

DECARBONIZATION AND SEQUESTRATION FOR MITIGATING GLOBAL WARMING

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ABSTRACT

Mitigating the global warming greenhouse effect while maintaining a fossil fuel economy, requires improving efficiency of utilization of fossil fuels, use of high hydrogen content fossil fuels, decarbonization of fossil fuels, and sequestering of carbon and CO₂ applied to all the sectors of the economy, electric power generation, transportation, and industrial, and domestic power and heat generation. Decarbonization means removal of carbon as C or CO₂ either before or after fossil fuel combustion and sequestration means disposal of the recovered C or CO₂ including its utilization. Removal and recovery of CO₂ from power generation plants and sequestration in the ocean represents one possibility of making a major impact on reducing CO₂ emissions to the atmosphere. This paper will briefly review the progress made in ocean disposal and present some alternative schemes.

Key Words: Decarbonization, sequestration, ocean disposal, methane hydrates, methanol, fuel cells, carbon

INTRODUCTION

Through a series of UN sponsored International World Meetings in Japan, Brazil, Germany and other locations, the world has recognized the problem of global warming due to emission of greenhouse gases especially carbon dioxide.⁽¹⁾ Through a series of scientific and technical meetings⁽²⁾, CO₂ mitigation technology has gained a great deal of attention. Many methods and concepts of dealing with preventing CO₂ from entering the atmosphere have been proposed and developed. Although the connection between fossil fuel combustion and utilization for energy purposes with the physics and chemistry of atmospheric CO₂ content and energy absorption has gained undisputed acceptance, the issue of global warming with respect to climate change and its effect on the global environment has elements of uncertainty. Because the implementation of CO₂ mitigation technologies could potentially result in severe economic penalties, a number of countries has been reluctant and slow to endorse and adopt these measures. However, the world can ill-afford to ignore the possible consequences resulting from global warming. Thus research must proceed in developing CO₂ mitigation technologies in order to minimize the potential economic penalties.

The major mitigating technologies conceived of so far are listed as follows:⁽³⁾

1. Improve efficiency of conversion of fossil fuels and the use of the energy produced by fossil fuels.
2. Switch to fuels that have higher hydrogen content such as natural gas.

3. Decarbonization of fossil fuels which means the removal and recovery of carbon either as CO₂ or as elemental carbon prior to combustion, or removal and recovery of CO₂ post combustion from central power stations.
4. Sequestration which means the disposal of the recovered CO₂ in the following sinks:
 - a) the ocean
 - b) aquifers
 - c) depleted oil and gas wells, enhanced oil recovery (EOR)
 - d) in mineral matter
 - e) salt domes
 - f) in deep coal deposits displacing adsorbed methane
 - g) in ocean sediments displacing methane in hydrates.
5. Plant trees and grasslands to increase photosynthesis of atmospheric CO₂
6. Use of non-fossil energy sources: biomass, nuclear and solar
7. Convert CO₂ to chemicals, materials and alternative fuels

Ocean Sequestration

Marchetti⁽⁴⁾ first proposed disposal of CO₂ in the ocean by pointing out that if CO₂ were injected in the Mediterranean at the Straits of Gibraltar, the CO₂ would be swept into the Atlantic by the undercurrent stream spilling into the Atlantic Ocean. Recognizing that the surface ocean is in equilibrium with the atmosphere, and that there is no CO₂ dissolved in the ocean below the thermocline, at Brookhaven National Laboratory we made the first studies of ocean disposal of CO₂ separated from central power plant stacks by pumping CO₂ below the thermocline at depths of 500 m and 3000 m.⁽⁵⁾ We also recognized that at below 3000 m the density of the liquid CO₂ is greater than the density of the ocean at that depth and that liquid CO₂ will sink to the bottom and form a lake on the ocean floor. We now know that hydrates can be formed which lowers the activity of the liquid CO₂ so that its dissolution in the ocean is further reduced. Our first studies indicated that the cost of production of electricity with CO₂ removal, recovery and ocean disposal from power plants would increase by between 75 and 100% over current costs. Due to more recent improvement in removal and recovery processes, which represents the bulk of the cost, this economic penalty can be reduced to about 50% increase in cost which, however, strongly depends on how far the power plant is located from the ocean. We also indicated that of the three physical forms for disposal of CO₂, gaseous, liquid and solid, due to compression cost, liquid disposal was the most economical.

International CO₂ Sequestration Projects

Much subsequent studies on ocean disposal has been made in the U.S. particularly at MIT⁽⁶⁾ and in Japan⁽⁷⁾ which you will much further learn about in this symposium. These studies have lead to an international experiment involving the U.S., Japan and Norway, which is currently in progress, designed to demonstrate the technology and the effects of pumping liquid CO₂ into the Pacific Ocean at the rate of about a Kg/Sec off the coast of Hawaii. The experiment is designed to determine the diffusion of the CO₂ from the point of entry and to measure pH changes among other aspects.

Although not exactly direct ocean disposal, a project that has been underway for more than a year by Statoil, a Norwegian oil company in the North Sea. CO₂ is separated from natural gas wells under the sea and the recovered CO₂ is pumped back into aquifers under the North Sea. About one million tons of CO₂ per year is disposed of in this fashion. Norway has a \$50/ton carbon tax, thus the company saves this cost and appears to be a benchmark for the cost of removal, recovery and disposal of CO₂.⁽⁸⁾

A project has been initiated between the U.S. and Canada concerning the sequestration of CO₂ in coal bedded methane. The deposits of coal are deep and usually cannot be economically mined. However, they contain adsorbed deposits of methane and could develop into economically productive gas wells. The concept is to pump CO₂ down into these deposits and displace the CH₄ with CO₂. The adsorption affinity and capacity of these coal deposits for CO₂ is about twice that of CH₄ and so the CO₂ remains sequestered while the methane is removed^(9, 9a). In some respects this method is similar to the use of CO₂ in enhanced oil recovery (EOR) in which compressed CO₂ is used to force oil out of depleted oil wells.

Another project involve pumping CO₂ into saline aquifers underground is progressing in the U.S.⁽¹⁰⁾

Advanced Concepts

Displacement of Methane Hydrates

There is increasing interest in methane hydrates under the ocean as an energy source. It is estimated that there is more than twice the amount of fossil fuel energy deposited in methane hydrates than in all fossil fuel coal, gas and oil deposits existing in the world.⁽¹¹⁾ The problem is how to recover this methane in an economical manner. From a CO₂ sequestration point of view, it may be possible to pump CO₂ into these hydrate deposits and displace and recover the methane while tying up the CO₂ as hydrate. Thermodynamically the CO₂-hydrate is more stable than CH₄-hydrate so CO₂ should drive out the methane.

Production of Hydrogen-Rich Fuels Utilizing CO₂

Most CO₂ sequestration methods deal with removal and recovery of CO₂ emitted from central power plant stations. However, in the U.S., this represents only about 30% of the emissions. As much as 40% comes from the automotive transportation sector, while the remaining 30% from the industrial and domestic heating sectors. Thus, to deal with reducing this major transportation emission source, we must rely on improving energy utilization efficiency, switching to other energy sources such as solar, nuclear and to a hydrogen-rich fuel source. Much work is now progressing towards using hydrogen-rich fuels in efficient fuels cells. A major problem is how to produce hydrogen without CO₂ emissions. For this purpose I have been trying to develop an efficient process for the production of hydrogen by the thermal decomposition of natural gas, (methane) while sequestering the elemental carbon. This is an alternative process to the conventional one for producing hydrogen by the steam reforming of methane in which large amounts of CO₂ is emitted and must be sequestered.⁽¹²⁾ The thermal efficiency of hydrogen production is estimated to be about the same for either of the two processes (about 60%) when sequestration is taken into account for the steam reforming system, even though carbon is not used as an energy source in the methane decomposition process. However, the steam reforming process has been practiced for a long time industrially but the methane decomposition process has only been practiced on a limited scale

for the production of carbon black. Another advantage of the thermal cracking process for hydrogen production with zero CO₂ emission is that it is much easier to store solid elemental carbon than it is to sequester gaseous CO₂ from the steam reforming process.

Hydrogen can be used directly in internal combustion engines as well as in efficient fuel cells. However, the current infrastructure makes use of liquid fuels. Therefore, the hydrogen can be catalytically reacted with CO₂ from coal or gas-fired power generating plants to produce such liquid fuels such as methanol, dimethyl oxide and higher oxygenated hydrocarbon fuels. Figure 1 indicates the Carnol system which utilizes CO₂ from the power generation sector to produce liquid methanol for use in automotive vehicles. Estimates indicate that with fuel cells the overall system reduction of CO₂ can exceed 75% compared to current emissions from the power generation and transportation sectors.⁽¹³⁾ The elemental carbon can be used either as a materials commodity or it can be sequestered. The elemental carbon may also be used in efficient power generation schemes such as in clean combustion turbines for combined cycle power or in highly efficient carbon fuel cells, if they can be developed, so as to produce power with much less CO₂ emissions. Nevertheless, in order to reduce CO₂ emissions completely, sequestration of elemental carbon may still be necessary and this may require ocean disposal as an option.

Combining Carbon and CO₂ Sequestration

An advanced concept which combines both the sequestration of elemental carbon from hydrogen production and CO₂ from fossil fuel power generation plants can be conceived which may synergistically be beneficial to both sequestration needs. As shown by Aya, Yamone and Shiozaki,¹⁴ the shallow dissolution method of CO₂ in the ocean has environmental and relatively short-lived sequestration problems. The deep ocean storage method has less environmental problems and the CO₂ can be stored for more than an order of magnitude greater period of time than the shallow dissolution method. However, because of the relatively small density differences between liquid CO₂ and the ocean, the CO₂ liquid must be injected at a depth, such that the heat transfer from the ocean to the droplet of CO₂ which becomes coated with a layer of hydrate does not make it become buoyant before it reaches the critical depth of 2700 meters (9000 ft). The critical depth is the depth at which the density of the liquid CO₂ is greater than that of the ocean at that depth so that the CO₂ is no longer buoyant and will sink to the ocean floor. This means that the droplet size must be quite large, on the order of 1 meter for a reasonable delivery pipe release depth. If we adsorb the CO₂ in a denser medium, the adsorber will carry the CO₂ down faster. Elemental particulate carbon should act as an ideal adsorber for liquid CO₂. A furnace carbon black of 19 nm particle size has a void volume of 64 cc/gm which translates to a 58.4% void volume using 2.20 gm/cc carbon density shown in Table 1.⁽¹⁵⁾ If this carbon is saturated with liquid CO₂ at less than -40°C, and pressure greater than 10 atm, adsorption should condense the CO₂ equivalent to a solid in the pore void volume of the carbon with a density of 1.56 gm/cc. The saturated CO₂-C composite will have a density of 1.82 gm/cc and contain 49.9% CO₂-50.1%C by weight as shown in Table 2. These liquid CO₂ saturated carbon particles may be pressed into blocks coated with ice and dumped into the ocean to sink rapidly. The composite density is much greater than the ocean density at all depths so that the composite will sink rapidly. Heat transfer calculations will determine the size of blocks that would allow melting the surface ice and form a CO₂ hydrate over the C-CO₂ composite on the way down in the ocean. There is also the possibility that carbon will catalyze the formation of CO₂-hydrates. In this manner both the CO₂ and carbon can be sequestered in the bottom of the ocean with the CO₂ locked up in the carbon. It should also be noted that activated

elemental carbon can be used in an adsorption/stripping pressure swing adsorption (PSA) unit to remove CO₂ from coal-fired power plant stack gases, however, the CO₂ will have to be compressed and liquefied to saturate and be slurried with the porous carbon. Figure 2 indicates the Carnol system in which methane thermally decomposes to carbon and hydrogen. The hydrogen is utilized either in stationary or mobile fuel cells and the carbon is used to extract CO₂ from coal efficient fired power plant stacks. The CO₂ is slurried with the carbon for producing a dense composite for sinking and sequestering in the ocean. This is an excellent way to simultaneously sequester both the large amounts of carbon and carbon dioxide produced from the power generation and transportation sectors.

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Table 1
Properties of Elemental Carbon Black

Particle Size	-	19 nm
Surface area	-	120 m ² /gm
Void volume	-	64 cc/100 gm
Carbon density	-	2.20 gm/cc
Bulk density	-	0.91 gm/cc

Table 2
Properties of Composite Liquid CO₂ Saturated Elemental Carbon Black
 For Ocean Disposal

Pressure	-	≥ 10 atm
Temperature	-	≤ 40 °C
Apparent CO ₂ adsorbed in carbon pore volume	-	1.56 gm/cc
Composite composition	-	50.1 wt% C - 41.6 vol% C
	-	49.9 wt% CO ₂ - 58.4 vol% CO ₂
Composite density	-	1.82 gm/cc