Conversion of Carbon Dioxide to Products of Value

Submitting Organization: Catelectric Corp.
Peter D. Pappas, President
33 Island Circle South
Groton, CT 06340-8823
Phone 860-912-0800
Fax 860-536-2227
Email peter@mcmil.com

Contributing Organization: University of Connecticut
Department of Chemistry
Dr. Steven Suib, Department Head
55 North Eagleville Road, Unit 3060
Storrs, CT 06269-3060
Phone 860-486-2797
Fax 860-486-2981
Email STEVEN.SUIB@uconn.edu

Key Words:
Climate Change, Energy Independence, Carbon Dioxide, Greenhouse Gas, Catalysis
Executive Summary

This is a proposal to initiate funding opportunities for chemical processes which have the promise of efficiently converting carbon dioxide (CO₂) into hydrocarbon products of commercial value. CO₂ constitutes 85% of the undesirable greenhouse gas in our troposphere and most comes from human activity.

Because CO₂ is an inert, highly stable compound, previous funding opportunities have assumed that no feasible means of converting (activating) CO₂ can be developed. The deployment of such technology addresses the critical national needs of mitigation of climate change and promotion of energy independence as the hydrocarbon products are largely made from components of fossil fuel.

The alternatives currently in development for mitigation of CO₂ atmospheric discharge, such as cap and trade or sequestration and storage are not feasible long term solutions. Under those solutions CO₂ is still produced and will eventually escape into the atmosphere. A solution that eliminates the gas is the only long term answer.

Evidence of Critical National Need and Policy

Climate Change

White House Press Briefing on the Second International Panel on Climate Change, April 6, 2007

Participants: Dr. Sharon Hays, White House Office of Science and Technology Policy, Jim Connaughton, Chairman, White House Council on Environmental Quality

“This report further underscores what the President has been saying for some time about the seriousness of this challenge, a point the President emphasized in the State of the Union this year of the need to confront the challenge.”

“The President has set a national goal through 2012 of improving our greenhouse gas intensity economy-wide by 18 percent.”

Reflections on the Science and Policy of Energy and Climate Change, American Geophysical Union Fall Meeting, December 10, 2007, by Dr. John Marburger, Director, Office of Science and Technology Policy, Executive Office of the President

“...Earth's heat balance is already tilted and some effects of massive CO₂ production are already evident. The current annual release from the world’s energy economy, by far the largest contributor to increased atmospheric CO₂, is about 27 billion tons of CO₂...”

“The energy balance of the Earth – the difference between energy absorbed from the sun and other sources and energy re-emitted back into space – is being affected by human activity.”

Understanding and Responding to Climate Change, Highlights to National Academies Reports, National Academy of Sciences, National Academy of Engineering, Institute of Medicine, National Research Council, 2008 Edition

“How do we know that human activities are changing the Earth’s climate? The concurrent increase in surface temperature with carbon dioxide and other greenhouse gases during the past century is one of the main indications. Prior to the Industrial Revolution, the amount of carbon dioxide released to the atmosphere by natural processes was almost exactly in balance with the amount absorbed by plants and other “sinks” on the Earth’s surface. The burning of fossil
fuels (oil, natural gas, and coal) releases additional carbon dioxide to the atmosphere. About half of this excess carbon dioxide is absorbed by the ocean, plants, and trees, but the rest accumulates in the atmosphere, amplifying the natural greenhouse effect.”

**Consequences of Climate Change (from U.S. Environmental Protection Agency)**

**Public Health** - “Extreme temperatures can lead directly to loss of life, while climate-related disturbances in ecological systems, such as changes in the range of infective parasites, can indirectly impact the incidence of serious infectious diseases.” ii

**Agriculture** - “The forces that shape our climate are also critical to farm productivity. Human activity has already changed atmospheric characteristics such as temperature, rainfall, levels of carbon dioxide (CO\textsubscript{2}) and ground level ozone. The scientific community expects such trends to continue.” iii

**Ecosystems and Biodiversity** – “The overwhelming majority of studies of regional climate effects on terrestrial species reveal consistent responses to warming trends, including poleward and elevational range shifts of flora and fauna. Responses of terrestrial species to warming across the Northern Hemisphere are well documented by changes in the timing of growth stages (i.e., phenological changes), especially the earlier onset of spring events, migration, and lengthening of the growing season”. iv

**Coastal Zones and Sea Level Rise** – “Sea level is rising along most of the U.S. coast, and around the world. In the last century, sea level rose 5 to 6 inches more than the global average along the Mid-Atlantic and Gulf Coasts, because coastal lands there are subsiding. Higher temperatures are expected to further raise sea level by expanding ocean water, melting mountain glaciers and small ice caps, and causing portions of Greenland and the Antarctic ice sheets to melt. The IPCC estimates that the global average sea level will rise between 0.6 and 2 feet (0.18 to 0.59 meters) in the next century.” v

**Water Resources** – “All regions of the world show an overall net negative impact of climate change on water resources and freshwater ecosystems. Areas in which runoff is projected to decline are likely to experience a reduction in the value of the services provided by water resources. The beneficial impacts of increased annual runoff in other areas are likely to be tempered in some areas by negative effects of increased precipitation variability and seasonal runoff shifts on water supply, water quality and flood risks.” vi

**Energy Independence**

ENERGY INDEPENDENCE AND SECURITY ACT OF 2007 (Public Law 110–140)vii

“An Act To move the United States toward greater energy independence and security, to increase the production of clean renewable fuels, to protect consumers, to increase the efficiency of products, buildings, and vehicles, to promote research on and deploy greenhouse gas capture and storage options, and to improve the energy performance of the Federal Government, and for other purposes.” vii

**The Feasibility of Carbon Dioxide Activation and Conversion**

Converting CO\textsubscript{2} into valuable hydrocarbons is thermodynamically uphill. This process takes a product of combustion and makes a precursor to combustion. For example, the simplest possible reaction by which CO\textsubscript{2} and water can be converted into an alkane would be methane:

\[
\text{CO}_2(g) + 2\text{H}_2\text{O}(g) \rightarrow \text{CH}_4(g) + 2\text{O}_2(g)
\]

This is an endothermic reaction, requiring an input of 818.5 kilojoules of energy (delta G) per mole of methane produced. Like the reverse reaction, combustion, the bulk of the energy requirement is thermal.
The likely process is catalytic, as catalytic reactions are driven by the kinetics of thermal energy. There are two ways that a catalytic activation of CO$_2$ could be accomplished with economic feasibility. The first method uses waste heat. Fossil fuel plants try to turn as much heat out of the combustion as possible to energy, so the flue gas after the preheater is at about 150 °C, too low for efficient catalysis. Nuclear power plants, on the other hand, have a far greater waste heat dissipation need. Channeling that waste heat into CO$_2$ conversion would have the dual benefit of generating carbon credits and reducing thermal pollution from the plant.

The second way the process can work economically is in existing applications that require thermal energy. For example, formaldehyde is produced industrially by the catalytic oxidation of methanol. In the more commonly used FORMOX process, methanol and oxygen react at 250-400°C. The thermal energy is already invested in the process. The economic advantage of CO$_2$ activation in this process is the substitution of a less expensive feedstock and, again, carbon credits, with the added strategic benefit of elimination of the fossil fuel derived feedstock.

**Alternative Solutions**

Because of the recognized urgent problem of climate change, significant investment has been made in research, development, and actual deployment of CO$_2$ mitigation measures:

**Sequestration and storage** – capturing and storing CO$_2$ in the earth or ocean. “The greatest reductions in future U.S. electric sector CO$_2$ emissions are likely to come from applying carbon capture and storage (CCS) technologies to nearly all new coal-based power plants coming on-line after 2020.” Problems associated with sequestration and storage are limited capacity, CO$_2$ escape to the atmosphere, ocean acidification, and a containment duration requirement in excess of nuclear waste.

**Agricultural Modification and Reforestation** – modifications include containment of decaying biomass to eliminate escape of methane. Such modifications do reduce greenhouse gas but do nothing regarding CO$_2$. These measures are limited by capacity. Reforestation may be a popular solution, but it is inadequate: to further reduce U.S. carbon dioxide emissions by 7%, as stipulated by the Kyoto Protocol, would require the planting of "an area the size of Texas [8% of the area of Brazil] every 30 years."

**Energy Conservation** – The “low hanging fruit” has been mostly taken. Further measures, such as equipment and motor replacement with more energy efficient units are capital intensive.

**Alternative Energy** – the “green alternatives, such as wind and solar are inefficient and not economically feasible without subsidy. Nuclear is capital intensive, has a long lead time and issues on spent fuel storage are unresolved.

There have also been studies on adaptation – Changes in water management, land use (coastal habitation), agriculture policy, etc. These areas address the worst case scenario that climate change cannot be stopped.

Pollution abatement measures such as the Clean Coal Power Initiative (CCPI) by the National Energy Technology Laboratory (NETL), address pollutants other than CO$_2$, which is the inevitable product of hydrocarbon combustion. Indeed, the project will result in near pure CO$_2$ stack gas, the perfect environment for a catalytic CO$_2$ conversion reactor as some of the abated pollutants can cause catalyst poisoning.
Certain gasses are known to promote radiative forcing and have become known as “greenhouse gasses”. The effect of radiative gasses in a planet’s atmosphere is proven. The atmosphere of Venus, for example, is 96.5% carbon dioxide and the planet’s surface temperature is over 870°F.

<table>
<thead>
<tr>
<th>Greenhouse Gas</th>
<th>Preindustrial Level</th>
<th>Current Level</th>
<th>Increase since 1750</th>
<th>Radiative forcing (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>280 ppm</td>
<td>384 ppm</td>
<td>104 ppm</td>
<td>1.46</td>
</tr>
<tr>
<td>Methane</td>
<td>700 ppb</td>
<td>1,745 ppb</td>
<td>1,045 ppb</td>
<td>0.48</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>270 ppb</td>
<td>314 ppb</td>
<td>44 ppb</td>
<td>0.15</td>
</tr>
<tr>
<td>CFC-12</td>
<td>0</td>
<td>533 ppt</td>
<td>533 ppt</td>
<td>0.17</td>
</tr>
</tbody>
</table>

i (http://www.epa.gov/climatechange/effects/health.html)

iii http://www.epa.gov/climatechange/effects/agriculture.html

iv http://www.epa.gov/climatechange/effects/eco.html

v http://www.epa.gov/climatechange/effects/coastal/index.html

vi http://www.epa.gov/climatechange/effects/water/index.html


viii The Power to reduce CO2 Emissions: The Full Portfolio, The EPRI Energy Technology Assessment Center, August 2007

ix William H. Schlesinger, dean of the Nicholas School of the Environment and Earth Sciences at Duke University, in Durham, North Carolina.

x Climate Change 2007: Synthesis Report, Intergovernmental Panel on Climate Change

xi http://www.netl.doe.gov/technologies/coalpower/cctc/