a 90% permeate. Stookey and Pope believe this scheme to be technically viable, but feel it is likely to be uneconomic for quite some time, because of compression costs. The continuing growth of membrane use in associated gas recovery, as well as the upgrading of low-Btu fuel gas to medium-Btu gas, should provide some incentives for further technical improvements.

5.4 Cryogenic Distillation

Using reduced temperatures can modify the relative volatility of mixtures containing CO_2 . In theory, this should make cryogenic separations of CO_2 fairly easy, but in practice, certain complications occur that make such separations more difficult (Holmes et al. 1985). One factor is the tendency of CO_2 mixtures to solidify under the conditions one would choose for separation. In particular, solid CO_2^{-1}

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 CH_4 mixtures can be formed at pressures higher than the critical pressure of CH_4 , so a phase of pure CH_4 cannot be recovered at constant pressure without passing through the solid phase. Similar problems occur for mixtures of CO_2 and N_2 , although at different temperatures and pressures. CO_2 can be recovered cryogenically from flue gas at high pressures, which would require precompression. According to Holmes, inlet composition must be at least 20%, and the feed must also be dried. Another drawback is the presence of 15%-30% CO_2 in the residual product; further recycling would be necessary to increase the overall recovery of CO_2 . Alternatively, one can take advantage of the tendency of CO_2 to form azeotropes by adding a third component (e.g., butane) to the CO_2 -N₂ or CO_2 - CH_4 mixture. The distillation can then be operated at higher temperatures and pressures, preventing freezing and lowering refrigeration requirements. CO_2 recovery is increased, and more flexibility of feed conditions is allowed.

5.5 <u>Electrochemical CO₂ Carriers</u>

SERI is currently evaluating electroactive CO_2 carriers for use aboard spacecraft (Bell et al. 1988). Preliminary results indicate the potential for very low-energy CO_2 transport.

5.6 Separation Energy Requirements

The theoretical and practical (state-of-the-art) energy requirements for separation of CO_2 from flue gas are summarized in Table 5-1. The state-of-the-art data for the chemical solvent processes were calculated directly from the base case and the optimistic designs of Anada et al. (1982). Both thermal and electrical energy were included, although for these processes, thermal energy accounts for more than 99% of the total energy consumption. The actual energy consumed is greater than the theoretical by factors of between 12 and 27, implying that further energy savings could be achieved. Note the significant energy savings of the potassium carbonate process over MEA, mainly because of lower operating temperatures. These processes are still about equally employed, proving that energy savings do not always govern the process economics. The optimistic designs, which incorporate both lower operating temperatures and lower solvent loading ratios, result in energy savings of 25%-30% compared to the base case designs.

Table 5-1.	Theore	tical versu	is Sta	ate-of	-the-A	rt Ei	nergy
Requireme	ents for	Separatio	n of	CO₂ :	from	Flue	Gas
-		(kWh/	kg)				

	Theoretical	Practical (State-of-the-art)
Chemical solvents:		· · · · · · · · · · · · · · · · · · ·
MEA		
base case	0.05 (work)	2.96 (heat)
optimistic	0.05 (work)	2.10 (heat)
K ₂ CÔ ₃	•	
base case	0.05 (work)	1.74 (heat)
optimistic	0.05 (work)	1.28 (heat)
membranes	0.05 (work)	0.98 (work)

Sources: Anada et al. (1982); Mazur and Chan (1982)

For the membrane system, the energy requirement takes the form of compression work (Mazur and Chan 1982). Although less energy is required for this process than for the chemical solvent process, there is still room for significant energy savings. The current state of the art for membrane separation of flue gas requires high membrane feed pressures: 515 psia or more. Technical improvements in selectivity and permeability could allow lower operating pressures, lowering the energy consumption for these processes.

6.0 CONCLUSIONS

The results of our study indicate that there are several large sources of CO_2 that could support microalgae-based fuel production. The possible quantities and costs of CO_2 are listed in Table 6-1.

The lowest cost sources of CO_2 are from systems that produce CO_2 at high pressure and in high concentration. These systems include liquid and gaseous synthetic fuel plants, and gasification-combined cycle power plants. From these sources, a total of 260-1050 x 10⁹ kg (5.0-20.1 TSCF) per year of CO_2 could be available at a price of \$0.012-\$0.016/kg (\$0.64-\$0.85/MSCF). CO_2 costs will be higher or lower because of variations in flow rate, allocation of costs between main product and CO_2 , process operating pressures, and other factors. Based on a requirement of 80 x 10⁹ kg CO_2 /quad (10¹⁵ Btu) of microalgae-derived liquid fuel, we estimate that sufficient CO_2 from these sources is available to support 3.3-13.1 quads annually of microalgae-based liquid fuel production. Gasification-based combined cycle power plants have been included in this total, even though only one commercial plant of this design exists. If this type of plant design gains favor with electric utilities, a significant portion of the estimated 790 x 10⁹ kg/yr of CO_2 could actually be produced.

If these sources were not adequate or available in a particular location, low-pressure, high-purity sources could be exploited. These sources include recovery from ammonia plants, ethanol fermentation plants, and depleted oilfields that have been flooded with CO_2 in EOR operations. A total of 17-41 x 10⁹ kg (0.3-0.8 TSCF) per year is potentially available from these sources. The costs of recovering CO_2 from these sources range from \$0.009-\$0.016/kg (\$0.47-\$0.85/MSCF). This CO_2 would support an additional 0.2-0.5 annual quads of microalgae-based fuel production, bringing the total from high-purity sources to 3.5-13.6 annual quads.

An additional 321-1159 x 10^9 kg (6.1-22.2 TSCF) per year of CO₂ could be available from high- and low-pressure dilute streams, primarily flue gas from coal-fired power plants and biomass anaerobic digestion plants. This quantity, which could be available in a 10-state region in the sunny part of the United States, is enough to support 4.0-14.5 annual quads of microalgae-based fuel production. However, except for special cases, e.g., high demand for biogas leading to natural gas pipeline companies bearing the cost of CO₂ separation from biogas, recovery of CO₂ from such dilute streams is expensive, ranging from \$0.029-\$0.095/kg (\$1.50-\$5.00/MSCF). For flue gas, the situation is further complicated by the presence of sulfur compounds. Unless improved separation processes are developed, these sources may not be economical for microalgae-based liquid fuel production.



CO ₂ Source		Potential CO ₂ (10 ⁹ kg/yr)	Estimate (1986 \$/kg) (19	
Concentrated, high-pressure sour Liquid synthetic fuels plants Gaseous synthetic fuels plants	ces:	40 220	0.012-0.016	0.64-0.85
Gasification-based combined cyc power plants	cle	0-790		
	Subtotal	260-1050		
Concentrated, low-pressure source Enhanced oil recovery ^{ab} Ammonia plants Ethanol plants	ces:	8-32 9 < 0.1	0.009-0.016	0.47-0.85
	Subtotal	17-41		
Dilute, high-pressure sources: Noncommercial natural gas ⁴ Refineries ⁶		52-100 13	0.011-0.053 0.054-0.095	0.57-2.77 2.80-5.00
Dilute, low-pressure sources: Anaerobic digestion (biomass) Anaerobic digestion (wastes) Cement plants Fossil-steam power plants ^{&}		130 100 26 0-790	0.011-0.084 0.051-0.084 0.029-0.048	0.57-4.40 2.78-4.40 1.50-2.50
	Subtotal	321-1159		<u></u>

Table 6-1. Potential Sources of CO₂ for Fuel Synthesis in 2010

a Assumes 25-yr depletion

b Based on 20% recycle of CO₂ used for EOR

c Includes FCCU and hydrogen plants

d Totals for 10-state region (AL, AZ, CA, FL, GA, LA, MS, NM, OK, TX)

e Based on DOE projections for 2010

Sources: Zimmerman et al. (1979); Anada et al. (1982); DOE (1983, 1987); Nelson (1983)

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7.0 REFERENCES

- Anada, H., D. King, A. Seskus, M. Fraser, J. Sears, and R. Watts, 1982, *Feasibility and Economics of By-Product CO*₂ Supply for EOR, DOE Report No. DOE/MC/08333-3.
- Anada, H.R., M.D. Fraser, D.F. King, A.P. Seskus, and J.T. Sears, 1983, "Economics of By-Product CO₂ Recovery and Transportation For EOR," *Energy Progress*, Vol. 3, No. 4, p. 233.
- Ballou, W.R., 1978, "Carbon Dioxide," in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., NY: Wiley Interscience, Vol. 4, p. 725.
- Barry, G.F., C.S. Wang, K.C. Chang, A.M. Wolsky, and U.S. Choi, 1986, A Modeling Study of Pulverized Coal Combustion in CO₂/O₂ Atmospheres, ANL Report No. ANL/CNSV-57.
- Bell, W.L., A. Miedaner, J.C. Smart, D.L. DuBois, and C.E. Verostko, 1988, Synthesis and Evaluation of Electroactive CO₂ Carriers, submitted to the 18th Intersociety Conference on Environmental Systems, San Francisco, July 11-13.

Chemical and Engineering News, November 26, 1984, p. 20.

- Chemical and Engineering News, May 19, 1986, p. 16.
- Chemical and Engineering News, June 8, 1987, p. 27.
- CRC Handbook of Chemistry and Physics, 1979, Weast, R.C., ed., Boca Raton, FL: CRC Press, p. F-198.
- Ember, L.R., P.L. Layman, W. Lepkowski, and P.S. Zurer, 1986, "Tending the Global Commons," *Chemical and Engineering News*, November 24, p. 14.
- Froning, H.R., D.D. Fussell, and E.W. Heffern, 1982, "Petroleum (Enhanced Oil Recovery)," in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., NY: Wiley Interscience, Vol. 17, p. 168.
- Goodman, B., 1988, unpublished data.
- Hare, M., H. Perlich, R. Robinson, M. Shah, and F. Zimmerman, 1978, Sources for Delivery of Carbon Dioxide for Enhanced Oil Recovery, DOE Report No. FE-2525-24.
- Holmes, A.S., 1985, "Recovery of Carbon Dioxide from Man-Made Sources Using Cryogenic Distillation Techniques," in *Recovering Carbon Dioxide from Man-Made Sources: Proceedings of* a Workshop Held in Pacific Grove, CA January 11-13, 1985, A.M. Wolsky and C. Brooks, eds., Argonne National Laboratory Report No. ANL/CNSV-TM-166, p. 63.

Information Resources, Inc., Alcohol Outlook, July 1987.

- Klass, D.L., 1980, "Fuels from Biomass," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., NY: Wiley Interscience, Vol. 11, p. 334.
- Laurmann, J.A., 1985, "Market Penetration of Primary Energy and its Role in the Greenhouse Warming Problem," *Energy*, Vol. 10, No. 6, p. 761.
- Laurmann, J.A., 1986, *Future Energy Use and Greenhouse Gas Induced Climatic Warming*, Presented at the CEC Symposium on CO₂ and Other Greenhouse Gases: Climatic and Associated Impacts, Brussels, Belgium, November 3-5.

SERI 🏶

- Linder, K.P., and M.J. Gibbs, 1987, Potential Impacts of Climate Change on Electric Utilities: Project Summary, presented at Air Pollution Control Association Annual Meeting, New York, June 21-26.
- Lowenheim, F.A., and M.K. Moran, 1975, "Urea," in Faith, Keyes, and Clark's Industrial Chemicals, 4th Ed. NY: Wiley-Interscience, p. 854.
- Mazur, W.H., and M.C. Chan, 1982, "Membranes for Natural Gas Sweetening and CO₂ Enrichment," *Chemical Engineering Progress*, Vol. 78, No. 10, p. 38.

Mohun, R., 1988, personal communication, March 2.

- Neenan, B., D. Feinberg, A. Hill, R. McIntosh, and K. Terry, 1986, Fuels from Microalgae: Technology Status, Potential, and Research Requirements, Report No. SERI/SP-231-2550, Golden, CO: Solar Energy Research Institute.
- Nelson, S.H., 1983, Availability of Carbon Dioxide for Production of Microalgal Lipids in the Southwest, Argonne National Laboratory Report No. ANL/CNSV-42.
- Schendel, R.L., 1985, "CO₂ Recovery by Liquid Absorption Processes," in *Recovering Carbon Dioxide from Man-Made Sources: Proceedings of a Workshop Held in Pacific Grove, CA January 11-13, 1985*, A.M. Wolsky and C. Brooks, eds., Argonne National Laboratory Report No. ANL/CNSV-TM-166, p. 46.
- Snyder, W.G., and C.A. Depew, 1986, Coproduction of Carbon Dioxide (CO₂) and Electricity, Report No. AP-4827, Palo Alto, CA: Electric Power Research Institute.
- Steinberg, M., H.C. Cheng, and F. Horn, 1984, A Systems Study for the Removal and Disposal of Carbon Dioxide from Fossil Fuel Power Plants in the U.S., DOE Report No. DOE/CH/00016-2.
- Stern, K.M., 1986, "Review of Current and Potential Future CO₂ Sources," *Energy Progress*, Vol. 6, No. 3, p. 191.
- Stookey, D.J., and W.M. Pope, 1985, "Application of Membranes in Separation of Carbon Dioxide from Gases," in *Recovering Carbon Dioxide from Man-Made Sources: Proceedings of a Workshop Held in Pacific Grove, CA January 11-13, 1985*, A.M. Wolsky and C. Brooks, eds., Argonne National Laboratory Report No. ANL/CNSV-TM-166, p. 53.
- Taber, J.J., 1985, "Need, Potential and Status of CO₂ for Enhanced Oil Recovery," in *Recovering Carbon Dioxide from Man-Made Sources: Proceedings of a Workshop Held in Pacific Grove, CA January 11-13, 1985*, A.M. Wolsky and C. Brooks, eds., Argonne National Laboratory Report No. ANL/CNSV-TM-166, p. 11.
- Tornabene, T.G., A. Ben-Amotz, S. Raziuddin, and J. Hubbard, 1983, "Chemical Profiles of Microalgae with Emphasis on Lipids," Final Report for SERI Subcontract No. XK-2-02149-1 (portions also published in *Screening for Lipid Yielding Microalgae*, Final Subcontract Report SERI/STR-231-2207), Golden, CO: Solar Energy Research Institute.
- U.S. Department of Commerce, Bureau of Census, 1987, Current Industrial Reports: Industrial Gases.
- U.S. Department of Energy (DOE), Energy Information Agency, 1986a, *Coal Production 1985*, DOE Report No. DOE/EIA-0118(85).
- U.S. Department of Energy (DOE), Energy Information Agency, 1986b, Inventory of Power Plants in the United States 1985, DOE Report No. DOE/EIA-0095(85).

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- U.S. Department of Energy (DOE), Energy Information Agency, 1987a, U.S. Crude Oil, Natural Gas, and Natural Gas Liquids Reserves 1986, DOE Report No. DOE/EIA-0216(86).
- U.S. Department of Energy (DOE), Energy Information Agency, 1987b, *Electric Power Annual 1986*, DOE Report No. DOE/EIA-0348(86).
- U.S. Department of Energy (DOE), Office of Policy, Planning, and Analysis, 1983, *Energy Projections* to the Year 2010, DOE Report No. DOE/PE-0029/2.
- Watson, K.D., and D.G. Siekkinen, 1986, "Sheep Mountain CO₂ Project Development and Operation," *Energy Progress*, Vol. 6, No. 3, p.155.
- Wolsky, A.M., 1985, "A New Approach to CO₂ Recovery from Combustion," in Recovering Carbon Dioxide from Man-Made Sources: Proceedings of a Workshop Held in Pacific Grove, CA January 11-13, 1985, A.M. Wolsky and C. Brooks, eds., Argonne National Laboratory Report No. ANL/CNSV-TM-166, p. 76.
- Wolsky, A.M., and D.J. Jankowski, 1986, "The Value of CO₂: Framework and Results," J. Petroleum Technology, September, p. 987.
- Yeager, K.E., and S.B. Baruch, 1987, "Environmental Issues Affecting Coal Technology: A Perspective on U.S. Trends," *Annual Reviews of Energy*, Vol. 12, p. 471.
- Zimmerman, F.W., C.W. Perry, and P.L. Shaw (Appendix) 1979, Naturally Occurring Carbon Dioxide Sources in the United States, DOE Report No. FD-2025-38.

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