

HYDROGEN PRODUCTION USING BIOMIMETIC CARBON SEQUESTRATION AND PHOTOCATALYSIS APPROACH

Renu Yadav, Darshika Nigam, Anubhav Jain, Priyadarshini Gupta, Udita Tiwari*

Department of Biochemistry, School of Life Sciences, Khandari Campus, Dr. B.R. Ambedkar University Agra, Uttar Pradesh, India

Corresponding Author:

Dr. Udita Tiwari

Department of Biochemistry, School of Life Sciences,
Khandari Campus, Dr. B.R. Ambedkar University Agra, Uttar Pradesh, India

Abstract: There are many inventions related to a process for generation of hydrogen based on biomimetic carbonation and photocatalysis. A path breaking way has been developed for generation of solar fuels in specific hydrogen by coupling biomimetic carbonation with photocatalysis. Worldwide efforts are being made to mimic the reaction for fixation of anthropogenic CO₂ into calcium carbonate using carbonic anhydrase (CA) as a biocatalyst. CA is being employed to accelerate the rate of hydration of CO₂ to form carbonate ions and proton which is further reacted with aqueous solution of calcium carbonate given a suitable saturation of calcium and carbonate ions by addition of appropriate buffer. This approach may prove to be a revolutionary technical advancement required for hydrogen economy demanding carbon neutral hydrogen production. In addition to carbonates as end products, also the production of hydrogen during biomimetic carbonation may make the process commercially viable to be adopted by industries which emit CO₂. This breakthrough thus opens new horizons in the area of carbon sequestration by virtue of the fact that end product of carbon sequestration is not only environmentally benign product of calcite but it would lead to the generation of clean greener energy including hydrogen, methane and methanol. Maximum hydrogen evolution has been observed up to 101.14 μmoles/mg of free CA, 156.8 μmoles/mg of immobilized CA and 101.14 μmoles/mg of CA, 6684.5 μmoles/mg of stabilized CA using TiO₂/Zn/Pt as photocatalyst.

Keywords: green technology, immobilization, single enzyme nanoparticles, carbon dioxide, hydrogen, photocatalysis.

1. Introduction:

The phenomenon of global warming which poses threat to the environment can be related to the increasing levels of green house gases. Carbon dioxide is considered to be one of the major contributors towards the global warming. In recent times, there have been several attempts to manage the flow of CO₂ into the atmosphere either by curbing the net emissions or by sequestration of CO₂ into long term sinks. The impact of CO₂ on global warming and ways to mitigate CO₂ is gaining center stage in the eyes of all environmentalists. The CO₂ reduction technology can be divided into two main categories namely 1) physical method and 2) chemical method. The physical methods involve capturing CO₂ from the atmosphere and storing it underground or under the sea bed using high pressure compression but the major drawbacks of this method are that, it cannot cope up with large amount of CO₂ and leaking back of CO₂ into the atmosphere (Petersen et al., 2005). The chemical method involves the conversion of CO₂ to value added products is associated with Carbon Capture and Sequestration (CCS).

2. Different ways to convert CO₂ to value added products:

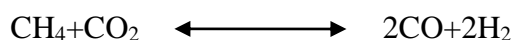
CO₂ can be utilized as reactant in various catalytic and non-catalytic reactions. However, the use of CO₂ is limited to very few processes like synthesis of urea and salicylic acid, reforming of CO₂ to form syngas and reduction of CO₂ to Carbon monoxide (CO). There are several ways to convert CO₂ into various value added products which may involve the use of homogeneous or heterogeneous catalysts. The processes can be summarized as following:

- 1) Catalytic Conversion
- 2) Electro-chemical conversion
- 3) Photo-chemical/catalytic
- 4) Thermo-chemical Conversion
- 5) Bio- chemical/ Enzymatic Conversion

2.1 There are many **chemical methods** involved for conversion of CO₂ into various value added products.

2.1.1 Carbon dioxide reforming of methane:

The reforming of methane by CO₂ has gained significant attention. Syngas is a mixture of carbon monoxide and hydrogen (CO+H₂). It can be produced in several ways like gasification of coal or by steam reforming of methane (Wet Reforming). However, the most relevant reaction is reforming of methane by CO₂ and this process is termed as “dry” reforming.



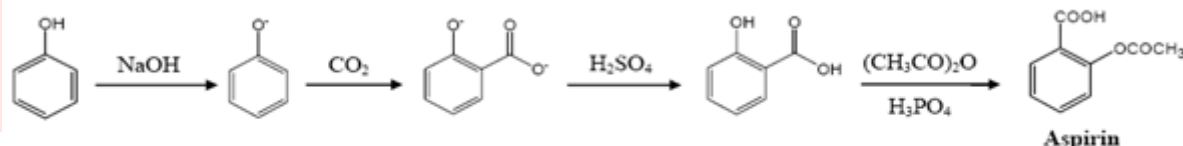
The major drawbacks associated with this reaction are that it requires high operating temperature of 800°C and deactivation of catalyst takes place owing to carbon deposition. Several authors have studied the catalytic reforming of carbon dioxide over Ir, Ni, Co–Ni, Ru, and Rh on different supports like silica, magnesia, alumina, Zirconia and lanthanum oxides (Song et al., 2000; Bradford & Vannice, 1999). Pietraszek et al., (2011) have recently reported monometallic and bi-metallic catalysts supported on Ce-Zr supports, which have proved to be effective in dry reforming of methane. Some La-Ni based perovskites have also shown good stability and resistance to carbon deposition (Dupeyrat et al., 2005; Gallego et al., 2006). Photo catalytic reforming of methane has also been reported by Yuliati et al. (2008) wherein conversion of CH₄ and CO₂ to yield CO and H₂ over Ga₂O₃ under UV radiation was studied.

2.1.2 Reduction of carbon dioxide to carbon monoxide:

One of the routes of carbon dioxide valorization is the reduction of CO₂ to CO by the utilization of solar energy under mild conditions. The pioneering work on photo reduction of CO₂ to CO was reported by Lehn et al., (1982) by using Ru and Co polypyridine complexes. (Lehn et al., 1982; Hawecker et al., 1983). The photo reduction of CO₂ in the presence of H₂ has been reported over Rh/TiO₂ (Kohno et al., 1999; Kohno et al., 2001) ZrO₂ (Kohno et al., 1997; Kohno et al., 2000) and MgO (Kohno et al., 2001; Teramura et al., 2004).

2.1.3 Synthesis of Salicylic acid by carbon dioxide:

There are several organic processes for the synthesis of salicylic acid amongst which Kolbe-Schmitt is widely used. Salicylic acid is used to synthesize aspirin which is the most safe and common analgesic. The synthesis of salicylic acid by phenol and CO₂ by radiation has already been investigated as a part of radiation induced carboxylation technology related to CO₂ utilization (Getoff, 2006; Kirimura & Ishii, 2017).



Kolbe-schmitt reaction

2.2 There are many **enzymatic methods** involved for conversion of CO₂ into various value added products.

- The synthesis of methanol (CH₃OH) and formic acid
- The production of carboxylates (RCOOH); and
- Relevant compounds such as carbamic esters and will compare the chemical routes with natural processes that use enzymes as catalysts.

2.2.1. Natural carboxylation's and RuBisCO genetic engineering:

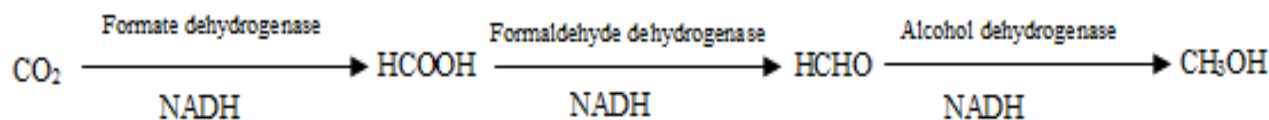
In nature carboxylation processes use either CO₂ or its hydrated form HCO₃⁻, which is available in cells at a higher concentration than gaseous CO₂, this reaction is catalysed by an enzyme Ribulose 1,5-bis(phosphate) carboxylase oxidase (RuBisCO) (Akazawa et al., 1987), requires a metal cation as co-factor eg.: Mg²⁺, Mn²⁺, Co²⁺, Fe²⁺. The mechanism of action is quite complex: it has been observed that, for both carboxylase and oxidase functions, RuBisCO have an activation site, constituting a lysine residue and a catalytic site, both placed in the large sub-unit. Today researchers are focused on RuBisCO genetic manipulation (Satagopan et al., 2017; Svab et al., 1990), directed towards increasing its specificity for CO₂ (Reynolds et al., 2000). Despite the many efforts made so far, there is not yet a clear indication of the feasibility of such a biotechnological approach (Andrews et al., 2003; Parry et al., 2003; Finn et al., 2004) that has a high potential for the natural conversion of excess anthropogenic CO₂.

Thaueraromatica bacteria can convert phenol into CO₂ and water under anaerobic conditions. The first step in the degradation pathway is the carboxylation of phenol-phosphate to 4-hydroxybenzoic acid (upper part) which is then dehydroxylated to benzoic acid (Aresta et al., 1991). The carboxylation of phenol is carried out by a new type of lyase

(Schuehle et al., 2004) i.e., phenolcarboxylase enzyme. The enzyme was isolated from the cytoplasmic portion of the cell and the cells are grown on low-melting-agar, and used in vitro for the carboxylation of phenolphosphate, mimicking the natural system (Aresta et al., 1998). Interestingly, the phenol carboxylase enzyme also works in sc-CO₂ (super critical CO₂) (Aresta et al., 2006).

Many researchers mimic many enzymatic reactions in vitro such as the production of acetic acid from CO₂ by using carbon monoxide dehydrogenase catalysis where Ni is the active center in S₄Fe₄-Ni enzymes for both the coordination of CO and the coupling of CO with CH₃ to afford the acetyl moiety (Aresta & Dibenedetto, 2005).

2.2.2. CO₂ converted to methanol:



Many challenging work is focusing on the efficient fixation of the green house gas CO₂ into methanol as a raw material and clean fuel by using formate dehydrogenase (FateDH), formaldehyde dehydrogenase (FaldDH) and alcohol dehydrogenase (ADH) encapsulated in silica gel prepared by modified sol-gel process as catalysts (Hong et al., 2003) or within titania particles through a facile and mild biomimetic mineralization process (Sun et al., 2009), tetraethyl orthosilicate (TEOS) as precursor, NADH as an electron donor (shown in scheme 1).

Scheme 1: Production of methanol from CO₂

2.2.3. CO₂ converted to carbon monoxide:

Carbon monoxide is also one of the value added product and can readily be converted into methanol for use as a liquid fuel. Woolerton et al. (2010) had worked on TiO₂ nanoparticles (NPs) modified with a photosensitizer and the CO₂-reducing enzyme, carbon monoxide dehydrogenase (CODH) from the anaerobic microbe *Carboxydotherrmus hydrogenoformans* (Ch), which act as a catalyst for CO₂ photoreduction. They observed the turnover frequencies of up to 40000 s⁻¹ have been reported for CO oxidation by Ch CODHs.

2.2.4. CO₂ converted to acetate:

Most acetogenic bacteria are able to grow on hydrogen plus CO₂ as sole energy sources, which catalyze the conversion of CO₂ into acetate in their energy metabolism. Acetate synthesis from CO₂ with H₂ as the electron donor must necessarily be coupled to a net synthesis of ATP. This was confirmed for the methylene-tetra hydrofolate (THF) reductase in the acetogen *Clostridium thermoautotrophicum*. If the methylene-THF reduction is coupled to sodium translocation, the sodium gradient could either directly be used for the synthesis of ATP via sodium translocating ATP synthase or be transformed via a sodium/proton antiporter into a proton gradient, which could then serve as the driving force for the synthesis of ATP catalyzed by a proton translocating ATP synthase. Evidence was presented for the presence of a Na⁺/H⁺ antiporter as well as a proton translocating ATP synthase in the acetogen (Nevin, 2010; Drake, 2008; Muller, 2003). The acetogen *Clostridium ljungdahlii* has been genetically engineered to produce the substitute of gasoline, butanol from acetyl-CoA (Kopke, 2009).

2.2.5 CO₂ converted to hydrogen:

Yadav (2011) and Rayalu (2012) worked on the mimicing reaction for fixation of anthropogenic CO₂ into calcium carbonate using carbonic anhydrase (CA) as a biocatalyst. The production of hydrogen in addition to carbonates as end products during biomimetic carbonation was further coupled with photocatalytic process. During the process of carbon sequestration they are not only able to produce calcite (environmentally benign product) but also some value added products such as hydrogen, methane and methanol. Maximum hydrogen evolution has been observed up to 101.14 μmoles/mg of, free CA, 156.8 μmoles/mg of immobilised CA and 101.14 μmoles/mg of CA, 6684.5 μmoles/mg of stabilised CA using TiO₂/Zn/Pt as photocatalyst (Rayalu et. al., 2013; Rayalu et al., Patent 2013).

3. Summary:

CO₂ valorization is an attempt to use CO₂ as a feedstock for producing various value added products. It can prove be a clean and sustainable approach towards utilization of CO₂. However it requires renewable energy resources like solar energy to be used as energy input to carry out the various reactions. Photochemical/ Photocatalytic conversion of CO₂ by solar energy can greatly help in carbon recycling. Development in solar energy chemical conversion and recent advances in catalysis definitely make this approach promising in future. Currently, there is no single technology which can reduce CO₂ emission as required by Kyoto protocol. Hence, a combination of processes each able to utilize CO₂ and leading to some value added products are required to meet the ultimate goal of reducing the amount of CO₂ in the

atmosphere. Carbon dioxide reforming is an attractive option from the viewpoint of carbon dioxide fixation. Photocatalytic pathways for conversion and utilization of CO₂ can hold great promise. Concerted research and efforts are required in this direction to develop less energy intensive pathways for the CO₂. CO₂ valorization is the only technology which can lead to valuable products and contribute to reduction of global emission.

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