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ANL/ES/CP 96052

METHODS TO REDUCE CO_2 RELEASE TO THE ATMOSPHERE

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INTRODUCTION

The U.S. anthropogenic emission of CO_2 is over 5.5 billion tons a year. Over 1/3 of it is emitted by power plants, and 90% of all power plant emissions is released by coal fired units. Figure 1 shows the amount of coal used and the amount of electricity generated from coal over a several year period. Burning one lb of coal produces about 2.1 lbs of CO_2 and about 1 kWh of electricity, or a 1000 MW coal-fired plant emits over 1000 tons of CO_2 per hour. Therefore, power plants are good candidates for reducing CO_2 emissions. Emissions can be reduced by conserving energy, fuel and oxidant treatment prior to combustion, using fuels with higher H/C ratios, and by capturing the CO_2.

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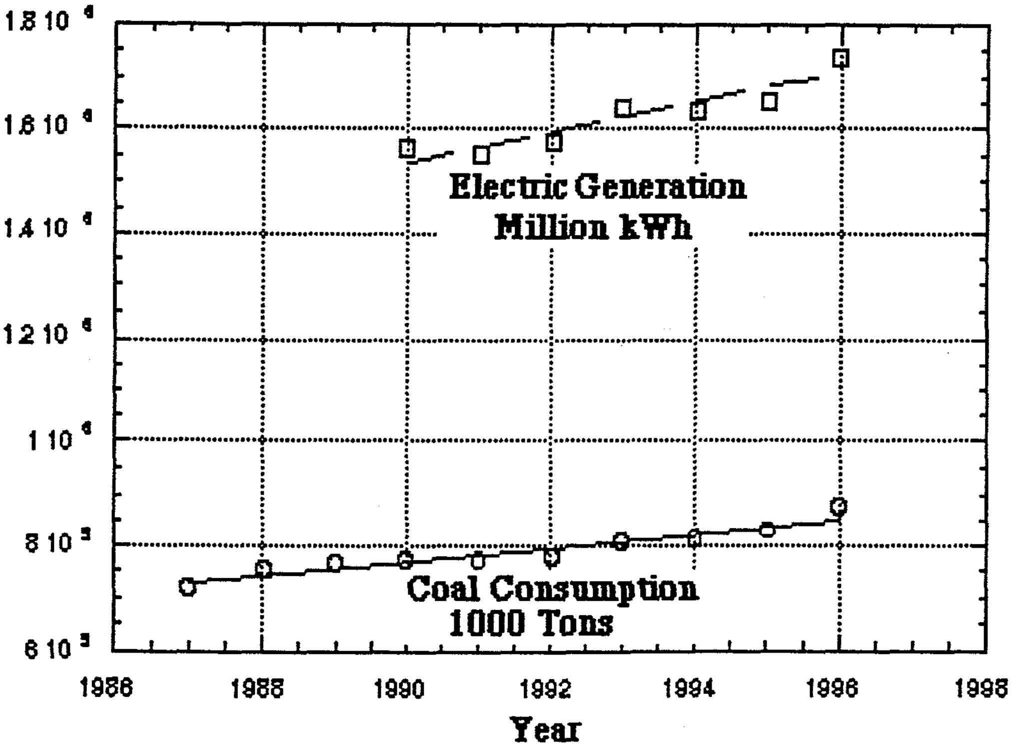

Figure 1. Electric Utility Coal Consumption and the Corresponding Electric Output [1]

ENERGY CONSERVATION

Energy conservation can be achieved by reducing the electric energy use, and by using more efficient equipment and processes. Reducing electric energy use is something we all have to plan for and practice. Among the few options available to the power industry is to reduce power losses associated with power transmission by locating smaller generating stations closer to the end users. These units may be less economical unless they are designed for cogeneration. Achieving higher efficiencies than the present value of about 33%, is presently not cost effective. Such options include

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increasing the number of reheat loops and feed water heaters. However, increasing efficiency by design modifications is likely to increase the cost of power generation by only a small fraction of what it costs to capture and sequester the CO_2 after it is produced. Replacement of older equipment with more modern units, such as replacing old gas turbine units with the new 2350 °F gas turbine, will also reduce CO_2 emissions. Figure 2 shows the reduction in CO_2 emissions that will result if the power plants operate at efficiencies higher than the present 33% value. Efficiencies in the lower 40% range using advanced combined cycles have already been demonstrated. Another approach to increase the efficiency in steam power plants, which might become more economically attractive when trying to reduce CO_2 emissions, is using off-peak power to produce storable heat sinks during off-peak hours, to allow expansion of the steam in the turbine down to a pressure of about 0.1 psia instead of the existing practice of about 1 psia [2]. Implementation of this requires modification of the turbine design. Operating at higher inlet temperatures and pressures also increase efficiency, but limited by materials' constraints.

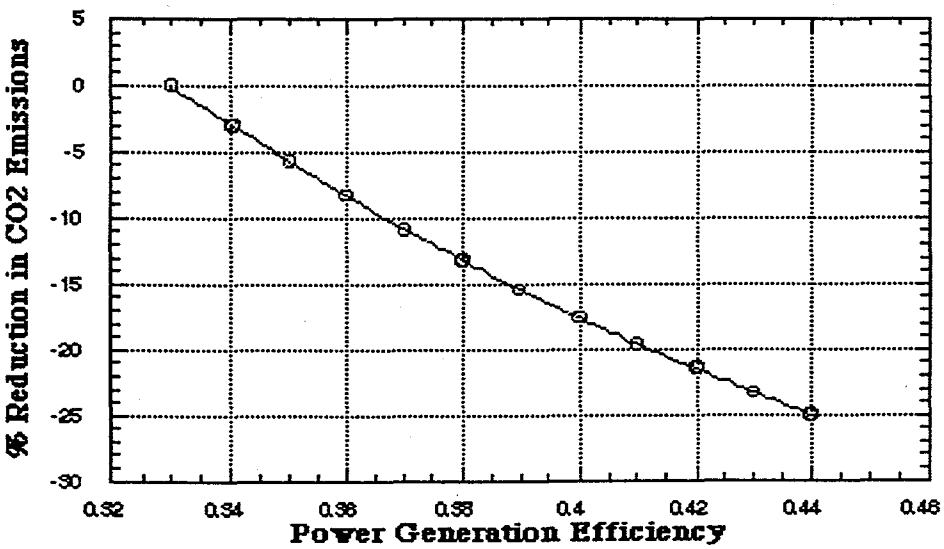

Figure 2. Reduction in CO_2 Emissions due to Increased Power Generation Efficiency

Cogeneration systems which normally achieve overall efficiencies greater than 65%, can reduce the overall CO_2 emissions, while opening new markets for utilities. Figure 3 shows the anticipated reduction in CO_2 emissions when cogeneration systems having different efficiencies are used, compared to producing the same amount of electricity from a power plant operating at 33% efficiency, and producing the thermal energy in an 85% efficient boiler when both alternatives use the same fuel.

FUEL/OXIDANT TREATMENT

Fuel/oxidant treatment involves separation of the carbon from the fuel and N_2 from the combustion air. Separation of the carbon from the fuel by techniques such as thermal cracking (Figure 4) is technically feasible and can be achieved without much energy loss. However, the thermodynamic irreversibilities in the process result in significant loss in availability or exergy, specially when applied to solid fuels. Since exergy is the maximum work that can theoretically be derived from a fuel, the loss in exergy should be addressed. When carbon is separated, the carbon can be burned separately using an O_2 stream to produce a highly concentrated CO_2 stream, which can be utilized as a product. The H_2 can be burned with air and discharged. Cryogenic systems for separating air are commercially available. Over 20% of the electrical output will be consumed by the air separation plant. ANL developed and tested a process which burns coal with O_2 and recycles a split stream of the flue gas back to the combustion chamber in order to achieve similar heat transfer characteristics as experienced when coal is burned with air; the purpose being to minimize the number of changes necessary to the existing hardware. To investigate the technical feasibility of this concept, three series of large-scale experiments were conducted in conventional equipment. These tests showed that coal could be burned with CO_2/O_2 as the oxidant at CO_2-to-O_2 mole ratios of 2.23 to 3.65 and achieve high combustion efficiencies. No noticeable effects on the performance of either the boiler or the space-heating system were observed. The tests also showed that transition from air-fired to oxygen-fired operation did not present any difficulties and that no extraordinary training of the plant operators would be required; the modified unit was operated by utility personnel[3,4]. Separation of moisture and inerts (ash) from the coal prior to combustion can increase the efficiency of the power generation process by reducing the portion of the coal energy that goes to heating the moisture and the ash. However, it is unlikely that the energy used to separate the ash and the moisture will be less than that saved by not letting the ash and moisture go through the combustion process.

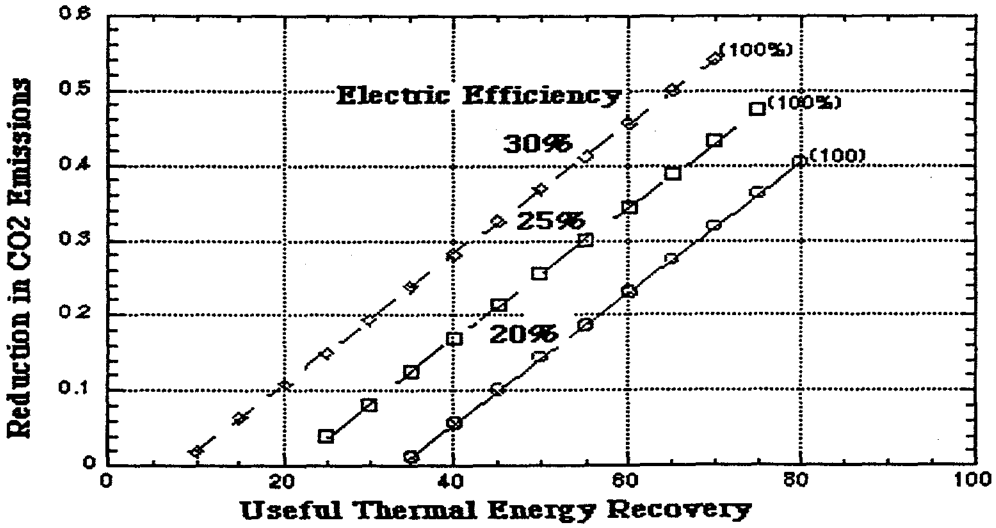

Figure 3. Reduction in CO_2 Emissions That Can Be Achieved By Cogeneration Systems

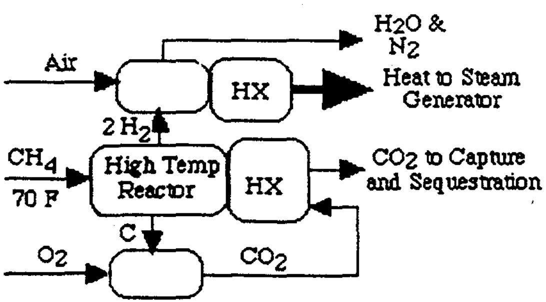

Figure 4. Thermal Cracking Unit Integrated With a Combustion System

SWITCHING TO FUELS WITH HIGHER H/C RATIOS

As the H/C ratio of the fuel increases the amount of CO_2 produced per kWh of electricity generated decreases (Figure 5). The ideal fuel for reducing CO_2 emissions is natural gas, which is primarily CH_4. Historically coal has enjoyed a cost advantage over natural gas, and concern over long term supplies is an issue. The ultimate fuel which does not produce CO_2 is H_2. However, one should consider the process by which H_2 is made. For instance, most of the H_2 available today is produced by reforming natural gas, and all of the CO_2 that would be produced if the natural gas is burned, is now produced by the reforming and the water-gas shift reactions. Therefore, in this case there is no net reduction in CO_2 emissions unless the CO_2 produced by the reforming process is sequestered, while the CO_2 produced by the combustion process is not. Plastics also have higher H/C ratio than coal. For example, the ratio for polyethylene and polypropylene is 2/1 while it is only 0.8 for coal. Many of the organic solvents, such as alcohols (methanol has a ratio of 4/1), and volatile organic compounds (VOC) also have higher ratios than coal. Therefore, waste streams that are rich in plastics or waste solvents offer an opportunity to reduce CO_2 emissions when burned. Major modifications are sometimes needed to be able to use waste as a fuel. Reducing CO_2 emissions may provide the needed economic impetus. Some of the waste materials are biodegradable and if not used as a fuel will release the same amount of CO_2 over a period of time anyway, and some of the VOCs are themselves greenhouse gases. Therefore, recovery of these materials also reduces greenhouse gas emissions.

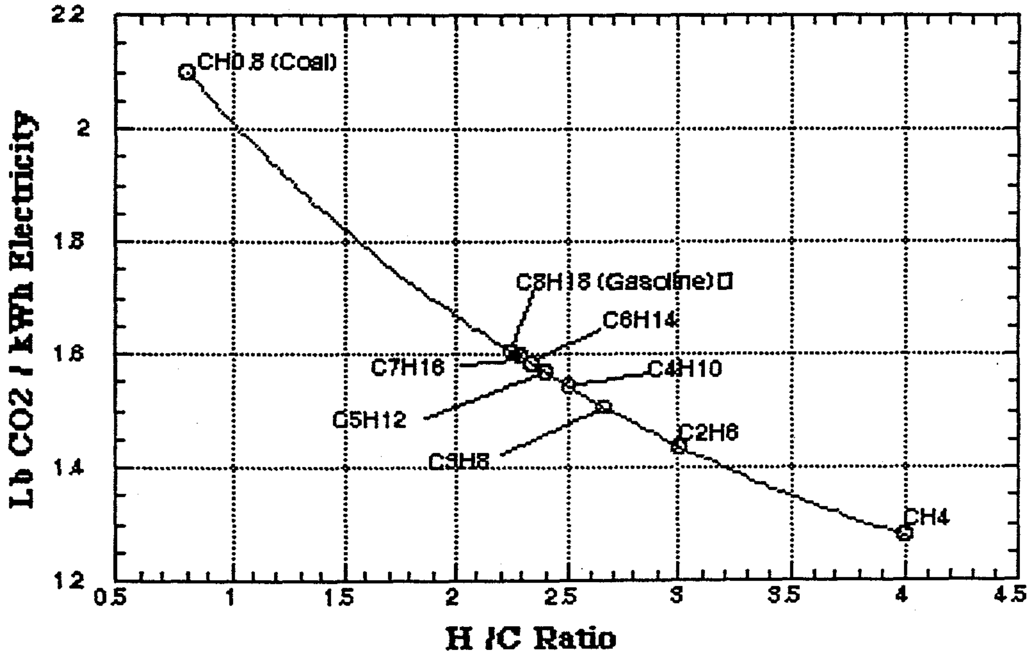

Figure 5. CO_2 Production Per kWh of Electricity Generated Using Different Fuels

REMOVAL OF CO_2 FROM THE FLUE GAS

Capturing CO_2 from flue gas is technically feasible. Figure 6 shows technologies that can be used to separate the CO_2. At least one plant was built to recover commercial grade CO_2 from the flue gas of utility boilers. However, CO_2 recovery from flue gas is expensive and energy intensive. Figure 7 shows the minimum theoretical energy required for separating CO_2 from the flue gas of coal fired boilers. Normally, 4 to 10 times the theoretical minimum is required because of the numerous thermodynamic irreversibilities involved. The reasons for the high energy requirement and high cost of separating the CO_2 from the flue gas include: (1) CO_2 is present in the flue gas at low partial pressures. When coal is burned with 110% theoretical air the CO_2 concentration in the flue gas is about 15 mole% . It is even lower for oil (~ 13%) and natural gas (~ 9%). To increase the CO_2 pressure we need to reduce the N_2 pressure by separating some of it prior to the combustion process. Membrane systems are presently operating to produce relatively pure N_2 from air for industrial use. These systems reject a stream that is about 30% O_2. Using such a stream when available, increases the concentration of CO_2 in the flue gas by about 50%. (2) Both N_2 and CO_2 require very low temperatures and/or high pressures to condense (CO_2 condenses at -78.6 °C and N_2 condenses at -195.8 °C, at atmospheric pressure). (3) The large number of species present in the flue gas and their corrosive nature.

Many of these technologies were developed for reasons unrelated to climate change — to clean up acid gases, to recover CO_2 for use in enhanced oil recovery and in the beverage industry. The logical evolution of these technologies is to investigate how these technologies can be modified and optimized to reduce CO_2 emissions from existing and from future power plants efficiently and economically. For example, chemical absorption of CO_2 involves one or more reversible chemical reactions between CO_2 and another material such as mono-, di- or tri- ethanol amines, diisopropanol amine, sodium hydroxide, sodium carbonate and potassium carbonate, to produce liquid or solid species which, upon heating, breakdown to liberate CO_2 and regenerate the material used to react with CO_2.

Energy savings can be realized, if a solvent that has high absorption capacity can be developed, or if a solvent that can be regenerated at higher pressures is used. In this case the CO_2 can be produced at the high pressure, and thus does not require recompression prior to final disposal. If that solvent is chemically stable upon thermal recycling, and can be used after regeneration in an organic Rankine power cycle, where instead of wasting the heat it gained in the regeneration process, the regenerated solution can be externally heated to produce a superheated vapor that can be expanded in a turbine to produce mechanical work. This concept will be particularly attractive for recovering CO_2 from the exhaust of gas turbines.

Cryogenic separation of gas mixtures is a mature technology. Separation of CO_2 from combustion gas streams is more involved than separating air, but the principle is the same. It involves compression and cooling of the gas stream to low temperatures in order to induce a phase change in CO_2 and thus its separation from the mixture. The water vapor present in the flue gas has to be removed down to a dew point that is less than the lowest temperature encountered in the separation process, prior to the cooling process. The drying process requires that, after the bulk of the water is removed by conventional means, a desiccant material must be used to absorb the residual water. After the CO_2 separation is accomplished, the effluent stream will consist essentially of the N_2 and the excess O_2 used in the combustion process. Recompression of the CO_2 is required. CO_2 can also be separated as a solid. At pressures below its triple point, CO_2 forms a nearly pure solid on cooling from a vapor mixture that may contain gaseous impurities.

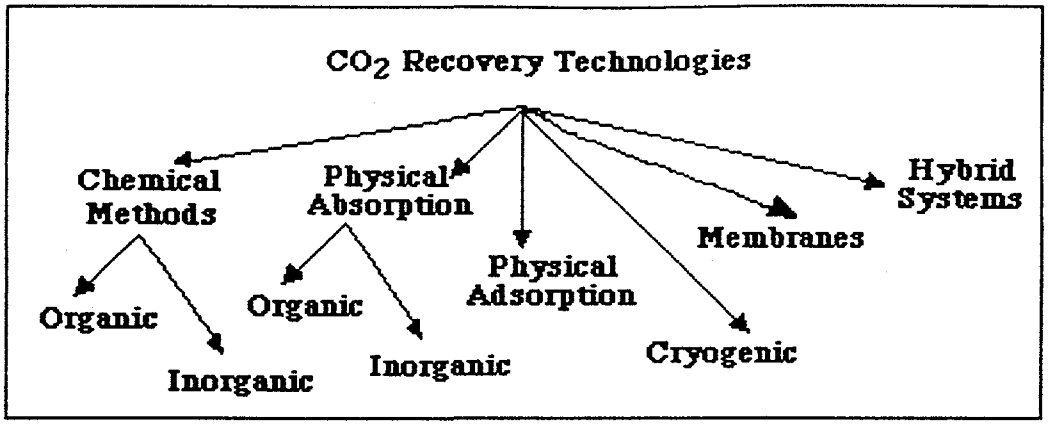

Figure 6. Technologies For The Capture of CO_2 From Flue Gas Streams

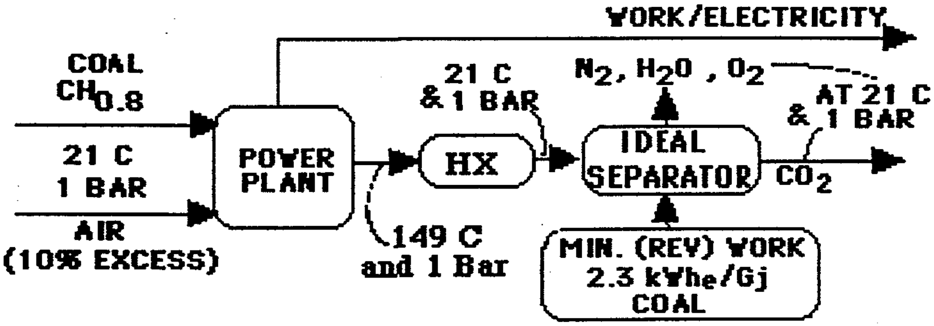

Figure 7. Minimum (Reversible) Work Required to Separate CO_2 From Coal Combustion Products

ACKNOWLEDGMENT

This work was sponsored by the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, under Contract No. W-31-109-Eng-38.

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