ETM

ENGINEERING & TECHNOLOGY MANAGEMENT

MINNING THE AIR, CO2 RECICLYING

Course Title: MANAGING TECHNOLOGICAL INNOVATION
Course Number: 549
Instructor: Charles Weber
Term: Spring
Year: 2017
Author(s): Jesús González Mendoza

ETM OFFICE USE ONLY

Report No.:
Type: Student Project
Note:

ABSTRACT

Carbon Dioxide is considered by many in the scientific community as the latest earth enemy, and it's believed to be one of the principal contributors to climate change. Governments from all over the world have been trying to figure out ways to reduce the carbon footprint. This has given big impulse to CO2 research, some resulting in new techniques and technologies to "recycle" CO2 and convert it to fuels such as methanol, and some methods even convert it to gasoline.

The porpoise of this investigation it's to show the latest innovations, not only about reducing the CO2 levels accumulating in the atmosphere, but ways to reuse the CO2, the challenges, and what can we expect in the near future from these new technologies.

INTRODUCTION

Some studies and researches have focused on Carbon dioxide "sequestration", which consists in methods to capture the CO2 and put it away in safe storage.

CO2 recycling are the different techniques to utilize the capture CO2 to obtain fuels, plastic, and in some cases oxygen therefore reducing the levels of CO2 that may accumulate in the atmosphere and reducing the risk of potential leaks in CO2 "storage".

Production of Carbon Dioxide has been consider as a problem by many for quite some time now, many researchers linked it directly as a main factor for climate change and the greenhouse effect. The race for the CO_2 recycling business is very competitive since there are several research programs around the globe and, as of right now, the process it's somehow complicated and expensive.

In this paper I intent to show new fuel obtaining methods and the different ways we have to reuse contaminants that we are producing and convert them into a usable fuel or plastic material, this is a way to reduce pollution as well as giving us an alternative fuel source. Throughout this research some of the techniques that will be mention will be some of the most common methods for CO_2 recycling; one of them is the Sabatier reaction. The second method that will be cover is the CO_2 stable homogeneous catalyst and the different ways in which they have been implemented. One of the methods is the CO_2 stable homogenous catalyst Another technique is to grab the CO_2 at its source, then add water and electricity to obtain liquid fuels and chemicals such as ethylene glycol and glycolic acid. A different approach is to mix in the same pot CO_2 and molecular Hydrogen to achieve direct CO_2 capture and conversion to methanol. And Last, we have the capture of CO_2 by porous membranes, then the captured CO_2 goes into a reactor were epoxide is added to obtain plastics.

The methods and researches for CO_2 recycling are on an early stage, but even climate change deniers can't think of these methods as something negative, Shell is founding one of the researches (The membrane capture method). I'm conducting a couple of phone interviews and exchanging emails with the people conducting some of the projects as well as obtaining information from their companies and universities websites that give data and show their progress.

THE SABATIER REACTION.

The Sabatier reaction was discovered in 1902 by Paul Sabatier and Jean-Baptiste Senderens. This discovery is the base for the conversion of CO_2 into alternative fuels.

The Sabatier reaction involves the CO_2 reaction with H_2 (hydrogen) over a metal catalyst to produce methane, also called “methanation” , has been studied extensively. [1]

The Methanation of both CO and CO_2 are highly exothermic reactions increasing the temperature in the reactor by 600 C per % of CO_2 reacted. Though many different metals have been used to catalyze these methanation reactions, nickel and ruthenium are two of the most effective.

$$CO_2 + 4\ H_2 \quad = \quad CH_4 + 2\ H_2O$$

The figure below (Figure 1) [2] shows the last five steps of the combustion of hydrocarbons, ending in the CO_2 gas. The Sabatier reaction concept consists in reversing this process starting with CO_2 and ending with CH_4.

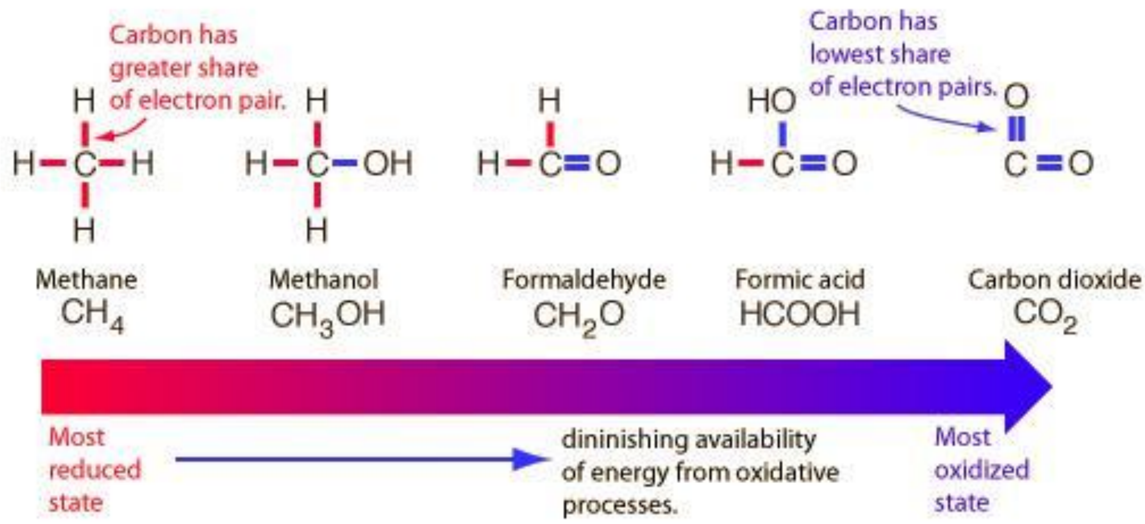

Figure 1

The CO2 in an engine or turbine exhaust can be reacted with renewably produced H2 to generate CH4 that can be recycled back into an engine or turbine, reducing greenhouse emissions and increasing the engine/turbine efficiency. [3]

Figure 1 (below) shows the model that was used by Curt Robbins in 2009 at the Dessert Research Institute during their Sabatier method research. [4]

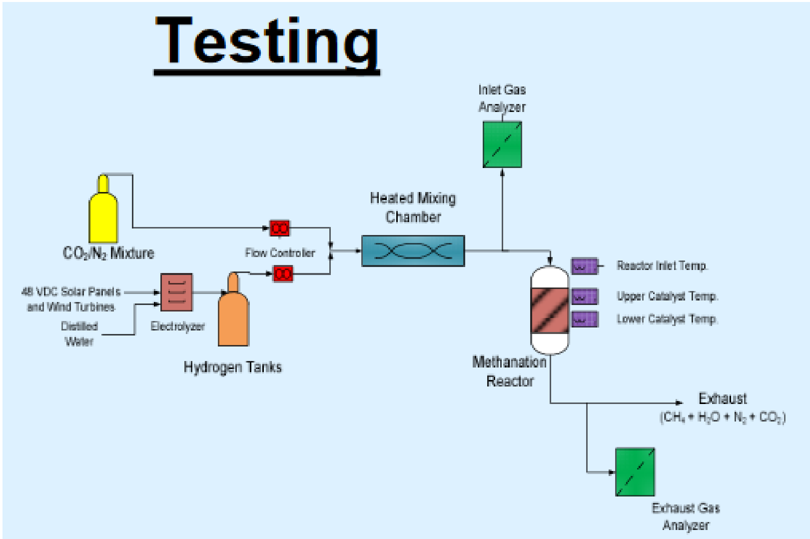

Figure 2

The next 2 figures (Figure 2 and Figure 3) show the test results. Figure 2 shows the exothermic reaction and how the % ofCO2 decreased while the CH4 increased. Figure 3 shows the CO2 reaction with the increase of H presence. [4]

Both graphs show very positive results in the reduction of CO2 levels.

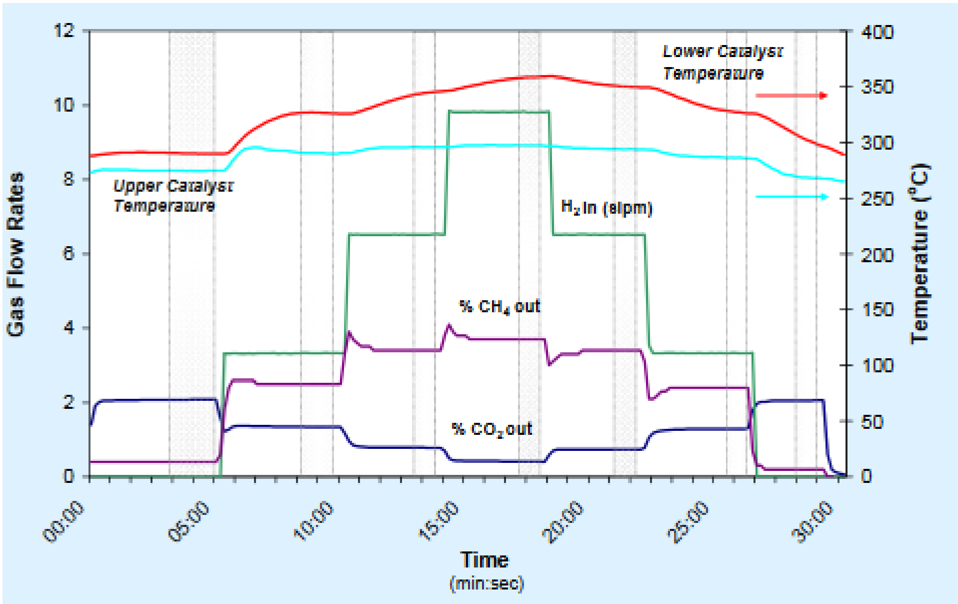

Figure 3

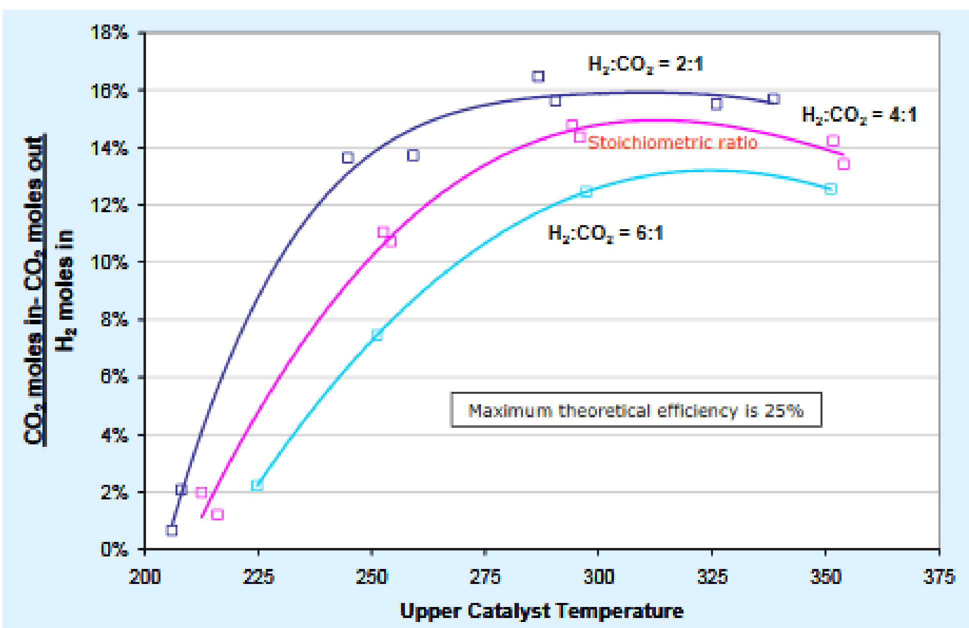

Figure 4

CO_2 STABLE HOMOGENEOUS CATALYST

The production of Methanol, specifically, is of high interest for some researches due to the fact that Methanol it can be used as an alternate fuel to gasoline. There are different ways of achieving a stable homogeneous catalyst.

The Sabatier method is used in chemistry to obtain a homogeneous catalyst; this is the product of the catalysis in a solution by a soluble catalyst. Strictly speaking, homogeneous catalysis refers to catalytic reactions where the catalyst is in the same phase as the reactants (wiki). By using this method, CO_2 gets reduce to CO which then can be used to produce carbon base fuels like methanol, ethanol and diesel by using the same "methanation" method to hydrogenate the CO, resulting in the formation of CH_4 (methane) or formic acid (HCOOH) [5].

As a first step in this direction, the electrochemical reduction of CO_2 to CO requires catalysts, usually derived from transition metal complexes. A very efficient, electro-generated iron-porphyrin catalyst was obtained by introducing both pendant acid groups and fluorine substituents in the molecule. New studies have discovered better yields in the methanol conversion with the introduction of different metals like rhodium, ruthenium, palladium, and the most widely investigate material, nickel, popular for its high production and low cost.

ULTRAEFFICIENT HOMOGENEOUS CATALYST

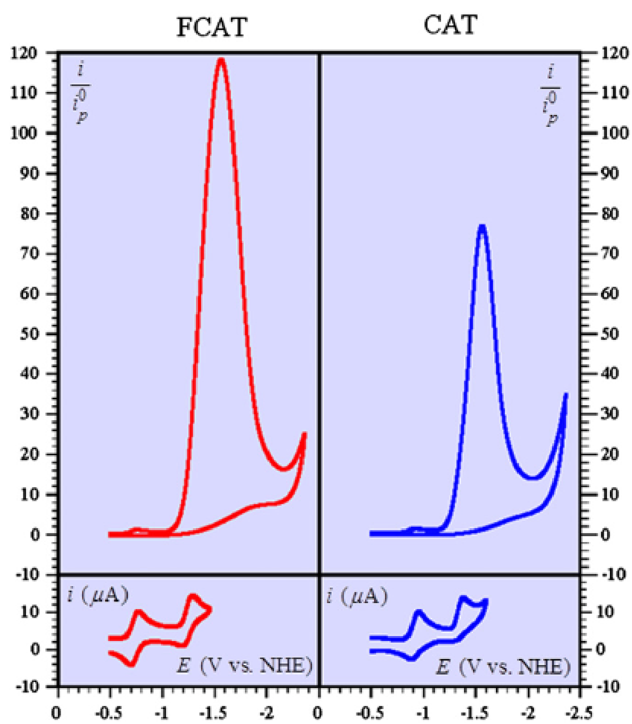

Fig. 1. CV of 1-mM FCAT (*Lower Left*) and CAT (*Lower Right*) in neat DMF + 0.1 M n-Bu_4NPF_6 at 0.1 Vs^{-1}. The same, *Upper Left* and *Upper Right*, respectively, in the presence of 0.23 M CO_2 and of 1 M PhOH. i_p^0, the peak current of the reversible Fe^{II}/Fe^{I} wave is a measure of a one-electron transfer.

In the race for CO conversion to fuels, a more efficient CO2 to CO electrochemical conversion method was developed; it is an ‘ultraefficient” homogeneous catalyst. Different low-oxidation-state transition metal complexes have been proposed to serve as homogeneous catalyst; electrochemically generated Fe0 complexes have been shown to be good catalysts, provided they are used in the presence of Brönsted or Lewis acids [6].

The figure show the comparison between the Fe0 Catalyst reaction (in red) and a catalyst reaction without the introduction of the Fe0 (in blue) [6]

DIRECT CAPTURE AND CO2 TO CO CONVERSION

Nobel Prize winner George Olah and Surya Prakash from the University of Southern California have been conducting research to obtain methanol directly from the small concentration of carbon dioxide in the atmosphere. They presented their findings in a paper published on the Journal of the American Chemical Society.

Up to recently, the idea of a direct conversion from capture CO_2 from the atmosphere to CO was just a concept, but it now has been done by Olah and Prakash's method. They used milder conditions than existing carbon dioxide-to-methanol processes. This is considered the first successful step for the "production" of fuel from gasses in the air.

And, even though, Harvard University's David Keith, a leading expert on 'air capture' of carbon dioxide from the atmosphere, is skeptical the new process can deliver on that promise. Earlier this year, another team, led by Dr. SUN Jian and Prof. GE Qingjie in Dalian Institute of Chemical Physics has succeeded in preparing a highly efficient, stable, and multifunctional $Na\text{-}Fe_3O_4/HZSM\text{-}5$ catalyst for the direct production of gasoline from CO_2 hydrogenation. Jian Wei et al, Directly converting CO_2 into a gasoline fuel, Nature Communications (2017). Figure 5 [8] (bellow) shows a simplified diagram of the process to obtained gasoline.

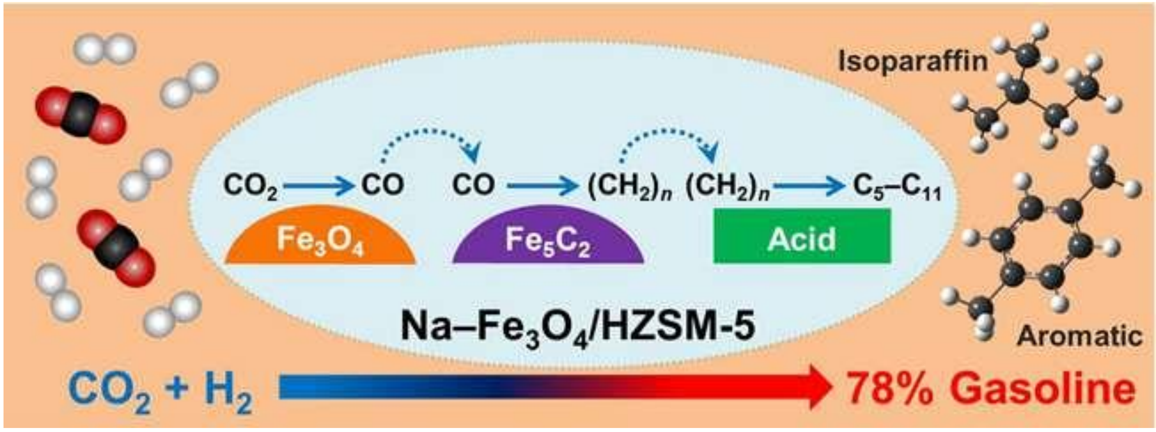

Figure 5

Membrane Capture method

The next method mention in the introduction was the "membrane capture" method, or, as I like to called it, the "artificial photosynthesis".

This research is been funded by Shell, and consists in artificial "plants" with cover in a tungsten-diselenide membrane that captures the CO2 and mimics the photosynthesis process (the way to do the photosynthesis is a homogeneous catalyst) to obtain sugar carbohydrates. Unfurtunately this process is fairly new and there is not a lot of information available to the public yet.

ARTIFICIAL PHOTOSYNTHESIS

Then next figure (Figure 6) shows a picture of an artificial leaf. [9]

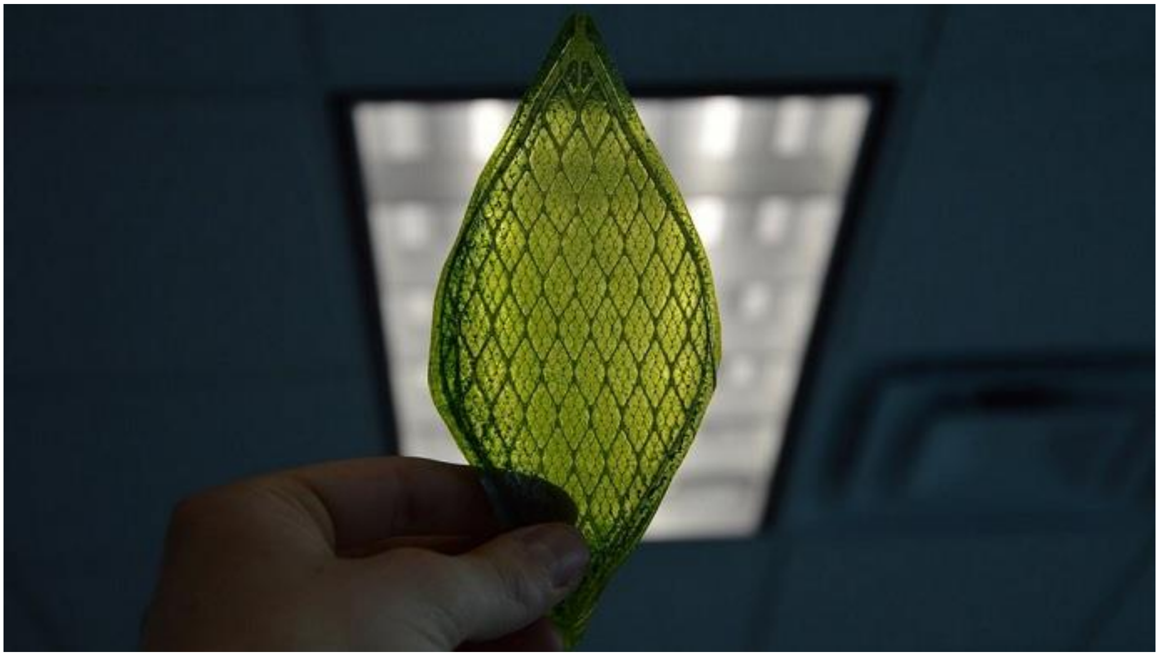

Figure 6

This artificial leafs are photoelectrical cells that mimic the photosynthesis process from natural plants.

It uses solar energy, water and CO2 and generates “Clean gas” an electric energy. This process it’s been develop in the University of California in Berkeley by scientis for the U.S. Department of Energy.

“In natural photosynthesis, leaves harvest solar energy and carbon dioxide is reduced and combined with water for the synthesis of molecular products that form biomass,” says Chris Chang, an expert in catalysts for carbon-neutral energy conversions. “In our system, nanowires harvest solar energy and deliver electrons to bacteria, where carbon dioxide is reduced and combined with water for the synthesis of a variety of targeted, value-added chemical products.” The system starts with an “artificial forest” of nanowire heterostructures, consisting of silicon and titanium oxide nanowires, developed earlier by Peidong Yang and his research group.

“Our artificial forest is similar to the chloroplasts in green plants,” Yang says. “When sunlight is absorbed, photo-excited electron−hole pairs are generated in the silicon and titanium oxide nanowires, which absorb different regions of the solar spectrum. The photo-generated electrons in the silicon will be passed onto bacteria for the CO2 reduction while the photo-generated holes in the titanium oxide split water molecules to make oxygen.”[7]

The team is currently working on the second generation of artificial leafs and is expected that once it reaches an efficiency of 10% of solar to chemical energy conversion the technology may be commercially available.

MASS PRODUCTION PROJECTS.

In 2014 the German company Sunfire built a rig that uses water and harvests CO2 from the air to produce high quality hydrocarbon fuels (gasoline and diesel). It creates water steam, and then it separates the H2 from the steam to be utilized for the CO2 conversion. The efficiency of this rig in 2014 could not compare yet to an oil rig (the average oil rig produces about 250 barrels of gasoline per day while the Sunfire CO2 rig only produced 1 barrel of fuel) [10]. The challenge presented is related to the CO2 capturing process, and it can be greatly improve if the rig is connected to a CO2 collector from which it can pull higher quantities of concentrated CO2. Of course this rig is in the early stages of development, and the company is still trying to figure out ways to make it cost efficient to put the product on the market.

Carbon Engineering, a Canadian company funded by Bills Gate, is part of a crop of companies behind the Squamish plant in British Columbia (A CO_2 capturing plant).

Adrian Corless, CEO of Carbon Engineering, told The Huffington Post during an interview that “The world is not ready yet”. “There will need to be some global coordination of effort, but for now, there’s no global strategy in place.”

In the meantime, companies like Corless‘ are attempting to turn carbon capturing into a viable business.

There are about a half dozen companies worldwide tackling direct air capture technology, which Corless compared to very efficient trees sucking up carbon dioxide already emitted into the atmosphere. At least three of these firms are relying on so-called “air-to-fuels” to be their golden goose. [11]

CONCLUSION AND IMPLICATIONS.

In the course of this research, I came across many different new methods that are been develop, most of them are related to the same principle of the homogeneous catalyst, the differences between this methods are in the CO_2 capture and storage methods and some technologies capturing and transforming straight from the air, as well as the different new materials that are being research to make the catalyst more efficient in both yield as well as reduce cost (lower energy and less time for reaction reducing energy costs).

For now, extracting fossil fuels is still the cheapest option, and fossil fuels will be around for a long time. And there seems to be a consensus in the scientific community that the current CO2 capturing and processing technologies may not be the real solution to stop global warming, but, there is an expectation that these methods will help slow down the global warming and give more time for scholars and researchers to find a long term solution.

Because of this reason, my predictions for this method to become a mainstream source of fuels and other carbohydrates materials are not yet positive from an economy point of view, most of this research it's been funded because of the environmental concern point of view. Most of the governments and scientist have come to a consensus in the direction of stopping global warming and the tendencies are to focus more on renewable energy.

For the researchers in the U.S. currently they are facing another obstacle, the current policies on environment protection are not very favorable for this kind of researches to get federal funding at this moment. There are some official efforts to try to revive the coil industry. And, even though, some major companies in the energy sector are funding some projects, and after my research, I have become skeptical about the future of the commercial use of these processes, the reason why is because as a “fuel” resource, solar energy has improved a lot and is already growing as a market.

CO_2 removal projects are being funded in several countries, such as China, Germany, Canada, Iceland and even some third world countries like India and Mexico. But my projection is that CO_2 recycling will remain being a small scale research that it’s going to depend on governmental funding and is going to be utilize as a tool to reduce the carbon dioxide levels going into the atmosphere but as a business model it’s not very cost efficient in the long run.

REFERENCES

[1] Ralston, John, The Sabatier Reaction, Possible Solution to CO2 Emissions, march 4th 2010.
[2] http://hyperphysics.phy-astr.gsu.edu/hbase/Chemical/redoxea.html
[3] DRI Renewable research center, Kent Hoekman, Amber Broch, Curt Robbins 2009
[4] https://images.indiegogo.com/medias/1059390/files/20131003130747-sabatier_alchemy.pdf?1380830869
[5]https://phys.org/news/2016-01-carbon-dioxide-captured-air-methanol.html
[6] Cyrille Costentin, Guillaume Passard, Marc Robert, and Jean-Michel Savéan.Ultraefficient homogeneous catalyst for the CO2 to CO electrochemical conversion. 2014
[7] News center of Berkeley lab website
[8] https://phys.org/news/2017-05-scientists-efficient-multifunctional-catalyst-co2.html
[9] http://wonderfulengineering.com/this-artificial-leaf-is-10-times-more-efficient-than-a-natural-leaf-in-photosynthesis/
[10] https://www.geek.com/news/german-company-can-make-gasoline-from-water-and-airborne-co2-1609987/
[11] http://www.huffingtonpost.com/entry/carbon-capture-fuel_us_577a177ae4b0a629c1aa7669

Other reading materials

- https://phys.org/news/2017-05-scientists-efficient-multifunctional-catalyst-co2.html-
https://www.chemistryworld.com/news/carbon-dioxide-to-methanol-catalyst-ignites-fuel-from-air-debate/9339.article
http://www.pnas.org/content/111/42/14990.full.pdf
https://phys.org/news/2016-01-carbon-dioxide-captured-air-methanol.html
http://e360.yale.edu/features/pulling_co2_from_atmosphere_climate_change_lackner
https://www.netl.doe.gov/publications/proceedings/01/carbon_seq/7b1.pdf
http://www.muyinteresante.es/ciencia/articulo/una-nueva-tecnica-para-reciclar-dioxido-de-carbono-911470123399
http://www.abc.es/ciencia/abci-reciclar-para-convertirlo-combustible-201512021652_noticia.html
http://www.greyrock.com
http://www.FlaretoFuels.com
https://www.researchgate.net/publication/269288005_Comparison_between_two_methods_of_methanol_production_from_carbon_dioxide

Capturing Carbon Dioxide From Air (Klaus S. Lackner, Patrick Grimes, Hans-J. Ziock)