Greenhouse Gases: Mitigation and Utilization CHEMRAWN XVII, Part II: Sequestration and Mitigation Strategies

by John Malin

This is the second part of a conference report on the CHEMRAWN XVII Conference on Greenhouse Gases: Mitigation and Utilization, held 8-12 July 2007 at Queens University in Ontario, Canada. The first part of this conference report (Jan.-Feb. 2008 *CI*, p.35) covered policy issues and strategies. This article covers the sequestration of greenhouse gases (GHG) and their mitigation and utilization.

The essential question is this: If the goal is to reduce net CO_2 emissions to zero, how can humankind provide for its energy needs? Timo Makinen, manager for Shell's climate change and GHG strategy, stated that since world oil demand is projected to increase, humankind is destined to remain in the fossil fuel age for the next generation or two. In Canada, oil sands are projected to provide some 75 percent of all gasoline by the year 2020. However, industry is adopting voluntary standards to reduce GHG emissions.

Sequestration Options

Rob Seeley, general manager for Sustainable Development and External Affairs, Oil Sands, for Shell Canada Energy, further described how, starting in the year 2012, the Shell "Quest" project proposes to capture 1.2 million tons of CO₂ generated per year by Shell's Scotford Upgrader facility at Ft. Saskatchewan, which produces synthetic crude oil from oil sands bitumen. After liquefaction, the CO₂ will travel through a 150-kilometer pipeline to oil fields at Pembina and



Swan Hills, where it will be used in enhanced oil recovery and/or will be stored in depleted wells. The two fields have the combined potential to store some 150 Gtons of CO_2 over two to five decades after startup in 2012. Shell is also evaluating a project to sequester CO_2 in a deep aquifer, with completion of a test well scheduled for 2008.

Although some costs can be recouped by selling ${\rm CO_2}$ to companies engaged in enhanced oil recovery, Seeley pointed out that there is an inherent "economic gap" in the project. Shell does not propose to cover all the costs of this project on its own and is requesting that the province of Alberta and/or the Canadian federal government provide a financial subsidy.

David Keith of the University of Calgary summarized how variations in patterns of land use and the accelerated burning of fossil fuels have modified the global carbon cycle and are on track to produce climate change of uncertain magnitude and impact. Framing climate change as an unintentional and thus unmanaged byproduct of our industrial society, he described the need for management and the prospects for capture and storage of fossil fuel carbon. Currently, Keith noted, there are only two CO₂ sequestration projects operating at the megaton-per-year level. Keith listed a "toolbox" of techniques, including injection of CO₂ into the deep ocean, storage of CO₂ in deep geological formations, and integration of biomass with industrial carbon capture. He also discussed the possibility of using high-altitude nanoparticles to increase the earth's albedo by shading the poles. All these approaches, he warned, would have to be evaluated for safety. The potential for accidents would be high, particularly if these activities were carried out in remote, unpoliced regions.

For example, Farzam Javadpour explained the advantages of CO_2 flooding of depleted oil and gas pools and the challenges of this method, but pointed out that CO_2 stored in geological formations would not be safe from earthquakes. Regarding the sequestration of carbon dioxide as clathrates under deep ocean sediments, Salman Alava of the University of Waterloo noted that liquid CO_2 is more dense than water. At high pressures encountered at depths of around 2 600 meters, it forms clathrate hydrates. If stored beneath undersea sediments, CO_2 clathrates should be stable for millions of years. However, because methane clathrates are also present on the ocean floor, Alava and coworkers performed modeling studies to determine whether a CO_2 clathrate would

be more or less thermodynamically stable than a clathrate-containing methane. They calculated that in a double cage structure, one of the two methane molecules would be replaced by CO_2 . Thus the method is at least thermodynamically feasible and could even be a basis for recovery of methane from clathrates. The caveat was added that methane is some 20 times more effective than carbon dioxide as a GHG, so a net release of methane to the atmosphere should be avoided.

The mechanics of post-combustion capture of CO_2 by clathrate hydrate crystallization of carbon dioxide from flue gas was described by Rajnish Kumar of the Clean Energy Research Center, Department of Chemical and Biological Engineering, University of British Columbia. And Kathryn Sheps, MDS Research, described a process by which the formation of carbon dioxide clathrates can be used to achieve simultaneous CO_2 sequestration and desalination of seawater.

The use of landfills to generate methane, which can be converted subsequently to CO_2 with the generation of energy, was described by Rodrigo Diaz of Argentina's Versus Goliath Project Solutions, Inc. P.A. Douglas of the University of Waterloo offered a plan for CO_2 capture and sequestration at a power generation plant on Ontario's Nanticoke Island. Sanni Eloneva of the Helsinki University of Technology described how CO_2 might be utilized with blast furnace or steel furnace slag to produce calcium carbonate. Susana Garcia discussed her preliminary assessment of ferriciron bearing sediments as sequestration media.

Disposal of an unwanted material can be costly; economists characterize such materials as having "negative value." Consequently, finding uses for captured carbon dioxide was a central theme of CHEMRAWN XVII/ICCDU XII. Charles A. Eckert, coauthor with profesors Charles L. Liotta and Philip G. Jessop, discussed four roles that CO_2 can play in solvents for sustainable technology: (1) supercritical CO_2 as a solvent, (2) gas-expanded liquids, (3) reversible acids, and (4) reversible ionic liquids. A presentation by Jackson Ford further elucidated the catalytic properties of gas-expanded solvents.

An age-old method for CO_2 sequestration is the planting of trees. Jean-François Boucher of the University of Quebec described the effectiveness of forests for this purpose. A paper by N. Scott of Queen's University emphasized that "Canada has enormous potential to use its biological capital to help mitigate rising GHG emissions. With improved man-

agement, Canada might be able to sequester 70 Mt ${\rm CO_2}$ per year" Robyn Foote of Queen's University discussed how, over a period of a century, carbon is captured in abandoned agricultural land, in association with mineral particles within 10 cm of the surface.



Utilization Efforts

At present rates, humankind consumes each year an amount of fossil fuels equivalent to 400 years of accumulation during prehistory. Jorg Schwender of the Brookhaven National Laboratory in the United States discussed the efficiency of the most abundant protein on earth, RuBisCO, the enzyme in plants that binds 10¹¹ tons of CO₂ per year.

Eric Beckman of the Mascaro Sustainability Initiative at the University of Pittsburgh described a number of components, characterized graphically as "wedges," that could be combined to effect GHG mitigation while energy is still produced. These include $\rm CO_2$ capture and storage, coal gasification, conservation and improved efficiencies, nuclear technology, solar energy, and wind energy. He noted that creating a "wedge" of wind energy would require increasing present-day capacity by a factor of 50—that is, by the installation of 2 million windmills. A solar electricity "wedge" would require utilization of approximately 3 percent of the U.S. land area for solar collectors.

Beckman discussed uses of carbon dioxide as a raw material in chemical production. This attractive option represents, unfortunately, only a small component among potential solutions to the climate change problem because human technology emits far more ${\rm CO_2}$ into the atmosphere than can be utilized as industrial products. For example, Beckman noted that if all methanol production worldwide (approximately 33

million tons) were converted to a $\rm CO_2$ -based process, it would consume less than 1 percent of the $\rm CO_2$ generated by human activity. Additional targets for substitution are the production of chlorine and ammonia. The use of atmospheric $\rm CO_2$ as a feedstock for high-value products such as diphenyl carbonate and various isocyanates would be too small to have a significant impact on the accumulation of atmospheric $\rm CO_2$, but it could contribute to an industry's profitability, which might provide an added incentive if a "cap and trade" system of $\rm CO_2$ credits were created. Beckman noted that $\rm CO_2$ reforming and synthetic biology should be especially viable areas for future research.

Yuhan Sun of the Institute of Coal Chemistry at the Chinese Academy of Sciences described the synthesis of cyclic carbonates from CO_2 and propylene oxide. Jessica Anderson of Notre Dame University described how carbon dioxide is highly soluble in ionic liquids such as imidazolium tetrafloroborate. Ionic liquids may not be sufficiently common to absorb massive amounts of CO_2 , but they are likely to be useful in creating membranes for separating the gas from other components. G. Wytze Meindersma noted that ionic liquids have a "designer ability" that can be employed for separation of CO_2 selectively from hydrocarbons. Angela Dibenedetto of the University of Bari in Italy discussed the synthesis of organic carbonates from aliphatic alcohols and CO_2 .

M. Halmann of the Weizmann Institute in Israel described how a considerable savings of energy and a reduction in CO_2 emissions could be realized by employing solar energy in the commercial Pidgeon process of calcining dolomite. Richard H. Heyn of the University of Oslo in Norway explained the use of metal-organic frameworks as low-temperature adsorbants of carbon dioxide. Chang-Jin Liu of Tianjin University described how plasmas can be used to prepare effective catalytic surfaces for the reforming of synthesis gas ($\mathrm{CO} + \mathrm{H}_2$) from methane and carbon dioxide. This could eliminate the need for separation when biogas contains large amounts of CO_2 and hydrocarbons.

Daniel Hoornweg of the World Bank noted that 80 percent of GHG emissions are produced in or for cities, specifically by activities that generate electricity and heat and by transportation, commercial, and manufacturing operations. He pointed out that, ironically, residents of cities are probably the most vulnerable to events such as flooding that could be caused by climate change. Hoornweg outlined measures that are

being taken in cities to reduce emissions, particularly water conservation, energy efficiency, and improved transportation. The World Bank, he said, has projects that include producing an index of GHG emissions and energy use, sending SWAT teams to pilot cities, and serving as an "honest broker" to encourage use of best practices worldwide.

Venkata Pradeep Indrakanti outlined his theoretical and experimental studies on photochemical reduction of CO_2 at surfaces of La-doped and undoped titania. R. Mann from the University of Manchester in the United Kingdom presented an analysis by K. Winch on how electricity derived from wind power could be used to resynthesize jet fuel from CO_2 isolated from stationary power plants. The price of this transformation is projected to be some 36 pence per liter. By 2020 this price could well be competitive with the cost of jet fuel from conventional sources.

John Macdougall of the Alberta Research Council explained that fixation of ${\rm CO_2}$ using photosynthetic algae in ponds shows promise for producing renewable biofuels and biomaterials. A project by Innoventures Canada (ICAN) to use microalgal mass cultivation has the potential to convert concentrated streams of ${\rm CO_2}$ (flue gases) into microalgal biomass. The products can be processed and fractionated to produce value-added compounds.

Kruamas Smakgahn of the National Institute for Agro-Environmental Sciences in Tsukuba, Japan, described how changes in the cultivation of field rices can minimize production of GHGs. Elevation of the concentration of ferric ion and the incorporation of rice straw into the soil, combined with appropriate field drainage, causes decreased production of methane. And appropriate field drainage and the application of fertilizers minimizes the production of nitrous oxide.

Rob Stephenson described how anaerobic digestion of sewage sludge in a wastewater treatment plant can create burnable hydrocarbons. These can be utilized in a generator, and the resulting electricity can replace the power consumed in operating the plant. Shirley Thompson of the University of Manitoba described how diversion of waste destined for landfills back into the production scheme can help Canada reach its Kyoto goals. Wei Wei of the Institute of Coal Chemistry at the Chinese Academy of Sciences discussed how magnesium-aluminum complex oxides can absorb CO₂, after which it could be used in synthesis. Yasuhiko Yoshida of Toyo University described

combinatorial screening of catalysts and processes for ${\rm CO_2}$ copolymerization. It was found that ${\rm C_{60}(OH)_n}$ is a useful catalyst for the process and that the use of plasmas is effective.

In sum, a large number of policy, sequestration, and mitigation strategies were proposed at CHEMRAWN XVII/ICCDU-IX. Adroit decisions and numerous effective technologies will be required to bring GHG emissions under control. As one conferee phrased it, "There is no silver bullet solution to the GHG problem, but there is silver buckshot."

As conference cochairs Keith Marchildon and Philip Jessop wrote: "This combined event . . . is more than just an exercise in organizational synergy and more than just the sum of two events that happen to have a substance, CO_2 , of common interest. Some methods of CO_2 utilization are, or could be, on a large enough scale as to be able to contribute to mitigation efforts; an obvious example is enhanced oil recovery. But many smaller uses of CO_2 also share with mitigation the objective of sparing the earth's environment. So all parts of the conference have the same laudable environmentally beneficent objective, and all participants can take satisfaction in being part of an event that helps further this great cause.

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in 2007; he has been involved with the committee since 1998.

Mendeleev Congress on General and Applied Chemistry

by Natalia Tarasova

The XVIII Mendeleev Congress on General and Applied Chemistry took place in Moscow 23-28 September 2007. The Congress celebrated the 100-year anniversary of the Mendeleev Congresses in Russia and the forthcoming 175th birthday of Dmitry Ivanovitch Mendeleev in 2009.

The congress was organized under the auspices of IUPAC, and the President of the Russian Federation, Vladimir Putin, and the first deputy to the chairman of the Russian Government, Sergey Ivanov, both sent warm greetings to the participants. The president of IUPAC, Bryan Henry, welcomed the Congress on behalf of the global chemical community, and the mayor of Moscow, Jury Luzhkov (a professional chemist by trade and education), in an emotional speech stressed the importance of chemistry worldwide and specifically for Russia and Moscow.



The winners of the IUPAC Poster Prize for young chemists and the winners of the Special Prize for young chemists in the session "Catalysis, Petrochemistry, Refining," shown together with Oleg Nefedov (front row, center), president of Mendeleev Congress, and Natalia Tarasova (front row, second from left), chairman of the congress's International Advisory Committee.

More than 3 850 scientists—among them more than 1 000 young scientists and students—came to the Russian capital for the conference, representing 53 Russian towns and 7 countries in the Commonwealth of Independent States. Numerous representatives from the Russian Academy of Sciences, from Russian ministries and other governmental organizations, and from national chemical societies abroad were also in attendance.

The program included 17 plenary lectures on mainstream directions in fundamental chemistry, innovations in chemistry and chemical technology, and chemistry education. Lectures by Nobel Prize laureates J.-M. Lehn (France), R.R. Schrock (United States), and J.I. Alferov (Russia) drew particularly large crowds, as well as media attention. All told, 430 scientists made oral presentations during 77 sessions of 9 sections and 5 satellite international symposia. In addition, 2 173 posters (representing 13 500 authors) were presented, and 3 560 abstracts were published in the congress proceedings.

The most advanced directions in research, the newest approaches, and various perspectives on the different branches of chemistry were discussed at the conference, including nanotechnology, space research, synthesis of the new elements of the periodic table, energy and resource conservation, renewable energy sources, and health care. A symposium on "The Social Responsibility of Chemists: Green Chemistry" was particularly well attended, and aimed at disseminating new educational materials related to responsible stew-