Liquid Fuels from CO$_2$: State of the Art

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Introduction

• Finite fossil fuel reserves dictate that new solutions must be found to reduce energy consumption and decrease carbon use. New processes must be developed to handle renewable feedstocks such as CO₂.
• Conversion of CO₂ to fuels is a very active research area that presents great challenges and opportunities for industry, along with great benefits to society.
• Recycling of CO₂ via its conversion into a high-energy content fuel, suitable for use in existing HC-based energy infrastructures, provides a very important option, if the process used is energy profitable and economical.
The GCC countries have consistently ranked high, in per capita C emissions. A lifestyle with a high ecological footprint in a fragile ecosystem can affect the regional environment, prosperity and social stability.

[Int. J. Energy Sector Management, 7(2) 2013, 223-242]
# Possible Methods of CO$_2$ Reduction

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio-chemical (using nuclear energy)</td>
<td>$\text{CO}_2 \xrightarrow{\gamma \text{radiation}} \text{HCOOH, HCHO}$</td>
</tr>
</tbody>
</table>
| Chemical reduction by metals (~ High T) | $2\text{Mg} + \text{CO}_2 \rightarrow 2\text{MgO} + \text{C}$  
$\text{Sn} + 2\text{CO}_2 \rightarrow \text{SnO}_2 + 2\text{CO}$  
$2\text{Na} + 2\text{CO}_2 \rightarrow \text{Na}_2\text{C}_2\text{O}_4$ |
| Thermo-chemical                     | $\text{CO}_2 \xrightarrow{\text{Ce}^{4+}, T>900^\circ \text{C}} \text{CO} + \frac{1}{2}\text{O}_2$ |
| Photo-chemical                      | $\text{CO}_2 \xrightarrow{\text{hv}} \text{CO, HCHO, HCOOH}$ |
| Electro-chemical                    | $\text{CO}_2 + x e^- + x H^+ \xrightarrow{e^V} \text{CO, HCOOH, (COOH)}_2, ...$ |

Possible Methods of $\text{CO}_2$ Reduction ...

<table>
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</tr>
</thead>
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<tr>
<td><strong>Bio-chemical (methanogenesis)</strong></td>
<td>$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td><strong>Bio-photo-chemical</strong></td>
<td>$\text{CO}_2 + \text{oxoglutaric acid} \xrightarrow{\text{Enzyme, } \text{hv}} \text{isocitric acid}$</td>
</tr>
<tr>
<td><strong>Photo-electro-chemical</strong></td>
<td>$\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \xrightarrow{hv, eV, \text{Semiconductor}} \text{CO} + \text{H}_2\text{O} + \ldots$</td>
</tr>
<tr>
<td><strong>Bio-electro-chemical</strong></td>
<td>$\text{CO}_2 + \text{oxoglutaric acid} \xrightarrow{\text{Enzyme, eV, Methylviologen}} \text{isocitric acid}$</td>
</tr>
<tr>
<td><strong>Bio-photo-electro-chemical</strong></td>
<td>$\text{CO}_2 \xrightarrow{hv, \text{Enzyme, p}–1\text{nP, eV, Methylviologen}} \text{HCOOH}$</td>
</tr>
</tbody>
</table>

Strategies for Renewable Fuel Synthesis and Utilization

http://www3.imperial.ac.uk/electrochemicalengineering/research/currentprojects/co2reduction
The Carbon Redox Cycle in Nature

Madigan et al., 2003. 10th ed. Prentice Hall, Fig. 19.23, p. 654)
Photocatalyst vs. Chlorophyll

1. Chlorophyll of plants is a typical natural photocatalyst.

2. The differences between chlorophyll photocatalyst and artificial photocatalyst are
   - Chlorophyll usually captures sunlight to turn $\text{H}_2\text{O}$ and $\text{CO}_2$ into starch, oxygen and organic compounds:
     \[
     6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{Light, Chlorophyll}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2
     \]
   - On the contrary, artificial photocatalysts create strong oxidation agent and electronic holes to breakdown the organic matter to $\text{CO}_2$ and $\text{H}_2\text{O}$ in the presence of light.

3. But we want the artificial photocatalysts to do a similar job as that of the Chlorophyll.
Photocatalyst vs. Chlorophyll ...
Photocatalysts so far tested in CO$_2$ Reduction

1. TiO$_2$ suspensions with metals such as Pd, Rh, Pt, Au, Cu, or Ru.

2. TiO$_2$ suspensions with other metals such as Hg, Cd, Pb, Tl, In, Sn, Pt, Ni, Fe, Ti, Au, Ag, and Zn.

3. TiO$_2$ suspensions with other non-metals such as C, S, N, F.

4. Photocatalysts such as ZnS and CdS work well.

5. Zeolites and solid-gas systems.

6. Transition metal (e.g. Ru, Rh, Co) complexes; proved much success.
Photocatalysts so far tested in CO$_2$ Reduction ...
VB, CB and Band Gap potentials of various semiconductors compounds (eV). Also shown Redox Potentials (Volt) vs. NHE (Normal Hydrogen Electrode) for half-cell reactions at pH 7 in aqueous solution.

Thermodynamic potentials (Volt) vs. NHE (normal hydrogen electrode) for half-cell reactions at pH 7 in aqueous solution.


<table>
<thead>
<tr>
<th>Chemical Equation</th>
<th>Thermodynamic Potential (Volt) vs. NHE</th>
<th>#</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ + e⁻ → CO₂⁻</td>
<td>-2.000</td>
<td>(1)</td>
</tr>
<tr>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>-0.410</td>
<td>(2)</td>
</tr>
<tr>
<td>CO₂ + 2H⁺ + 2e⁻ → HCOOH</td>
<td>-0.610</td>
<td>(3)</td>
</tr>
<tr>
<td>CO₂ + 4H⁺ + 4e⁻ → HCHO + H₂O</td>
<td>-0.520</td>
<td>(4)</td>
</tr>
<tr>
<td>CO₂ + 2H⁺ + 2e⁻ → CO + H₂O</td>
<td>-0.480</td>
<td>(5)</td>
</tr>
<tr>
<td>CO₂ + 6H⁺ + 6e⁻ → CH₃OH + H₂O</td>
<td>-0.380</td>
<td>(6)</td>
</tr>
<tr>
<td>CO₂ + 8H⁺ + 8e⁻ → CH₄ + H₂O</td>
<td>-0.240</td>
<td>(7)</td>
</tr>
<tr>
<td>H₂CO₃ + 2H⁺ + 2e⁻ → HCOOH + H₂O</td>
<td>-0.166</td>
<td>(8)</td>
</tr>
<tr>
<td>H₂CO₃ + 4H⁺ + 4e⁻ → HCHO + 2H₂O</td>
<td>-0.050</td>
<td>(9)</td>
</tr>
<tr>
<td>H₂CO₃ + 6H⁺ + 6e⁻ → CH₃OH + 2H₂O</td>
<td>+0.044</td>
<td>(10)</td>
</tr>
<tr>
<td>2CO₃²⁻ + 4H⁺ + 2e⁻ → C₂O₄²⁻ + 2H₂O</td>
<td>+0.478</td>
<td>(11)</td>
</tr>
<tr>
<td>2CO₃²⁻ + 3H⁺ + 2e⁻ → HCOO⁻ + 2H₂O</td>
<td>+0.311</td>
<td>(12)</td>
</tr>
<tr>
<td>2CO₃²⁻ + 8H⁺ + 6e⁻ → CH₃OH + 2H₂O</td>
<td>+0.209</td>
<td>(13)</td>
</tr>
<tr>
<td>2C₂O₄²⁻ + 2H⁺ + 2e⁻ → 2HCOO⁻</td>
<td>+0.145</td>
<td>(14)</td>
</tr>
<tr>
<td>HCOO⁻ + 5H⁺ + e⁻ → CH₃OH + 2H₂O</td>
<td>+0.157</td>
<td>(15)</td>
</tr>
</tbody>
</table>
Example: Photocatalytic Production of CH$_4$ from CO$_2$ and H$_2$O on TiO$_2$ Catalysts

• This process has a low energy conversion efficiencies so far.
• The shape and size of the photocatalyst are very important.
• The products depend upon the photocatalyst itself and the reaction conditions as well. For example,
  \[
  \text{CO}_2\text{(aq)} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH} \text{ (formic acid)} \\
  \text{HCOOH} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCHO} \text{ (formaldehyde)} + \text{H}_2\text{O} \\
  \text{HCHO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{OH} \text{ (methanol)} \\
  \text{CH}_3\text{OH} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_4 \text{ (methane)} + \text{H}_2\text{O}
  \]

Overall reaction:
  \[
  \text{CO}_2\text{(aq)} + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 \text{ (methane)} + 2\text{H}_2\text{O}
  \]
TiO\textsubscript{2} Photocatalytic Enhancement vs TiO\textsubscript{2} Modification Techniques.

Visible Light Responsive (VLR) Photocatalysts used for CO$_2$ Reduction.


- Capable of utilizing solar energy which is 45% of solar spectrum.
- Co-metal doped, sensitized and novel sensitizers are very effectual to enhance yield and selectivity.
- Higher yield and selectivity is possible under mild operating conditions. Methanol is possible by using co-metal and sensitized catalysts. Cu is good for methanol production.
Example on Photocatalyst Modification for CO₂ Reduction

Matrix isolated TiO₂ clusters encapsulated inside the cavities of Y zeolite acting as photocatalyst for CO₂ reduction by H₂O

N-doped TiO₂ NT array acting as solar light photocatalyst for CO₂ reduction by water

*Int. J. Mol. Sci.* 2014, 15, 5246-5262
Mechanism of Photocatalytic CO\textsubscript{2} Reduction and H\textsubscript{2}O Oxidation on TiO\textsubscript{2} Catalyst

Reaction Scheme:

• Electron \((e^-_{cb})\) plus hole \((h^+_{vb})\) pairs are photo-generated:

\[
\text{TiO}_2 \xrightarrow{hv} (e^-_{cb}) + (h^+_{vb})
\]

• Photo-reduction of CO\textsubscript{2} to form carbon radical C• and oxygen O\textsubscript{2}:

\[
\text{CO}_2 + \text{UV} - \text{Visible light} \xrightarrow{doped \text{ metal oxide}} \text{C•} + \text{O}_2
\]

• Photo-oxidation of H\textsubscript{2}O to form H\textsuperscript{+} and hydroxyl radicals OH•:

\[
\text{H}_2\text{O} + h^+_{vb} + \text{UV} - \text{Vis light} \xrightarrow{doped \text{ metal oxide}} \text{H}_2\text{O}^+ \xrightarrow{} \text{OH•} + \text{H}^+
\]

• Overall Photoreaction:

\[
a \{(\text{C} + \text{O}_2)\} + b\{\text{OH•} + \text{H}^+\} + c\ e^- \rightarrow d\ \text{C}_x\text{H}_y\text{O}_z + e\ \text{H}_2\text{O}
\]
Reaction scheme for the production of HCs during photocatalytic CO$_2$ reduction and H$_2$O oxidation

- For example, the hole (h$^+$) of TiO$_2$ breaks apart the H$_2$O molecule to form H$^+$ gas and •OH$^-$ radical. The electron (e$^-$) reacts with CO$_2$ to form super active •CO$_2^-$ radical. The other steps toward HCs production are as illustrated below. This cycle continues when light is available.
Mechanism and Pathways for Photocatalytic Processes

\[ \text{electron, } e^- \]

\[ \text{light} \]

\[ \text{hole, } h^+ \]

\[ (\text{CO}_2) \]
Requisite Components for Construction of Solar Fuels System

• The design of highly efficient, non-biological, molecular-level energy conversion “machines” that generate fuels directly from sunlight, water, and CO$_2$ is both a formidable challenge and an opportunity that, if realized, could have a revolutionary impact on our energy system.

• Requisite Components for Construction of Solar Fuels System are
  (1) Light Absorbers
  (2) Catalysts
  (3) Membranes
  (4) Linkers

Joint Center for Artificial Photosynthesis (JCAP) http://solarfuelshub.org/research/overview/
Requisite Components for Construction of Solar Fuels System ...

1. **Light Absorbers**: Discover and develop light absorbers that consist of robust, Photo-chemically stable, Earth-abundant elements to provide the needed voltage and current density to effect fuel formation from sunlight, water, and CO$_2$, as the only inputs.

2. **Catalysts**: Discover and develop a variety of catalysts to drive the key fuel-producing reactions of interest, such as oxidation of water and reduction of CO$_2$ to energy-rich fuels.
3. **Membranes**: In natural photosynthesis, energy conversion depends upon an inter-connected network of membranes that separate the reactants and products, and that provide a physical matrix that supports the whole process. It is needed to design and synthesize photo-electro-chemical membrane layers that provide ionic pathways and good optical and light-scattering properties, while remaining impermeable to the product fuels and to oxygen.

4. **Linkers**: The design of the artificial system must provide “linkers” that efficiently couple light absorbers and catalysts for optimal control of the rate, yield, and energetics of charge carrier flow at the nanoscale, so that the complete macroscale system can achieve maximum conversion of solar energy into fuel.

Joint Center for Artificial Photosynthesis (JCAP) http://solarfuelshub.org/research/overview/
Among the open challenges that need to be solved in order to make future technology in this area successful are

1. CO₂-to-fuel conversion technologies seem not fully economical in comparison to conventional ones.
2. Worldwide, fuel market is about 2 times higher than that of chemicals.
3. Since CO₂ emissions are mainly associated to energy production - the impact of CO₂ conversion on global emissions will be rather moderate.
4. The elaboration of cost-efficient processes of CO₂ conversion to valuable products / chemicals needs research.
Photoreduction of CO₂ Perception - Unsolved Problems!

1) Mole reduction products of CO₂/mole catalyst are still low.

2) Efficiencies of the reactions are unsatisfactory – both the amounts of reduction products of CO₂ (usually C₁ products) and oxidation products of the sacrificial donor (e.g. H₂O).

3) The tuning of the single components with respect to their redox potentials, life times and selectivity is not well understood.

4) It is necessary to device systems which do not require sacrificial donors.

Photoreduction of CO$_2$ Perception
- Unsolved Problems! ...

6) Light energy is also used for degradation of the sacrificial donors, thus unfavorably influencing the energy balance of the reactions.

7) Macro-cyclic complexes of transition metal ions – satisfy the requirements of a useful relay. They may play a dual role as catalysts and relays.

8) Even with transition metal complexes – reduction products have not been of great economic value (usually only C$_1$ products).

9) Multi-component systems containing photoactive centers, electron relays and/or molecular electro-catalysts, in addition to possible micro-heterogeneous systems, may be discovered.

Photocatalytic CO$_2$/H$_2$O Redox Reactions on metal oxide semiconductor surfaces – Challenges

1. The process centers around the activation of two thermodynamically most stable molecules; CO$_2$ and water.

2. The process has extremely low conversions (< 1 %) achieved so far that are occurring at very slow rates.

3. Catalysts tend to get deactivated over a short period of use.

4. CO$_2$ photoreduction process is highly complex, involving multi-electron transfer and non-selective, leading to a range of HC products (C$_1$-C$_3$).

5. Design of catalysts, consisting of photocatalysts and co-catalysts aided by metal ion / anion doping and light harvesting components / sensitizers, is equally complex.

6. Ideal catalysts are expected to display maximum efficiency towards solar energy absorption and possess requisite band energy level characteristics to drive the redox reactions.

7. The process involves splitting of water and reduction of CO$_2$, which is thermodynamically more favorable. Since CO$_2$ reduction involves multi-electron transfer, the rates are very slow relative to water splitting. These two steps are to be synchronized to achieve higher yields of hydrocarbons.

8. Nevertheless, research efforts on these fronts are being pursued with full vigor by many laboratories around the globe.

9. Design of efficient catalyst systems and achieving higher yield of desired products are the two key issues being pursued by the researchers.

Rajalakshmi, MSc Thesis, ITT, Madras, India, May 2011
Final Words...

- The CO₂ conversion to HC Fuels is a multidisciplinary challenging project that needs chemists, physicist, Engineers and others to collaborate.

- Enough supporting resources (Interested Specialists, Fully Equipped Research Labs, Sophisticated Instrumental Analysis Facilities, Rewarding Budget, etc.)

- The Research Team should be released from other work in order to be really productive and devote their time to such future promising project.
Thank You

Any Questions?
It has been discussed and agreed that

1. CO₂ sequestration and capture technologies that allow separation of CO₂ from process streams with further storage or recycling are commercially available.

2. The production of value-added products, materials and fuel from CO₂ feedstocks could help to close the carbon cycle and would be an example of sustainable future technologies that aimed in saving natural resources and energy. CO₂ can also be considered an energy vector for efficient use of solar energy, as well.

3. The use of algae to convert CO₂ indirectly into high-value products is an interesting option and current investigations in this field confirm the great potential.

4. There is a strong need for research to help bringing new or improved technologies to market.
## CO$_2$: From Waste to Value
European Commission Workshop, Brussels, 30/3/2011 …

Among the identified areas of future/further research to overcome the existing challenges:

1. Production of chemicals from CO$_2$.
2. Advanced catalysts for CO$_2$ recycle technologies: Research in the field of catalysis is necessary to develop photocatalysts for splitting water and novel catalysts to be used for the direct methanol synthesis from CO$_2$.
3. Production of liquid fuels from CO$_2$/H$_2$O using solar energy (C-based energy vectors).
5. New enzymes to design artificial metabolic routes for CO$_2$ conversion on molecular level.
6. Mineralization technology as an alternative for CO$_2$ storage.
7. Artificial bioconversion of CO$_2$. 
Scientists have developed a new photosynthetic solar cell that converts CO$_2$ to hydrocarbon fuel using sunlight.

The new solar cell can remove CO$_2$ from the atmosphere — like trees do — that use such cells as artificial leaves “could produce energy-dense fuel efficiently.

The fuel produced by the cell is — synthesis gas, a mixture of H$_2$ and CO$_2$, which can be burned directly, or converted into diesel or other hydrocarbon fuels.
Scientists achieved “synthetic photosynthesis” by combining nanoscale semiconductors and genetically modified bacteria.

By marrying nanoscience and biology, a biologically inspired, but completely artificial, system has been created that uses long nanoscale filaments to turn sunlight into electrons, which bacteria use to convert CO$_2$ and water into butanol fuel and more complex molecules such as acetate.

Also nanowires wrapped with hydrogen-loving bacteria has been used to turn CO$_2$ into methane.
Combination of Synthetic Light Converters and Natural Catalysts — Is it the way of the Future?
University of Toronto

1. Intended to create an artificial photosynthetic system.
2. Integrate bacterial catalysts with semiconductor technology. This lets us understand and optimize a truly synthetic photosynthesis system.
3. Learn and develop a synthetic catalyst with performance similar to the bacteria.
5. Meanwhile, this approach represents an intermediate step that lets us learn about artificial photosynthesis in new ways.
Novel Catalytic Mechanisms for the Chemical Reduction of CO$_2$ to Energy-Dense Liquids


Recommended Research Concentration Areas include:

1. Developing efficient processes and high turnover catalysts for the efficient reduction CO$_2$ to produce energy-dense fuels containing carbon-carbon bonds;

2. Identifying and understanding the molecular mechanisms of the processes of CO$_2$ reduction and C-C bond formation

3. Identifying appropriate electrode materials that make efficient use of the solar spectrum to produce electrons needed for CO$_2$ reduction and understanding the detailed mechanisms of production, transport and donation of electrons

4. Understanding and developing a predictive modeling capability for the multiple-electron and multiple-proton processes needed to avoid pathways with high activation energies in CO$_2$

5. Developing novel material designs for electrochemical systems to convert CO$_2$ to chemical fuels.
Novel Catalytic Mechanisms for the Chemical Reduction of CO$_2$ to Energy-Dense Liquids
University of California San Diego, Institute of Technology, Stanford University, and Princeton University

Recommended Approach:

1. Combine in situ spectroscopic studies using synchrotron radiation and density functional theory (DFT) investigations to develop a fundamental understanding of CO$_2$ reduction at metal electrode surfaces.

2. Combine photo-electro-chemical, spectroscopic and theoretical studies to understand how metal oxides and other semiconductor surfaces can have their band energy profiles matched to the solar spectrum to facilitate CO$_2$ reduction.

3. Elucidate homogeneous and heterogeneous reaction pathways to determine branching ratios for (photo-)electrochemical reduction of CO$_2$ to methanol and other liquid fuels.

4. Design high efficiency semiconductor interfaces by functionalizing semiconductor photoelectrode surfaces with metal nanoparticles and aromatic amine (pyridinium) catalysts for CO$_2$ reduction.

5. Apply combinatorial methods for the discovery of new homogeneous and heterogeneous catalysts and semiconductor photoelectrode materials for CO$_2$ reduction.
Electro-chemical and Photo-electro-chemical Activation of CO$_2$


1. One need to consider the bonding scheme of CO$_2$ and evaluate which mode of activation is feasible and possible.
2. Which site in the molecule has to be activated and why?
3. What selectivity or product slate one wants?
4. What is the basic difference between electro-chemical activation and other modes of activation, if it exists?
5. Do we need CO$_2$ reduction alone or both reduction and decomposition? If so, how?
Some Concepts at this Stage!

• Electro-chemical activation is possible but being a gas under normal conditions, the yields and selectivity depend on potential nature of electrodes and medium that can be employed.

• Direct photo-chemical activation may be possible but cannot be selective.

• Combined photo-chemical and electro-chemical, i.e. photo-electro-chemical mode can be one of the choices now at hand to activate CO₂.

• Do you have any challenges to pose!
Combined Mode of CO$_2$ Activation: The photo-electro-chemical catalytic cell
References

• *Int. J. Energy Sector Management*, 7(2) (2013) 223-242


• [http://www3.imperial.ac.uk/electrochemicalengineering/research/currentprojects/CO2reduction](http://www3.imperial.ac.uk/electrochemicalengineering/research/currentprojects/CO2reduction)

• European Workshop "CO₂: From Waste to Value“, Brussels, 30/3/2011


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• C. R. Graves, Recycling CO$_2$ into Sustainable Hydrocarbon Fuels: Electrolysis of CO$_2$ and H$_2$O, PhD, Technical University of Denmark, 2010.