REVERSING GLOBAL WARMING:
CHEMICAL RECYCLING AND UTILIZATION OF CO_2

Report of the National Science Foundation-Sponsored Workshop
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EXECUTIVE SUMMARY

Nature recycles carbon dioxide by photosynthesis in plants. Humankind needs to supplement nature and recycle CO_2 into useful fuels and products. —George A. Olah, Nobel Laureate, Loker Hydrocarbon Research Institute, University of Southern California

The buildup of carbon dioxide (CO_2) in the atmosphere, its effect on global climate, and the dwindling supply of fossil fuels are critical problems that will require innovative, global-scale science and policy interventions. The National Science Foundation (NSF) and the Loker Hydrocarbon Research Institute at the University of Southern California brought together a multidisciplinary group of experts to discuss a bold solution to these problems—the capture, recycling, and use of the world's excess CO_2—and the necessary, fundamental, and transformative research to enable it. The approach that was explored at this workshop involves isolating CO_2 from concentrated sources and the atmosphere, and then converting it chemically into liquid fuels, such as methanol and related feedstocks, with the goal of creating a carbon-neutral energy cycle (Fig. 1). The research effort complements work being sponsored by the Department of Energy that targets the sequestration of excess CO_2 in geological formations.

Fig. 1 – The recycling of CO_2 could enable a carbon-neutral energy economy that will provide abundant liquid fuel without adverse effects on the climate (Courtesy George A. Olah).

The biggest challenge to recycling CO_2 is the chemistry of activating, or reenergizing, it. CO_2 is a highly stable, noncombustible molecule, so a great deal of energy is necessary to activate and convert it into fuels or other synthetic hydrocarbons. Today, the fundamental chemistry of CO_2 and its reactions is not fully understood. Filling these gaps in our knowledge base will go a long way toward implementing its sustainable and economical reuse. Moreover, fossil fuels are finite and may last a couple of centuries at most. In addition to the basics of capturing CO_2, the other major area of inquiry is the conversion of captured CO_2 using electro-, photo-, and thermochemical reactions (utilizing electricity, light, and heat, respectively). Because reducing excess CO_2 in the atmosphere is of critical importance, these reactions would have to be powered by renewable, clean energy sources. The goal of this approach is to preserve the carbon-based energy and materials economies so that hydrocarbon fuels and feedstocks can continue to be used— with existing infrastructure—in a manner that is economical and environmentally carbon-neutral.

At the workshop, scientists and engineers from universities, national laboratories, and private industry outlined their current approaches to capturing CO_2 and converting it into a variety of useful products, as well as the strategic and policy aspects of the problem. The experts were then divided into three groups to discuss the fundamentals of CO_2 capture and conversion, electrochemical conversion reactions, and photo- and thermochemical approaches. The participants in the first group concluded that efforts to capture CO_2 should focus in the short term on concentrated point sources, such as coal-burning power plants, cement plants, breweries, and natural gas wells. New liquid and solid absorbents to capture CO_2 need to be investigated. Over the long term, CO_2 can also be separated from the air, which will provide the additional benefits of reducing its concentration in the atmosphere and potentially reversing climate change.

The experts discussing the electrochemical conversion of CO_2—reactions driven and guided by electricity—concluded that fundamental research is required into catalysts, electrodes, electrolytes, and full-cell reactions to enhance the efficiency,

rate, mass transport, stability, and scalability of the processes.

Photo- and thermochemical conversion reactions are welcome options for converting CO_2 to usable products, according to the workshop participants, because the sun provides a useful, efficient, and inexhaustible power source for both approaches. However, these are also areas that will require breakthroughs before the approaches can be implemented. Basic research is needed into interfacial boundaries, catalysts, oxygen transport in solids, chemistry of the excited state, and other areas.

The obstacles to CO_2 recycling are daunting but can be overcome with a concerted, multidisciplinary research effort. Even modest investment in the field will likely produce key innovations and tangible progress. The organizers of the workshop concluded that CO_2 recycling, more than any other possible future energy scenario, allows for the flexibility and desirable products that a sustainable global system will demand. The workshop members urged the NSF to further enable fundamental research into CO_2 recycling and utilization to create a sustainable energy storage mechanism and stable global climate.

INTRODUCTION AND BACKGROUND

There is no shortage of energy itself on Earth—the sun provides a virtually endless source of light and heat. However, we have problems capturing, storing, and using that energy. Our renewable energy systems have not yet achieved the efficiency, capacity, and cost-effectiveness to provide for our evergrowing energy needs. So we turn, as we have since the dawn of the industrial revolution, to fossil fuels—oil, coal, natural gas. Fossil fuels, which long ago captured and stored the energy of the sun via photosynthesis, have two very obvious long-term problems: they will eventually run out, and burning them for energy creates carbon dioxide (CO_2) and contributes significantly to global climate change. We need alternative methods of capturing, storing, and using energy that are renewable, inexhaustible, and environmentally neutral.

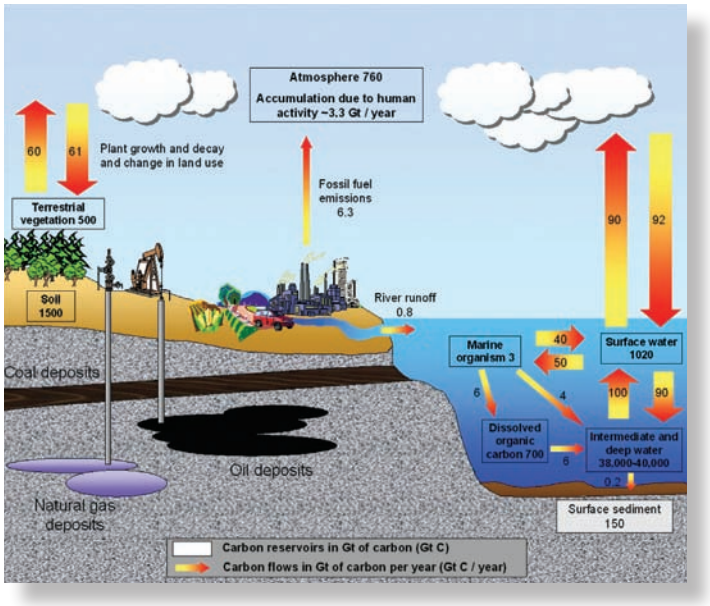

Fig. 2 – The carbon cycle is the balanced natural flow of carbon. Our CO_2 emissions have altered this system (Courtesy George A. Olah).

Despite its reputation, CO_2 is no villain; it is a fundamental component of the biosphere that needs only to be managed. Nature has a very effective system for this management: photosynthesis, the process by which plants convert CO_2 in the air, with water and sunlight, to organic compounds. This is part of the larger carbon cycle (Fig. 2), the natural movement of carbon through the atmosphere, oceans, sediments, soils, geological formations, and living creatures. Our use of stores of carbon that have long been locked away has upset this cycle. The conversion of biomass to fossil fuels took place on a geologic time scale. Yet we have reintroduced much of that energy and carbon in just decades. Perhaps mimicking through chemistry nature's plan for the gas, converting it from a problem to a resource, can address both our energy and climate problems on a human time scale.

Simulating the effects of photosynthesis transforms carbon from waste product to energy carrier. To do this, first CO_2 must be captured, either from point sources, such as natural gas wells and power plants, or the air. Once captured, that CO_2 can either be locked away or reenergized (using renewable energy sources) through complex chemical reactions to create stable fuels or feedstocks for a variety of chemical and industrial processes.

Under ideal circumstances, once these synthetic fuels are burned for energy, the CO_2 they produce could be recaptured and used again. This would close the anthropogenic carbon loop, allowing us to continue to use carbon-based fuels without affecting the atmosphere. As opposed to limited and environmentally problematic fossil fuels, hydrocarbon fuels made from recycled CO_2 would be essentially limitless and environmentally neutral. In fact, if CO_2 is captured from the air for recycling, the concentration of CO_2 in the atmosphere can actually decline, potentially reversing global climate change.

There are many scientific, organizational, and economic obstacles to a carbon-neutral future through recycling CO_2. A massive multidisciplinary scientific effort, covering everything from basic chemistry to advanced engineering, will be necessary. CO_2 presents, on a scientific level, quite a challenge. It is a highly stable, noncombustible molecule, and it takes a great deal of energy, known as its activation energy, to convert it into a product that can be used for chemical synthesis. To recycle carbon practically, this energy—in the form of electricity, light, or heat—must come from a renewable source. The fundamental chemistry of the molecule and its reactions is not yet fully understood, and it is not yet clear whether recycling it will be economically feasible.

This three-day workshop brought together an appropriately diverse population of experts— scientists and engineers from national labs, universities, and industry—to

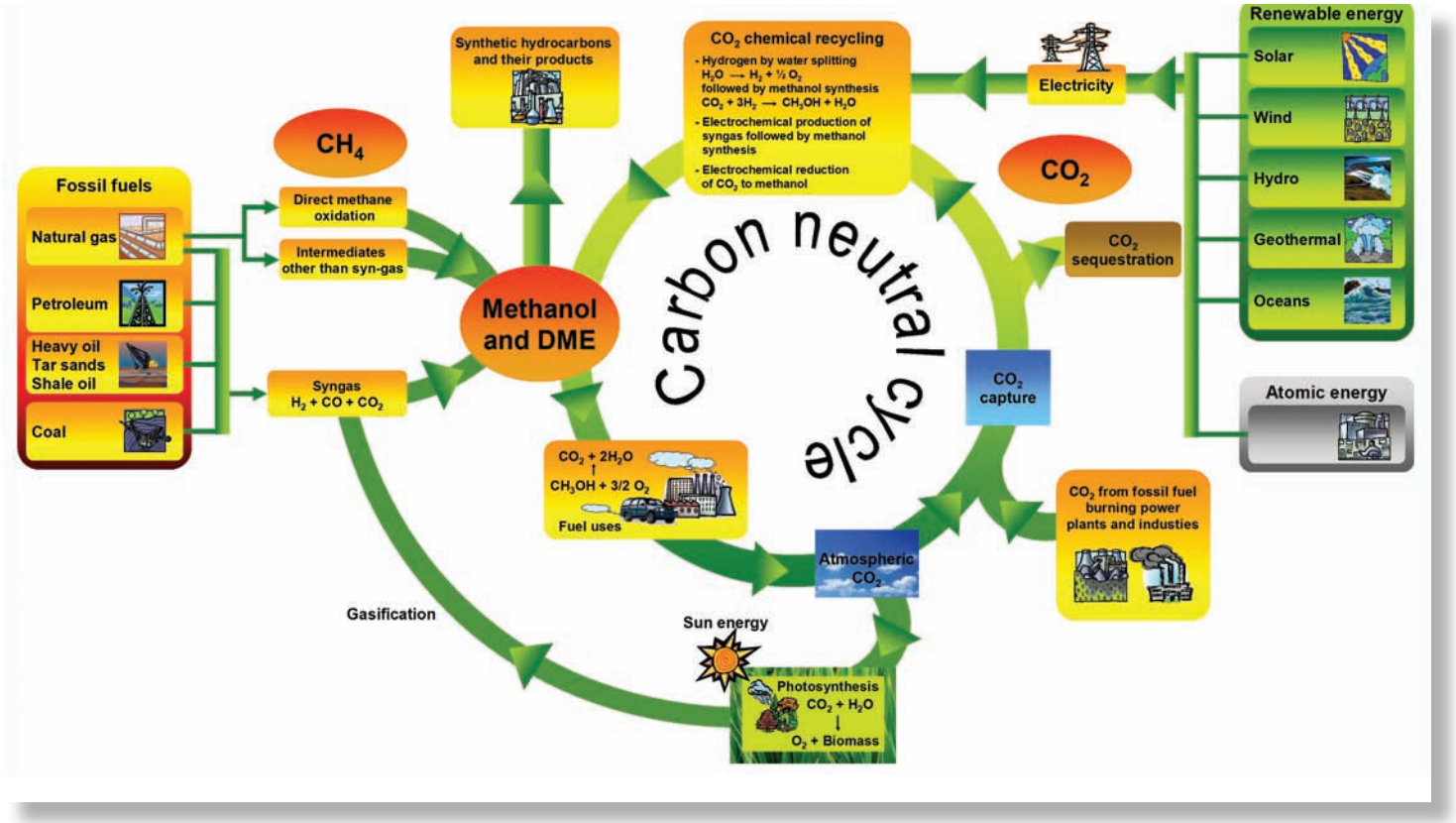

Fig. 3 - The goal of the workshop was to assess the current state of research and discuss steps for moving toward a carbon-neutral energy economy using renewable energy sources to recycle CO_2 into hydrocarbon fuels and products (Courtesy George A. Olah).

discuss innovative chemical methods to capture, recycle, and use excess CO_2 and reinvent the carbon-based energy economy (Fig. 3). They were asked to review current research approaches and identify the necessary, fundamental, and transformative future research that will make this all possible, especially those areas that will require scientists of different disciplines to come together.

The workshop, like this report, was structured around three avenues of inquiry: issues of policy and strategy; updates on research being conducted at universities, national labs, and private companies across the United States and Europe; and breakout sessions in which the experts were tasked with analyzing the current status of research into CO_2 recycling; the scale of the effort necessary to deal with climate change; the organization of large-scale research efforts; alternative energy sources; short-, mid-, and long-term goals; and the best ways to partner with industry and the international community.

This workshop represents a critical step in marshaling the collective expertise and research energy of a broad spectrum of scientists and policymakers toward the goal of slowing or reversing global climate change while simultaneously providing a model for a coherent, stable, and environmentally neutral global energy regime.

POLICY AND STRATEGY

In addition to great scientific and technical effort, creating a carbon-neutral energy economy through capturing and recycling CO_2 will require an equally massive feat of planning, coordination, and cooperation. Several workshop presentations focused on the strategic and policy aspects of this effort. The talks addressed a range of topics, from the advantages of methanol and related feedstocks, to the National Science Foundation's support for innovative and high-risk research, to the role of private industry in bringing these ideas to reality.

Nobel-Laureate chemist George A. Olah, of the Loker Hydrocarbon Research Institute at University of Southern California, presented a rationale for CO_2 recycling and a case for methanol and dimethyl ether as appealing liquid fuels and feedstocks that can be synthesized from CO_2.

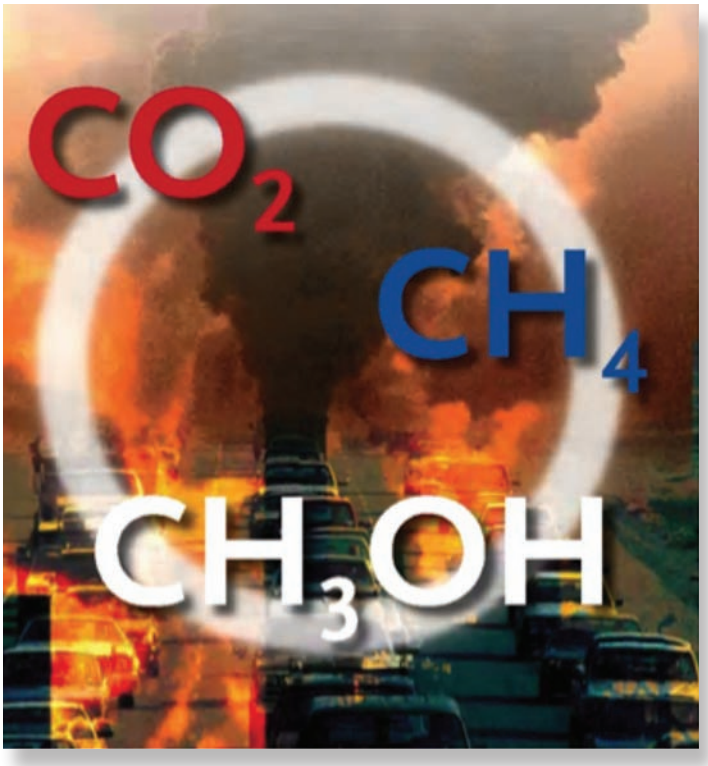

Fig. 4 – One possibility for a carbon-neutral energy economy can be based around captured CO_2, natural gas, and methanol (Courtesy Wiley VCH).

Olah began by outlining the energy challenges the world will face in the coming decades: increasing population and demand for energy, dwindling fossil fuels, and global climate change caused by excess CO_2. Donald Rapp of Jet Propulsion Laboratory of the National Aeronautics and Space Administration later offered a contrarian view of the problem, emphasizing that Earth's climate is complicated, and for that reason it is difficult to estimate the effect of CO_2 alone on climate change. While conservation and energy efficiency will go some way toward addressing these problems, it has become increasingly clear that they will not be enough—eventually CO_2 will have to be recovered from emissions and the atmosphere. The Department of Energy has supported research on methods of capturing and sequestering CO_2, primarily in geologic formations. The NSF would like to focus on exploring the capture and recycling of CO_2 as an alternative and complementary approach.

In the book Beyond Oil and Gas: The Methanol Economy (Wiley VCH, 2006), Olah, Alain Goeppert, and G.K. Surya Prakash argue for an energy economy based around the capture of CO_2 and its conversion to methanol (CH_3OH) (Fig. 4). Methanol is an excellent fuel with a high octane rating for internal combustion engines, and also a convenient liquid fuel for direct- oxidation fuel cells. It can also be converted to dimethyl ether (CH_3OCH_3), which is a high cetane diesel substitute. Methanol is safe to use and transport and would fill the need for a new, essentially inexhaustible liquid fuel source. Energy is required to convert CO_2 to methanol, but that energy can and should come from renewable sources—providing a flexible, renewable liquid fuel that takes advantage of our existing transportation and fuel infrastructure. In addition, methanol and dimethyl ether can serve as feedstocks for the manufacture of chemicals today derived from petroleum. And because methanol, apart from a single C-O bond, has only C-H bonds, its conversion from CO_2 is expected to be energy efficient and convenient.

There are a number of difficulties with the capture and conversion of CO_2. Today, it is energy intensive, inefficient, and expensive. Confronting these complications is a multidisciplinary problem with chemistry at its core. The scientific challenges will be discussed in greater detail in the "Technology and Research" section of this report. To even begin to address the problems will require clever and innovative advances in policy and funding. Olah observed that the U.S. government has spent time and money studying an energy economy based around hydrogen, an approach he sees as unrealistic and impractical. Alternatively, China, Japan, Korea, Iceland, and others have invested more in CO_2 conver-

sion (Fig. 5). Methanol will be made from captured CO_2 in the near future, Olah said, and the United States should be part of this effort.

Luis Echegoyen, Director of the NSF's Division of Chemistry, spoke at the workshop about the role of the federal institution in promoting sustainability. Sustainability, as he defined it, is ensuring the continued availability of the resources necessary for human survival, without harming the environment and with careful management and monitoring of the impacts of human economic activity.

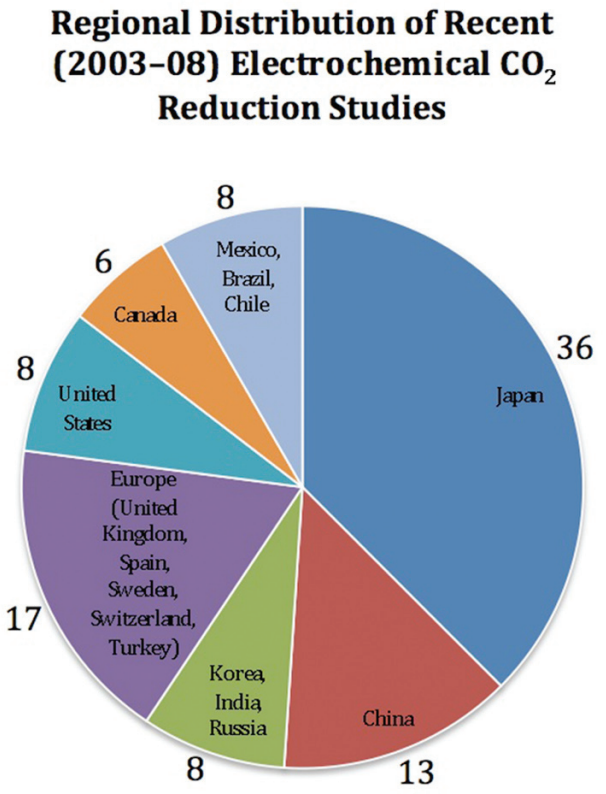

Fig. 5 – Less than 25 percent of recent electrochemical reduction studies have originated in the Americas; the United States is responsible for only 8 percent.

The NSF supports basic, high-risk, transformative research into the science and engineering of sustainable development. This means supporting work into the fundamental chemistry of CO_2, as well as innovative, disruptive ideas to deal with problems of energy needs and global climate change. The NSF is in a unique position to support CO_2 recycling research. The problem is vast and complex, and the NSF's emphasis on inter- and multidisciplinary research may be able to provide the focus, coherence, and communication necessary to be a research hub, Echegoyen said. There is clear opportunity for growth in NSF's support of chemical research, and Echegoyen expressed a hope that new ideas would emerge from the workshop that span all of the NSF's divisions and capabilities, and perhaps draw in partners such as the Department of Energy, the Environmental Protection Agency, and international institutions. The NSF's Early Concept for Exploratory Research (EAGER) program, which offers grants for up to two years at $200,000, is designed to support high-risk, high-payoff projects, and is ideally suited to supporting the CO_2 capture and reuse research effort.

NSF support will be critical in increasing the understanding of the basic chemistry of CO_2 reactions, but the implementation of CO_2 recycling will also require a great deal of money and the participation of industry. To gain traction in a market accustomed to cheap, easy fossil-fuel based energy, energy alternatives must be efficient, cost-competitive, and provide a return on investments.

Oddur Ingólfsson, of Carbon Recycling International (CRI), a private company based in Reykjavik, Iceland, provided an early model for how industry and private enterprise can help push toward a carbon-neutral energy future. Sustainable chemistry, as he described a broad idea that includes CO_2 recycling, holds the potential to maintain the world's standard of living without burdening future generations. Iceland is blessed with an extensive network of geothermal wells, which provide both concentrated streams of CO_2 (as does the country's aluminum smelting industry) and a source of energy by which to convert it to usable products. The company is following the model proposed by Olah—conversion of CO_2 and hydrogen into methanol and dimethyl ether. Even under favorable conditions provided by Iceland, there are difficulties. The cost of the process, including capture, conversion, purification, and transportation of the liquid fuel, must be balanced against the benefits. Furthermore, the process and price vary based on the source of the CO_2.

CRI currently is building a 10-ton-per-day demonstration plant in which CO_2 will be converted to methanol using a proprietary catalyst (Fig. 6). Any location with geothermal resources, including the United States, Japan, and the Philippines, could also support the process CRI is developing, Ingólfsson said. One goal, he continued, is to provide transportation fuel for Iceland, freeing it from fossil fuel imports and establishing a small-scale model for addressing

both the technical and economic challenges of recycling CO_2. Whether this can be done successfully and economically on a large scale remains to be seen.

Alan Knight, a professor at the University of Southampton and an advisor to the Virgin Group of companies, presented another early, industry-driven mechanism for supporting basic research into CO_2 capture, sequestration, and reuse—the Virgin Earth Challenge. The challenge, launched in February 2007, is a prize of $25 million for a commercially viable design that removes greenhouse gases from the atmosphere each year for at least ten years without harmful side effects. So far there have been 600 entries for what is dubbed the largest industrial prize ever offered, and they fall into four

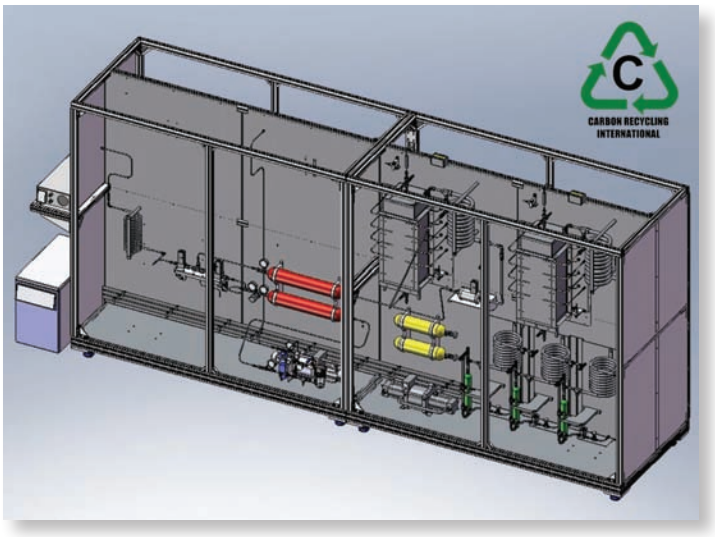

Fig. 6 – Carbon Recycling International is developing a test plant in Iceland for the conversion of CO_2 to methanol (Courtesy CRI).

broad categories: new machines or devices, new trees, old trees, and oceans and plankton. A viable CO_2-recycling plan would certainly be eligible for the prize. A winning plan must address all greenhouse gases (not just CO_2), store them long-term, be scalable, be credibly measured, provide a return on investment, and have clear ownership of the intellectual property involved. Commercial viability probably represents the most significant difficulty. Knight also made the point that the goal of the prize is to prepare Virgin to influence energy policy toward sustainability, and not to mask the fact that many of Virgin's businesses contribute to atmospheric CO_2.

Some participants in the workshop opposed the inclusion of Knight's presentation at a meeting of scientists and engineers. Knight responded that because CO_2 recycling is a new venture, new methods of funding and support will be necessary, and that scientists must become more adept at speaking with investors. Other participants supported the relatively novel approach. Perhaps the entrepreneurial spirit will lead to fresh, easily implemented ideas.

Strategically, the effort to recycle CO_2 still is young. The key priorities of the effort and the mechanisms by which to support basic research are still being determined. These talks provided a framework, a few immediate steps, and much material for future discussion.

RESEARCH AND TECHNOLOGY

There are many technical obstacles—ranging from basic science to advanced engineering—to utilizing CO_2 as part of a carbon-neutral energy economy. Most of the workshop's presentations were dedicated to updates on research into CO_2 capture; electro-, photo-, and thermochemical conversion of CO_2; and the fuels and other usable products that can be derived from it. These presentations indicated areas that can most benefit from a coordinated effort toward a practical, economically feasible system for recycling CO_2.

The first technical challenge in the process of recycling CO_2 is capturing it, either from point sources or the atmosphere. CO_2 is produced in concentrated streams from natural gas and geothermal wells; power, cement, and fermentation plants; and aluminum and iron ore smelters, among other sources. These sources of concentrated CO_2 present the best targets for early CO_2 capture efforts. Carl A. Koval of the Energy Initiative at the University of Colorado at Boulder is working on the problems associated with capture from two directions— with membranes and with electrochemistry.

Collecting CO_2 from air—more than half of human-produced CO_2 comes from distributed sources, such as homes, businesses, and transportation— presents special difficulties because CO_2 concentration in the atmosphere is low (currently approximately 385 parts per million) compared with point sources. Efficient new absorbents must be developed to make this viable. For now it is probably most feasible to focus on places where the CO_2 stream is concentrated. In Europe, Asia, and the United States, membranes are currently being used commercially to separate CO_2 from gas mixtures. Driven by differences in pressure, temperature, concentration, or energy, gases diffuse across such membranes. Koval and his colleagues are working on refining these processes by improving selectivity and flow of the membranes—that is, the ability of the membrane to allow CO_2 in particular to pass through at sufficient rates (Fig. 7). Polymer or ionic liquid membranes that separate CO_2 from methane or nitrogen are one possible strategy, but will need to see improvements in permeability, selectivity, cost, and stability.

The other approach to the capture and concentration of CO_2 involves electrochemistry, or the use of electricity to drive or control chemical reactions with an electrode and an electrolytic solution. A process of electrochemically modulated complexation is one approach researchers at the Energy Initiative are investigating for separating and concentrating CO_2, though it requires a better fundamental understanding of the reactions involved. Researchers with the Energy Initiative are also studying new electrodes, solutions, and catalysts. The separated CO_2 could be used as a feedstock for producing liquid fuel ($CO_2 + 2H_2O \rightarrow CH_3OH + 3/2\ O_2$).

In his talk on the "Methanol Economy," George A. Olah highlighted some of the challenges of the next step in CO_2 recycling— converting the captured gas into something else, such as methanol and dimethyl ether. Several approaches have been shown to be possible in concept, but fine-tuning them will require a greater understanding of these reactions at a basic level.

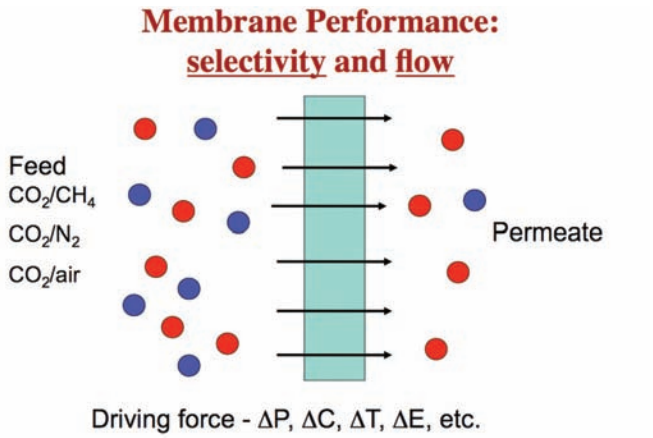

Fig. 7 – Membranes are an option for the separation of CO_2 from gas mixtures, provided they can be designed to be selective for CO_2 and allow enough flow to pass through (Courtesy Carl Koval).

To turn CO_2 from a stable molecule into something that can be burned for fuel, for example, requires chemical reduction—the reaction that creates a hydrocarbon feedstock from CO_2 and water or other ingredients. The reduction of CO_2 to other forms is a highly complex reaction, studded with chemical and engineering problems, but potentially with multiple solutions. The reenergizing reaction is slow, inefficient, and requires sophisticated catalysts. Most significantly, it requires a great deal of energy, which can not, for obvious reasons, come from CO_2-producing sources. Addressing these problems is of critical importance and is the target of a number of research teams.

The CO_2 conversion reaction may be designed to create methanol directly or may first go through an interme-

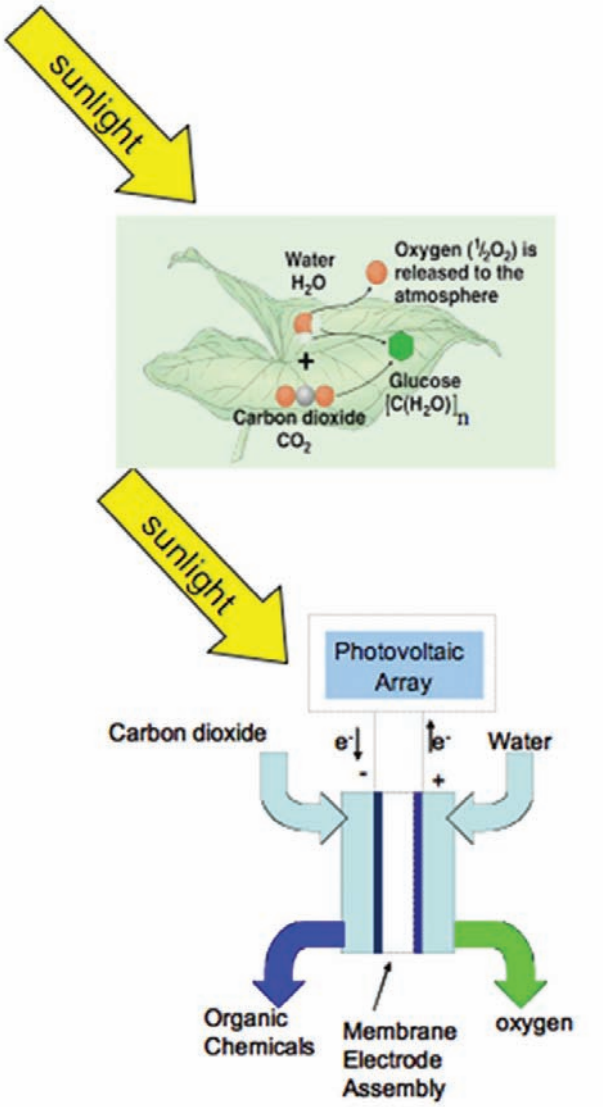

Fig. 8 – Electrochemical conversion of CO_2 to organic chemicals mirrors, especially when powered by sunlight, the natural process of photosynthesis (Courtesy S.R. Narayan).

diate stage that can be further manipulated. Syngas, a mixture of carbon monoxide and hydrogen, is one such intermediate that can be guided into a variety of hydrocarbon products. Currently, methanol is obtained using syngas, often produced from coal gasification or natural gas, or from agricultural products or other forms of biomass. Olah discussed new approaches to creating methanol that are under investigation, such as converting natural gas to methanol directly, without syngas as an intermediate step. Other processes would use captured CO_2, including catalytic hydrogenation or electrochemical reactions.

S.R. Narayan of the Jet Propulsion Laboratory and California Institute of Technology is working on electrochemical conversion of CO_2, using photosynthesis as a model (Fig. 8). He explained three varieties of electrochemical conversion processes: direct reduction, indirect reduction, and two-step reduction.

- Direct reduction to carbon-containing products (examples):

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$$
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$

- Indirect reduction followed by carbon-fixing reaction:

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2 \text{ (water electrolysis)}$$
$$\text{Sabatier reaction: } 4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$
$$\text{Homogeneous hydrogenation: } H_2 + CO_2 \rightarrow HCOOH$$

- Two-step reduction:

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2 \text{ (water electrolysis)}$$
$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \text{ (direct reduction)}$$
$$\text{Fischer-Tropsch: } (2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$$

However, reducing CO_2 is a slow reaction compared with the production of hydrogen from water, the other reagent necessary to synthesize hydrocarbon fuels. Provided the CO_2 reduction reaction can be improved— made more rapid, energy efficient, and likely to produce usable hydrocarbons— electrochemical conversion of CO_2 to fuel feedstock has a number of advantages, according to Narayan. Any source of electricity, including solar, wind, hydro, geothermal, tidal, and atomic power, can be used to drive the reaction. The reactions can be tailored to create specific fuels for specific uses, and the process can be scaled up to industrial levels. Development in catalysts, improved electrodes, and chemical conditions currently are necessary to refine the process.

Andrew Bocarsly of the Frick Laboratory at Princeton University also is investigating electrochemical conversion, in addition to photoelectrochemical conversion, or using a combination of electricity and sunlight to convert CO_2 into methanol. In electrochemistry, electrons drive the reaction. In photochemistry, photons serve the same purpose. The Frick Lab was the first to demonstrate photoelectrochemical reduction of CO_2 and water to methanol. However, this process still faces problems in efficiency and the particular difficulty that only a small portion of the light spectrum actually pushes the reaction along. Basic research to understand the mechanism of photochemical charge transfer in the reduction reaction that converts CO_2 to methanol will be needed to improve the process.

The photochemical approach also is under investigation by Etsuko Fujita and colleagues at Brookhaven National

Laboratory. They have explored a number of paths and approaches, and established that photochemical reduction of CO_2 is viable. But, as other research groups have found, the reaction is stubbornly slow and not selective enough. More understanding of the mechanism of CO_2 reduction is necessary, and efficient, inexpensive, and stable catalysts must be developed. Studies at Brookhaven dealing with artificial photosynthesis include work on sunlight absorption by band-gap narrowed semiconductors and metal complexes, water oxidation by Ru dinuclear complexes and cobalt hydrous oxide, photogeneration of NADPH-model complexes, and CO_2 and proton reduction by photogenerated hydrides (and/or hydrogenase model complexes). Fujita concluded that the sun provides the most promising source of energy—either through electricity generated by solar cells or with the light itself—needed to recycle CO_2.

The third approach, alongside electro- and photochemical conversion and also driven by the sun, is thermochemical, or driving the reaction with heat. While the other approaches are likened to photosynthesis, James E. Miller from Sandia National Laboratories said that thermochemical conversion more resembles the opposite of combustion, a process that creates much of the anthropogenic CO_2 in the first place. In concept, it is similar to the other forms of CO_2 reduction, only using the sun's heat as its energy source. Miller and his research team are using a unique new reactor system, the CR5. It is a heat engine that can create temperatures above 1000°C—hotter than a nuclear reactor—through a parabolic dish that concentrates solar energy (Fig. 9). The two-step heat reaction (with two temperature levels) uses metal oxides as catalysts, particularly Fe_2O_3 and ceria-based composite materials. With the system, the researchers have split CO_2 to carbon monoxide, which could be an interesting feedstock for downstream chemical and fuel conversions, and they plan to continue to refine the kinetics and bulk performance of the reaction. Testing is still in the early stages, but Miller believes the lab has found experimental conditions that are promising, and is working on managing the energetics of the reaction to improve its efficiency over what is possible with electrochemistry. This avenue of research will benefit from additional effort in improving the performance of the materials they use in the reactions (the temperatures are so high that some materials melt before the full reaction can take place), changing the design of the reactor, fine-tuning the system as a whole, and integrating the heat engine with systems to convert the feedstock they create from CO_2 into usable fuels.

Fig. 9 – The parabolic dish used with the CR5 reactor system at Sandia National Laboratories harnesses concentrated sunlight to drive CO2 conversion (Courtesy James Miller).

While creating new liquid fuels is the thrust of many research efforts in this area—owing to the critical dual problems of climate and energy— CO_2 recycling can also be used to make many of the other carbon-based products that have been traditionally made from fossil fuels. CO_2 is already used as a solvent or in synthetic chemistry, where it is used to make products for the chemical industry, such as urea, Plexiglas™, dimethyl carbonate, and others. But that use comprises only 0.5 percent of current emissions. Daryle H. Busch of the Center for Environmentally Beneficial Catalysis at the University of Kansas proposes using recycled CO_2 in a number of ways to create, efficiently and cleanly, a variety of chemical products that can be used by industry.

Some of their pioneering work focuses on employing supercritical CO_2 media for chemical synthesis, as well as CO_2-expanded liquids, which can be used in several industrial processes. For example, they have developed new catalytic oxidations with oxygen gas and hydrogen peroxide in CO_2-expanded liquids. Some challenges are finding alternatives for the synthesis of terephthalic acid, used in the creation of polyester for clothing and bottles, and new methods of producing propylene oxide, used in the manufacture of polyurethane plastics. The same processes that Busch and others are investigating might be used to create ethylene oxide, a precursor to chemical products such as automotive coolant and antifreeze, a process that is one of the biggest producers of CO_2 in the chemical industry. All of these compounds have numerous, large-scale industrial uses and are predominantly synthesized from fossil fuels. Early experiments in these areas involving captured CO_2 have been encouraging.

GOALS, CHALLENGES, AND RECOMMENDATIONS

Following presentations on the policy and technical challenges of recycling CO_2, the assembled experts were divided into three groups to discuss and document gaps in knowledge, opportunities for collaboration, and short and long-term recommendations. The breakout groups were divided into three subject areas: CO_2 capture and the fundamentals of conversion, electrochemical conversion, and photo- and thermochemical conversion. A set of recommendations culled from the breakout sessions follows the subject reports.

Capture and Conversion Fundamentals

Participants in this session were asked to discuss CO_2 capture from point sources and the air, and its chemical conversion to fuels, feedstock, and products.

Before CO_2 can be used as a raw material for the creation of synthetic fuels, technology and strategies for its capture must be developed and refined. The experts in this breakout session concluded that the most attractive and viable sources of CO_2 are point sources—natural gas and geothermal wells, and industrial operations that produce concentrated CO_2 as a byproduct. Scrubbers are needed to extract it from emissions, and the energy companies themselves could process the CO_2 into fuel and other applications. Over the long-term, scrubbers and absorbents can be developed to accomplish the more difficult task of extracting CO_2 from the air, where it exists in low concentrations.

To accomplish these goals, research energy must be dedicated to assessing point sources of CO_2, studying the basic science of separating and capturing it, evaluating conversion methods, and deciding which products can be produced. Other issues, which the participants raised but did not discuss in detail, include the cost of CO_2 capture, economic aspects of CO_2 cap-and-trade systems, and what effect these practices might have on atmospheric CO_2 concentration and climate change.

Coal-based power plants, cement plants, breweries, natural gas wells, and certain chemical plants could provide streams of CO_2 that can be assessed. Each type of source, however, produces CO_2 in a different concentration and with different impurities, meaning that each will require a different separating system. Once the CO_2 is isolated from a mixed gas flow, it must be captured in a way that is easily reversible, so the captured CO_2 can be freed for conversion and recycling with minimum energy penalty. Membranes, chemical capture, and efficient absorbents are possibilities that require further investigation.

The next step is the process of CO_2 conversion, which requires energy. Off-peak energy at power plants could be used to chemically convert CO_2 to useful products—an example of efficient power-load management and energy storage. Research is needed on the catalysts presently used in conversion, and on the basic chemical processes of conversion itself. To make the processes cheaper and more efficient, researchers must understand them at a fundamental level. Converting CO_2 to carbon monoxide is the most important battle, because it creates an intermediate that can be converted to many useful products and fuels. Products that can be made from CO_2 (with hydrogen) include methanol, dimethyl ether, ethylene, propylene, dimethyl carbonate, polycarbonate (Plexiglas™), gasoline, diesel, benzene, terephthalic acid, and a variety of others. With a greater understanding of the fundamental chemistry of CO_2 conversion, products can be developed for specific uses, and markets for them identified. Automotive fuels such as methanol and dimethyl ether are promising, but using them will release CO_2 into the atmosphere that must be accounted for. CO_2 itself can also be used as a recyclable and green solvent.

Electrochemical Conversion

Participants in this session were asked to address the electrochemical conversion of CO_2 in aqueous and non-aqueous media, using electrocatalysis to improve selectivity of the conversion reaction, and the economic aspects of electroreduction of CO_2 using alternative energy sources.

Electrochemistry, reactions induced and guided by the application of electricity, is a commonly discussed method for reducing captured CO_2 to a form that can be used in new carbon-based products and fuels. The experts in this session agreed that the electrochemical conversion of CO_2 is certainly viable, but that there are a number of outstanding questions about the basic chemistry involved. Improved fundamental understanding of CO_2 reactions will help increase the rate and efficiency of CO_2 reduction. It will also enable the development and refinement of superior electrodes, electrolytes, and

catalysts, as well as optimal operating conditions, including pH, temperature, and pressure, to optimize the reaction. Greater understanding of basic chemistry also will help guide the reactions toward the simplified, direct creation of desirable fuels and intermediates, as well as determine whether it can be scaled up to industrial scale.

The experts concluded that just a small fraction of the funds that have been directed to fuel cell research could lead to substantial advances in the electrochemical conversion of CO_2. The viability of any electrochemical approach also depends to a large extent on the availability of renewable energy to feed into the reaction, so that new fuels and products will be carbon-neutral or even carbon-negative.

Photo- and Thermochemical Conversion

Nature converts CO_2 to useful plant matter with the aid of photosynthesis. Participants in this session were asked to discuss artificial photosynthesis— photo- and thermochemical reactions— to transform CO_2 into useful products.

The experts in this session report that refining photo- and thermochemical reactions will require a multidisciplinary effort to decrease the energy required to drive the reactions and increase their efficiency. Multidisciplinary cooperation of this sort is a challenge for any single institution, and may be achieved through deep and complex cooperation between investigators at universities, government laboratories, and private corporations. Regular meetings— based on models established by the Department of Energy— provide one avenue to broad cooperation, and fresh eyes and open communication will assist all avenues of the research effort. The cost of such a research effort will naturally be high, and the NSF can play a role in marshaling those resources.

Over the short term, this multidisciplinary effort in photo- and thermochemical research should focus, much like for electrochemical conversion, on a greater understanding of the basic chemistry of the reactions, such as the details of oxygen transport and chemistry of the excited state, combined with a refinement of the equipment and conditions of the reactions, including catalysts and reactive surfaces. The long-term goals include further understanding of the kinetics, structure, and reactivity of CO_2 conversion reactions—the nuts and bolts of refining a complex and detailed chemical process— through both experiments and modeling.

RECOMMENDATIONS

The breakout sessions produced a number of key recommendations for moving toward viable, efficient, cost-effective CO_2 recycling:

- Identify and assess point sources of CO_2 for its separation and capture
- Create and refine absorbents and membranes for separating CO_2 from mixed gases
- Develop greater understanding of the basic chemistry of CO_2 and reduction reactions
- Identify better catalysts and reaction conditions for improving the efficiency and selectivity of the conversion of CO_2 to usable fuels and feedstocks— including the electro-, photo-, and thermochemical processes
- Identify funding sources, including particular NSF funding mechanisms, to support this basic research
- Propose mechanisms, such as the use of off-peak electricity, that can make the CO_2 conversion process more cost-efficient
- Study the scalability of any CO_2 recycling process to be sure that it can be conducted cost-efficiently on an industrial scale
- Examine the potential products that can be created from CO_2 to determine potential uses and markets
- Identify other industrial chemical processes in which captured CO_2 can be used
- Improve communication between the NSF, universities, national laboratories, private industry, other government entities, and international partners to create consortiums and encourage cooperation
- In the long-term, find and refine absorbents that can be used to extract CO_2 from the air efficiently, which may reverse global climate change
- Continue work to improve and utilize sources of sustainable, renewable energy that can be used to drive the CO_2 conversion process

CONCLUSIONS

The shift to a CO_2-neutral energy cycle is not yet a reality, but experts agree that it is possible and that there are a number of key challenges that must be addressed. The organizers of the workshop concluded that CO_2 recycling, more than any other possible future energy scenario, allows the flexibility and desirable carbon-based products that a sustainable global system will demand. The workshop members urged the National Science Foundation to support fundamental research into CO_2 recycling and utilization to create a sustainable energy storage mechanism and stable global climate for the future.

It has become increasingly obvious that energy conservation and efficiency, though of critical importance, will not be enough to address the global climate crisis and provide a sustainable vehicle for energy when fossil fuels run out. With appropriate investment now, the scientific community is in position to undertake transformative, disruptive research that will herald a new energy age in which mankind closes the loop on its use of carbon and has an endless supply of versatile, environmentally neutral fuel to power the energy and carbon-based materials economies of the future.

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REVERSING GLOBAL WARMING:

CHEMICAL RECYCLING AND UTILIZATION OF CO_2

A workshop sponsored by the National Science Foundation and Loker Hydrocarbon Research Institute, University of Southern California July 9–10, 2008 at the USC Davidson Conference Center, 3415 S. Figueroa Street, Los Angeles, CA 90089-0871.

Wednesday, July 9, 2008

Morning Session:

8:00–9:00 am	Registration and Continental Breakfast
	Session Chair: G.K. Surya Prakash, University of Southern California
9:00–9:10 am	Welcome
9:10–9:40 am	Luis Echegoyen, National Science Foundation, "Sustainability and the Role of NSF"
9:40–10:25 am	George A. Olah, University of Southern California, "Beyond Oil and Gas: The Methanol Economy"
10:25–10:55 am	Coffee Break
10:55–11:25 am	Oddur Ingólfsson, Carbon Recycling International, "Capitalizing on Geothermal Energy: Conversion of CO_2 to Methanol and Fuels"
11:25–11:55 am	Carl Koval, University of Colorado, "Membrane and Electrochemical Separationand Concentration of CO_2 from Gas Mixtures"

Afternoon Session:

12:00–1:30 pm	Lunch
	Session Chair: Stuart Licht, National Science Foundation
1:30–2:00 pm	S.R. Narayan, JPL-NASA, "Prospects and Challenges in the Electrochemical Reduction of CO_2"
2:00–2:30 pm	Andrew Bocarsly, Princeton University, "The Electrocatalytic Reduction of CO_2 to Methanol at Metallic and Semiconducting Electrodes"
2:30–3:00 pm	Etsuko Fujita, Brookhaven National Laboratory, "Photochemical CO_2 Reduction: Current Status and Challenges"
3:00–3:30 pm	Coffee Break
	Session Chair: Nancy Jackson, Sandia National Laboratories
3:30–4:00 pm	James Miller, Sandia National Laboratories, "Solar Thermal CO2 Conversion to Carbon-Neutral Liquid Fuels"
4:00–4:30 pm	Daryle Busch, University of Kansas, "Benefits and Challenges of Conducting Liquid Phase Chemical Reactions in Dense Phases of Pure CO_2 and Mixed Solvents Based on CO_2"
4:30–5:00 pm	Donald Rapp, JPL-NASA, "Energy and Climate"
6:00 pm	Dinner, USC Town and Gown

Thursday, July 10, 2008

Morning Session:

8:00–9:00 am	Continental Breakfast
	Session Chair: Stuart Licht, National Science Foundation
9:00–9:45 am	Alan Knight, University of Southampton, "The Virgin Earth Challenge: An Update"
9:45–10:15 am	Coffee Break
10:15 am–noon	Breakout Sessions

Afternoon Session:

12:00–1:30 pm	Lunch
1:30–2.45 pm	Breakout Sessions
2:45–3:15 pm	Coffee Break
3:15–4:15 pm	Breakout Sessions
4:15–5:00 pm	Workshop Wrap-up