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ENERGY FOCUS

Reduction of CO_2 to Chemicals and Fuels: A Solution to Global Warming and Energy Crisis

We are living in an era of unprecedented technological innovation, progress, and prosperity driven by energy. The industrial revolution, since the 1860s, and the exponential urbanization during last 2 decades caused a dramatic increase in carbonaceous emissions into the atmosphere, which contributed to most of the unprecedented global warming over the past decade. Smog hanging over cities is the most familiar and apparent form of air pollution that has become a regular phenomenon. However, a more serious and harmful form of air pollution occurs through enormous anthropogenic (or industrial) emission of carbon dioxide (CO_2), a nonvisible greenhouse gas. Over millions of years, plants used to assimilate CO_2 into energy-rich compounds (carbohydrates) by a process called photosynthesis, through which nature used to maintain its own carbon cycle to present us a sustainable environment. Unfortunately, the industrial revolution and modern civilization during the last few centuries necessitated the use of excess fossilized sunlight (fossil fuels) accumulated over millions of years. Consequently, the CO_2 that was stored as carbohydrates by photosynthesis over millions of years is being returned back to the atmosphere at an incredibly alarming rate. These activities have substantially impacted the natural carbon cycle, which is no longer sufficient to maintain the carbon balance over the various sectors of the environment. The CO_2 concentration in Earth's atmosphere is rising drastically more than ever in the Earth's history, and this phenomenon is expected to have major impacts on the Earth's climate and human civilization as well. Thus, it is correctly envisioned that the oil age will end much before the Earth actually runs out of oil, being restricted by emission regulations of fossil fuel usage.

There are various sources of CO_2 emissions that can generally be classified as stationary, mobile, and natural sources, as listed in Table 1.[1−3] Among them, power generation and manufacturing sectors contribute the majority of the CO_2 emissions to the environment. The flue gas stream from coal and natural gas power generation basically consists of various gases including nitrogen, CO_2, water vapor, oxygen, soot, CO, nitrogen oxides, and sulfur oxide. In the past 150 years, such activities have pumped enough CO_2 into the atmosphere to push the atmospheric CO_2 level beyond the deadly 400 ppm mark. There are no standard technologies developed to efficiently convert CO_2 from these streams due to the presence of water vapor and all pollutants, which is likely to decompose/poison most of the catalysts and decrease the efficiency of the conversion of CO_2.

Table 1. Various Sources of CO_2 Emission

stationary	mobile	natural
fossil fuel based electric power plants	cars and sports utility vehicles	humans
independent power producers	trucks and buses	animals
manufacturing plants in industry (cement, limestone, hydrogen, ammonia, soda, fermentation, chemical oxidation)	aircrafts	plant and animal decay
commercial and residential buildings	trains and ships	land emission
flares of gas at fields	construction vehicles	volcano
military and government facilities	military vehicles and devises	earthquake

There are a variety of measures that need to be taken to curb global warming, starting from private homes to large industry scale. The "carbon footprint" (the amount of CO_2 a person is responsible for putting into the atmosphere) can be controlled at a personal level by various activities such as driving and flying less, recycling, using less energy consuming appliances, etc. To fully address the threat of global warming on a larger scale, governments are taking measures to limit emissions of CO_2 and other greenhouse gases. The Paris meeting, also known as COP21,[4] was the annual gathering of the Conference of Parties (COP) to the United Nation's Framework Convention on Climate Change (UNFCC). Policy experts, scientists, and climate economists from 118 countries in COP21 voluntarily agreed to take measures to combat climate change, with the ultimate goal of keeping the postindustrial global temperature rise below 2 °C. Another method is to put taxes on carbon emissions or higher taxes on gasoline, so that individuals and companies will have greater incentives to conserve energy and pollute less. The EPA (United States Environmental Protection Agency) has implemented several rules to reduce the carbon emission from power plants, called a "clean power plan".[5] The Obama administration in the U.S.A. designed the plan to lower emitted CO_2 by power generators in 2015.[6] A few other goverments attempted to implement a comprehensive set of climate solutions that includes expansion of renewable energy usage, increased vehicel fuel efficiency, building a clean energy economy with the help of fundamental science and translational technology, restricting the carbon emission by introducing a carbon tax, reducing tropical deforestation, etc. Although these above-mentioned large- and/or small-scale efforts can help in controlling pollution, they are not sufficient enough to tackle the problem due to exponential urbanization.

Apart from all of these controls, the scientific world is already in action to control the excess CO_2 by various methods such as capturing[7] and sequestration.[8] However, these methods have severe limitations as there are saturation/permanency limits to the capture or sequestration of CO_2. Therefore, the ultimate

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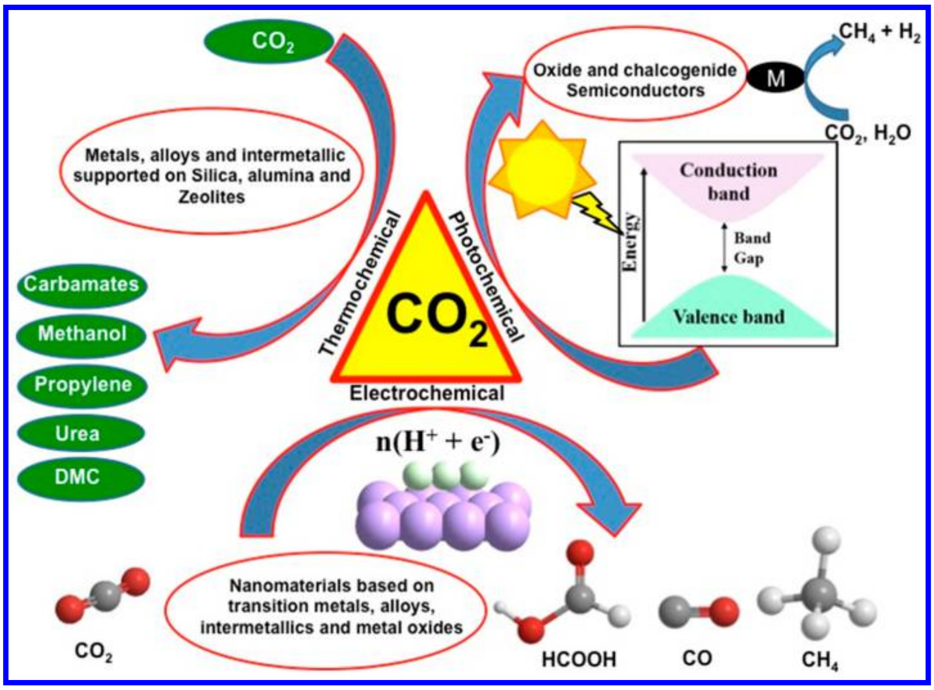

Figure 1. Different methods employed for the CO_2 reduction to various products.

solution without hampering the industrial development and urbanization is the utilization of CO_2, which is to efficienctly convert it into fuels, chemical feedstock, concrete, household items, and anything that can be consumed in our routine life.[9−13]

The CO_2 reduction to other chemicals can be done by different methods such as thermochemical, photochemical, and electrochemical pathways (Figure 1). The choice of catalysts and process technology is very crucial as it heavily depends on the methods employed. For example, the catalysts should be stable at higher temperature in a thermochemical reaction, the catalyst should able to minimize the competitive H_2 evolution reaction expected in the electrochemical method, and an appropriate semiconductor with a minimum band gap of 1.23 eV is required for the photochemical method.

The chosen products of CO_2 reduction should have a considerable global market size and demand to act as a big enough carbon sink (e.g., transportation fuel substituents, chemical feedstocks). This approach will create an artificial human maneuvered carbon cycle that will complement the natural cycle to give a sustainable environment. Catalyzing the reduction of CO_2, however, is a challenging chemical process due to the myriad of possible products and complicated interconnected reaction pathways, and "business as usual" has not yielded a viable catalyst so far. It is reported that the reduction of CO_2 leads to 17 different chemical/fuel products (Table 2) depending on the materials and/or methods employed.[14] The complexities of the reaction clearly necessitate a rational design approach and the ability to scan a sufficiently large chemical space.

Table 2. Expected Products during the CO_2 Reduction Process

1	methanol	7	allyl alcohol	13	carbon monoxide
2	formate	8	acetaldehyde	14	dimethyl ether
3	methane	9	glycolaldehyde	15	hydroxyacetone
4	ethylene	10	n-propanol	16	ethylene glycol
5	ethanol	11	acetone	17	propionaldehyde
6	glycerol	12	acetate		

We need a portfolio of solutions to address this scientific challenge in various ways. NRG COSIA Carbon XPRIZE is a global competition to inspire and drive various scientists and engineers to come together as a team to address this issue.[15] As the competetion says "the $20M NRG COSIA Carbon XPRIZE will challenge the world to reimagine what we can do with CO_2 emissions by incentivizing and accelerating the development of technologies that convert CO_2 into valuable products. These technologies have the potential to transform how the world approaches CO_2 mitigation, and reduce the cost of managing CO_2." The competition was initiated in 2015 with two tracks in three rounds of the selection process, one focused on testing technologies at a coal power plant and the second one at a natural gas power plant. Each track will operate as a separate competition on the same timeline with a **total prize of $20 million**. Twenty-seven teams from a total of 47 teams in Round 1 advanced to Round 2 in 2016, which further reduced to 10 teams (5 each in coal and natural gas tracks) representing 5 countries, including Canada, China, India, the U.S.A., and the U.K.

The coal track includes five teams that will demonstrate conversion of CO_2 emissions at a coal-fired power plant in Gillette, Wyoming, U.S.A.:

- **Breathe** (Bengaluru, India) − Led by Dr. Sebastian Peter, the team is producing methanol, a common fuel and petrochemical feedstock, using a novel catalyst.
- **C4X** (Suzhou, China) − Led by Dr. Wayne Song and Dr. Yuehui Li, the team is producing chemicals and biocomposite foamed plastics.
- **Carbon Capture Machine** (Aberdeen, Scotland) − Led by Dr. Mohammed Imbabi, the team is producing solid carbonates with applications to building materials.

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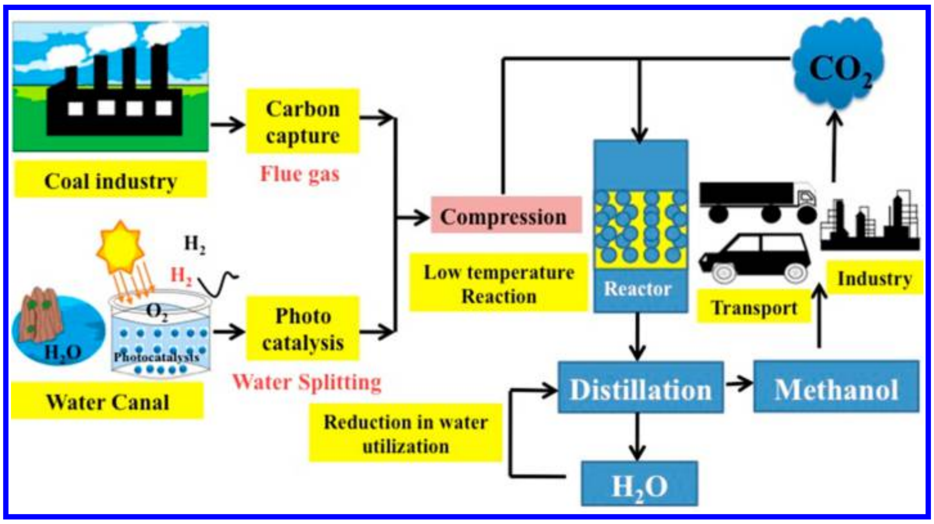

Figure 2. Schematic of the overall technology designed by team BREATHE for the efficient conversion of CO_2 originating from a coal power plant into methanol and other high-value products.

- **CarbonCure** (Dartmouth, Canada) – Led by Jennifer Wagner, the team is producing stronger, greener concrete.
- **Carbon Upcycling UCLA** (Los Angeles, CA, U.S.A.) – Led by Dr. Gaurav Sant, the team is producing building materials that absorb CO_2 during the production process to replace concrete.

The natural gas track includes five teams that will demonstrate conversion of CO_2 emissions at a natural gas-fired power plant in Alberta, Canada:

- **C2CNT** (Ashburn, VA, U.S.A.) – Led by Dr. Stuart Licht, the team is producing carbon nanotubes.
- **Carbicrete** (Montreal, Canada) – Led by Dr. Mehrdad Mahoutian, the team is producing cement-free, carbon-negative concrete that uses waste from steel production as an alternative to traditional cement.
- **Carbon Upcycling Technologies** (Calgary, Canada) – Led by Apoorv Sinha, the team is producing enhanced graphitic nanoparticles and graphene derivatives with applications in polymers, concrete, epoxies, batteries, and pharmaceuticals.
- **CERT** (Toronto, Canada) – Led by Dr. Alex Ip of the Sargent Group at the University of Toronto, the team is producing building blocks of industrial chemicals.
- **Newlight** (Huntington Beach, CA, U.S.A.) – Led by Mark Herrema, the team is using biological systems to produce bioplastics.

The teams that moved into the final round shared $5 million, and the winner in the final will be awarded a $7.5 million grand prize in each track. The competition has been designed by conducting extensive research and consultation with industrial leaders and experts in the field and aims at catalyzing the growth of innovative commercial technologies that can significantly arrest environmental degradations. The idea of NRG COSIA Carbon XPRIZE is to inspire the brightest minds around the world to come together and tackle a significant challenge and solve the climate change problem.

The development of technologies for chemical/fuel production from industrial CO_2 waste will simultaneously boost the economic growth of the energy sector and mitigate the overall CO_2 emissions in developing countries. While a matured TRL value (4–7) for CO_2 reduction technology is indicated by the presence of some industrial global endeavors (the methanol production plant by Carbon Recycling International (CRI) in Iceland, dimethyl ether production by Korean Gas Cooperation (KOGAS) in South Korea, the methanol plant in Japan by Mitsui Chemicals, the methanol production plant at the Lünen power plant, Germany), there are still several substantial technological challenges that have to be addressed to make the overall end-to-end technology a commercially viable and well-established one.

This technology will have big impact in developing countries like India and China as these countries are heavily dependent on nonrenewable energy resources and top the list in total CO_2 emissions in the world. Economic development requires access to energy. There is, however, a drastic conflict between improving the living conditions of billions in the developing world and mitigating climate change because increased energy demand implies increased CO_2 emissions, especially in the developing world where renewables are not as accessible. Developing countries will tap into their natural resources to satisfy increasing energy demands. For many countries, it can be coal or natural gas. It will lead to a very complex geopolitical problem to restrict any developing country in exploiting their own resources to improve living conditions, and thus, global environmental norms may seldom emerge as a true and practical solution to the climate change problem. The more viable solution, therefore, is to find ways to reduce the additional emission of CO_2 on a significant scale or reduce it into useful fuels and chemicals.

For example, BREATHE representing India is one among the 10 finalists of the NRG COSIA Carbon XPRIZE competition. BREATHE aims to convert CO_2 originating from a coal power plant to methanol and other value added products (Figure 2). India is currently the fourth largest emitter of CO_2, with a current annual increase of emissions by about 5%. A threshold country, India, is currently looking at rapid social changes and urbanization. The increasing living standards, however, are closely linked to increased energy consumption. India recorded the largest increment to CO_2 emissions of all countries for a third consecutive year in 2016, growing by 113.7 Mt or 5% for the last 3 years. Intense international pressure threatens to curtail economic develop-

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ment if energy consumption cannot be decoupled from CO_2 emission. The mitigation potential via "carbon capture and sequestration" is limited due to geological conditions in India too, calling for the alternative approach of reducing CO_2 to added-value products including methanol, ethanol, dimethyl ether, etc. CO_2 capture technology is comparatively well established and readily available, and hence, the focus is primarily on conversion technology development and integrating it with different CO_2 capture subsystems to offer a complete solution.

India has vast resources of coal. There is strong economic incentive to meet the raising energy demand through significant indigenous coal resources rather than "cleaner" natural gas imports. The amount of CO_2 emitted from various sectors such as power generation (coal and oil), cement industries, chemical industries, and automobiles in India is around 2100 Mt at the moment. This value is in stark contrast with the estimated storage capacity of India, which is only about 4.7 Mt/y, with a significantly higher cost of implementation. Alternative technologies are urgently needed to maintain growth and increasing living standards while simultaneously managing CO_2 emissions. However, fundamental research activities in India need to be improved for scientific foundations for innovation and attract more industrial sectors to lead innovation.

CO_2 reduction technology is comprised of 6 parts: (1) CO_2 capture from coal energy flue stream, (2) H_2 production, which is used as the reductant, (3) design and development of the catalyst, (4) engineering of the reactor and process, (5) thermochemical CO_2 reduction, and (6) purification of the products depending on the market demand. Methanol is going to be one of the most important products in the Indian energy sector, which is a commodity consumed extensively in a wide variety of industries like energy, transportation fuel, chemical feedstock, pharmaceuticals, plastics, etc. India presently consumes about 2 million tons of methanol, only 20% of which comprises domestic production, and the rest is imported. The size of the methanol market in India alone amounts to around \$1 billion, which is anticipated to grow with the introduction of the Methanol Economy.[16] The government is already taking measures in this direction by mandating the introduction of methanol by blend in gasoline (transportation fuel), incentivizing usage of cleaner cooking stoves, etc. While methanol is the present target of BREATHE's technology, CO, a related product having a niche market, can be readily made with a suitable change in the catalyst and operating conditions.

To summarize, NRG COSIA Carbon XPRIZE has stimulated the formation of an excellent team of researchers with complementary expertise in chemistry, engineering, and applied physics. The market of CO_2 conversion plants has widespread scale, from hundreds of kgs/day to thousands of kgs/day. To keep up with its timeline, teams have pushed themselves to a limit, combining simulations and experiments and developing an indigenous technology for CO_2 conversion. The XPRIZE competition has incentivized teams' work and is expected to have a notable impact on global position in technologies for a clean environment and recyclable energy. Ultimately, the impact of the prize will go far beyond the critical demonstration of innovative technologies by inspiring transformation, enabling new markets, and empowering people to be part of the solution to one of our world's grandest challenges. In the final round of the competition, the teams in coal and natural gas tracks need to build a demonstration plant in Wyoming (U.S.A.) and Alberta (Canada), respectively, to demonstrate the technology, and the winners will be announced in 2020. The prize will help identify the most promising pathways for CO_2 conversion and prove they can be deployed at power plants and other industrial facilities. In addition to mitigating CO_2 emissions, this would also reduce reliance on imported fuel and chemicals. To achieve this goal, each team should push the boundaries by employing an integrated materials-by-design approach for a highly complex reaction. By predicting reaction pathways with the help of theoretical analysis, one can scan a much larger chemical space for promising catalysts. Through close coupling with experimental synthesis and advanced characterization, the teams will validate and optimize their design methodology and also ensure the upkeep of industrial interests to take their findings forward at the end of the competition. Finally, the prize will incentivize development of new and emerging CO_2 conversion technologies, accelerating their transformation from the laboratory testing stage to the demonstration stage under real world conditions.

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Notes

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