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Technology for CO₂ Emission Monitoring and Control

E.L. Joyce Jr.*, P.J. Unkefer, J.H. Pendergrass,
W.J. Parkinson, V.W. Loose and J.R. Brainard

Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). We examined three specific areas relative to CO₂ emissions and controls: (1) the effect of deregulation of the utility industry on emissions, (2) the role of advanced power systems in reducing emissions, and (3) developing CO₂ mitigation technologies. In this work the Energy Technologies program office at Los Alamos attempted to initiate an integrated approach that includes a range of tasks involving both point and distributed CO₂ control.

Deregulation, or more generally, restructuring of the electric utility industry has been a widely debated topic on the national scene over the past several years. The largest impact of such moves will be on the generation of electric power. Traditional, rate-of-return regulated public utilities are losing their monopoly franchises in the service territories with industry entry now open to any and all suppliers (generators). After restructuring, suppliers of electric power will be motivated by an entirely new set of incentives. Consumers will have a choice of supplier and will make that choice based upon relative price and possibly other marketing incentives. Price per kWh will be the most important selection criterion and this will force generators to choose the most cost-effective technologies/fuels. Standard private industry financial/ economic/cost analyses will prevail and this may put coal and coal conversion technologies at a disadvantage..

A rationale and the desirable characteristics have been established for the modeling, simulation, and analysis (MS&A) of end-to-end, coal-based, electric-power production and delivery systems. These range from fuel source through generation stations with CO₂ capture to transmission of electricity to customers and transport of CO₂ for sequestration. The MS&A is to provide the information on materials flows (including emissions), energy flows, performance (including efficiencies), costs, risks, and descriptive materials that decision makers need to efficiently and effectively allocate resources and direct technology research, development, demonstration, evaluation, testing, and commercialization of new technologies.

We have examined evolving mitigation (separation and sequestration) technologies for CO₂ disposal. The separation of hydrogen gas from high-temperature CO₂-containing streams is a critical component of carbon

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dioxide mitigation technology, and cost-effective point sequestration will require separation of CO_2 from H_2 . We investigated four types of separation techniques: two high-temperature membrane technologies, an intermediate-temperature membrane technology, and a separation technology based on the formation of CO_2 hydrate compounds through reaction of CO_2 with water at near freezing conditions. At Los Alamos, sequestration technologies are being developed along three principal areas: mineral sequestration of CO_2 , the enhancement of natural sinks using biotechnology methods, and the conversion of CO_2 to methanol using high-temperature photolysis.

Background and Research Objectives

Economic growth in 21st century America will depend on plentiful, reliable, low-cost electric energy and stable, domestic fuel supplies at affordable prices. Most Americans want these economic benefits to be realized in an environmentally responsible manner. To maintain our current way of life, near-, mid-, and long-term options for capture utilization, and disposal of carbon dioxide from fossil energy usage need to be investigated.

Coal, oil, and gas currently account for about 90% of the world's energy production. The size of the market into the next century will be determined by the ability of fossil fuel technologies to meet environmental requirements at costs that keep it competitive with other energy alternatives (nuclear and renewable energies). The situation is particularly acute because the worldwide demand for energy will increase dramatically in the coming decades due to unprecedented population growth as well as dramatic increases in per capita energy usage. Fossil fuels will provide for much of the rising energy demands of a growing world population, especially in large third-world countries with extensive coal reserves. However, the environmental impacts of growing fossil fuel use, in particular CO_2 emissions, must be dealt with. In line with the low/no CO_2 technologies, mitigation (separation and sequestration) technologies should be considered.

While great strides have been made in the understanding and control of some components of emissions generated from burning fossil fuels, most experts agree that the global issue of CO_2 is the major environmental challenge facing the fossil fuel industry. Many leading climate-change scientists suspect that the use of fossil fuels is contributing to significant changes in the global climate that could have severe ecological and sociological ramifications. The purpose of this project was to develop a technical assessment of the necessary CO_2 avoidance and mitigation control technologies to maintain fossil fuel usage. To accomplish this goal will require the development of a broad understanding of where the technology is and where it should be directed in the future.

Importance to Los Alamos Science and Technology Base and National R&D Needs

This project leveraged Los Alamos core competencies in complex experimentation and measurement, analysis and assessment, earth and environmental systems, and bioscience and biotechnology. Additionally, this project directly supported DOE strategic objectives to foster a secure and reliable energy system that is environmentally and economically sustainable, and to support continued United States leadership in science and technology.

Scientific Approach and Accomplishments

This project examined three specific areas relative to CO₂ emissions and controls. These consisted of examining the effect of deregulation of the utility industry on emissions, the role of advanced power systems in reducing emissions, and lastly understanding developing CO₂ mitigation technologies.

Impact of Electric Industry Deregulation on the Coal Industry (V.W. Loose)

Deregulation, or more generally, restructuring of the electric utility industry has been a widely debated topic on the national scene over the past several years. Over the past year or so, the discussion has moved beyond debate as an increasing number of states; notably California, Rhode Island, and a number of other New England states; have passed legislation to implement restructuring by a date certain. Rhode Island set July 1, 1997 and California set January 1, 1998 as start dates. The largest impact of such moves will be on the generation of electric power. Traditional, rate-of-return regulated public utilities are losing their monopoly franchises in the service territories with industry entry now open to any and all suppliers (generators).

After restructuring, suppliers of electric power will be motivated by an entirely new set of incentives. Consumers will have a choice of supplier and will make that choice based upon relative price and possibly other marketing incentives. An analogy to what may evolve in the electric power industry is provided by long-distance telephone service. Price per kWh will be the most important selection criterion and this will force generators to choose the most cost effective technologies and fuels. Standard private industry financial/economic/cost analyses will prevail and this may put coal and coal conversion technologies at a disadvantage. However, if there is currently excess generating capacity as is generally believed, the industry technology trend may not be very evident for some years.

We conducted background research and analysis in the context of restructuring and its impact on the industry. Staff attended a conference focused on the impact of restructuring on the coal industry and made valuable industry and government contacts and obtained information on the issue. This information provided useful background to future staff participation in various aspects of fossil energy programs. The most notable was the initiation of a multi-year program titled "The Clean Coal Technology Compendium," which was established in FY 1997 and funded by the DOE Office of Fossil Energy at \$1M/yr for five years at Los Alamos.

Understanding the Role of Advanced Power Systems in Reducing Emissions (J.H. Pendergrass)

Modeling, Simulation, and Analysis for End-to-End Fossil-Energy-Based (Especially Coal) Electric Power Production and Delivery Systems

We have established a rationale and the desirable characteristics for the modeling, simulation, and analysis (MS&A) of an end-to-end, coal-based, electric-power production and delivery system. These range from fuel source through generation stations with CO₂ capture to transmission of electricity to customers and transport of CO₂ for sequestration. The MS&A provides information in such categories as materials flows, including emissions, energy flows, performance, including efficiencies, costs, risks, and descriptive materials that decision makers need to efficiently and effectively allocate resources and direct technology research, development, demonstration, evaluation, testing, and commercialization of new technologies. Important aspects of the MS&A environment are:

- new technologies for individual elements can be examined as parts of integrated systems, which may include both conventional and new technologies, e.g., in retrofit, repowering, and life-extension projects, rather than in isolation;
- emphasis on external factors, such as impacts on the environment, the economy, human health and safety, and social institutions; and
- efficiency and ease of use owing to models that represent only the essentials to answer the kinds of questions required for decision making of the kinds described above, and a modular structure.

Facility-Siting, Fuel-Choice, and Technology-Choice Tradeoffs When Transport of CO₂ Materials is Added to Fuel Delivery and Electric Power Transmission Costs

The tradeoffs involved in selecting fuels types, fuel sources, fuel delivery technologies, generating technologies, transmission technologies, and the siting of facilities relative to fuel sources and customers are generally well understood under present

conditions, although special local and/or transient factors can complicate some of the tradeoffs. New factors resulting from the introduction of the transport of

- raw materials that may be required for some approaches to capturing and sequestering CO₂ for electric power production and delivery systems that utilize fossil energy sources, and
- CO₂ or CO₂-bearing materials for ultimate disposal

can significantly alter the outcomes of such tradeoff studies.

CO₂ is substantially heavier per carbon atom than are any of the common fossil fuels. The situation is generally far worse for raw materials that might be used to capture CO₂ and have to be transported for long distances and the resultant CO₂-bearing materials that might also then have to be transported long distances for sequestration. The distances for transport from plants in the Upper Midwest of the United States to beyond the continental shelf to deep ocean basins for disposal can be thousands of miles. The new costs, risks, ES&H impacts, technology choices that might be forced, and siting issues involved have generally been examined in only the most cursory fashion. A start has been made in examining such tradeoffs more accurately and thoroughly.

Negotiations are underway to establish a national simulation effort to evaluate various energy scenarios and the associated tradeoffs to reduce CO₂ emissions. This effort is being developed with the DOE Office of Fossil Energy, and should be supported at a rate of approximately \$1M/yr at Los Alamos. This effort will directly complement the Clean Coal Compendium Project mentioned earlier.

CO₂ Mitigation (Separation and Sequestration Technologies) (E.L.Joyce)

Solutions to the perceived climate change problem warrant international collaboration. Currently, our national investment in CO₂ mitigation is very limited in comparison with the other developed nations. It has been our intent in this effort to determine what the technical and economic possibilities for the future are in the area of CO₂ mitigation and with DOE support to establish a "Center of Excellence in CO₂ Mitigation" at Los Alamos.

Developing efforts in the area of Fossil Energy Plexes, called "Vision 21" Technology, look to high efficiency systems that generate H₂ from fossil fuels, with associated CO₂ capture and disposal or utilization schemes. Analysis of the technologies in this area requires examination of proposed processes for CO₂ capture, disposal, and utilization, realizing that these must operate within the "Vision 21- Energy Plex" scheme. As one begins the business of evaluating process needs for CO₂ mitigation technologies, it is

noteworthy to examine the actual process scale required of separation and sequestration unit operations in a typical utility. If one uses current technology as the baseline, a 1-Gigawatt (GW) coal plant, operating at 33% efficiency, produces roughly 300 kg/s of CO₂. At standard temperature and pressure (25°C and 1 atmosphere), this equates to 6×10^5 m³/hr. Current estimated cost targets for CO₂ mitigation technology are on the order of \$5 to \$50/tonne of CO₂. This wide range of costs includes the low cost associated with dispersed control technologies, as well as active capture systems, and lastly the upper limit being the Norwegian CO₂ tax. In reality the actual cost target will likely be toward the lower end of these estimates, since competitive alternative energy sources (renewable and nuclear) will set the acceptable costs for overall electricity production with a system that includes CO₂ mitigation.

Capture Technologies

The separation of hydrogen gas from high temperature CO₂ containing streams is very critical component of carbon dioxide sequestration technologies. Versatile cost effective sequestration will require separation of CO₂ from H₂, it is generally felt that separation at high temperatures is preferable to increase overall process efficiency, though at the same time this presents a more difficult set of operating conditions. In all, four types of separation techniques were investigated. These included: two high temperature membrane schemes and an intermediate temperature Zeolite thin film scheme and lastly a low temperature CO₂ Hydrate separation process. Research in these separation areas is very recent, with the overall need focused on lower costs and increased process efficiencies and throughputs, through the deployment of advanced materials and process development.

High Temperature Permeation Membranes (F. Garzon)

Many technologies envisioned for carbon dioxide sequestration involves the catalytic processing of a hydrocarbon or coal combined with water vapor at elevated temperatures to yield hydrogen gas and carbon dioxide. A high-temperature hydrogen-permeation membrane thus enables the isolation of the hydrogen fuel from the carbon dioxide waste. Los Alamos has developed hydrogen ion-conducting membranes that separate hydrogen from other gases at temperatures from 600-900 °C.

These ceramic membranes are based on rare-earth-doped SrCeO₃, BaCeO₃, CaZrO₃, and SrZrO₃ perovskites. The motivation for most of this work derives from the desire to utilize these materials for high-temperature, hydrogen-fueled, solid-oxide fuel cells. In a reverse operation mode, if metal or metal-oxide electrodes are deposited onto a dense pellet of this material and are heated to temperature T, the application of an electric potential to the

electrodes will cause a hydrogen partial pressure difference across the pellet according to the Nernst equation:

$$\Delta V = -\frac{RT}{zF} \ln \frac{P'_{H_2}}{P_{H_2}} \quad (1)$$

where F is Faraday's constant and z is the number of electrons transferred upon oxidation and reduction. We have demonstrated the separation of hydrogen gas from other gases and from high-temperature electrolysis using these materials.

The introduction of electronic conductivity into these perovskite materials via either chemical doping reaction or two-phase ionic/electronic conductor composites would eliminate the need for electrodes. The gas separation could be then performed using pressure gradients rather than electrical power. Initial results for the separation of H_2 from a number of feed streams is shown in Figure 1.

Figure 1. Hydrogen permeation data for solid-state, ceramic proton pumps.

Liquid Membrane Technologies (D. Devlin)

A membrane system based on the reactive solubility of CO_2 in molten salts is being explored for the separation of CO_2 from hydrogen at high temperatures. The separation mechanism relies on the reversible reaction, shown in Equation 2,

to facilitate the transport of CO_2 as a carbonate ion through the ionic melt. Reactive solubility of CO_2 in carbonate/oxide melts can be very high. Eutectic compositions can be in the range of 60 to 80 mole percent. Hydrogen solubility on the other hand is expected to be physical, obeying Henry's law and in the range of 10^{-7} to 10^{-6} mol/mol-atm. The large difference in solubilities should result in good separation. Operation of the membrane will require maintaining low partial pressures of CO_2 on the downstream side to enhance decomposition of the carbonate back to CO_2 .

Zeolite Thin Films (R. Dye)

Pulsed laser deposition (PLD) is uniquely suited to form novel thin-film zeolites for intermediate-temperature gas separation and catalytic supports [1-3]. Separations at 600°C have been performed at Los Alamos with these membranes. Novel thin-film zeolite materials with known pore sizes have been grown by PLD. Having this class of materials in thin-film form marks a major breakthrough in gas separations. Los Alamos with Dow Chemical was the first to have successfully deposited zeolitic thin films and demonstrated their usefulness as novel membranes and chemical sensors. The absence of binders in the fabrication of the zeolitic films by PLD allows for operation of the membrane at high temperature. Initial data in conjunction with a Polymer Electrolyte Membrane (PEM) are shown in Figure 2.

Figure 2. Polymer Electrolyte Membrane (PEM) operation in simulated reformer gas, with and without membrane separator.

CO₂ Hydrate Processing

This process uses thermal-chemical compression to form CO₂ hydrates/clathrates, as opposed to doing it with higher-value mechanical energy and clathrate-log pipelining, which is an analog of the emerging technology of coal pipelining for more efficient delivery of coal over long distances. The nominal operating conditions for the process are approximately 300 psi and 0°C [4]. To date, this promising process has been run at rates high as 1000-kg/hr CO₂ and has had significant process design and analysis, conducted by Semtech and Gilbert Commonwealth - Parson's Power, with cost estimates of approximately \$8/tonne CO₂ capture.

Disposal Technology

Geologic Disposal

Research into understanding disposal in deep aquifers, coal mines, and natural gas wells is needed. Issues of long-term stability of this disposal option need to be evaluated, which involve studies in areas related to CO₂ transport, fixation, and release. This presents a clear opportunity for Los Alamos geoscience expertise to contribute to this evolving national need.

Mineral Sequestration (E.L. Joyce)

Research has been conducted to develop processes that bind CO₂ in mineral substrates (mineral fixation). This process may produce an entirely new industry as more than ample supplies of the necessary minerals are available. An excellent review of the mineral reserves is given by Goff et al [5]. This approach permits a permanent storage option because of the thermodynamic stability of MgCO₃. Mineral fixation is an option currently under development at Los Alamos. This technology encompasses extraction of an alkali-silicate mineral, with recovery as an alkali hydroxide and subsequent conversion to an alkali carbonate. The overall reaction for the process is shown by Equation 3. Analysis of

the envisioned process indicates that the dissolution of mineral and recovery of the alkali-hydroxide are critical process steps because of energy management costs [6]. The feasibility of this reaction has been demonstrated by an aqueous route; however, the specific process

lacks sufficient energy management for a cost-effective implementation. Work aimed at removing this obstacle is currently underway.

Additionally, the carbonation of the hydroxide to a mineral carbonate is another critical unit operation. Currently, the necessary residence time for the solid phase is about 1/2 hour; in this time approximately 600 m³ of Mg(OH)₂ and 1.6 x 10⁴ m³ of CO₂ will be processed [7]. The reaction is shown as Equation 4. Currently the most encouraging

operating conditions for carbonation are 550°C and 50 atm. Because of the fine nature of the solid reactant, on the order of 50-150µm, a fluidized bed is a likely choice. An initial design and cost estimate, based on a 1-GW coal power plant producing 300-kg/s of CO₂, is presented below.

Costs based on a solid content of 6 x 10⁵ kg Mg(OH)₂, which assumes a density of 1g/cm³ for the polycrystalline solid [8,9] in the fluidized bed, have been estimated to be on the order of \$100M [7]. This cost estimate for the carbonation system should be considered optimistic in regard to necessary reactor volume. The reactor will likely require some additional volume for two reasons. The first depends on the particle size; for this case 50 - 150µm particles can require a void fraction of about 0.50 - 0.70 to initiate fluidization [10], and the second is the need for freeboard or disengaging volume above the fluidized bed. The experimentally determined effect of particle size on fluidization is shown in Figure 3. To reduce this required volume will require further optimization of the carbonation reaction.

The following discussion should be useful in scale-up and optimization of the carbonation process. This relates to the gathering and analysis of the experimental data, and extending these results to the design and scale-up of a functional reactor system.

Figure 3. Void fraction at the onset of fluidization for various materials [9].

Examination of the temperature dependency of the rate constant for the gas-solid kinetic results [7,11] indicates evidence of multiple mechanisms as shown in Figure 4 (note the change in slope). In estimating the kinetic parameters, the authors interpreted the results via a parabolic rate law or first-order reaction mechanism (with a second parameter estimated as a time constant) as the controlling step in the carbonation process. A review of the experimental technique (thermogravimetric analysis) employed [11] and the geometry of the gas-solid sample contact (flow around a crucible rather than flow through a porous mesh basket) lead us to conclude that a mixed-control model yields the most likely interpretation of this data (and the time constant). The mixed-control model includes gas film mass transfer, pore diffusion through the changing solid matrix, and interfacial chemical reaction control.

The classic result [12,13] is shown in Figure 5 and several sets of similar experimental data for the oxidation of zinc sulfide are shown in Figure 6. It is known that ignoring the mass transfer resistance can lead to a diffusional "corruption or falsification" of the apparent activation energy if a model based on chemical control is fit to data subject to transport resistances. The resulting "corrupted or falsified" kinetics makes it difficult to accurately determine the impact of changes in operating parameters such as temperature, pressure, and flow velocity on the "global" kinetics. That is, optimization of the reactor performance will prove difficult to achieve.

As shown in Equation 5, the numerical representation of the mixed-control mechanism relates the total time necessary for a given extent of conversion to the sum of the time for each individual mechanism [14]. One can then delineate the contribution of each of these mechanisms to the overall reaction by studying the experimental system for flow characteristics (gas film control) and the solid to separately account for the pore-diffusion effect. It is often the case in these types of reaction studies that one raises the flow

$$T_{\text{total}} = T_{\text{film alone}} + T_{\text{ash alone}} + T_{\text{reaction time}} \quad (5)$$

rates in the system to avoid gas-film mass transfer, but as Figure 7 and Equation 6 show, this relationship is exponential and as such often needs to be identified separately.

Figure 4. Arrhenius plot of rate constants for the dehydroxylation and simultaneous dehydroxylation and carbonation of $\text{Mg}(\text{OH})_2$ in helium and carbon dioxide, respectively. The rate constants were calculated using a contracting sphere model [11].

Figure 5. The minimization of external mass transfer or pore diffusion effects by operation at lower temperatures [12].

Figure 6. The rate of zinc sulfide oxidation according to numerous investigators. Polycrystalline spheres and plates: O, Denbigh and Beveridge; Δ , Natesan and Philbrook; ∇ , Gerlach and Stichel. Single crystals:

$\blacktriangle$, Ong *et al.*; $\blacksquare$, Cannon and Denbigh¹³

Figure 7. The minimization of external mass transfer effects by operation at high gas velocities [13].

Equation 6 is known as the Ranz-Marshall correlation for forced-convection mass transfer, expressed here as a function of Schmidt and Reynolds numbers. The identification of these contributions, often allows the experimenter to avoid excessive experimental costs

$$N_{sh} = A + B(N_{Sc})^m(N_{Re})^n \quad (\text{for a sphere } A=2, B=0.6, m=0.33, n=0.5) \quad (6)$$

by operating in a mixed-control regime, while still collecting the necessary intrinsic kinetic information. These constants are normally determined independently for the experimental system by studying a reaction known to be controlled by gas-film mass transfer (naphtha evaporation is a common surrogate) [15]. Since the molar density of the reactant $Mg(OH)_2$ is greater than the product $MgCO_3$, one can also expect to see pore closure and enhanced pore-diffusion control as the reaction proceeds. To determine the effect of pore-diffusion control, one normally examines the evolving pore structure as a function of extent of reaction; again several commonly employed techniques are shown in the text by Szekely *et al.* [16]. The intrinsic kinetic information, once extracted from the experimental data, can then be used for reactor design with added confidence when scaling the system.

The results of a mixed-control model, which incorporates both gas-film mass transfer and first-order chemical reaction (note: the parabolic rate law has a first order expression) as

the controlling mechanisms in the carbonation, is shown in Figure 8. As one can see the agreement between this simple model and experimental results is quite good. The binary gas-diffusion coefficient was estimated to be $3 \text{ cm}^2/\text{s}$ and the characteristic length as 0.1 cm , which yields a mass-transfer coefficient of 30 cm/s . The temperature ranged from 350 to 475°C , and pressure ranged from ambient to -0.78 Bar . The resistance due to chemical-reaction control was estimated as a multiple of the mass-transfer resistance; for these cases these ranged from $1000:100:1$ with increasing temperature.

Figure 8. Comparison of a mixed-control model for carbonation with experimental results for carbonation.

More complex models are available in the literature; a good starting source again is the text by Szekely, Evans, and Sohn [16]. General Mixed Control Models (multiple controlling mechanisms), like the "Grain Model," are discussed. These models are capable of describing both well-defined reactant/product interfaces (topochemical) and diffuse reactant/product distributions (non-topochemical) kinetics.

These models have great flexibility in regard to handling a variety of chemical reaction types as well as multiple reactions, while also being capable of accounting for both volume/morphology, and non-isothermal conditions within the particle. These model types have been applied extensively, in both the metals industry for both the gaseous reduction of metal oxides and the roasting of sulfide ores, as well as, in various desulfurization processes

for fossil-energy-based off gases. For several others who have also made significant contributions in this area, the reader is directed to the works of G. Bitsianes, K. Li, G.P. Martins, W.O. Philbrook, P.R. Taylor, N.J. Themelis, E.T. Turkdogan, and C.Y. Wen.

The current state of this effort indicates a need to understand the mass transfer and pore diffusion effects in the data, so that one can identify the necessary intrinsic kinetics for the carbonation reaction. Using something like the "Grain Model" for simulation of the polycrystalline (submicron crystallites) within particles may prove to be useful, as may experiments of the type described above.

Ocean Disposal

Storage of CO₂ is normally foreseen at depths greater than 1000m in the form of CO₂ hydrates/clathrates. A more clear understanding of hydrate formation as well as near surface phenomena and recirculation mechanisms is needed. The direct injection of clathrates is particularly attractive, as it permits direct processing of the off-gas stream rather than a pretreated stream (see previous section on capture technology). Additionally, various forms of CO₂ storage on the ocean floor in the form of bicarbonates or solid CO₂ are also being investigated. All these ocean storage techniques require knowledge regarding stability of the proposed end product, as well as its effects on marine life. A last technology subset related to ocean disposal is that of iron fertilization, whereby CO₂ is absorbed from the atmosphere and converted via vegetation/phytoplankton to form carbohydrates that ultimately die and are deposited on the ocean floor. Research is necessary into the level of iron loading, stability of the phytoplankton product, food cycle of marine life associated with plankton, amount of CO₂ sequestered and associated issues. This last technology again offers the potential for direct capture from air, with little to no energy cost.

Utilization Technology

Research is needed in CO₂ recycle by means of microalgae processes that produce biomass for subsequent conversion to liquid or gas synfuels. Additionally, research to utilize CO₂ to generate widely applicable feed materials such as methanol or dimethyl ether, via photochemical dissociation of CO₂, is ongoing.

Biological Fixation of CO₂ (P.J. Unkefer)

A general assessment of the potential of biological carbon dioxide fixation was examined to reflect a number of parameters. These parameters included global pools, movement between the pools, and basic economic drivers for technology implementation and acceptance.

Consideration was given at the global level to the major pools and their sizes and the fluxes between these pools and the atmosphere. The major pools are ocean, soil, atmosphere, and land plants. The atmosphere and land plants are of the same order of magnitude. The average residence times of carbon in these four pools were considered; all are on the order of several years except for the deep ocean pool (a subpool of the ocean), which is several hundred years. The flux between the pools is significant in all cases. Thus all pools were deemed appropriate as potential candidates to help with carbon dioxide fixation.

The general economic drivers for land systems are feasible if one uses biomass as co-fuel with other fuels because it will then have value as a fuel. To increase the economic position, there are two avenues: increase production per acre or decrease biomass handling costs (mechanical issues). LANL technology in development was identified that addresses the former. Another economic driver for land systems is through agricultural production. Increased plant growth rates or plant size are economic products in agriculture and thus would provide drivers for their own perpetuation and adoption in broad use. The above mentioned LANL technology also positively contributes to this economic driver for its increased carbon dioxide fixation.

Success of the project will depend on a detailed understanding of the competing technologies and where they fit in terms of economic and technical feasibility and applicability. It will be necessary as the assessment is developed to invest in judicious "proof-of-principle" experiments such as head-to-head comparisons of the various mitigation scenarios (including selected schemes for CO₂ capture) with either utilization or disposal. Up to now the researchers working in global climate change have had relatively little interaction with energy technology researchers. This work enables us to create a strong linkage between fossil energy and the environment. The opportunity exists to explore some of the relevant cutting-edge technologies that relate to global warming and the economic and political tradeoffs associated with energy alternatives. For the nation and the world, the possibilities range from continuing business as usual to drastic cuts in CO₂ emissions with the resulting high economic costs or an inability to meet energy demands.

Solar Thermal Recycling of CO₂ to Methanol (E.L. Joyce/W.J. Parkinson)

This effort involved developing an engineering process flow diagram for the conversion process. The photochemical process chemistry is shown in Equation 7, with potential H₂ production schemes shown in Equations 8 and 9, and the methanol conversion reaction shown in Equation 10. This effort was undertaken in order to determine the economic viability of the process. This process in reality represents an interesting class of

processes, which would be most appropriately labeled "hybrid" processes. One could easily imagine supplementing fossil energy in an effort to reduce the carbon loading with any one of several alternative energy sources. In this case, if one looks at the total system (utility + recycle), the process supplements fossil energy with solar energy to decrease carbon loading.

The heat and material balance for the process has been done with the ASPEN flowsheet simulator. From a thermodynamic standpoint, the process appears feasible, though some challenges exist. A cost analysis is difficult, since many of the components are custom items. The plant as initially designed would not operate 24 hours per day; this presents both startup and shutdown problems on a daily basis. Such a design would require additional capital equipment for startup and shutdown as well to store the large quantities of either CO or CO₂, since the photochemical reactor is intended to operate in conjunction with a methanol plant. Therefore the design requires supplying surge capacity or storage tanks.

The initial design envisioned quenching the hot product gas (approximately 2000 - 3000°C) with cold CO₂ in a 5:1 ratio. This results in a requirement to reprocess large amounts of gas, while removing very little CO₂ from the system. Other cooling mechanisms are certainly possible; examples might include fluidized bed cooling or expansion cooling, though these will add additional cost to the process and possibly allow active sites for recombination of the carbon monoxide and oxygen. Separation of the CO₂, CO, and O₂ as designed used cryogenic technology. Carbon dioxide is removed as a solid and then cryogenic distillation used to separate the carbon monoxide and oxygen. This will likely be expensive and difficult to control, because of the transient nature of the process.

Because methanol is the intended product, hydrogen must be generated to produce methanol. This can be accomplished by either the water-gas shift reaction or the reforming of methane (Equations 8 and 9). Methanol is then produced by the reaction of hydrogen with carbon monoxide (Equation 10).

To determine the overall chemistry for methanol production, one can combine either Equation 8 and 10 or Equation 9 and 10 depending on whether methane is used in the process. The overall conversion is shown by Equations 11 and 12, respectively. These

two reactions point to the maximum conversion for each process path assuming 100% conversion and capture of the product carbon monoxide in the photochemical step.

If one employs the water-gas shift reaction to generate H_2 and subsequently produces methanol, then the maximum conversion of CO converted to methanol is 33%, as shown by Equation 11. If one reforms methane to generate H_2 , then the maximum to methanol will be 67%, as shown by Equation 12. One should remember that any operating inefficiencies from the photolysis, quenching, and separations processes will lower these estimated conversions.

In conclusion, the major challenges facing this process involves quenching the products of the photochemical process, cost effective separation of the CO , CO_2 , and O_2 , and optimization of the methanol conversion reaction.

Summary

As can be seen from the above discussion, Los Alamos has many capabilities to bring to bear in the area of carbon management. This effort has allowed us a chance to understand national and international needs and in turn look at how we might apply the Laboratory's science and technology capabilities toward addressing those needs. These capabilities range from systems analysis to the development of new unit operations or the development of entirely new processes. In the past year, we have been successful in looking at requirements in power generation technology and a new program in this area has been established. Additionally, we have begun significant development and understanding of new approaches to mitigation technologies that offer opportunities to continue to use valuable fossil energy reserves while at the same time satisfying the ever developing concerns about "greenhouse" gases and their potential effect on climate. As a result of this, DOE Fossil Energy - Coal and Power Systems Office (CPS) has asked Los Alamos to consider creating a Center for Carbon Management and Sequestration at the Laboratory.

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