Utilization of Carbon dioxide- A global endeavour

CO_2 and global warming

CO_2, as available in nature,has always played a beneficial role, serving as the source of carbon for photosynthesis of plants and crops and simultaneously releasing oxygen, a component so critical for all forms of life on this earth. The level of CO_2 in atmosphere,till recently, was of 0.039 % or 389 parts per million by volume(ppmv). However, it is increasing continuously, due to the emission of carbon dioxide into the atmosphere, released mainly by the burning of fossil fuels. All types of human activity generate about 37 billion tons (37 Gt) of CO_2 emissions each year, with about 30 Gt of this coming from energy-related emissions. Burning 1ton of carbon in fossil fuels releases more than 3.5 tons of carbon dioxide. Total emissions were less than 25 Gt twenty years ago, and are projected to rise to over 50 Gt in twenty years from now. The Earth's surface temperature has risen by approximately 0.6 K in the past century, seriously affecting the weather conditions and patterns of rain, with significant warming trends.

The realization that carbon dioxide is the major cause for global warming, the fact that fossil fuels are bound to continue as the major source of energy for several decades into the future and the world's insatiable demand for energy, have propelled carbon dioxide management (capture, storage and sequestration)to the centre stage.Controlling global warming or the greenhouse effect has emerged the key global issue. Since the issue is complex in nature, it needs to be addressed in several ways.

Approaches towards reduction in CO_2 emission

Attempts in this direction are in progress, adopting major approaches:

1. Efficient use of carbon-based energy sources,
2. Use of alternative or carbon-free energy sources,
3. Use of a post treatment using carbon-capture technology.

While considerable advances have been achieved on all the three fronts, carbon capture technology has gained prominence, with the usage of fossil fuels and consequent CO_2 build up becoming inevitable. Carbon capture refers to the removal of CO_2 from industrial flue gas/any source by a gas separation process prior to release to the atmosphere. Ideally, the captured and stored CO_2 could then be recycled by conversion into useful fuels and chemicals, thereby control the global warming.

Carbon Sequestration

Carbon sequestration (storage and conversion) is the isolation of carbon dioxide (CO_2) from the earth's atmosphere so as to avoid continued CO_2 buildup in the atmosphere.Several process technologies such as gas absorption into chemical solvents, permeation through membranes, cryogenic distillation, and gas adsorption onto a solid sorbent are available for the capture of CO_2 from any given source.

Geological sequestration involves storing CO_2 underground in rock formations/sea bed that can retain large quantities of CO_2 for long periods of time. The CO_2 would be held in small pore spaces inherent in rocks. However, it is difficult in practice, to store billions of tons of CO_2 in this manner and the long term consequences on the environment could defeat the purpose. It is possible that CO_2 injection into coal seams and mature oil fields could assist in the extraction of coal bed methane or oil that would otherwise be left in the ground, which could help offset the costs of sequestration. In this context, chemical/biological/catalytic fixation of CO_2 or CO_2 mitigation/conversion emerges as a viable alternative.

CO_2 conversion

CO_2 is the most oxidized form of carbon, and therefore the only chemical transformation at normal conditions that would be possible is to reduce it. A wide range of CO_2 conversion techniques are under investigation which include:

i. Chemical Reduction by metals at high temperatures
ii. Thermo chemical Conversion
iii. Radio chemical Method
iv. Photo-Chemical Conversion
v. Bio-Chemical Conversion
vi. Electro-Chemical Conversion
vii. Bio Photochemical conversion
viii. Electro photochemical conversion

Conventional catalytic reduction of CO_2 to chemicals (formic acid, methanol, methane etc.) with external hydrogen is feasible but hydrogen has to be produced via renewable resources to render it viable and sustainable.

Utilization of solar energy

The CO_2 reduction process is thermodynamically uphill as illustrated by its standard freeenergy of formation ($\Delta G° = -394.359$ kJ/mol). Economical CO_2 fixation is possible only if renewable energy, such as solar energy, is used as the energysource. Equally difficult is the reduction / splitting of water to yield hydrogen and hencerequires similar combination of activation steps. The most ideal and desirable processwould then be the simultaneous photo catalytic reduction of CO_2 and water to yield hydrocarbons, whichessentially works out to ***artificial photosynthesis.***

The utilization of solar energy via chemical storage can be achieved by photo catalytic or photo-electrochemical activation of light-sensitive catalytic surfaces. When comparingthe two systems, photo catalytic system is simpler, easy to construct and operate. Photocatalyticprocess occurs via the direct absorption of photons with energy greater than or equal tothe band gap of the photo catalyst to generate electron-hole pairs. The initial excitationand electron energy transfer to the adsorbed reactants on the photo catalyst makechemical reactions in the photo catalytic process possible. Both photo catalytic and photo electro catalytic reduction of $CO_2$are under investigation as the potential routes for effective CO_2 utilization. Utilization of solar energy renders these processes sustainable.

Photo catalytic and photo electro catalytic reduction of CO_2

Reports on photo catalytic reduction of CO_2 by water to yield hydrocarbons on semiconducting oxide catalysts gained prominence since 1979, though the first report on artificial photosynthesis appeared in 1921-22. Since then several metal oxides, including titania and modified titania, layered and perovskitetype oxides, niobates and tantalates have been explored as catalysts for photo reduction of CO_2.Besides hydrogen, methane and methanol are observed as products along with traces of ethane and ethylene. The process is in nascent stageand further improvements are needed as CO_2 conversion rates are extremely small, with products formed in terms of 1-10 micro moles/hr. One of the means of improving the process efficiency is to carry out electrochemical reduction of CO_2 using solar electric power, with an integrated Photo electrochemical cell (PEC).Yet another option is to reduce CO_2 to methanol using hydrogen produced using solar powered PEC

Given the fact that backward reaction of CO_2 reduction products reduce overall yield of hydrocarbons, efforts are under way to device a reactor system where in anode oxidation and cathode reductions are carried out in different compartments separated by a proton conducting membrane like Nafion. Nafion layer is expected to promote local proton activity within the layer, stabilize the intermediates during CO_2 reduction and inhibit the re-oxidation of the reduction products. Several binary and ternary oxide catalysts, which are active in the visible region and display higher stability under reaction conditions, are under development.