REDUCTION, CAPTURE and REMEDIATION OF CARBON DIOXIDE

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ABSTRACT

Technological approaches to reduction in carbon dioxide (CO_2) production are driven by philosophical and political considerations. Operational requirements for CO_2 reduction cannot be fully satisfied by economic redistribution, or green energy save, perhaps, nuclear energy. Future carbon management strategies must include CO_2 sequestration and CO_2 utilization. Each require new more efficient separation and capture methods. Source stream concentration, environmental issues, cost and scale-up issues predominate in method selection. We are developing new highly efficient methods for CO_2 capture suited to both ambient and off-gas CO_2 containing streams.

GREEK

1. INTRODUCTION

Carbon dioxide (CO_2) is the major contributor to greenhouse gases (GHG) and thus to global warming (GW). This is due to the huge volume emitted each year and its lifetime in the atmosphere. Yearly anthropogenic production is about 6 B MT with a resulting increment or burden of about 3 B MT allowing for uptake by terrestrial and oceanic systems. It is strongly believed that continued and increasing CO_2 emissions will result in severe and unpredictable changes in global weather patterns. There is a clear and positively sloped relationship between gross domestic product (GDP) and energy use, currently commensurate with CO_2 emissions. There is wide agreement, viz. accords reached at Rio and Kyoto, that CO_2 emissions must be reduced sharply and soon.

1.1 Philosophical and Strategic Approaches to CO_2 Reduction

At these meetings several philosophic positions and strategies have emerged to deal with GHG emissions and GW (Table I). One position is to alter the current energy economy by reducing demand, i.e., decreasing total energy use and likely altering lifestyle patterns. One strategy consistent with this position is to go on a massive energy diet, i.e., to reduce utilization of GHG producing chemicals. This would be realized by a combination of efficiency-based energy savings coupled with reduced demand by altered lifestyles. Another strategy in this direction is to move to a “cash economy,” i.e., to consume only as much energy as can be derived each year from renewable energy sources – biomass, wind, wave, geothermal, etc.

PHILOSOPHY	DESCRIPTOR	STRATEGY	CO_2 CAPTURE REQUIRED
Decrease Demand			
	Massive Diet		
		Reduced Lifestyle / Redistribute Pollution Allowances	
		Energy Efficiency	
	Cash Economy		
		Renewable Energy Sources	Yes
Maintain Demand			
	Alternate Fuels		
		Nuclear Energy	
		Decarbonized Fuels	Maybe
	New Uses		
		New Materials	Yes
		Chemically Reduce &	Yes

		Re-consume	
	Sequestration		
		Store in Mines & Wells	Yes
		Store in Ocean	Yes
		Store in Terrestrial Minerals	Yes

Table I. CO_2 Production / Use Alternatives

A second philosophic position supports the idea of continued high level energy consumption but relies on technological solutions to reduce GHG emissions. One approach consistent with this philosophy is to increase use of nuclear fuels. Another is to move to a decarbonized economy by converting carbon-containing fuels to carbon-free fuels, e.g., hydrogen. Another approach consonant with continued consumption is to continue to use fossil fuels but to remove as much CO_2 as enters the atmosphere so that the net carbon budget change is zero even negative. This could be accomplished by sequestering the CO_2, by using it in manufacturing processes to create new materials or by reducing it to another fuel to be burned once again. The sequestration options include deposition of the CO_2 as a gas, in abandoned wells or mines or in currently active oil or gas fields, or as a liquid, i.e., as clathrates, deep in the ocean, or as a solid in the ocean or on land.

1.2 Consideration of Alternate Philosophies and Strategies

Efforts to reduce demand or to redistribute pollution allowances to “equalize” opportunity for developing nations are likely to be strongly modified if not fail for several reasons. First, energy consumption is correlated with economic development thus, new more efficient plants excepted, the sheer increase in numbers of economically better off individuals the more energy use the more pollution. The efficiency savings are in no way commensurate with demand. Second, the inherent concept of a consumer economy is anathema to demand reduction.

Efforts to utilize solar, wind, waves, geothermal and biomass energy sources at best will satisfy only a small percentage of current not to mention future energy needs. Wind, wave and geothermal energy are limited to specific geographies. Solar energy capture efficiency continues to show strong increase and will be more of a contributor but an area about 0.8% of the U.S. would be needed to supply current U.S. energy needs. Similarly, at current efficiencies about 1/3 of the U.S. surface would have to be devoted to biomass production to satisfy current production levels. These technologies cannot replace fossil fuels without reduction in demand. Rather, their role is to supplement fossil fuel and thereby make a contribution to reduction in net CO_2 emission.

Alternate fuels are one way to maintain demand while reducing CO_2 emissions. The debate and concerns over nuclear energy are well known and require no further discussion.

Decarbonized fuels are a method for producing more hydrogen-enriched materials while trapping the carbon as a solid that can be stored as a terrestrial product. Were electric generating plants to become hydrogen producers by these methods their distribution would be broad enough to enable a hydrogen economy, for vehicles for example, with moderate, localized pipeline construction. While not likely to occur for one or more decades this approach has considerable promise.

In contrast to all of the foregoing solutions each of which serves to reduce CO_2 emissions the strategies of New Uses and Sequestration assume that carbon containing fuels, oil, gas and coal would continue to be combusted as they are today but that the emitted CO_2 would be captured and trapped. New Uses might involve new chemistries or enlarged use of existing carbon containing materials, e.g., wood, in construction where now metals or stone are used. Chemical reduction of CO_2 to a fuel - CO or CH_4 - implicitly assumes that solar energy is collected and used to power the reduction.

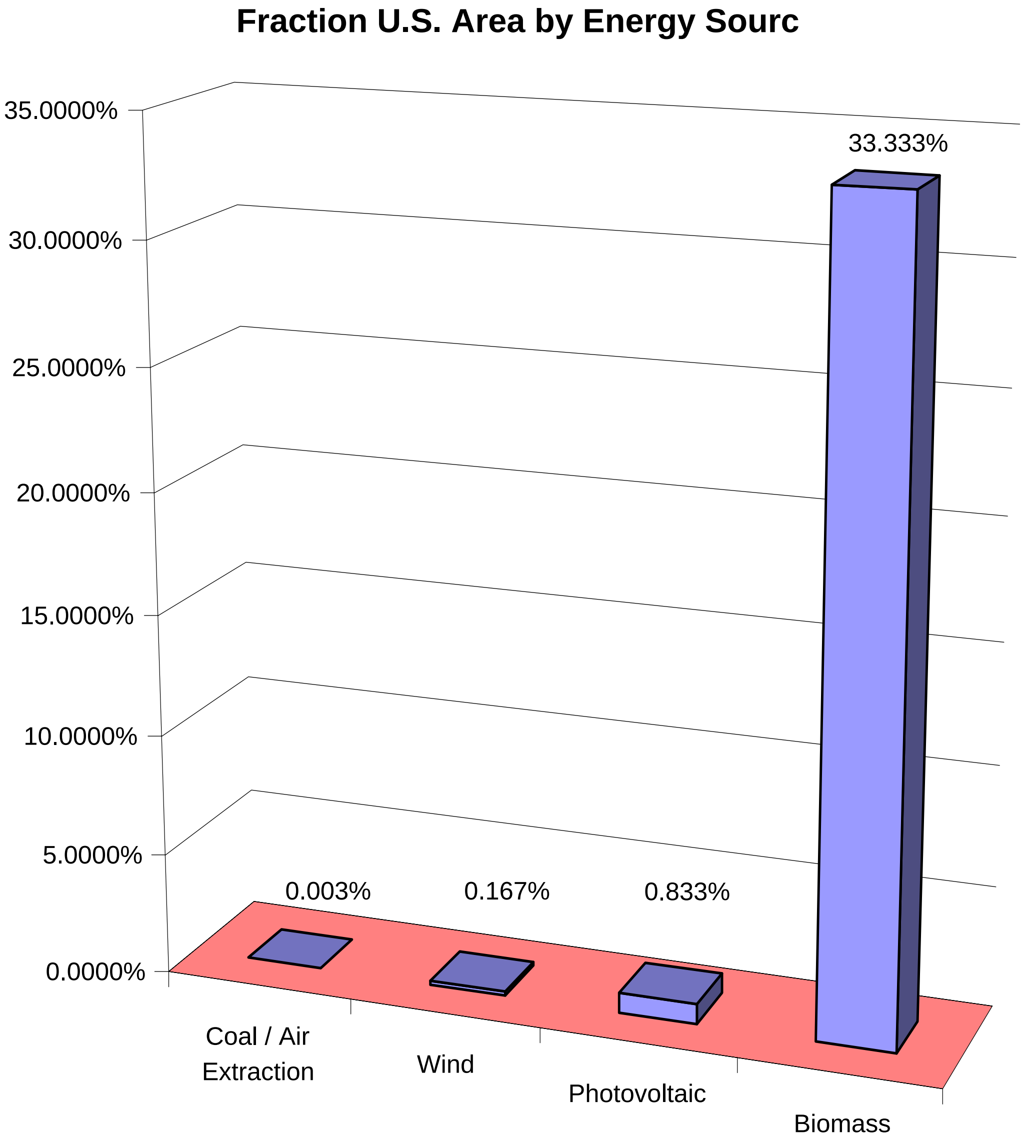

Fig. 1. Land area required for various CO_2 reduction options.

Sequestration is by far the largest magnitude option capable of storing all of the CO_2 emitted. Storage in mines and wells has some risk of release though, in some cases there are benefits such as enhanced gas or oil production. Ocean storage is difficult because of the depth required and because many point sources are quite far from deep ocean. Pipeline costs could be significant and would pose definable risks. Storage in terrestrial minerals is gaining attention, as there are sufficient cation reserves to sequester all of the CO_2 emitted.

With each of these solutions the technology is either not yet mature or too costly to be accepted. None-the-less one factor in common for many of these approaches is the need to capture large quantities of CO_2 either at ambient concentration (0.035%) or at smokestack concentrations which range from 4-24%. This distinction is important, as many current technologies are incapable of scouring CO_2 at ambient concentrations but would perform acceptably, though not economically, at the higher concentrations. The importance of an economical capture method is appreciated by realizing that the U.S. DOE estimates that capture accounts for as much as 3/4 of the cost of sequestration.

Due to the insensitivity of current capture methods, and considering the lesser volumes of gas which must be processed and the ease of identifying point sources traditional engineering would prefer stack gas cleanup. However, even fully efficient this approach would account for no more than 1/3 to 1/2 of the CO_2 emitted. In contrast extraction of CO_2 from ambient streams would allow an equitable distribution of costs in addition to being able to remove CO_2 from the atmosphere independent of emitting source.

Removing CO_2 directly from the atmosphere has several advantages compared to recovering CO_2 from point sources. The advantages include: elimination of the need for CO_2 compression, liquefaction transportation, and storage; allow the location of power plants and other industrial plants to be dictated by factors other than the cost of transporting CO_2 as the disposal or storage site would not have to be close to the site where CO_2 is generated; allow recovery from both point sources and distributed sources such that the cost of sequestration would not need to be borne disproportionately by a single industrial sector.

A rational choice between these two alternatives depends on a clear understanding of the relative costs – capital and operating, expressed in dollars, risk and uncertainty. These include not only the amount of gas processed but siting costs, transportation costs, pipeline development and operation, and safety.

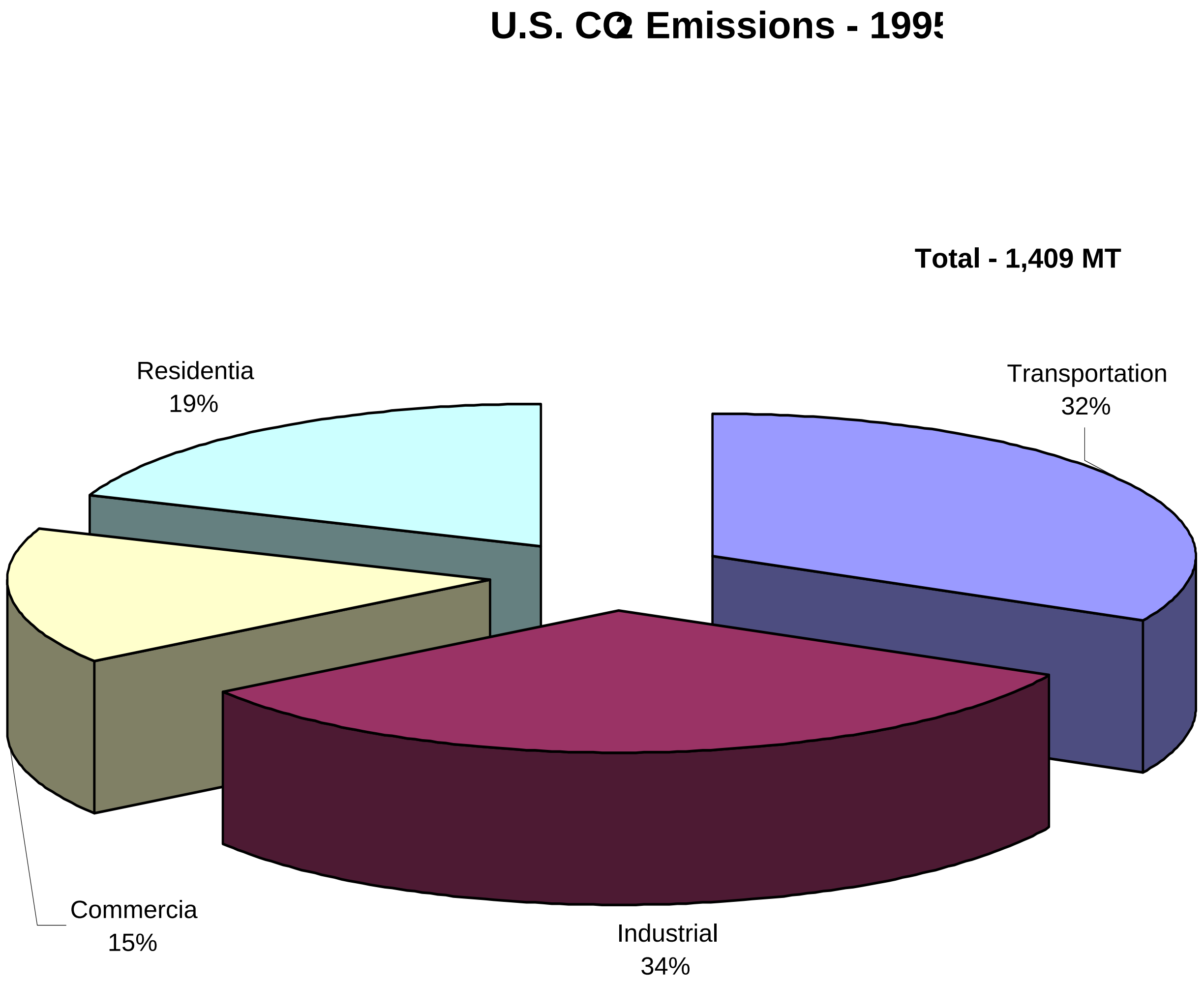

Fig. 2. U.S. CO_2 Emission by Sector

1.3 Biomimetic Capture of CO_2

To allow for each of these two options we have been developing a new class of enzyme enhanced facilitated transport liquid membranes for selective extraction of CO_2. These have high flux, high selectivity and high sensitivity yet capable of operating over a large range of CO_2 concentrations.

The enzyme carbonic anhydrase (CA – E.C. 4.2.1.1) is uniquely tailored to accomplish this goal. Millions of years of evolution have selected for its attributes as the premier CO_2 catalyst. It occurs naturally with considerable variation (isozymes) and they are found in virtually every species from bacteria to plants, to mammals. Any given isozyme can be selected for specific operating conditions, e.g., high operating temperatures. The enzyme reacts specifically with CO_2 to form bicarbonate and does so at a rate of as fast as 10^6 moles CO_2 mole Enz^{-1} s^{-1}. The reaction is carried out at ambient temperature and pressure and normal pH. All spent products are fully biodegradeable. This approach provides a new opportunity for management of the greenhouse gas CO_2. These membrane systems can capture CO_2 directly from air with separation ratios to oxygen (and nitrogen) of at least 200:1.

2.0 Experimental Results

As a homogeneous catalyst a CA-based facilitated transport reactor successfully removed CO_2 from air-CO_2 mixtures with pCO_2 ranging from 0.035 to 10%. The CO_2:O_2 separation ratios were 206:1 at 0.1% CO_2, 74:1 at 1% CO_2 and 26:1 at 10% CO_2. These corresponded to flux rates of about 10^{-8} moles CO_2 cm cm^{-2} kPa^{-1} s^{-1} at 0.1% CO_2 (equivalent to 0.224 cm^3 cm cm^{-2} kPa^{-1} s^{-1}). It is likely that there was insufficient enzyme reaction material at the gas interface to allow the enzyme to operate as efficiently at the higher concentrations as it did at the lower concentrations.

The enzyme is extremely stable, as it must to achieve our objective of a one-year lifetime. In our experience it can be stored under a variety of cold conditions in solution or lyophilized for period ranging from two to five years. At room temperature the solution lifetime is over one year and under operating conditions it is more than three months.

We have also carried out mutations of the enzyme to increase its stability and to foster immobilization of the enzyme in the reactor. These mutants can be bound to metal moieties in a reversible fashion to allow replacement of the active catalyst without replacement of the membrane reactor to which it binds covalently.

ACKNOWLEDGEMENTS
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