Biogenic Methane: A Long-Term CO_2 Recycle Concept

David J. Beecy; david.beecy@hq.doe.gov; 301-903-2787
U.S. Department of Energy
Office of Environmental Systems
Office of Fossil Energy
19901 Germantown Road
Germantown, MD 20874

Frank M. Ferrell; frank.ferrell@hq.doe.gov; 301-903-3768
U.S. Department of Energy
Office of Environmental Systems
Office of Fossil Energy
19901 Germantown Road
Germantown, MD 20874

James K. Carey; jcarey@energetics.com; 301-621-8432
Energetics, Incorporated
7164 Gateway Drive
Columbia, MD 21046

INTRODUCTION

Carbon sequestration is one of three major pathways to achieve stabilization of greenhouse gas concentrations. Compared to the other two pathways—improving the efficiency of energy use and reducing the carbon content of fuels—carbon sequestration is the newest approach and is less mature from a research and development perspective. In fact, it is a new field of science and technology, one in which there is a great opportunity for the identification and exploration of novel concepts. This paper explores some of these opportunities, identifies several current avenues for novel concepts, and focuses on one "value-added" concept.

Novel approaches to carbon sequestration can play an extremely important role in extending the boundaries of technology options for CO_2 capture, storage, and reuse. Opportunities include conversion to benign, stable compounds for long-term storage or to value-added products for reuse. For example, one area is CO_2 mineralization. One concept uses carbonic anhydrase enzyme to convert dilute, unseparated CO_2 to HCO_3^- and then to everlasting calcium and magnesium carbonates. This could offer a stable, essentially permanent storage option for carbon sequestration. Another area is biogenic methane. One concept is the geologic storage of CO_2 in depleting and depleted oil and gas reservoirs, with subsequent conversion of the CO_2 to CH_4 via designer microbes or biomimetic systems that operate either below or above ground. This could lead to "closed-loop" fossil systems, providing a sustainable methane economy with near-zero net CO_2 emissions.

A common element of many of these concepts is to enhance naturally occurring biochemical and geochemical processes. That is, to identify and replicate (at greater scale, faster conversion rates, etc.) natural processes that mediate interactions that are beneficial for the purposes of carbon sequestration. Microbial consortia in the ocean sediments, for example, are known to convert CO_2 to both CH_4 and carbonates through various biochemical pathways. The overall challenge is to 1) identify pathways of potential interest, 2) elucidate the biogeochemical processes involved, and (3) develop enhanced analogs through bioengineering or biomimetic approaches. Such approaches could yield breakthrough processes that are sustainable, environmentally benign, and cost-effective.

OBJECTIVE: ACHIEVING THE SEQUESTRATION VISION

The vision for the Sequestration R&D Program is to develop the scientific understanding of sequestration and develop, to the point of deployment, those options that ensure environmentally acceptable sequestration to reduce anthropogenic CO_2 emissions and atmospheric concentrations. In the near- and mid-term, the program will develop options for value-added geologic sequestration with multiple benefits, such as using CO_2 for enhanced oil recovery and for enhanced methane production from deep, unminable coal seams. Over the long-term, the technology products will be revolutionary and require less reliance on site-specific or application-specific factors to ensure their economic viability. The program seeks to use early successes in niche value-added applications to attract greater industry interest and participation in advanced sequestration concepts R&D.

Putting the Carbon Back in the Ground

With the passage of time, plus temperature and pressure, the carbon in plants and fossils buried underground has been converted to petroleum, coal, and other fossil fuels. These are the same fossil fuels that are the source of the CO_2 emissions that we now seek to reduce. The vision for geologic sequestration is “putting this carbon back in the ground.”

Under the surface of the earth, in the U.S. and many areas of the world, are structures that once were filled with oil and gas but now have space that could be used for storing CO_2. Under the right geologic setting, a portion of this injected CO_2 may be converted to fixed minerals or, in the presence of methanogens and other biologic agents, back to methane (1,2).

Other structural settings, lacking the presence of hydrocarbons, are filled with saline waters left over from pre-historic seas. These structures would also serve as sites for CO_2 storage, displacing the water in the structures or becoming dissolved in the saline water itself, much as is the case with natural mineral water.

Role of Natural Analogs

Opportunities exist for understanding the long term behavior and safety of these underground carbon dioxide storage sites from rigorous study of "natural analogs." In certain geologic and high temperature settings, the hydrocarbons or fossil fuels in a reservoir have been converted to CO_2. In other settings, CO_2 from deeper sources has migrated and become trapped in these underground structures (3). In either case, the CO_2 in these natural analogs has existed for millions of years. Understanding the interactions of carbon dioxide with formation water, rock and minerals and assessing the seals and leakage (if any) of natural CO_2 storage sites can provide valuable insights and data obtainable in no other manner.

Value-Added Geologic Sequestration

As introduced above, some of the geologic settings offer the potential for value-added byproducts, helping defray some of the costs of carbon sequestration. Notable examples are the injection of CO_2 for enhanced oil recovery and enhanced coalbed methane recovery. Numerous barriers still exist in using these options for CO_2 storage, such as reconciling the conflicts between achieving the lowest cost of oil/methane recovery and maximizing CO_2 sequestration. In all cases, adding appropriate long-term monitoring and verification to the CO_2 injection and storage process will be essential.

In the near term, the adaptation of these existing technologies can provide viable options for using geologic sequestration. In the longer term, considerable research and technology demonstration will be required to fully define and lower the costs of advanced options, such as saline formation storage, biomineralization, or even methane production through methanogens or biomimetic approaches.

APPROACH: THE SEARCH FOR VALUE-ADDED ADVANCED CONCEPTS

Value-added geologic sequestration provides a template for the desired attributes of advanced concepts. The only way we can expect to create new, advanced concepts which have a chance for achieving program goals is to pursue advanced concept options which can also achieve multiple benefits, or as we have called them, value-added benefits.

For the longer-term, we envision closed-loop fossil fuel systems. That is, systems in which the carbon rejected in the fuel production or use is "recycled". Envision systems such as shown conceptually in Figure 1. Conceptually, this is straight-forward. It is analogous to closed-loop biomass systems, where the "recycle module" is the growth of replacement standing biomass, over a 30-40 year interval. The challenges are formidable. CO_2 is not an attractive feedstock from an economic or energy efficiency viewpoint. But fortunately nature provides us some clues as to pathways we might pursue.

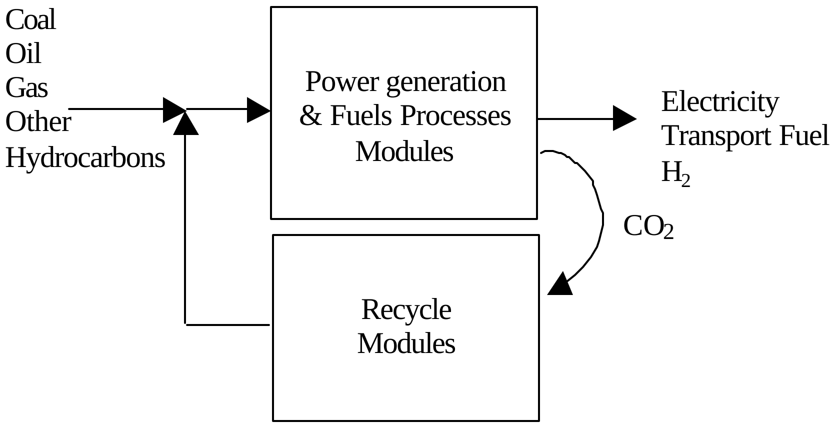


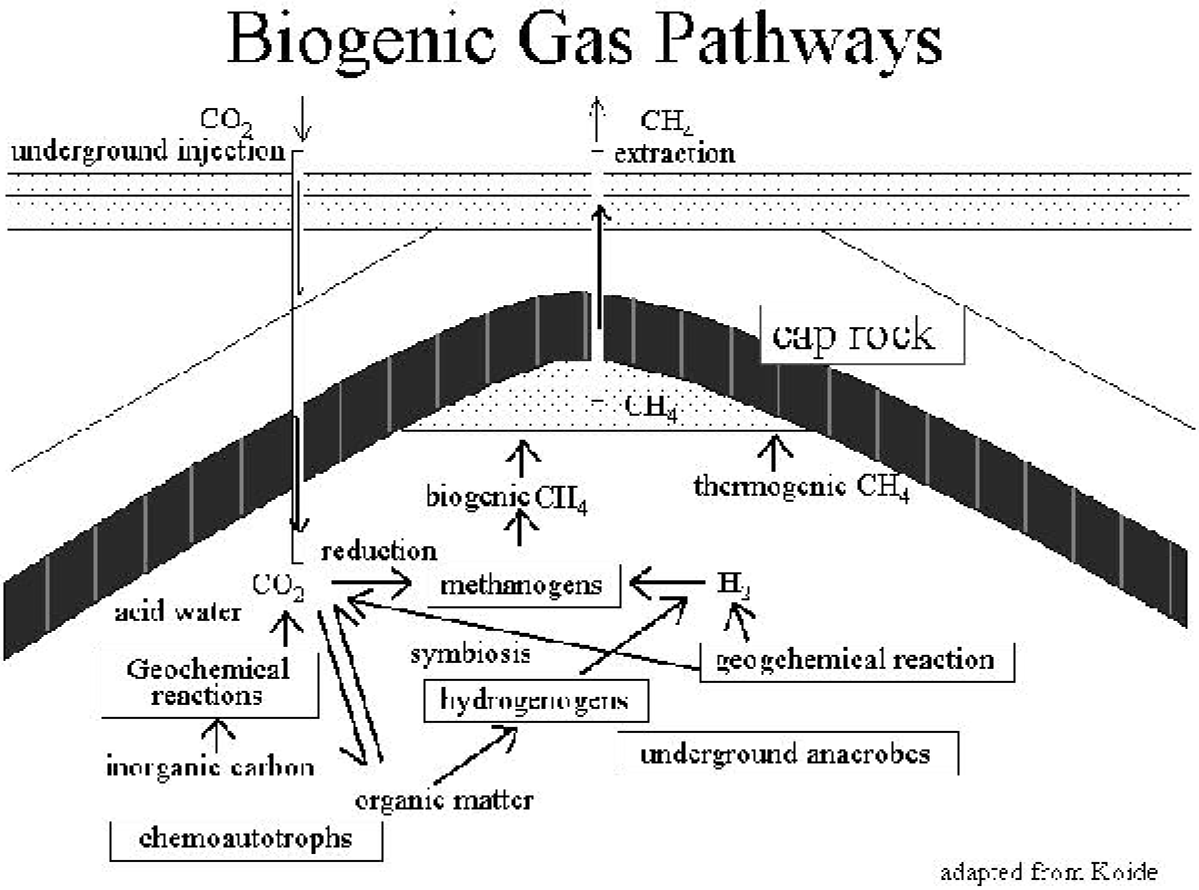
Figure 1 Closed-Loop

Several concepts identified to date are based on elucidating and enhancing naturally occurring processes. Two examples based on complex biogeochemical processes occurring in nature are mineralization and biogenic methane. Mineralization is the conversion of CO_2 to Ca and/or Mg carbonates that are stable in nature and constitute essentially permanent sequestration of CO_2. One concept uses carbonic anhydrase enzyme to convert dilute, unseparated CO_2 to HCO_3^- and then to calcium or magnesium carbonates (4,5). Biogenic methane arises from methanogenesis, a biological process widely found in nature in which bacteria generate methane by several pathways, including CO_2 reduction (6,7). One concept envisions closed-loop systems with injection of CO_2 into depleted (or depleting) oil or gas reservoirs, with the use of "designer" microbes to convert the CO_2 to CH_4 at commercially useful rates of gas generation. Alternatively, a process using biommetic catalysts could be carried out above-ground (2).

Unfortunately we have yet to find a mineralization concept that is value-added. Both of these examples are extracted from the field of biogeochemistry. What other examples exist? We have only recently started to seriously explore these phenomena. Can we create biomimetic pathways to produce "value-added" products from CO_2? The associated disciplines of biology, chemistry and catalysis offer a rich set of opportunities for future research to identify revolutionary new chemistry/biochemistry.

SCIENCE & TECHNOLOGY: BIOGENIC METHANE PATHWAYS

Biogenic methane is a term used to describe natural gas derived from the reduction of CO_2 via biogeochemical processes (8). The processes which contribute to the production are complex, poorly understood, but pervasive in nature (7). The operative processes vary from site to site where observations have been made, but generally have occurred over long periods of time. Biological processes include methanogenesis and hydrogenogenesis, but there are also geochemical processes that have been identified (9). Figure 2 provides a conceptual picture of the many possible pathways which may come into the process of conversion at any particular site (1,10).



adapted from Koide

Figure 2

Methanogenesis in Natural Systems

Methanogenic bacteria generate methane by several pathways, principally the fermentation of acetate and the reduction of CO_2 (6,15). Figure 3 diagrams the microbial chemistry that has been elucidated for the thermophile *Methanobacterium thermoautotrophicum* in the reduction of CO_2 to CH_4 (7). Generally a consortium, or food chain of microbial organisms, operates together to effect a series of biochemical reactions in the production of methane in energy-yielding cellular processes. Methanogens are anaerobic bacteria of the family Archaea, and are found in such diverse environments as landfills, digestive systems of animals, in deep ocean vents, and in coal seams. Chemosynthetic communities are found in close association with cold hydrocarbon seeps, for example, and demonstrate complex relationships that include the mineralization of CO_2 as well as methanogenesis (11). In one location, sampling of hydrocarbon gases from ocean-floor cold hydrocarbon seeps in Monterey Bay, California suggest that most of the methane produced is microbial in origin (12). In coal seams, methanogens may increase coalbed methane production. Laboratory study of microbially enhanced coalbed methane processes indicate that microbial consortia can increase gas production through conversion of coal and enhancement of formation permeability, leading to the potential for substantially increased methane production (13).

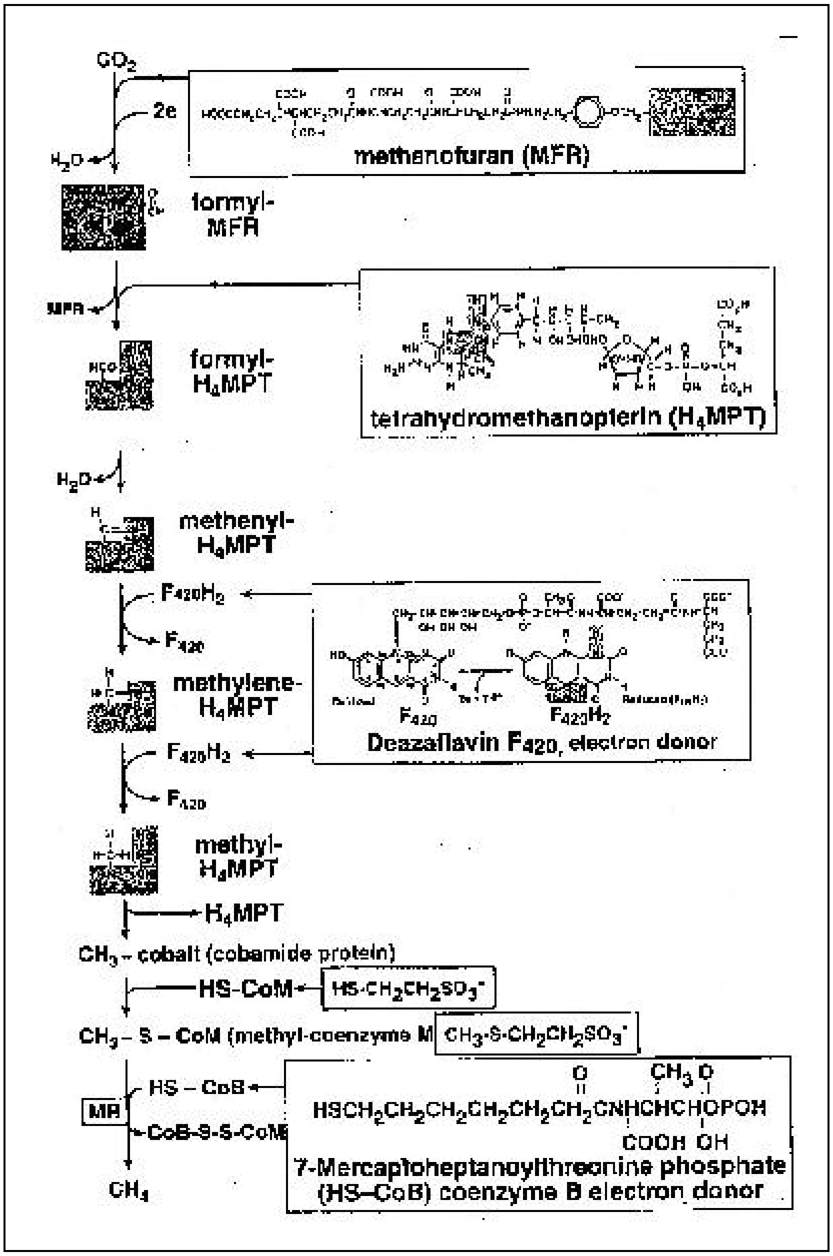


Figure 3. Microbial Chemistry of CO_2 Reduction to CH_4 [from Wolfe (7)]

In general, methane in the earth’s crust may be formed by both biogenic (that is, the conversion of organic matter) and abiogenic processes. The vast majority appears to be biogenic in origin, and results from a combination of microbial production and thermogenic processes (14). It is believed that 20% of the natural gas in the earth is from methanogens, of which 2/3 is by acetate fermentation and 1/3 by CO_2 reduction (15). While the portion generated by methanogen varies, there is strong evidence that it may be the predominant mechanism in some fields. For example, in the Terang-Sirusan Field in the East Java Sea, methane is generated exclusively by methanogens using the CO_2-reduction pathway (16). Furthermore, recent study of oil and gas fields in the Gulf of Mexico sheds light on the rate of methane evolution. It appears that there may be significant recharge of reservoir methane in a timeframe (decades) that is significant to commercial uses (17).

Where Are We Today?

Developments in genetic decoding, gene sequencing, identification of novel enzymes, and selection of desirable traits have the potential to result in enhanced CO_2 to CH_4 conversion processes. The potential exists for both improved biological processes using engineered biological systems, or processes that mimic biologically-based catalysts and processes (biomimetics). For example, advances in the "directed development" of microorganisms offers the potential for enhancing biochemical processes and pathways of interest for commercial applications (18). Also, for example, the supply of hydrogen via hydrogenogens to the methanogen-catalyzed conversion of CO_2 to CH_4 may be a major bottleneck in methane evolution. There is probably an optimum set of methanogen and hydrogenogens in a given system as well as a need in some, but not all, cases to inject organic matter to help supply hydrogen and thereby make the overall conversion of CO_2 to CH_4 go faster. Obviously, this is an area of high-potential research that can be explored and possibly exploited (7,10).

BENEFITS

The potential payoff is undeniably large. Low-cost, natural-process based systems could provide the foundation for the sequestration of large amounts of CO_2. Moreover, these processes would be both environmentally acceptable and sustainable. These are key factors for any systems that may be deployed worldwide in large numbers.

FUTURE ACTIVITIES

Given the amounts of CO_2 that will need to be sequestered to reduce global CO_2 concentrations, advanced concepts must play a pivotal role in providing viable and cost-effective science and technology options for the challenge ahead. Advanced concepts based on natural processes offer great promise but much basic and applied scientific research will be needed before the true potential can be assessed.

While there appears to be a sound fundamental basis for this and related approaches, several areas of research are indicated.

- A better understanding of existing natural analogs and emerging sequestration processes in various geological settings is required.

- The kinetics of known microbial conversions appear to be relatively slow; increases of many orders of magnitude will be required for commercial-scale processes.

- Related factors, such as growth cofactors needed to sustain a healthy microbial population, the source of hydrogen for CO_2 conversion, and the mechanisms to remove waste products in a geological setting must be identified.

- While the approach would build on natural geophysical and biochemical processes combined with novel or enhanced enzyme and energy pathways, our present understanding of these processes is fragmented in this context. A systematic assessment of the linkages and relationships of the geologic, chemical, and biological components will be necessary.

For approaches based on the evolution of biogenic methane, a number of specific biochemical pathways and mechanisms must be explained.

- The reaction pathways that occur in natural systems must be identified and the pathways of interest to sequestration selected.

- The specific mechanisms and enzyme systems that mediate these reaction pathways must be determined.

- “Fast” reaction pathways must be identified and/or the kinetics of slower pathways must be enhanced for commercially-useful rates.

- The specific heats of individual process steps must be understood to allow determination and refinement of process engineering and economic factors.

The authors wish to interest researchers from various disciplines in beginning an open and extended dialogue on the potential of novel concepts, such as the one discussed here, in developing science and technology options to mitigate global climate change. The role of novel science and technology approaches will be critical to the development of effective mechanisms to stabilize greenhouse gas concentrations.

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