

# Formation of Synthesis Gas Using Solar Concentrator Photovoltaics (SCPV) and High Temperature Co-electrolysis (HTCE) of CO<sub>2</sub> and H<sub>2</sub>O

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**Abstract:** Carbon dioxide is considered a greenhouse gas (GHG) that reflects solar radiation and consequently increases the temperature of the earth. Many countries are now considering putting a tax on CO<sub>2</sub> emissions that will increase the cost of products that are associated with those emissions. The most common method currently considered for dealing with CO<sub>2</sub> emissions is the capture of the gas, pressurization, and then sequestration in either rock formations or saline aquifers. This is relatively costly in both capital investment and operation of the equipment. Also, there is the possibility that this CO<sub>2</sub> will escape at some point in the future subjecting the company in question to an uncertain risk. Ceramatec has been investigating an alternative approach that converts the CO<sub>2</sub> into a useful product that can then be sold. Using solid oxide fuel cell materials in conjunction with a non-carbon source of energy it is possible to generate synthesis gas (CO and H<sub>2</sub>) and oxygen from CO<sub>2</sub> and H<sub>2</sub>O. SCPV (Solar Concentrator Photovoltaic) systems are the most efficient generators of solar electricity and generate high quality heat at the same time. HTCE (High Temperature Co-electrolysis) uses both the solar electricity and the heat to electrolyze the CO<sub>2</sub> and H<sub>2</sub>O at double the total cycle efficiency of traditional electrolysis. The synthesis gas that is produced can be used to produce synthetic fuels such as synthetic natural gas or Fischer Tropsch liquid fuels, or chemicals. This paper will discuss this alternative approach to the disposal of CO<sub>2</sub>. This approach has the following advantages: permanent disposal, usable product, storage of solar energy in fuel, reduction of GHG, reduction in solar radiation, and no additional GHG.

**Keywords:** high temp electrolysis; CO<sub>2</sub> conversion; high temp co-electrolysis; solar concentrator photovoltaics; CO<sub>2</sub> electrolysis; steam electrolysis

## Introduction

The system described in this paper combines two complimentary technologies (i.e. a solar concentrator photovoltaic system and high temperature co-electrolysis) to turn water and carbon dioxide into a useful industrial input (i.e. synthesis gas). The process in effect provides a method to store the energy from sunlight in a form that is easily transported and can be used at any time rather than just when the sun is shining. At the same time, these technologies present a pathway to converting a greenhouse

gas into useful product (i.e. synthetic natural gas, liquid hydrocarbons, or industrial chemicals).

Much debate on global warming has occurred but it is generally accepted that greenhouse gases (GHG) reflect solar radiation that would otherwise be radiated into space and thus retain heat within the atmosphere. In effect, GHG change the radiation balance by trapping some of the infrared heat associated with sunlight within the biosphere of the earth. The proposed technology attacks this problem in several ways.

1. The SCPV system captures the heat associated with solar radiation and passes that heat to the HTCE system where the heat energy is used to increase the efficiency of the electrolysis process. Thus, the combined technologies will store not only the electrical energy from the SCPV but also the heat component of solar energy. This significantly increases the captured solar energy and thus, the efficiency of the total system.
2. The system will convert captured carbon dioxide and water into a stream of pure synthesis gas (i.e. carbon monoxide and hydrogen) that can be used as mentioned above to store the electrical energy from the photovoltaic array and the associated heat energy in a useful form.
3. If the technology can be applied at sufficient scale, the use of carbon dioxide that would have been emitted to the atmosphere in the formation of synthesis gas has the potential to also favorably affect the radiation balance allowing more solar radiation to escape to space thus lowering the amount of heat captured within the earth's atmosphere. The combination of these technologies will have the potential to favorably affect the heat balance in the earth's atmosphere.

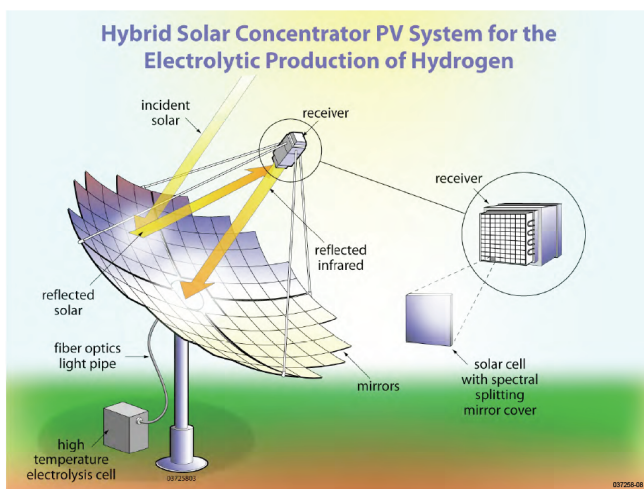
Obviously, since the system uses electric power to produce the synthesis gas, the source of electricity must be from a non-fossil energy source. Since it generates both electricity and heat, the solar concentrator photovoltaic (SCPV) array is ideal. The SCPV heat is generated at a temperature that is well matched with the HTCE cells and thus, contributes substantially to the overall system efficiency.

Based on ice core data and atmospheric measurements of carbon dioxide content, it can be shown that there have been significant increases in the amount of carbon dioxide

since pre-industrial time <sup>(1)</sup>. Measurements indicate a steady rise of about .9 ppmv (parts per million by volume) per year from a pre-industrial value of ~280 ppmv to a current value above 380 ppmv (NOAA, July, 2009). Several scientists (University California San Diego, et al) have hypothesized that the anthropomorphic CO<sub>2</sub> generated from various industrial sources can be shown to correlate well with the current increase in temperature associated with climate change.

Data gathered and reported by the Intergovernmental Panel on Climate Change indicates that fossil fuel use accounts for over 50% of total anthropogenic greenhouse gas emissions in 2004 <sup>(3)</sup>. The HTCE system described in this paper has demonstrated the ability to convert CO<sub>2</sub> and H<sub>2</sub>O into a stream of pure synthesis gas (CO and H<sub>2</sub>). Once the synthesis gas is formed it can be converted to synthetic natural gas (i.e. methanation reaction), liquid hydrocarbon fuels (i.e. Fischer Tropsch reaction), or various chemicals. In effect, the energy of the sun is used to capture the CO<sub>2</sub> for re-use.

**Solar Concentrator Photovoltaics:** The CO<sub>2</sub> disposal system utilizes a SCPV array that utilizes a spectral splitter to separate the infrared portion of the solar spectrum before the solar rays impact the high efficiency solar cells. This infrared portion of the total solar spectrum will be routed to the HTCE unit by light pipe to provide the heat required to operate in the highly efficient endothermic operating range of the HTCE unit. The photovoltaic array will be made up of ultra high efficiency, multi-junction cells that become economical to use because of the light intensification of the solar concentrator (see Figure 1).



**Figure 1:** SCPV combined with HTCE system

Solar Systems Pty Ltd has demonstrated proprietary SCPV technology on a pilot scale in Australia. Each SCPV dish and receiver will generate approximately 30 kW electric and approximately 45 kW thermal of high quality heat for

the HTCE system. Based on typical solar incidence, about 12 km<sup>2</sup> (i.e. ~4 square miles) of desert in the Southwest United States is sufficient to generate about 1000 MW of electric power and thus about 1500 MW of thermal energy (NREL data).

The high efficiency cells used in the described system have a solar to electricity efficiency of over 40%. Modeling of the system indicates that it will be possible to convert light into hydrogen at a total system efficiency exceeding 50% (*note: this is possible because of the use of the infrared portion of the solar energy*). If the HTCE is used in a co-electrolysis mode, the conversion of solar energy into synthesis gas has been modeled to slightly exceed 56%. This efficiency is calculated by comparing the energy content of the solar incidence versus the energy content of the generated synthesis gas on a lower heating value basis. This high efficiency is possible because of the inherent high efficiency of the HTCE system in utilization of electricity and heat.

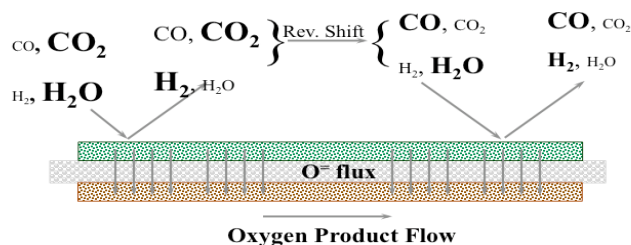
**High temperature Co-electrolysis:** Ceramtec has been actively developing planar SOFC (solid oxide fuel cells) systems for over 20 years. In the early 1990's, it was shown that the SOFC materials could be successfully used for the dry electrolysis of CO<sub>2</sub>. These experiments indicated that the electro-kinetics of dry CO<sub>2</sub> conversion to CO were an order of magnitude slower than the same cell exhibited with a conversion of steam to hydrogen.

In late 2006, a HTCE unit was operated in the steam electrolysis mode for 1000 hours and produced 1.2 m<sup>3</sup>/hour of hydrogen at the beginning of the test. The unit was then switched to a feed of steam and CO<sub>2</sub> and operated for an additional 1000 hours producing synthesis gas by co-electrolysis of steam and CO<sub>2</sub>. It was found that the kinetics of the co-electrolysis system was almost identical to that of the steam electrolysis unit and thus the electrolysis of CO<sub>2</sub> became much more practical. The mechanism for the electrolysis of steam and carbon dioxide is shown in Figure 2 below.

**Feed:** H<sub>2</sub>O, CO<sub>2</sub>, (minor H<sub>2</sub>, CO)

**Reverse Shift Reaction:** CO<sub>2</sub> + ↑ H<sub>2</sub> <=> CO + ↓ H<sub>2</sub>O

As steam is consumed and H<sub>2</sub> produced the RSR proceeds to the right



**Figure 2:** HTCE mechanism

The preference for the cell is to extract the oxygen from the steam (i.e.  $H_2O \rightarrow H_2$ ) with the oxygen being transported to the other side of the cell by the electrochemical process. As the steam is reduced and hydrogen generated, the reverse water gas shift reaction is forced by the equilibrium equation. There is some conversion of the  $CO_2$  to CO by the cell transfer of oxygen but most is believed to occur through the reverse water gas shift.

The experimental co-electrolysis cell uses a zirconia based electrolyte “stabilized” in the cubic phase by doping with a trivalent ion supplied as an oxide, typically yttria (i.e. YSZ – yttria stabilized zirconia) or scandium. The HTCE cathode (anode in SOFC operation) is a micro-porous metal-ceramic composite (cermet) commonly composed of micron scale particles of nickel and YSZ. The oxygen evolution electrode (the cathode in SOFC operation) is a micro-porous Perovskite ceramic such as a lanthanum manganite ( $LaMnO_3$ ). The experiments described in this paper use a proprietary composition for the nickel cermet hydrogen electrode and perovskite oxygen electrode system that has shown better performance in co-electrolysis mode than the conventional SOFC materials. There are no precious metals required for the cell or stack assembly. The SCPV infrared energy will be routed to the HTCE system to bring the cells to operating temperature and supply the heat assist to the electrolysis.

Ceramatec has demonstrated the ability to produce both synthetic natural gas and Fischer Tropsch liquids from the co-electrolysis of  $CO_2$  and  $H_2O$ . Table 1 shows the results of several tests using various inputs of steam and  $CO_2$  to the co-electrolysis unit and the resulting synthesis gas generated by co-electrolysis and synthetic natural gas from that synthesis gas. The ratio of CO to  $H_2$  can be varied by altering the ratio of  $CO_2$  to steam. It is also possible to produce Fischer Tropsch (FT) liquids by feeding the output of the co-electrolysis unit to a synthesis gas compression system and a FT reactor. The ability to vary composition of the synthesis gas is important dependent on the desired end product. For example, liquid Fischer Tropsch (FT) fuels are favored by a ratio of hydrogen to carbon monoxide of approximately 2:1 respectively. The formation of lighter hydrocarbons (e.g. synthetic natural gas) is favored by higher ratios. The higher hydrocarbons

would utilize greater amounts of carbon (i.e. more carbon dioxide per molecule generated; ~920 lbs  $CO_2$  per barrel of synthetic diesel) and would require a lower percentage of hydrogen.

Test #	From Co-Electrolysis		From Methanation Reactor		
	CO	H2	CH4	CO	H2
1	14.3	60.7	42.5	0	13.8
2	18.5	58.0	47.7	0	9.2
3	20.1	63.5	50.0	0	9.4
4	15.8	58.9	42.0	0	4.6
5	15.2	59.5	40.4	0	8.2

**Table 1:** Synthesis gas generated from co-electrolysis and synthetic methane from methanation reactor

### Summary

Ceramatec has demonstrated the ability to permanently dispose of  $CO_2$  using high temperature co-electrolysis to produce synthesis gas and then convert that synthesis gas into either synthetic natural gas or FT liquid fuels. By using non-carbon based sources of electricity (i.e. solar concentrator photovoltaics, wind power, nuclear, etc), the  $CO_2$  can be converted into usable products without generation of any additional GHG. The economic calculations show that there are reasonable scenarios where it is actually possible to make profits from the disposal of  $CO_2$  in this manner. In addition, this methodology eliminates any risk that a company will be held responsible for leakage of  $CO_2$  that has been sequestered in a geological formation.

### References

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2. “A Hybrid Solar Concentrator PV System for the Electrolytic Production of Hydrogen”; R.D. McConnell, et al; NREL
3. Intergovernmental Panel on Climate Change report filed in November, 2007, page 36.