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U.S. DOE Integrated Collaborative Technology Development Program for CO_2

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U.S. DOE Integrated Collaborative Technology Development Program for CO_2 Separation and Capture

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Electric power generation represents one of the largest carbon dioxide (CO_2) emitters in the United States. Roughly one-third of all the United States' carbon emissions come from power plants. Since electricity generation is expected to grow, and fossil fuels will continue to be the dominant fuel source, power generation can be expected to provide even greater CO_2 contributions in the future. Consequently, an important component of the United States Department of Energy's (DOE's) research and development program is dedicated to reducing CO_2 emissions from power plants by developing technologies to capture CO_2 for utilization and/or sequestration. A primary goal of this research is to develop technology options that dramatically lower the cost of eliminating CO_2 from flue gas and other streams by use of either pre- or post-combustion processes. This research is in its early stages, and is exploring a wide range of approaches, including membranes, improved CO_2 sorbents, advanced scrubbing, oxyfuel combustors, formation of CO_2 hydrates, and economic assessments. This paper presents an overview of the DOE research program in the area of CO_2 separation and capture, while specifically addressing the status of research efforts related to promising pathways and potential technological breakthroughs.

INTRODUCTION

Fossil fuels currently supply over 85% of the energy needs of the U.S., and their combustion is responsible for about 90% of the greenhouse gas (GHG) emissions in the U.S. [1]. Use of these fuels, domestically and internationally, is expected to increase well into the 21st century. The Energy Information Administration within the U.S. Department of Energy (DOE) projects U.S. consumption of coal, oil, and natural gas to increase by 40%, and carbon emissions to rise by 33% over the next 20 years (See Figure 1).

Carbon sequestration holds great potential to reduce GHG emissions at costs and impacts that are economically and environmentally acceptable. The DOE's Office of Fossil Energy's (FE) formal carbon sequestration effort began in 1997.

The Carbon Sequestration Program is pursuing five technology pathways to reduce GHG emissions:

- Separation and capture
- Geologic sequestration
- Terrestrial sequestration
- Oceanic sequestration
- Novel sequestration systems

These five pathways encompass a broad set of opportunities for both technology development and partnership formation for national and international cooperation. This paper deals mainly with the first of these pathways, namely separation and capture.

In addition to CO_2, methane (CH_4) and nitrous oxide (N_2O) are other major anthropogenic emissions that contribute to global climate change. On a pound for pound basis, both CH_4 and N_2O are more potent GHGs than CO_2. However, in terms of the quantity emitted, CO_2 far outstrips other GHGs and is, thus, the primary focus of mitigation efforts. Efforts to decrease non-CO_2 GHG emissions are included in the Sequestration Program, but are not discussed in this paper.

An important component of DOE's Carbon Sequestration program is directed toward reducing CO_2 emissions from power plants. Roughly one-third of the United States' anthropogenic CO_2 emissions come from power plants (See Figure 2). CO_2 emissions in the U.S. from electricity generation by fossil-fuel burning power plants increased by 23.5% between 1990 and 2000 [2]. Moreover, most power plants use air for combustion, which means that the major constituent of the flue gas is nitrogen. This makes it difficult and expensive to capture CO_2 as a concentrated stream, which is required for most storage, conversion, and reuse applications. One way of mitigating GHG emissions in a safe and environmentally-friendly manner is to capture CO_2 and store it in geological formations.

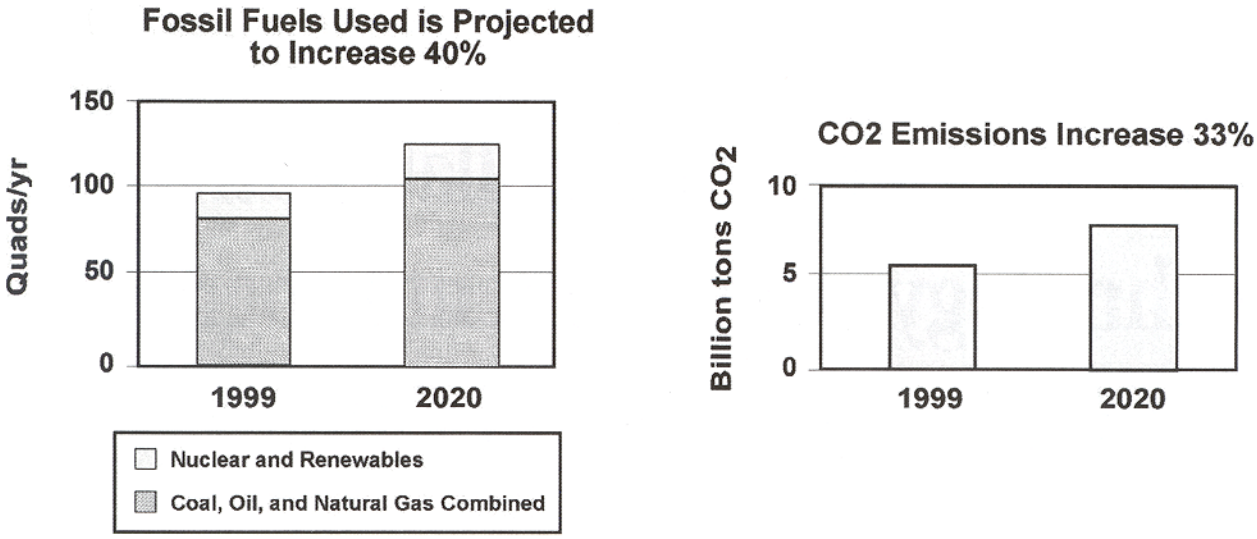

Figure 1. U.S. energy consumption and GHG emissions in 2020.

This has emerged as one of the most promising options for sequestering CO_2 from energy plants [3].

Carbon sequestration is an underexplored area of science and technology. In order for recovery/sequestration to work, improved CO_2 capture technologies are needed, and costs must be reduced substantially. Capture technology, based on the use of physical or chemical sorbents, such as amines, is in wide use today to remove CO_2 from natural gas, which can be used in the food industry and for tertiary recovery in oil fields. However, the cost is on the order of $50 per ton of CO_2 removed, or about 5 cents per kWh, too high for cost-effective GHG emissions reductions. Additionally, existing capture systems use substantial amounts of energy, reducing a power plant's net generation capacity, sometimes by as much as 30%. DOE's long-term goal is to achieve sequestration with only a modest increase in energy costs [4, 5]. The programmatic timeline is to demonstrate, at commercial scale, a portfolio of safe and cost-effective GHG capture, storage, and mitigation technologies by 2012.

CARBON SEQUESTRATION RESEARCH AND DEVELOPMENT PROGRAM

Before it can be sequestered, CO_2 must first be separated and captured. Therefore, the Carbon Sequestration Research and Development Program is exploring a portfolio of new and improved technologies to reduce the capital cost and energy penalty for CO_2 capture. During the FY2000 to FY2002 period, the DOE Carbon Sequestration Program issued a solicitation and selected 20 R&D projects in the areas of CO_2 capture and storage in geologic formations. These programs have up to a 40% non-DOE cost share. This research is in its early stages and is exploring a wide range of capture approaches, including membranes, improved CO_2 sorbents, advanced combustor concepts, advanced scrubbing, formation of CO_2 hydrates, and economic assessments. DOE is also a partner in the CO_2 Capture Project (CCP) with an international team of energy companies to develop a set of new technologies to reduce the cost of capturing CO_2 from fossil fuel combustion.

There are two general approaches to CO_2 capture: precombustion decarbonization and post-combustion capture. Either the carbon can be removed before the fuel is burned, or CO_2 can be recovered from the flue gas. In addition, the use of pure oxygen, rather than air, in combustion, known as oxyfuel combustion, has a high potential for reducing CO_2 separation and capture costs.

PRECOMBUSTION DECARBONIZATION

Precombustion decarbonization involves removal of carbon from a gaseous, liquid, or solid fuel before it is burned. Various approaches are possible. A very promising technology involves gasifying coal and then scrubbing the CO_2 from the fuel gas before combustion. The CO_2 is normally removed by a chemical or physical absorption system. Existing capture technologies operate at a low temperature, requiring the syngas produced in the gasifier to be cooled for CO_2 capture and then reheated before combustion in a turbine. Substantial cost reductions in CO_2 capture and separation are expected to come through integrated designs incorporating the use of membranes and other breakthrough recovery technologies.

CO_2 Selective Ceramic Membrane to Improve the Water-Gas Shift Reaction

This technology involves precombustion decarbonization with the addition of an innovative water-gas shift (WGS) reactor to increase the amount of CO_2 captured. The WGS reactor consists of ceramic tubes that incorporate a membrane permeable to CO_2, but not to other gases. The tubes are filled with catalyst. As the fuel gas from the coal gasifier passes through the WGS reactor, the CO_2 produced by the reaction, as shown in Equation 1, diffuses through the membrane, allowing the reaction to approach completion.

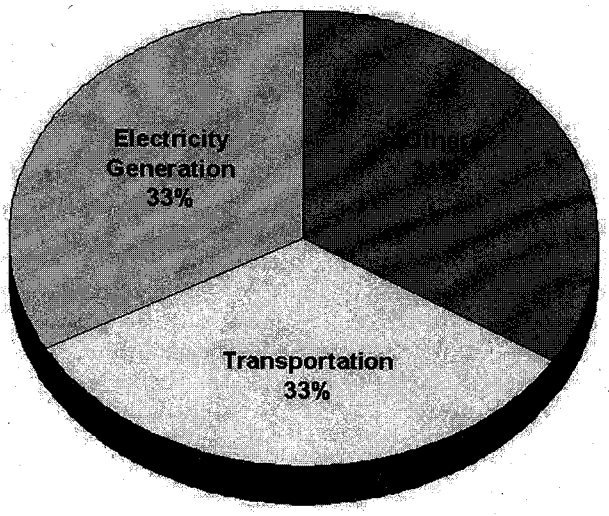

Figure 2. U.S. carbon emissions sources.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

This produces a hydrogen-rich fuel stream, while simultaneously producing a pure CO_2 stream for use or sequestration. The hydrogen can be sent to a fuel cell or burned in a combustion turbine. In either case, the only product is water, which is innocuous to the environment. This project is being conducted by Media and Process Technology, Inc., in partnership with the University of Southern California. They have developed a technique for depositing hydrotalcite in the pores of a ceramic substrate. The hydrotalcite is permeable to CO_2, but plugs the pores, preventing passage of other gases. The project team is currently working on improving production procedures and determining operating conditions to maximize CO_2 permeance.

POST-COMBUSTION CO_2 CAPTURE

Post-combustion capture involves the removal of CO_2 from the flue gas produced by fuel combustion. The major problem with this approach is that flue gas is usually at near atmospheric pressure, and the CO_2 concentration is low. The resulting low partial pressure of CO_2 results in only a small driving force for traditional adsorption/absorption processes. While post-combustion CO_2 capture may not have the greatest potential for step-change reductions in separation and capture costs, it has the greatest near-term potential for reducing emissions, since post-combustion processes can be retrofitted to existing facilities. Although the processes discussed below can be used to remove CO_2 from flue gas, the benefits of these developments will be equally applicable to the removal of carbon dioxide from gasifier product streams for the production of syngas or pure hydrogen.

Electric Swing Adsorption

Electric Swing Adsorption (ESA) is an advanced separation system for CO_2 removal from syngas being developed for use with the gasification of low hydrogen-to-carbon ratio fuels, such as petroleum coke. Oak Ridge National Laboratory has developed a novel process, which adsorbs CO_2 on a carbon substrate. After saturation of the carbon fiber adsorbent with CO_2, immediate desorption of the adsorbed gas is accomplished by applying low voltage across the adsorbent. This technology is being developed to remove CO_2 from the exhaust gas of a conventional turbine combined with a non-condensing steam turbine. Calculations based on available adsorption data indicate that it should be possible to develop an improved CO_2-separation process compared to existing technology.

Stable High Temperature Polymer Membranes

Many membrane systems used for industrial gas separation applications employ polymer membranes. Such applications include the production of high-purity nitrogen, dehydration and removal of acid gases from natural gas, and recovery of hydrogen from process streams. However, many gas separation applications require materials that are stable at high temperatures and pressures. Polymeric materials currently used commercially have thermal and mechanical limits too low for such applications. Consequently, there is a compelling need for membrane materials that can operate under more extreme conditions for extended periods of time while providing an acceptable level of performance.

Los Alamos National Laboratory is developing a high-temperature polymeric membrane with better separation performance by supporting a polybenzimidazole (PBI) film on a sintered metal support. PBI possesses excellent chemical resistance, a high glass transition temperature (450° C), and good mechanical strength. Tests for H_2, CO_2, CH_4, and N_2 permeability with the membrane oriented with the polymeric layer on the feed side have shown promising results. This type of membrane is highly selective and able to operate at flue gas conditions.

Advanced Gas/Liquid Scrubbing

A major problem associated with chemical absorption using amines is the degradation of the solvent through irreversible side reactions with SO_2 and other flue gas components. Such reactions lead to numerous problems, such as foaming, fouling, increased viscosity, and formation of stable salts in the amine. Amine degradation results in solvent loss, requiring a replacement rate of up to eight pounds of amine per ton of CO_2 captured. A focus of R&D activities at the National Energy Technology Laboratory (NETL) is a study of amine degradation under actual plant conditions.

This study will lead to a better understanding of the chemistry of solvent degradation, which is known to increase corrosion. Understanding this phenomenon will improve operations and decrease costs, since to reduce corrosion, solvent strength is kept relatively low, resulting in large equipment sizes and high regeneration energy requirements. In addition, several researchers have shown that blending amines increases the absorption rate. The work

at the University of Texas at Austin focuses on expanding the investigation of promoted potassium carbonate using piperazine as the amine.

Regenerable CO_2 Sorbent Development

A different approach for CO_2 capture employs dry scrubbing—a process that involves chemical adsorption with a dry sorbent. Such a sorbent can remove the pollutant, be regenerated to produce a concentrated stream of CO_2, and be recycled. This process can have economic advantages compared to commercially available wet scrubbing amine processes.

Research Triangle Institute has initiated development of a process that uses a regenerable, sodium-based sorbent for CO_2 recovery. Preliminary microreactor tests with sodium carbonate have indicated that absorbing CO_2 and steam to form bicarbonate, with subsequent regeneration to the carbonate, is a viable process. Because sorbent regeneration uses waste heat, the power requirement for capture of CO_2 is relatively small. Various system configurations are being simulated to define optimal heat management.

NETL has pioneered research to identify regenerable sorbents that can be used for CO_2 capture. The active component in a calcium-based sorbent being studied chemically bonds with CO_2 and is later regenerated using heat or a reducing agent. Packed bed testing is now in the planning stage. In another project, CO_2 is absorbed by a zeolite based sorbent, and a temperature/pressure swing is performed to recover the carbon dioxide. The project team (NETL and Carnegie-Mellon University) is currently working on simulation modeling to understand the performance of high-temperature sorbents and on high-pressure reactor testing of promising synthetic zeolites.

OXYFUEL TECHNOLOGY

Oxygen-Fired Combustion for CO_2 Capture

The objective of oxygen-fired combustion is to burn the fuel in enriched air or pure oxygen to produce a concentrated stream of CO_2. Oxygen-fired combustion presents significant challenges, but also provides a high potential for a technological breakthrough and a step-change reduction in CO_2 separation and capture costs. The barriers and issues include:

- Oxygen from cryogenic air separation is expensive and, because in oxygen-fired combustion, all the carbon in the fuel is converted to CO_2 using pure oxygen, rather than only part of the carbon with gasification, oxygen combustion consumes several times more oxygen than coal gasification followed by combustion of the syngas in air.
- Combustion of fuels in pure oxygen occurs at a temperature too high for existing boiler or turbine materials, while CO_2 recycle to control temperature increases the parasitic power load.

Development and costing of an optimized oxygen-fired combustion scheme requires an engineering study to identify and resolve the technical issues related to application of oxygen firing with flue gas recycle to the boiler and process heaters. Alstom Power has outlined an approach in which two sets of economic evaluations would analyze a fossil fuel-based (coal and petroleum coke) circulating fluidized bed (CFB) combustor, and a biomass-based CFB for power production. The first step is to identify and analyze normal baseline conditions for CFB combustion with air firing both without CO_2 capture and with a novel high-temperature CO_2 capture and sorbent regeneration process. Next, CFB-based power plants employing an oxygen/recycled flue gas mixture as the oxidizing agent will be studied to determine what operating conditions and gas clean-up processes are most economical. The CO_2 concentration in the flue gas can be greatly increased by using oxygen instead of air for combustion. Flue gas is recycled to moderate the combustion temperature.

Comparisons will also be made with Integrated Gasification Combined Cycle (IGCC) cases that have already been evaluated by Parsons Energy and Chemical Group. In this way, important features that can improve plant operations by utilizing oxygen firing will be explored, identified, and included in plant designs.

Integration of Membrane Air Separation

The economics of both oxygen-firing and IGCC can be improved by the application of advanced oxygen production technology. New air separation processes using high temperature oxygen ion transport ceramic membranes are being developed by several consortia. For oxygen-fired combustion applications, integration of an oxygen transport membrane (OTM) for oxygen production with the combustion system can provide a method for the cost-effective capture of CO_2 from power plants. Praxair, in conjunction with Alstom Power, has initiated the development of a novel technology that integrates a high-temperature OTM with boiler components to enhance both oxygen production and boiler efficiency (See Figure 3).

OTM membranes are based, in part, on Praxair-patented materials that have demonstrated ability for rapid electron conduction. A condensing heat exchanger will be used to take advantage of the high water content in the flue gas from combustion with pure oxygen. A high driving force across the ceramic membrane, due to pressurized air, and the high temperature environment inherent in combustion, result in a significant reduction in the power consumption for oxygen production. The resultant combustion process will not only lead to low NO_x and CO emissions, but also increase the CO_2 concentration in the flue gas sent to the capture system, thus leading to lower capital costs. The technical challenge is to develop materials with enhanced conductivity and stability, and to produce ceramic structures specifically suited to combustion applications.

NOVEL CONCEPTS

Carbon Dioxide Separation Using Hydrates

An entirely new concept for recovering CO_2 from process streams is the formation of hydrates, ice-like

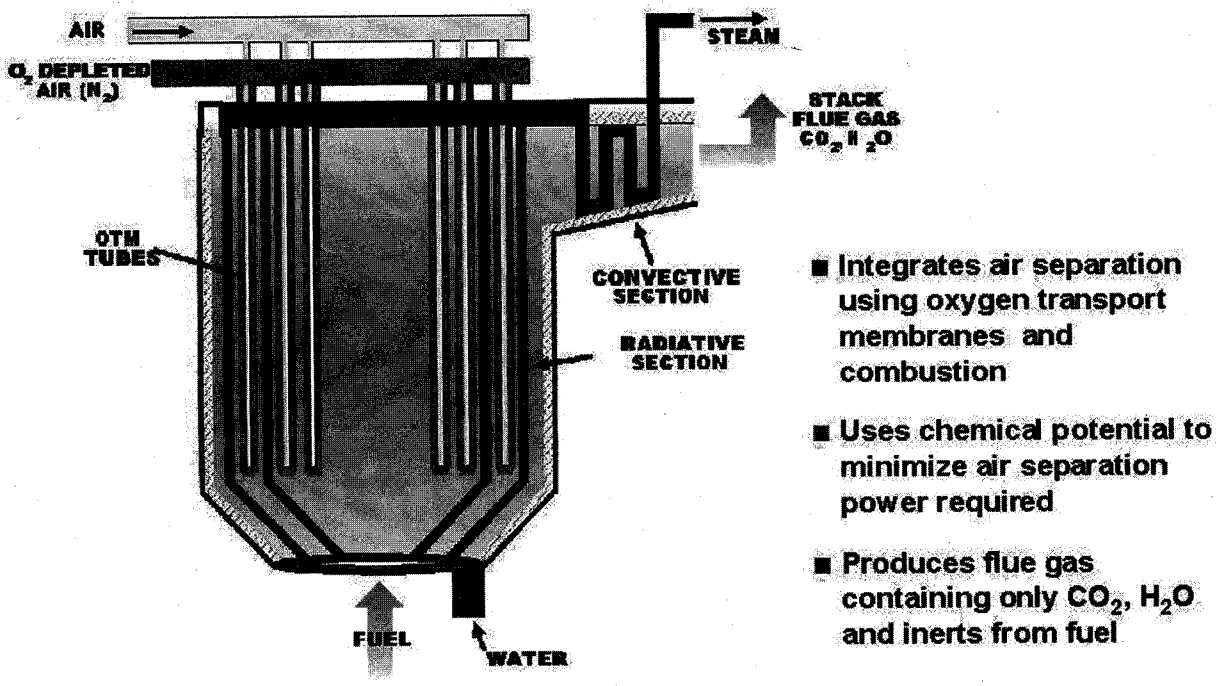

Figure 3. Praxair advanced boiler.

complexes of water and CO_2 molecules. Many people are familiar with methane hydrates, in which a methane molecule is enclosed in a cage of water molecules, but are unaware that CO_2 can form similar hydrates under suitable conditions. The California Institute of Technology has developed a bench-scale apparatus to produce CO_2 hydrates. The objective of the current project team (Los Alamos National Laboratory, Nextant, Inc., and SIMTECHE) is to develop this concept into the basis for a commercial process that removes CO_2 from flue gas by contacting it with water at low temperature (0° C) and high pressure (1-7 MPa) to form crystalline ice-like solids that can be removed from the system.

A new test unit has been constructed for experimentation. Figure 4 is a schematic of a CO_2 hydrate separation process operating on a synthesis gas stream that has undergone the WGS reaction. Water and CO_2 in a greater than 12/1 molar ratio flow through a venturi to achieve intimate contact, and then into a cooler to remove the heat of formation of the hydrate. The slurry and unreacted gas then flow to a separator. Work to date has demonstrated that hydrates can be formed in systems with very short residence times, and that continuous operation is possible, provided operating conditions are adjusted so that plugging does not occur.

The next step in the development process is the design, construction, and operation of a pilot plant. However, further data are needed before this can be done, including the physical properties of the hydrate slurry, practical ranges of the key process variables, and tests with $CO_2/H_2/H_2S$ mixtures. Using CO_2 hydrates to purify gas streams is a potentially less energy-intensive recovery method. It is also possible that CO_2 hydrate slurries could be pumped to sequestration sites without regeneration. Implementation of this technology will be best suited to gasification systems that operate at pressures higher than those of typical flue gas streams.

Chemical Looping

Indirect combustion of coal, sometimes referred to as chemical looping, will be evaluated by Alstom Power. In chemical looping, oxygen for combustion is provided by a metal oxide, rather than by air. Fuel gas (CO plus H_2) produced by the gasification of coal reduces a solid transition metal oxide in a fluidized bed reactor to a lower oxidation state, producing water and CO_2. The off-gas stream is cooled to condense water and produce a pure CO_2 stream for sequestration. The reduced metal containing solid is transferred to a second fluidized bed reactor, where it is reoxidized with air. This exothermic reaction heats the oxygen-depleted air, which is sent to power production.

OTHER ACTIVITIES

Modeling/Assessment

There is a need to develop a comprehensive economic model that that will enable different options for CO_2 capture from power plants to be systematically evaluated, including pipeline costs. Carnegie Mellon University is developing such a model. The initial focus includes current commercial technologies, such as amine-based CO_2 capture, shift conversion, pipelines, and geologic storage. The model is expected to be capable of establishing a common

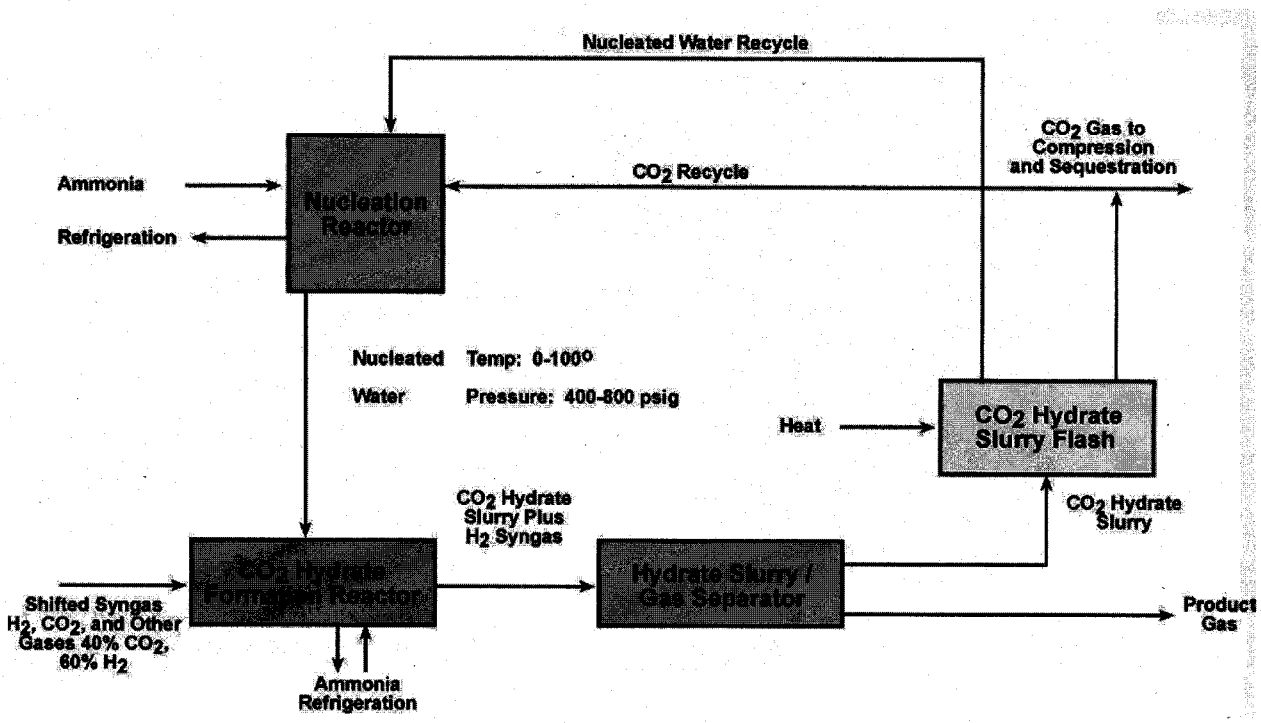

Figure 4. Conceptual process block flow diagram of a CO_2 hydrate process.

set of performance metrics and evaluating the overall cost of CO_2 sequestration, including the component costs of new separation and capture modules, transportation and sequestration in geologic reservoirs and unmineable coal seams, and use in enhanced oil recovery.

NETL and Science Applications International Corporation are developing a computer model-based technique for evaluating CO_2 recovery and sequestration technologies. With existing studies as a baseline, all technologies in the DOE portfolio will be evaluated to continually assess their potential technical and economic performance. This will ensure that the highest potential projects are kept at the forefront of the DOE development effort.

CO_2 Capture Project

To further enhance the effort to reduce GHG emissions, DOE is sponsoring the CO_2 Capture Project (CCP) with an international team of energy companies lead by BP, and including Chevron-Texaco, ENI (Italy), Shell, Norsk Hydro (Norway), PanCanadian (Canada), Statoil (Norway), and Suncor Energy (Canada). This joint industry project will demonstrate the feasibility of capturing the CO_2 produced from burning a variety of fuel types and storing it in unmineable coal seams and saline aquifers.

The CCP has issued contracts with technology developers in the U.S., the European Union, and Norway to carry out studies in various process areas, including geologic storage, post-combustion CO_2 separation and capture, precombustion decarbonization, and fuel combustion with pure oxygen [6]. The potential exists for many scientific breakthroughs from this project, such as the development and evaluation of a combined shift reaction and CO_2 separation system employing high temperature adsorbents. This process would selectively remove CO_2 from a reacting gas mixture, thereby increasing conversion and providing two gas streams requiring minimal further purification. Technology developed by Air Products and Chemicals involves the precombustion decarbonization of a hydrocarbon feedstock that has been gasified by reaction with steam and/or oxygen to produce a $H_2/CO_2/H_2O/CO$ gas mixture with trace contaminants. This concept has already been demonstrated at laboratory scale. Development needs are to apply the system to CO_2 capture and optimize the adsorbent and cycle for large-scale use.

Four membranes have been identified to achieve the CO_2 recovery target at a concentration above 97 mol %. Each of these membranes (Cu-Pd, supported zeolite, silica, and electro-ceramic) will be developed and characterized. For example, ECN Dutch Energy Efficiency Institute will develop silica membranes and provide mathematical models. Fluor Daniels will develop simulations of the overall process incorporating a model of the membrane reactor supplied by ECN.

Other potential scientific breakthroughs that could result from the CCP include:

- New solvents and/or contactors to reduce the cost of CO_2 separation.
- An emerging H_2 generation process integrated with CO_2 capture.
- Understanding the production of fuel-grade H_2 and its combustion properties.

- An enhanced understanding of controls and requirements for geologically sequestering CO_2.

Information on capture and sequestration options generated during the performance of these parallel and complimentary studies will maximize technology transfer and, hence, benefit CO_2 reduction efforts in the U.S and globally.

CONCLUSIONS

The DOE Carbon Sequestration Program is developing a portfolio of technologies that hold great potential to reduce GHG emissions. The programmatic timeline is to demonstrate a series of safe and cost effective GHG capture, storage and mitigation technologies at the commercial scale by 2012, with deployment leading to substantial market penetration beyond 2012. Developments are directed toward substantial improvements in performance and cost reduction compared to state-of-the-art alternatives. Wide deployment of these technologies holds great promise to slow the growth of GHG emissions in the near-term, while ultimately leading to stabilized emissions towards the middle of the 21st century.

This paper has presented a brief overview of the DOE Carbon Sequestration Program. More details on these and other R&D projects in the portfolio can be found at the referenced Web site [5].

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