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Elementary process identification of solar carbon dioxide (CO_2) fueling

By

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CERTIFICATION OF APPROVAL

Elementary Process Identification of Solar Carbon Dioxide Fueling

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A project dissertation submitted to the
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Approved by,

____

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UNIVERSITI TEKNOLOGI PETRONAS, TRONOH, PERAK
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SHARON LEE LAI PING

ABSTRACT

With the respect to the negative roles of carbon dioxide on our climates, it is obvious that it is the time for the development of processes that convert CO_2 into useful products. Many processes have been discovered by the researchers to crack and convert the CO_2 into fuels, hence completing the fossil fuel cycle. Yet, most of these advanced processes are requiring a large amount of energy because carbon dioxide is very stable. Therefore, solar energy which is freely available has been selected as the major source of energy for the process of CO_2 cracking. In this project, it is aimed to identify and understand the elements in the solar cracking process of the CO_2 and converting carbon dioxide to fuels. Analysis of the process and deciding on a framework consisting the complete cycle of capturing of carbon dioxide and convert them into fuels are considered. So far, a comprehensive literature review has been carried out to understand all the proposed technologies for CO_2 cracking. From the theories, in spite of the huge reflectors, solar CO_2 fueling is identified as promising technology since the source is clean and free.

ACKNOWLEDGEMENT

I would like to express my utmost gratitude to my supervisor, AP Dr Hussain Al-Kayiem for his tremendous guidance, advices and feedbacks for the completion of the project. With his guidance, I managed to learn many new things throughout the project period. In addition to that, I would like to take this opportunity to convey my deepest appreciation to my biggest supporter – my family. With their never ending love, care and encouragement, I managed to complete this project.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

The world has been awaken with the fact that the emission of carbon dioxide has increased rapidly as the technology develops from time to time. The sources and the factors are studied and they are conveyed below.

1.1.1 Carbon dioxide and world population

The increase in carbon dioxide emissions is caused mainly by human activities. Figure 1 shows the projection estimation and trends that starts from the year of 1900 to 2050. Starting from the year of 1960, the number of population bloomed rapidly until the year of 2020.

Also, the number of transportation increases to accommodate the mobility of human. In addition, technology development has contributed to an increase in the number of manufacturers. Combining these factors, they contributed to the great amount of carbon dioxide emission to the environment.

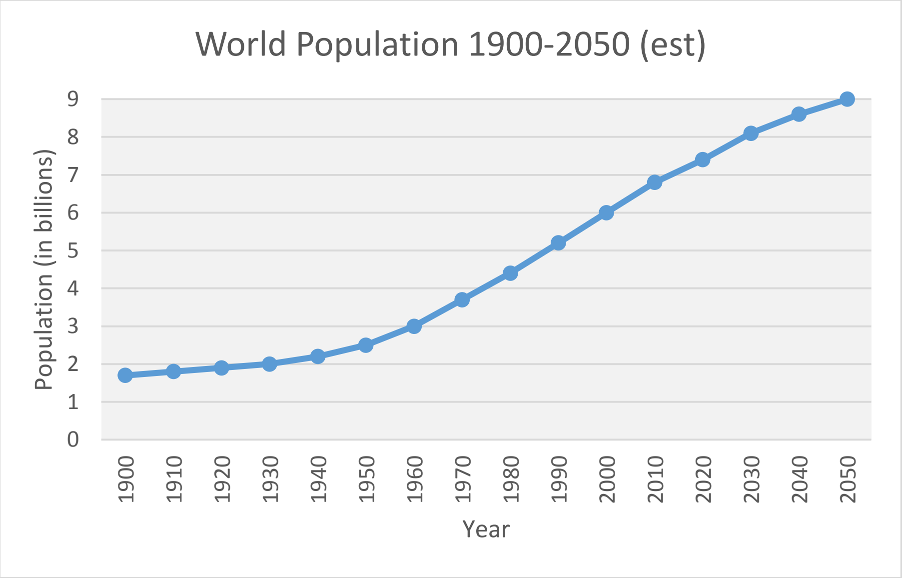


Figure 1: Population trends and estimated projections from the year of 1900 to 2050 [1]

1.1.2 Major sources of carbon dioxide production

Sources of carbon dioxide are studied into these sections: electricity generation, transportation, industry and residential. Figure 2 shows the percentage of the sources that contributed to the emission of carbon dioxide. The largest section is electricity generation which tallies with the blooming of population. Next in line, carbon dioxide is also emitted by vehicles.

The increase in the number of population has increased the number of vehicles used for mobility. Vehicles uses internal combustion engines and they are lacking in efficiency. Products of combustion are mainly carbon dioxide and also other harmful gases such as nitrogen dioxide, sulfur dioxide and carbon monoxide. Collectively, these harmful gases causes greenhouse gases and evidently harm the Earth. Fortunately, hybrid vehicles has been introduced, yet they are quite expensive for daily usage.

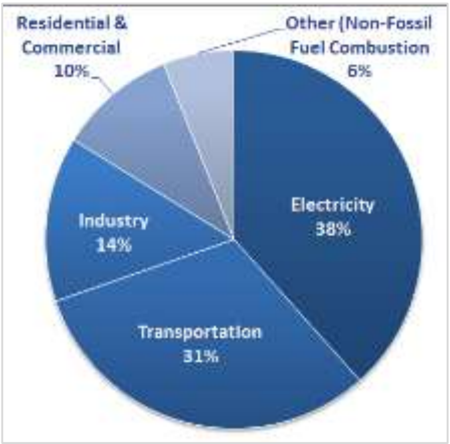


Figure 2: The constituents of contributors of carbon dioxide [2]

1.1.3 Industrial sources of carbon dioxide

Since it is known that most of carbon dioxide emission is also caused by the industry, a study has been done to record the sector that emit the most carbon dioxide and it is portrayed in Figure 3. The greatest sector is found to be solid fuel. Since the Industrial Revolution, solid fuels has been widely used for industrial purposes. Solid fuel is defined as any solid material that is used as a fuel to produce energy and heating such as coal or solid wastes. They are widely used because of the low running costs, convenience, and the variation of fuels [3]. Apart from that, the heat from solid fuels is guaranteed, therefore power cuts from the grid will not interfere with the plant's operation. Then, it is followed by liquid fuel, gaseous fuel, cement production and lastly from gas flaring.

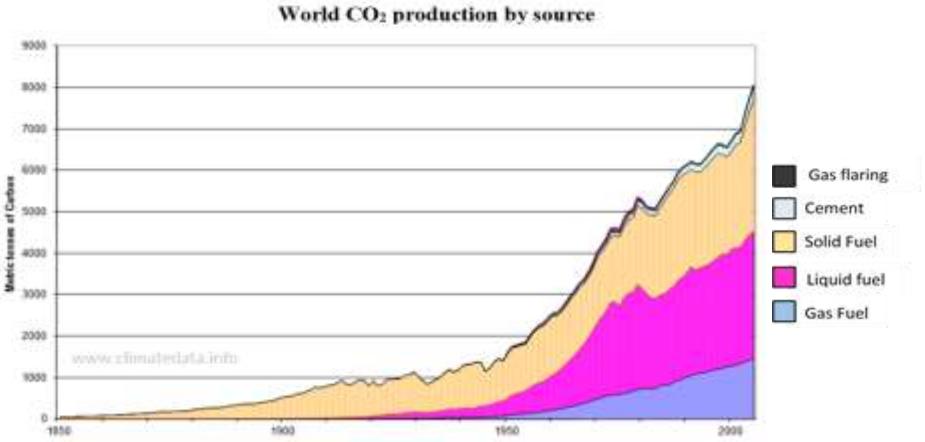


Figure 3: Sources of world carbon dioxide emission [4]

1.1.4 Sources of carbon dioxide according to regions

Then, carbon dioxide sources are categorized according to the regions. From the year of 1990, United States has recorded to be the largest supplier of carbon dioxide. The emission of carbon dioxide is somewhat constant throughout the year of 1990 to 2010. Similarly, this trend is followed by the EU countries, Japan, OECD countries and Russian Federation as shown in Figure 4. The figure shows the recorded amount of CO_2 in 1000 million tonnes from the year of 1990 to 2010, and is arranged by the regions.

Global CO_2 emissions per region from fossil fuel use and cement production

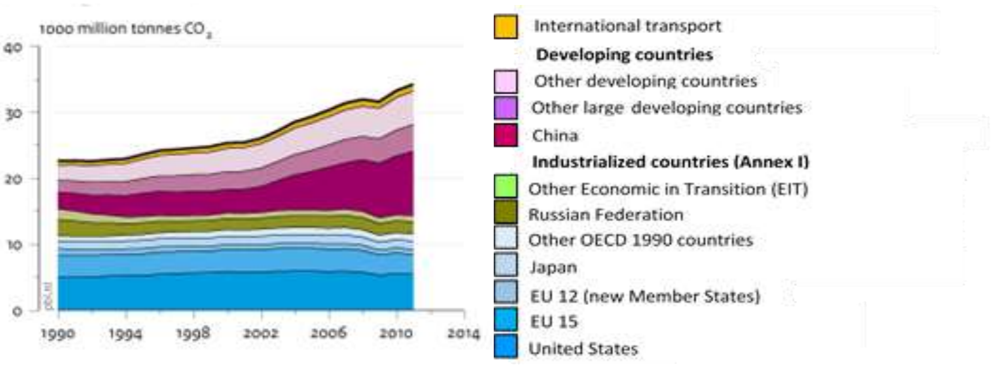


Figure 4: Estimation of world carbon dioxide emission by regions from the year of 1990 to 2030 [5]

In contrast to the trend, the carbon dioxide emission in China is observed to increase very rapidly starting from the year of 2002 and it is now the largest producer of carbon dioxide in the world. Due to technology advancement and cheap labor costs, most factories are situated in China and this explains the rapid increase in emission in China since the year of 1998. This can be supported with the fact that during the mid-1990s, mobile phone industries has started to grow due to demands.

Developing countries also recorded an increment in the emission of carbon dioxide. The reason being is that the countries are also options for manufacturing field as the labor cost is also cheap and affordable. Plus, international transport has also shows a slight increment from the year of 1990. Since then, more commercial aero planes are built and more international flights are introduced; more fuels are needed and more combustion products are emitted.

1.2 Renewable energy as sources of energy

Renewable energy such as wind and solar has gotten many attention in these few years. They are free, easily obtained, and most importantly sustainable. Therefore, synthesizing them will be an advantage. Recently, solar energy has become an outbreak as a source of clean energy. Common applications are solar water heaters, photovoltaic cells, solar concentrators, solar tower, solar furnace and many more. Most of these applications capture the heat from solar radiation and utilize them to produce energy in many ways.

A complete carbon cycle can be achieved by using renewable energy and it is shown in Figure 5. A carbon capture and storage system (CCS) is introduced to the commercial areas which captures excessive carbon dioxide, then transports some of them to a geological storage for the purpose of Enhanced Oil Recovery (EOR). Meanwhile, some of them are transported to a cracking plant, in this case, a methanol and DME synthesis plant which is powered by renewable energy such as solar or wind energy. The methanol is further synthesized into synthetic hydrocarbons which can be used as fuels. This framework is widely acknowledged, but the technology is not being implemented due to lack of researches on the cracking plant by utilizing renewable energy.

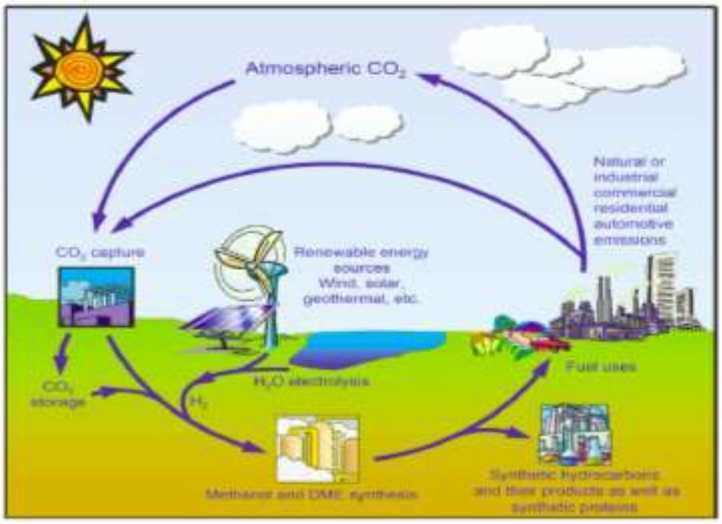


Figure 5: Carbon cycle [6]

1.3 Problem statement

As we all know, carbon dioxide (CO_2) emission has become a major problem which contributed to global warming and greenhouse effect. This situation first emerged because of the increase on the demands and people around the world which leads to a rapid increase in the number of power plants, transportation, and deforestation by combustion. If this situation is left untreated, it will deteriorate and will affect the balance of the environment. Therefore, one of the ways to curb this issue is to convert CO_2 to fuel. This project will identify elementary processes to convert fuel from CO_2 using solar energy.

1.4 Objectives

1. To identify the cracking process of CO_2
2. To identify and determine the capturing processes of CO_2
3. To asset the utilization of the solar energy as clean input to the process.

1.5 Scopes

Carbon dioxide is emitted from almost all the applications. A suitable process will be required to capture carbon dioxide from a specific place. Various technologies have been established and implemented for the system, however the effectiveness is still relatively low.

The heart of the project is to convert carbon dioxide into fuels by using solar energy. As mentioned before, solar energy is free and a form of clean energy. Therefore, it is selected as the input for the process. Many projects done by converting solar energy to electrical energy and it will be used to power the reactions. However, in this project, solar energy is used directly to crack the carbon dioxide captured. Applications such as solar collectors, solar photovoltaic, solar concentrators, and solar furnace are the options for the project.

For this project, a method is chosen based on the readings made by the student; then, the student is required to calculate the amount of energy needed to determine the size of solar applications needed as the solar intensity differs by locations. One of the scopes of the project is to study the working principles and operations of the solar application selected. There will be a certain operating conditions that each application offer.

CHAPTER 2

LITERATURE REVIEW

Carbon dioxide is described as one of two oxides of carbon which are bonded covalently and it is mostly obtained from the combustion of fossil fuels. Greenhouse gases effect is mainly affected by CO_2 due to the spike increment of emission of the gas in the atmosphere. [6] The applications of carbon dioxide is used for enhanced oil recovery, urea and polymer synthesis as a monomer feedstock, food and beverage industry as propellant and chemical production. This is true for just 1% of global carbon dioxide generated. The remaining of the CO_2 is released to the surroundings because there were no affordable technologies that can be implemented. [7]

2.1 Carbon capture and storage (CCS)

Carbon capture and storage (CCS) is the capture and secure storage of carbon dioxide. Components of a CCS system are usually divided to Capture, Transport, Injection and Monitoring. [8]

Capture is the process of separating CO_2 from an effluent stream and then compress them into a liquid or a supercritical state. The idea of capturing emerged when there is a need of capturing a large concentration of carbon dioxide for Enhanced Oil Recovery (EOR) operations. CO_2 is injected into reservoirs to increase the efficiency by improving the mobility of the oil. [9] CO_2 capturing processes from a power production plant fall into post combustion, oxy-combustion and pre-combustion capture. For the first two categories are suitable in the existing coal power plant while the last category requires an integrated gasification combined-cycle (IGCC) power plant.

2.2 Methods of capturing carbon dioxide

There are many methods of capturing carbon dioxide; some are available and some are still under research. In this section, all of them are explained thoroughly.

2.2.1 Absorption

The first technology of capturing carbon dioxide is through absorption. Basically, there are two types of absorption: chemical and physical absorption [10]. It is predicted that before 2030, chemical absorption by using aqueous alkanoamines is proven to be the most mature technology, however, it has several drawbacks. Alkanoamines corrodes the equipment at high rate besides from requiring a large amount of energy in regeneration [11].

In chemical absorption, the flue gas is passed through a scrubbing system which is made up of and absorber and desorber. The absorber absorbs carbon dioxide from the flue gas and then, they are stripped at the desorber with the aid of an aqueous alkaline solution (solvent). Hence, a pure stream of CO_2 is produced and is compressed while the regenerated solvent is returned back to the absorber. In contrast, physical absorption involves physical solvents to replace the chemical solvents which is used in chemical absorption. The processes are simple, however they impose great challenge in the terms of emissions and energy requirements [12]. In ideal situation, it is assumed that 1 mol of chemicals can absorb 1 mol of CO_2. However, due to irreversibility, more moles of chemicals are needed; and in degenerative systems, the chemicals are emitted to the environment.

2.2.2 Adsorption

Other than that, adsorption is also discovered to be feasible to capture carbon dioxide. Since absorption by using alkanoamines imposed drawbacks as mentioned above, physical adsorption can be used as an alternative. Adsorption is the separation of a substance from one phase accompanied by its accumulation or concentration at the surface. It require adsorbent which is the adsorbing phase and absorbate which is the surface of where the adsorption occurs [13]. Common absorbates are made up from zeolites, mesoporous silica and metal organic frameworks. Zeolites and metal organic frameworks are porous materials that have high selectivity of carbon dioxide [14]. Similar to absorption, adsorption is also divided into two types: chemical and physical [15]. The quality of an adsorption process is determined by the properties of adsorbent particles such as molecular size, molecular weight and polarity. Figure 6 shows a simple adsorption.

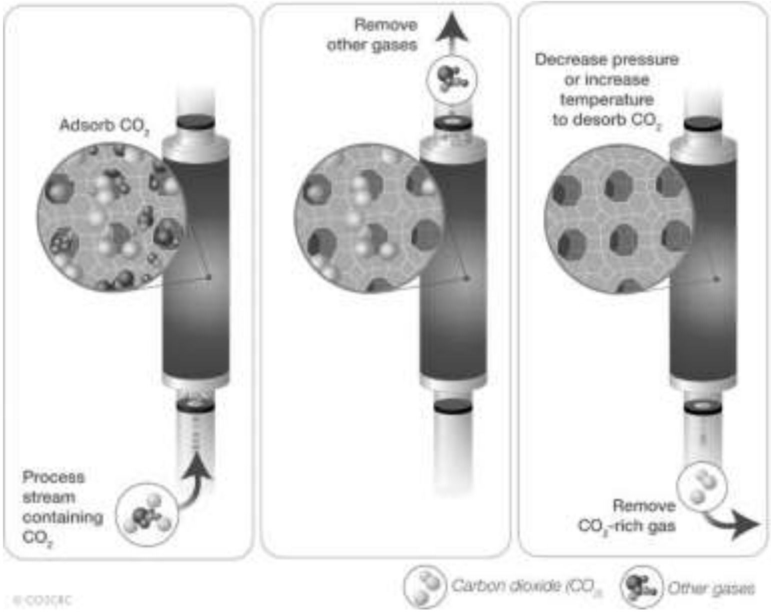


Figure 6: Adsorption of carbon dioxide process [16]

2.2.3 Membrane technology

Moving on, carbon dioxide can also be captured by using the membrane technology. It is recently discovered that membranes carry several advantages such as eco-friendliness, smaller footprint, simplicity apart from requiring lower energy when compared to amine processes [17]. Post-combustion capture by membrane separation requires pretreatment of flue gas, removal of impurities such as NO_x and SO_x, and finally passing the gases to the membranes to be separated. The basic process is shown in the Figure 7.

Of course, membranes technology have some limitations that hinder their applications in the industry. Firstly, for the stream which has low concentration of carbon dioxide, the membranes required must be of high selectivity. Furthermore, a compressor is needed to increase the pressure in order to keep the separation to be efficient. The membranes are also sensitive to temperature, therefore the gas must be cooled to below 100°C. Second stage membrane separation is often required as the efficiencies are low. Last but not least, it is difficult to produce a membrane that is resistant to flue gas impurities, aging and plasticization.

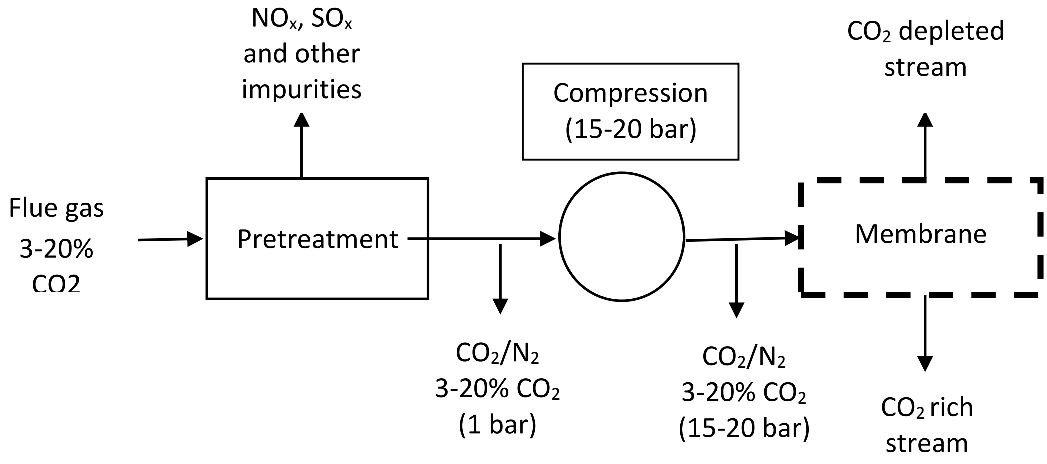


Figure 7: Simplified process flow diagrams of post-combustion capture by membranes [17]

2.2.4 Other alternatives of capturing carbon dioxide

Besides that, there are also alternatives that have been developed and is studied so that they can replace the available technologies in the future. This includes dissolving the flue gas containing carbon dioxide in ionic liquids or developing new sorbents by using palm empty fruit bunch [18]. It is possible to capture carbon dioxide by using solid waste materials [19] [20], biotechnology [21] and et cetera.

2.3 Methods of cracking carbon dioxide into fuels by using solar energy

Aforementioned, carbon dioxide has been utilized for so many useful applications in the industry. Apart from utilizing them in useful applications, carbon dioxide can also be converted into fuels under certain conditions. There are many ways that has been discovered, but the interest of converting carbon dioxide into fuels by using solar energy has captured the most attention. Solar energy is widely available and they should be fully utilized.

2.3.1 Direct solar reduction

The simplest method found to produce fuels from carbon dioxide by using solar energy is found to be the direct reduction of CO_2 to CO through the process of photolysis. A prototype has been created to prove the process and it is shown in Figure 8 [22]. The apparatus is made up of solar collectors, converter which is the heart of the apparatus, and the instrumentation to control the flow rate of gases plus, measuring the amount of gases formed. Solar collectors comprised of square mirrors, which reflects the solar radiation to the converters. Then, at the converter, the CO_2 is preheated, which will then will be converted. The carbon dioxide is preheated to a temperature of 1900°C to ensure direct photon absorption and avoiding back reactions from occurring (CO to CO_2). Equation (2.1) describes the photolysis of carbon dioxide to carbon monoxide in the apparatus.

$$CO_2 + \text{heat} \rightarrow CO + 1/2O_2 \qquad (2.\ 1)$$

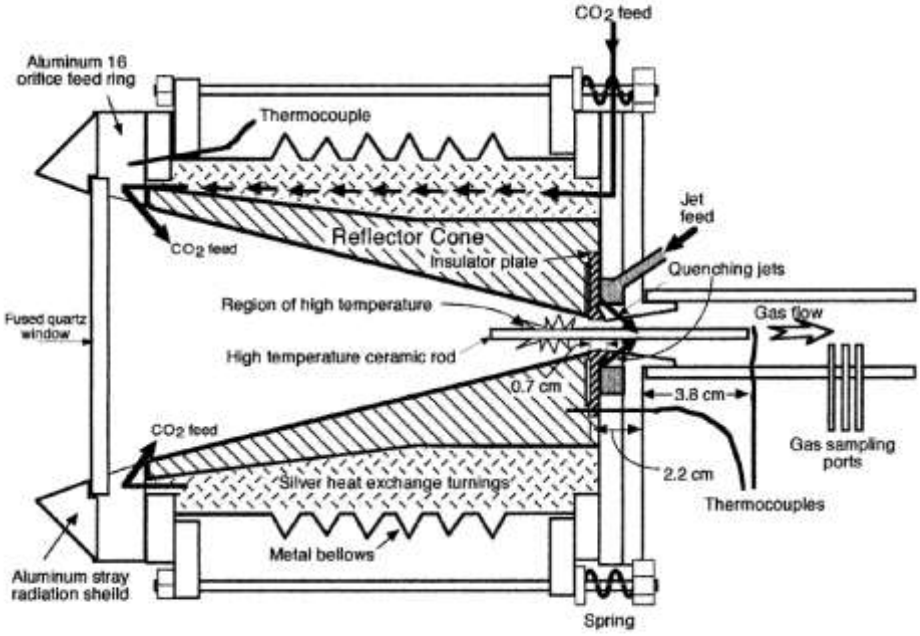


Figure 8: Converter assembly for direct solar reduction of CO_2. The overall length of the apparatus represented is approximately 20 cm and overall diameter about 16cm. [22]

2.3.2 Methane reforming

Methane can also be considered as a type of fuel and it can be easily reformed from carbon dioxide. This reaction produces an equimolar of syngas which consists of mixture of hydrogen and carbon monoxide from carbon dioxide and methane (CH_4). This method, however, is limited in the industrial application. [23] [24]. The product can be further utilized to higher-value added products such as higher hydrocarbons [25]. Apart from that, syngas is the building block of Fischer-Tropsch process and a major supplier of hydrogen in refinery processes. It is commonly used in the industries because it is suitable for the synthesis of oxygenated chemicals, provided that the ratio of H_2/CO is close to one. Despite the advantage, carbon deposition is still the main problem which causes catalyst deactivation which is consists of noble metal catalysts.

2.3.3 Photocatalytic reaction

Next, photo catalytic reaction is also proven able to convert carbon dioxide to fuels. The conversion involves thermochemical reaction which utilizing the energy from the Sun to dissociate carbon dioxide (CO_2) and water (H_2O) using metal oxide [26]. The oxides such as cerium oxide are reduced at higher temperature, releasing O_2 under concentrated solar radiation, and then react with CO_2 and H_2O at a lower temperatures.

To prove the reaction, an experiment has been set up using MgO as the oxide as reducing agent [27]. Naturally, MgO is an insulating material, yet its special characteristic enables CO_2 radical anion to be adsorbed at its surface and the $CO_2^{\cdot}$ radical anion will react with water to form CO. The role of sunlight in photocatalytic process is also shown here as there is no product formed at MgO catalyst when the apparatus is exposed in a dark surrounding. Instead, CO_2 radical anion is reduced to surface bidentate formate with the presence of H_2 and CH_4 [28].

2.3.4 Artificial photosynthesis

Solar energy can be harvested to create photosynthesis to produce solar fuels [29]. To produce solar fuels via artificial photosynthesis, a photoelectrochemical cell which consumes a biofuel to generate hydrogen gas. The set-up is shown in Figure 9. Anode is constructed with a photoactive component and it is covered with a glass with a transparent conductor such as indium tin oxide (ITO) or fluorinated tin oxide (FTO).

Meanwhile, the cathode bears a hydrogen producing catalyst such as platinum. The fuels in this study is hydrogen which can be used in hydrogen fuel cell to power hybrid vehicles. Hydrogen energy is stored in the batteries because the components of the hydrogen are expensive [30]. Other than that, artificial photosynthesis can also be used to split water besides from producing oxidized carbon as a byproduct. Water is the main components because it is a source of electrons for solar fuel production. Both processes utilizes illumination from solar energy. Yet, these systems will require a huge amount of dramatic improvements in efficiency.

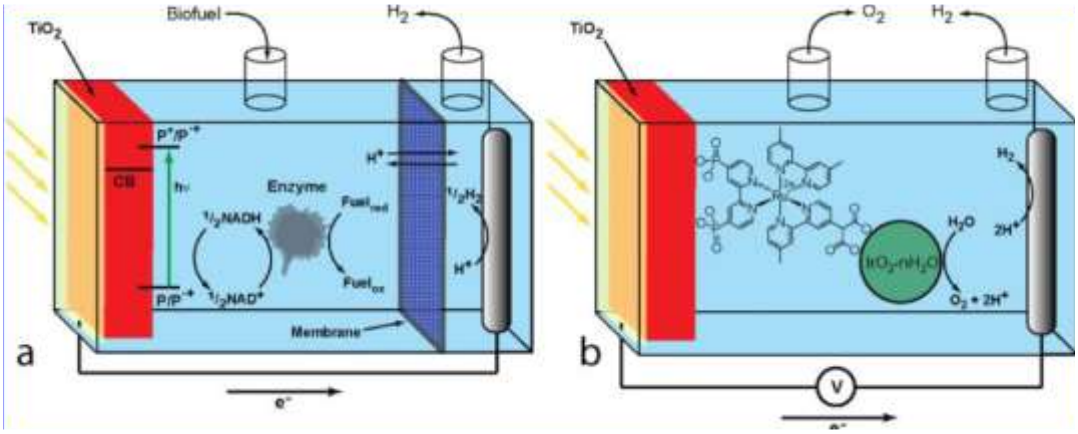


Figure 9: Photoelectrochemical biofuel cell that uses light to generate hydrogen [29]

2.3.5 Other alternatives for cracking carbon dioxide

Besides that, by using concentrated solar energy to reverse combustion, Sandia National Laboratories built a prototype to chemically ‘reenergize’ carbon dioxide into carbon monoxide [31]. This approach is called known as Sunshine to Petrol (S2P) and “Liquid Solar Fuel” will be the end product; many forms can be produced such as methanol and gasoline. The idea of S2P is to convert carbon dioxide to carbon monoxide and transported through a pipeline to a gas station; this is feasible since it is estimated that this technology will only be available in another 15 to 20 years. The same approach is used in this prototype in which carbon dioxide will be collected from the source where it is concentrated like power plants, smokestacks or breweries.

2.4 Conclusion

In a nutshell, there are many methods of capturing and the cracking of carbon dioxide. In the area of carbon dioxide capturing, there are some mature technologies that have been established and implemented in the industries; however there is still no recognized technologies that is applied in the industries largely. This is due to lack of study and also it is due to the low efficiency on these processes. Furthermore, the technologies in both areas are expensive. Refer to Appendix I for the summary for the cracking processes of carbon dioxide. It is noticeable that some of the references are not used in the report due to the recentness of the source. The references helped on the students’ further understanding on the project.

CHAPTER 3

METHODOLOGY

3.1 Flow chart

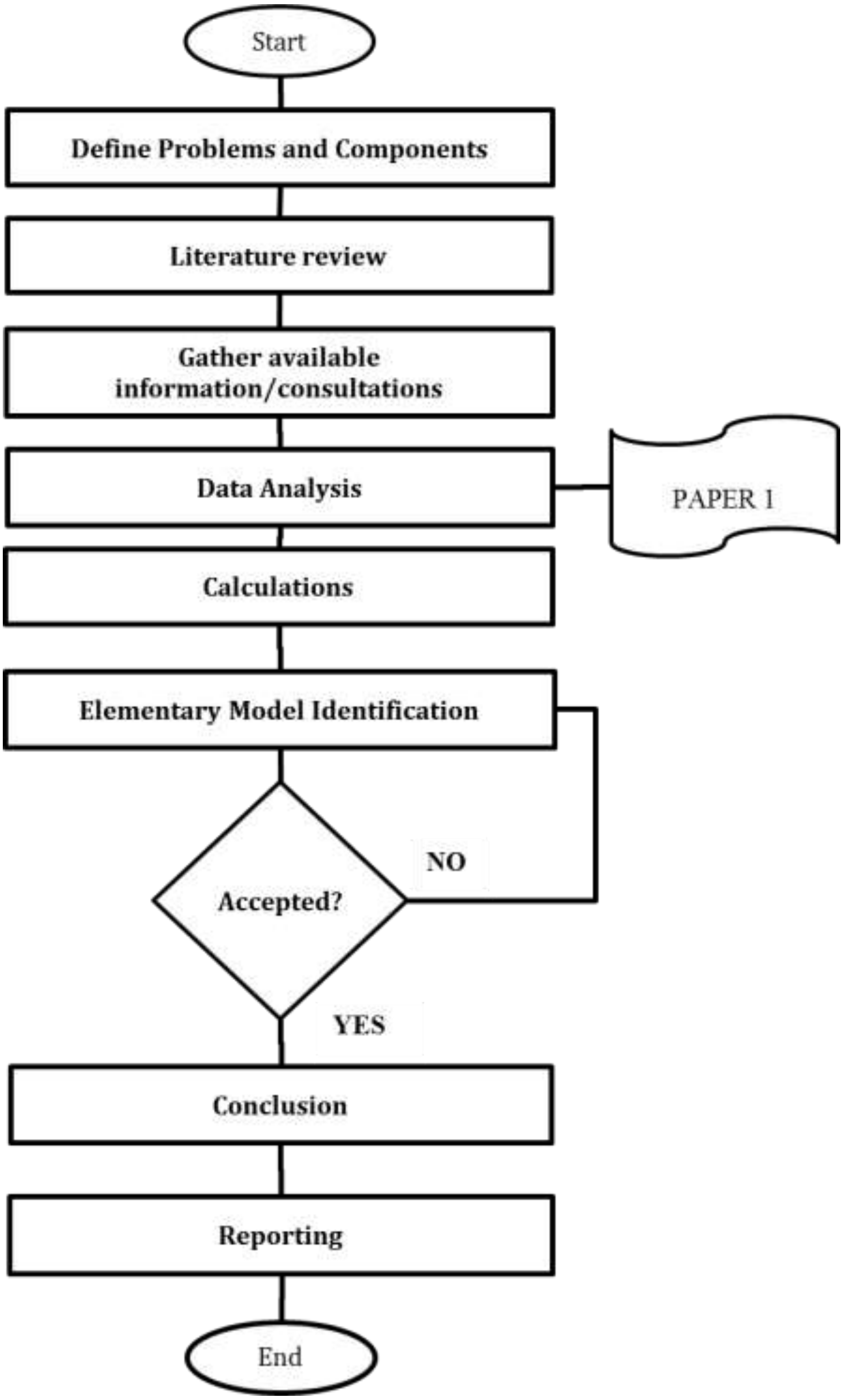


Figure 10: Flow chart for the project

3.2 Key milestones

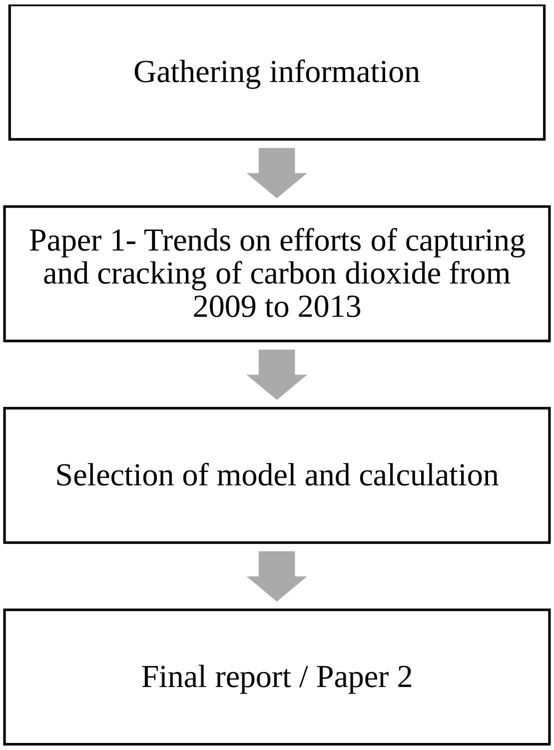


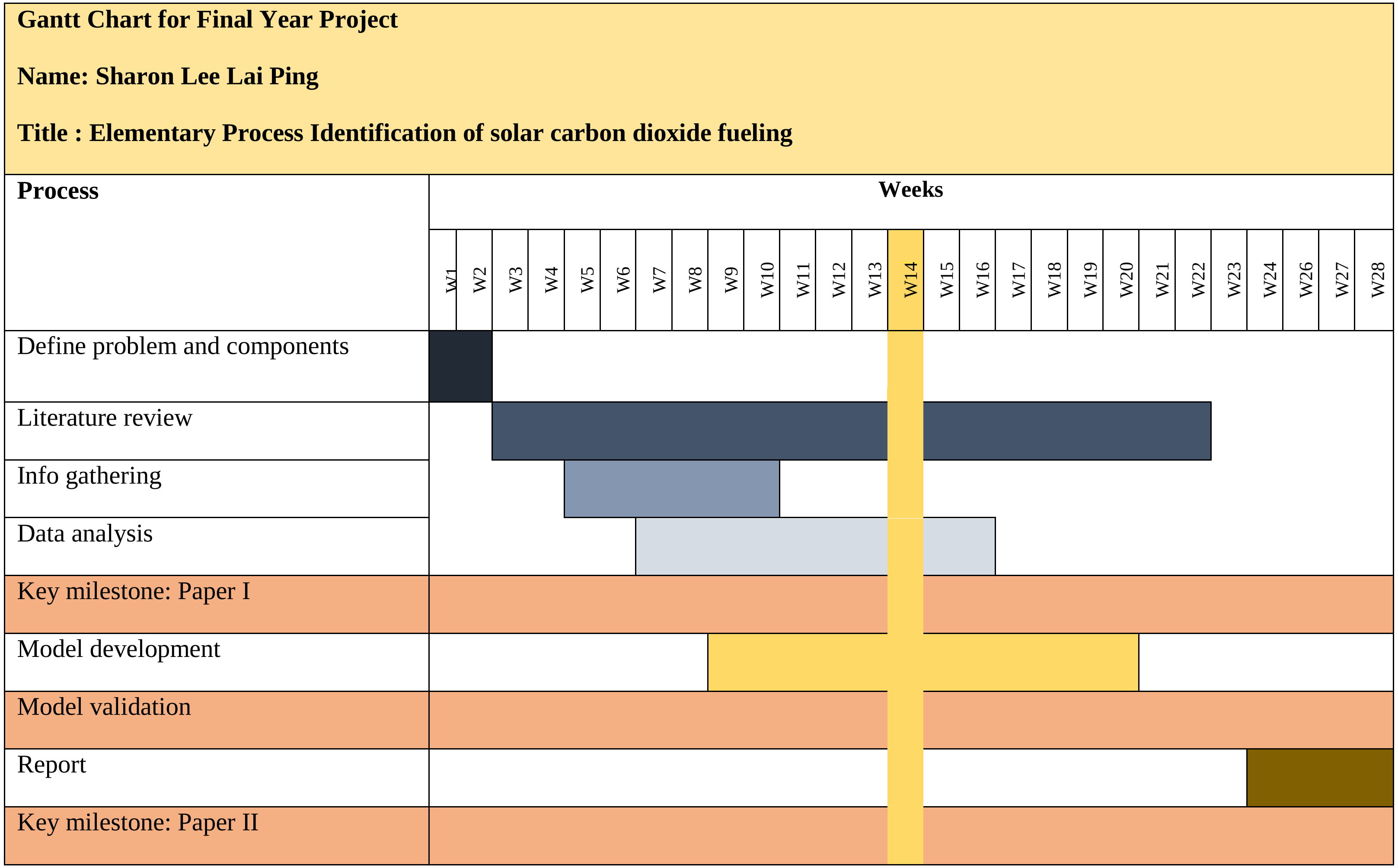
Figure 11: Key milestones of the project

This project is mainly to identify the elementary processes of cracking carbon dioxide by using solar energy. The development of the projects has been done by extensive research on the published paper available online.

Throughout the project, after gathering the information, a paper is produced by the combined efforts from the student and lecturer. The paper is predicted to be published in JESTECH and it studies the trends on the efforts made on carbon capturing and cracking in the year of 2009 to 2013. Nevertheless, the focus area on carbon dioxide cracking covers all methods; not only with the utilization of solar energy.

After studying a couple suitable methods of cracking of carbon dioxide, a model is chosen. The favorable model involves the conversion of carbon dioxide by direct reduction. The details about the model is studied and calculated to determine the energy needed and also the area of solar facility that are needed. Lastly, the process will be documented into a final report

3.3 Gantt chart



Gantt Chart for Final Year Project

Name: Sharon Lee Lai Ping

Title : Elementary Process Identification of solar carbon dioxide fueling

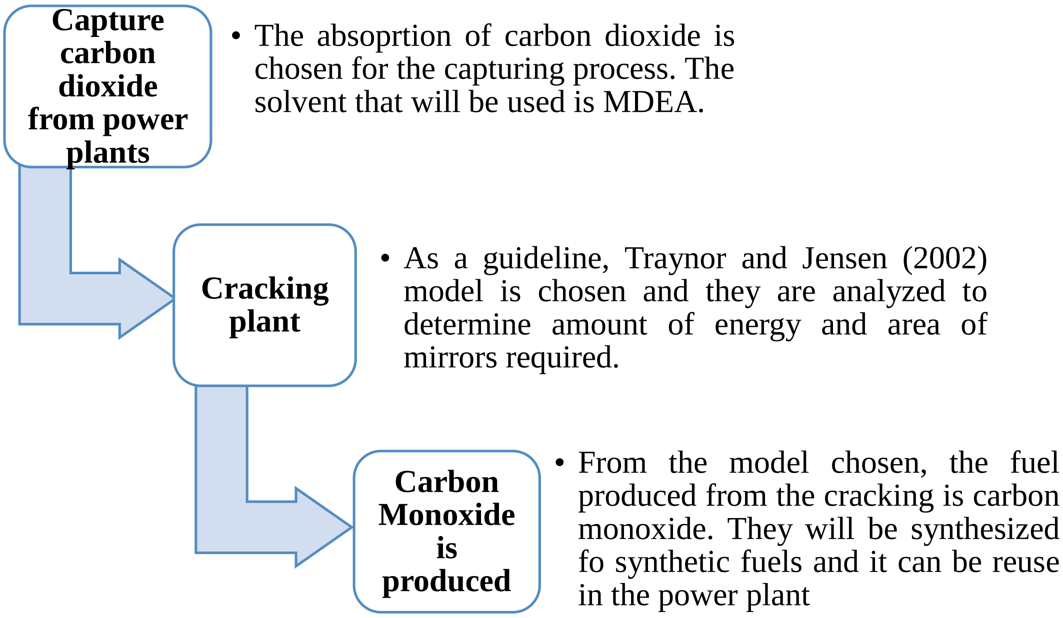
Process	**Weeks**																										
	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	W21	W22	W23	W24	W26	W27	W28
Define problem and components	■	■																									
Literature review			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■					
Info gathering					■	■	■	■	■	■																	
Data analysis							■	■	■	■	■	■	■	■	■	■											
Key milestone: Paper I																											
Model development									■	■	■	■	■	■	■	■	■	■	■	■							
Model validation																											
Report																								■	■	■	■
Key milestone: Paper II																											

Figure 12: Gantt chart showing the expected time period for each ste

CHAPTER 4

RESULTS AND DISCUSSIONS

Figure 13 shows the elementary process of solar carbon dioxide fueling. The main processes are described in the left hand side while the explanations are provided in the right rectangles. This visual aid is to provide a comprehensive flow so that the project can be easily understandable; the thorough discussions are done in the later part of this section.



- The absoprtion of carbon dioxide is chosen for the capturing process. The solvent that will be used is MDEA.
- As a guideline, Traynor and Jensen (2002) model is chosen and they are analyzed to determine amount of energy and area of mirrors required.
- From the model chosen, the fuel produced from the cracking is carbon monoxide. They will be synthesized fo synthetic fuels and it can be reuse in the power plant

Figure 13: Basic framework for solar carbon dioxide fueling process

4.1. Capturing CO_2 from power plants

Aforementioned above, the capturing process will be done by using absorption and methyl diethanolamine (MDEA) will be the solvent. This technology is currently the most mature technology available in the world.

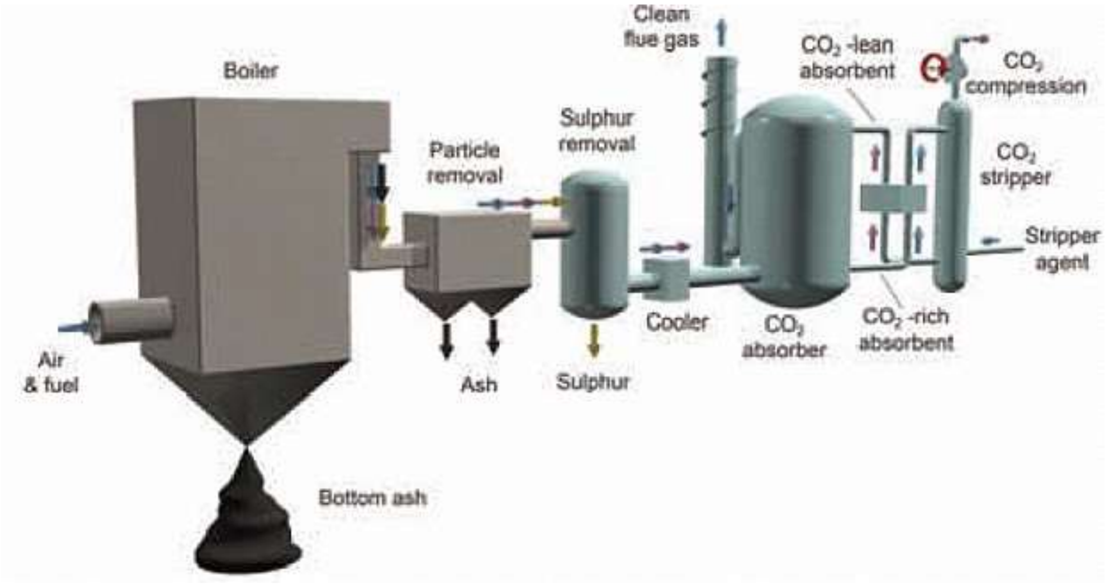


Figure 14: Typical post-combustion CO_2 capture [32]

4.1.1. Absorption process

In the literature review, a detailed explanation on the mechanism of absorption has been acknowledged. Similar procedures are used in this project; but with the usage of a specific solvent, MDEA.

4.1.2. Methyl Diethanolamine (MDEA)

First and foremost, alkanoamine can be divided into three major components of amine: primary, secondary and tertiary. MDEA is categorized under the tertiary amine group at which it has a rather low absorption rate as compared to the primary and secondary groups of amines; however it is still more efficient after taking into account other factors such as regeneration energy, corrosion tendency, cost and etc.

MDEA is used as it has many advantages. They have high solution concentration which is up to 50 to 55 wt%, high acid gas loading, low corrosion rate at high solution loadings, slow degradation rates, low heats of reaction and low vapor pressure and solution losses. However, they impose several drawbacks such as slow reaction rate with CO_2, tendency to foam at high concentration and it is rather costly [33].

To overcome the drawbacks, operating temperatures and filtrations systems are introduced into the plant for the problem of reaction speed and foaming respectively. As for the costs, MDEA is expensive but it can be compensated with the fact that the losses are very minimal; it can be mitigated by having the correct concentration of amines.

4.2 Cracking plant

To determine the size of the solar facility, calculations need to be done to determine the amount of energy needed.

4.2.1 Calculations

As a guide, the model from Traynor & Jensen (2002) is chosen. The prototype utilizes direct solar energy by constructing a cone which focuses solar radiation into the converter. Carbon dioxide is dissociated into carbon monoxide and oxygen. As mentioned before, the dissociation of carbon dioxide is done by just adding heat.

From the reactions, and by taking an initial 100 kW of solar energy, there is 8kW loss through the mirror, bringing about 92% of the solar power to the converter. At the converter, where the dissociation of carbon dioxide occurs, there is a large amount of loss in the form of heat (70kW). At the converter, only approximately 24% of the total energy received from the solar mirror is successfully converted to carbon monoxide. The percentage of energy breakdown through the prototype for better enlightenment.

Table 1: Table of percentage of energy breakdown through the prototype

Useful		**Waste**	
Electrical	**Fuel**	**Mirrors**	**Heat**
25%	20%	10%	45%

Figure 15 shows the breakdown of an initial 100kW solar power passing through the prototype.

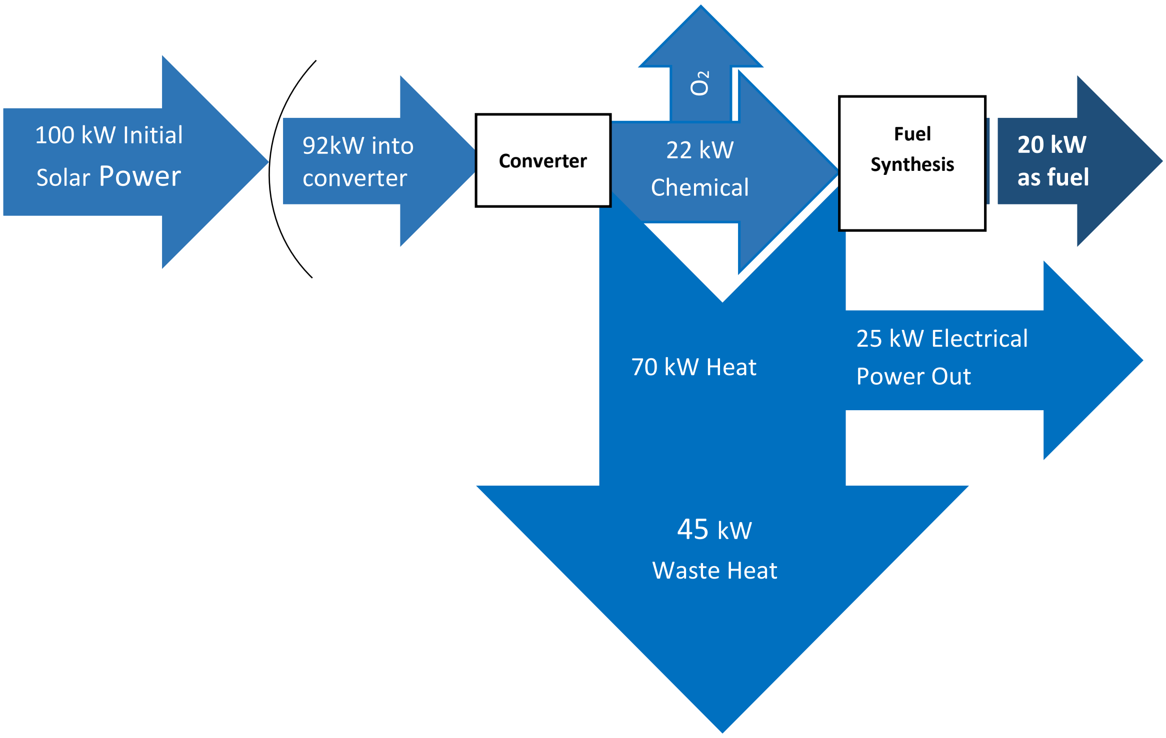


Figure 15: Schematic showing energy conversion goals for a direct solar reduction system based in 100kW initial solar input. [22]

In this experiment, the flow rate chosen is 10L/min with 100 kW solar power.

To convert the flow rate into mass flow rate, $\rho = 0.2682 kg/m^3$ as shown in Appendix II,

$$10\frac{L}{min} \times \frac{0.001\,m^3}{1L} \times 0.2682\frac{kg}{m^3} = 2.682 \times 10^{-3}\ kg/min$$

For this project, the range of mass flow rate of 0.5 to 2.0 kg/min are selected. The reason of having such small mass flow rates into the converter because the cracking process will require a relatively long time to complete. In order to calculate the energy required, the ratio of mass flow rate is used. The calculations are shown as below:

Considering 0.5 kg/min of carbon dioxide,

$$0.5 \times \frac{100\ kW}{2.682 \times 10^{-3}\ \ kg/min} = 18.64 \text{ MW}$$

Meanwhile for 1 kg/min of carbon dioxide,

$$1.0 \times \frac{100\ kW}{12.682 \times 10^{-3}\ \ kg/min} = 37.29 \text{ MW}$$

For 1.5 kg/min of carbon dioxide,

$$1.5 \times \frac{100kW}{2.682 \times 10^{-3}\ \ kg/min} = 55.93\ MW$$

Lastly, for 2.0 kg/min of carbon dioxide,

$$2.0 \times \frac{100kW}{2.682 \times 10^{-3}\ \ kg/min} = 74.57\ MW$$

Observing from the calculations, the minimum solar power required is 18.64 MW. The prototype that is used in Traynor and Jensen (2002) model will not be sufficient to supply this amount of energy as it is equipped with 9.2 m^2 of square quartz mirrors.

Therefore, the areas for the mirrors of solar facilities should be calculated, in order to obtain the power from the solar radiation. As shown in Appendix III, the ranges for the solar radiation in Malaysia is 100 to 900 W/m^2. The information is received from Malaysia Meteorological Department. The formula to calculate the areas is shown below and they are tabulated.

$$Solar\ power\ (W) = Solar\ Irradiation\ \left(\frac{W}{m^2}\right) \times area\ of\ collector\ (m^2)$$

Table 2: Calculation of areas for all the mass flow rates

Solar radiation (W/m^2)	Area (km^2)			
	0.5 kg/min	1.0 kg/min	1.5 kg/min	2.0 kg/min
100	0.19	0.37	0.56	0.75
200	0.09	0.19	0.28	0.37
300	0.06	0.12	0.19	0.25
400	0.05	0.09	0.14	0.19
500	0.04	0.07	0.11	0.15
600	0.03	0.06	0.09	0.12
700	0.03	0.05	0.08	0.11
800	0.02	0.05	0.07	0.09
900	0.02	0.04	0.06	0.08

Table 3: Tabulation of useful and energy losses from the clean input required to break down the selected mass flow rates

Mass flow rates (kg/min)	Clean input energy (MW)	Energy (MW)			
		Useful		Waste	
		Electrical	Fuel	Mirrors	Heat
0.5	18.64	4.66	3.73	1.86	8.39
1.0	37.29	9.32	7.46	3.73	16.78
1.5	55.93	13.98	11.19	5.59	25.17
2.0	74.57	18.64	14.91	7.46	33.56

Based on the tabulation, it is observed that most of the energy are turned into waste. Hence, efforts need to be established in order to reduce the wasted energy as much as possible. We must acknowledge that not all processes are perfectly effective.

The results are also plotted in order to analyze the relationship between solar radiation and the areas of collector.

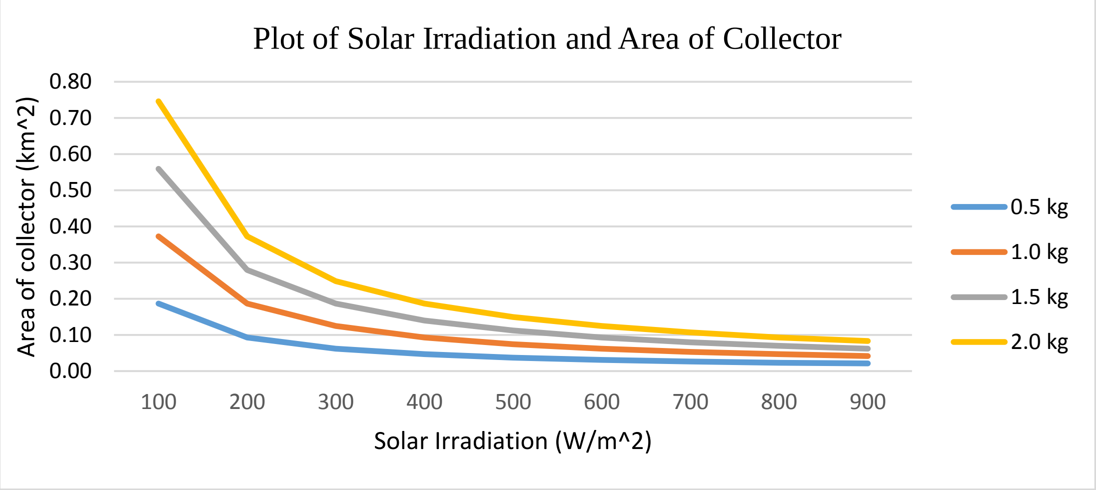


Figure 16: Relationship between solar radiation and areas of collectors

From the plot, it is observed that as the solar radiation increases, the areas of solar collectors get smaller. However so, the minimum solar radiation that is required in order to obtain constant solar power is 500 W/m^2.

4.2.2 Catalysts

Next, the catalyst for the dissociation of carbon dioxide to carbon monoxide is just water (H_2O). But, before the cracking process, it is preheated up to 1900^{o}C to enable photon absorption before passing through the converter. According to the requirements, the best solar application is a solar power tower or a solar furnace.

4.2.3 Solar Facility

Based on the Figure 16, the solar facility will require a maximum of 0.16 km^2. Other factor of deciding the suitable solar facility is the operating temperature. As mentioned in the model, the CO_2 flow is preheated up to 1900^{o}C; hence the facility need to withstand a high temperature. Based on the requirements, solar power tower and solar furnace can be considered.

4.2.3.1 Solar power tower

A solar power tower consists of collection of mirrors with a central receiver. The mirrors are attached to heliostats to track solar paths. The mirrors usually, cover an area up to kilometres to supply a large amount of power to heat the water in the receiver so that it can turn the turbine equipped to generate electricity.

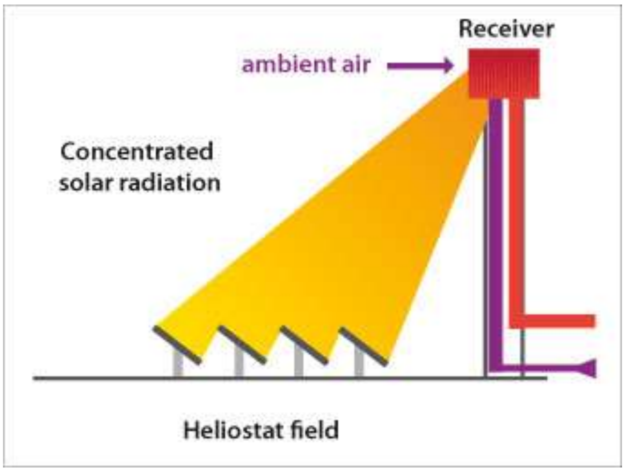


Figure 17: Working principle of solar power tower [35]

There are several advantages of using the solar power tower. Among one of them is that it uses clean solvent such as molten salt which is harmless to the environment apart from being recyclable. Other than that, it also can achieve a high temperature because of the number of mirrors focusing to the receiver. Plus, the installation of heliostats on the mirrors enable them to always track the radiation so that it can receive maximum radiation.

Nevertheless, they impose some disadvantages. First of all, a power tower will require a large area which receive large solar radiation. Hence, the suitable location for the installation would be at the deserts or empty fields. Else, a large deforestation or evacuation will be needed. The reflections from the mirrors might disrupt the ecology. Next, the constructions of the mirrors need to have rigid structure in order to withstand any natural occurrences such as wind and rain.

4.2.3.2 Solar furnace

On the other hand, solar furnace is made up of similar components used by the solar power tower. However, there is a small difference. In solar furnace, it is made up of 2 major mirror components. The first one is a large lens-shaped concentrator and the rest is made up of a single large-sized mirror or many single mirrors attached to heliostats. The total area is the combination of both mirrors and concentrator's area. The concentrator is built to have a fixed focal length. The large mirror or the mirrors attached to the heliostat track the radiation and focuses them into concentrator. The concentrator then focus the rays to the focal point where the receiver is located.

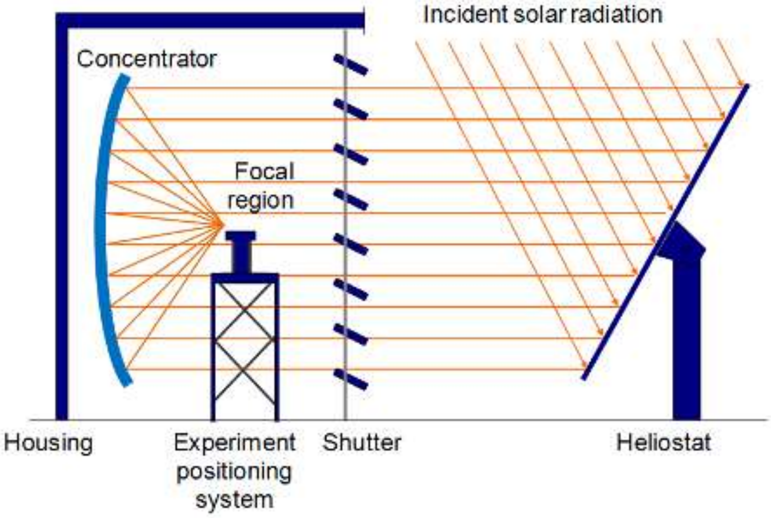


Figure 18: Working principle of a solar furnace [36]

Figure 19: Solar Furnace at Odeillo, France-Spain border. One of the largest solar furnace in the world [37]

Like the power tower, there are some benefits that solar furnace carries. Firstly, the solar furnace can heat up a point without contamination. This means that it is environmental-friendly. The temperatures also can be controlled easily by using the furnace. Unlike the solar power tower, the furnace contains fewer number of mirrors to control in order to adjust the amount of radiation focused to the focal length; means it has a simpler mechanism. High temperatures also can be achieved due to intense solar radiation.

However, there are some disadvantages of using a solar furnace. The construction cost itself is relatively larger as compared to the cost of installing a power plant, due to the sophisticated design of the concentrators. Besides that, unlike the solar power tower which can operate almost all the time during the day, solar furnace can only achieve to 4 to 5 hours max of operation times. Due to the location of the receiver at the focal length, therefore the high temperature area is very concentrated, hence efficient heat exchange only occurs at small areas.

4.3 Production of carbon monoxide

The product from the direct solar radiation cracking of CO_2 is consisted of carbon monoxide and oxygen. CO then, mixed with hydrogen, can be further synthesized to hydrocarbons via Fischer- Tropsch process.

Fischer- Tropsch can be achieved by three main methods: Gas-to-Liquid (GTL), Biomass-to-Liquid (BTL) and Coal-to-Liquid (CTL). The second and third method will require extended processes such as gasification, pyrolysis or torrefaction in order to produce syngas, which is made up from carbon monoxide and hydrogen. In GTL, the gases (mixture of CO and H_2) can be input directly into the bed reactor to be processed. Due to its state, fuels that are produced by GTL usually consisted strands of light hydrocarbons.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

In a nutshell, this project has achieved its objectives in identifying elementary processes for solar carbon dioxide fueling.

Carbon capturing will be done by the absorption method, with the medium of amine, MDEA. Next, the carbon dioxide is transported to the cracking plant which has a solar furnace or solar power tower; they are chosen due to their ability to capture high temperature solar radiation besides from providing sufficient power to crack carbon dioxide. Calculations regarding the power requirement and areas of solar facility are executed. Then, when the cracking is completed, the fuel is transported to the synthesizing area. The fuel produced which is carbon monoxide, mixed with hydrogen gas, and are synthesized through Fischer-Tropsch process.

However, we must acknowledge that this project is valid in the theoretical area because experiments will then need to be done to prove the theory. Provided the funding and facilities, the experiment can be done and it will an outbreak to the entire world, since it is a very new technology and it requires continuous development in order to be more efficient. To overcome the ineffectiveness of the aforementioned prototype, the mirrors should be of high reflectivity so that the radiation can be maximized. As for the waste heat, a binary system can be attached to the solar facility to add value into it by generating electricity or etc.

CCS was never a cheap technology, whilst the weather are not unpredictable, making this process harder to achieve. If this process can be realized, the benefits will definitely outstand the disadvantages. This is one of the methods that can curb the problem of global warming.

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APPENDIX I: Summary of cracking techniques

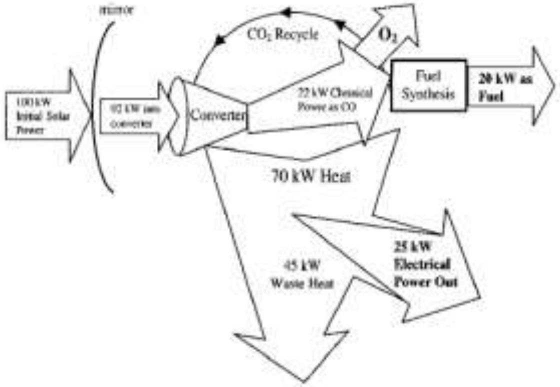
Research	Explanation	Technique	Results	Equation	Adv / Disadv
Dry reforming of methane [24]	• Sequestration of CO_2 from plants • Burial is not effective	• Produces syngas with H2 and CO from CH4 and CO2 • Only 2 industrial processes can do this • Dry vs steam reforming • Syngas can produce synthetic liquid gas eg: naphthalene, sulphur-free diesel via Fischer Tropsch synthesis and CH_4 $CO + H2 \rightarrow CH_3OH$	• Methanol and sulphur free diesel produced from steam reforming (for H_2) and dry reforming. • Syngas produces reacts to produce naptha. Energy is gained from natural gas. • High T and low P favors dry reforming, • T= 1023 K, P = 1 bar, $CH_4/CO_2 = 1/1$	Dry reforming: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\Delta H^0_{1023} = 261\ kJ\ mol^{-1}$ Steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H^0_{1047} = 226.2\ kJ\ mol^{-1}$	Dry reforming consumes 1.6 times E than steam reforming Produce more CO2(questionable) Production of synthetic fuels – valorisation of CO_2. Consumes some CO_2. High T and high P can alleviate carbon formation = catalyst deactivation in dry reforming

				Needs WGS (Water Gas Shift) + combustion of natural gas	
Electrochemical reduction of CO2 in methanol [38]	Methanol is a better solvent of CO_2 compared to H_2O Useful for Rectisol process	Ionophore – benzalkonium chloride Catholyte = benzalkonium chloride in double distilles methanol Anolyte = aqueous $KHCO_3$ 9 electrodes used = Ti, Fe, Co, Ni, Pt, Ag, Au, An, Sn.	Main products: • CO – Ag, Au, Zn, Sn • Methane- All electrodes • Ethane – Ni	CO2 $\rightarrow \cdot CO_2 \rightarrow$ CO Adsorbed CO_2 radical anion.	

Photocatalytic reduction of CO_2 in the presence of H_2 or CH_4 as a reductant over MgO [27]	Using adsorption on MgO surface	Under photoirradiation, CO_2 radical anion will be adsorbed on MgO Achieved at 2-4MPa, 1000K and Ni catalyst	Photoirradiation products: CO and H_2 after 5 hours CH_4 and H_2 = reductant In dark, no products formed. MgO is 5x ZrO_2	$CO_2 + H_2 \rightarrow CO + H_2O$ $CO_2 + CH_4 \rightarrow 2CO + 2H_2$	Cannot operate in dark environment
Dual Alkali Approaches for the capture and Separation of CO_2 [39]	The sequestration of CO2 is done by the absorption of CO2 by amine	Solvay process to convert CO2 to sodium carbonate Use ammonia as catalyst in Solvay process	Produce carbonate salts to be placed at the seabed	$CO_2 + NaCl + NH_3 + H_2O \rightarrow NaHCO_3 + NH_4Cl$ $2NaCl + 2CO_2 + CaO + H_2O \rightarrow 2NaHCO_3 + CaCl_2$	Limestone for the regeneration of ammonia renders the process ineffectively
Modification of semiconductor surface with ultrafine metal particles of	Photoelectrochemical (PEC) reduction of CO_2 with a	5<t<20mm, t= thickness	High energy barrier is formed	To get high efficiency:	Energy conversion efficiency is low

efficient photoelectrochemical reduction of CO_2 [40]	semiconductor electrode.	Photogenerated electrons come out to the surface near to p-Si Electrons transferred to metal particles and reduce CO_2		Control of atomic level for decrease in surface carrier Manometer-sized for obtaining a high barrier height and good-energy level between semiconductor and solution	High photovoltage and high catalytic activity
Selective Solar-Driven Reduction of CO2 to Methanol Using a Catalyzed p-GaP Based Photoelectrochemical Cell [41]	Driven by light energy	Selectively reduced CO2 to methanol	Produce CO and formic acid when use homogeneous photosensitizer with metal electrode with semiconductor colloids	-	Good faradaic efficiency
Reduction of carbon dioxide with water under concentrates sunlight using photocatalyst	Use apparatus with concave mirrors, thermocouple, reaction cell	Focus light intensity on the reaction cell using concave mirror	Reduce CO_2 into CH_4, HCOOH, HCHO ($Pt/K_2Ti_6O_{13}$)	-	Use high energy and temperature

combined with Fe-based catalyst [42]	Use Xe/Hg irradiation light 0.3g catalyst+7.7kPa of CO_2 and 4ml distilled water		Fe-Ce-K/DAY = additional CH_3Oh, C_2H_5OH		
High-Rate Solar Photocatalytic Conversion of CO2 and Water Vapor to Hydrocarbon Fuels [28]	Reduce CO2 to organic compounds Use nitrogen-doped titania nanotube arrays	Use titania – use surface area, modify gap band + cocatalyst nano particles Nanoparticles thickness lesser than minor carrier diffusion length Must be placed outdoor	Produced CO, methane, olein, paraffin and alkanes	-	Titania – powerful oxidation, superior charge transport + corrosion resistance High concentration of CO_2 compared to other techniques RH = 85%, covered with chemiadsorbed hydroxyls
Conversion to CO2 to CO and Hydrocarbons by Plasma Reaction [43]	Electrochemical reduction through plasma	Input electrical power = 1W, flow rate = 1.6mL/min	Products: CH_4, C_2H_4 + C_3H_6 CO is main product	$2CO_2 \rightarrow 2CO + O_2$ $H_2 + CO_2 \rightarrow CO + H_2O$	Cannot use faradaic efficiency. Because electricity used is too high.

			CO is produced more in Cu than Fe With H2, methane and diamond are formed		
Direct solar reduction of CO2 to fuel : First Prototype Results [22] Traynor, A., Jensen, R. (2002)	Photolysis	Heat up to 1900oC <u>Design:</u> 1. Solar concentrator dish 2. Converter- heat, convert, dissociating, limiting the back reaction 3. Instrumentation	CO and O_2 produced $CO_2 + \text{heat} \rightarrow CO + 1/2O_2$  **Figure 5.** Schematic showing energy conversion goals for a direct solar reduction system based on 100 kW initial solar input.		Increase negative Gibbs free energy Input = 100kW, only 92kW is transferred then 22kW is stored in CO as chemical reaction >70kW as heat

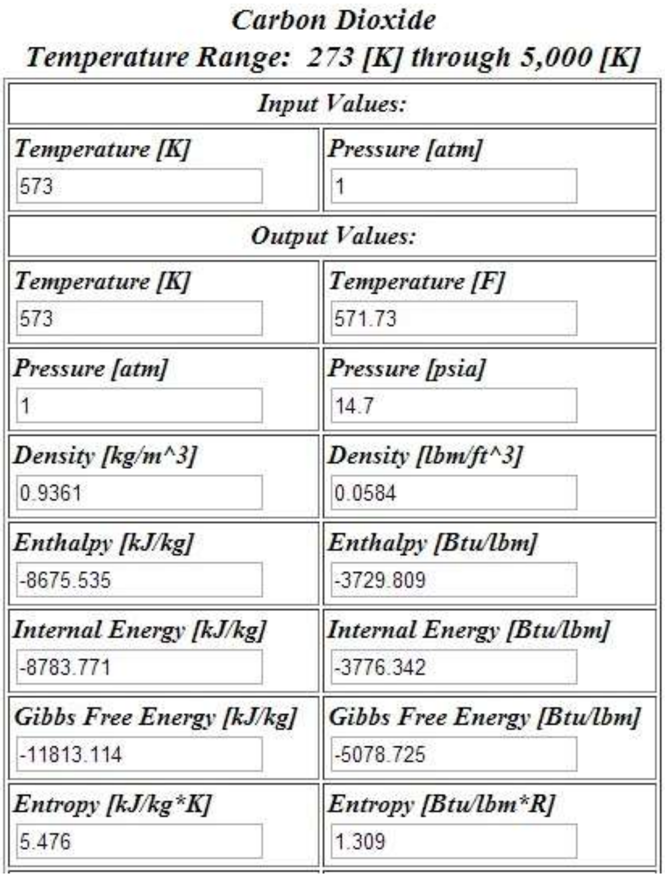
Electrocatalytic and homogeneous approaches to conversion of CO2 to liquid fuels [44]	Properties of CO_2	Convert CO_2 and H_2O to CO and H_2. Then use Fischer Tropsch process to form liquid fuels. ‘Hard way’ – Change directly CO_2 to hydrocarbons (electrocatalysts)	Metal complexes with macrocyclic ligands Metal complexes with bipyridine ligands Transition metal phospine complexes Catalyst = CODHs (carbon monoxide dehydrogenases) – obtained from anaerobic and archae/ aerobic and carboxydotropic	-	‘Hard Way’- need to find one catalyst that is kinetically low barrier
Opportunities and prospects in the chemical recycling of CO_2 to fuels [23]	Methods of converting CO_2 to fuels	4 approaches - high energy = hydrogen, low-energy synthetized targets = carbonates, shift equilibrium, supply physical energy	React with H_2 Reverse WGS Produce methanol Produce hydrocarbons Electrochemical Photoelectrochemical	-	Hydrogenation – uses a lot of H_2. If consumed from the burning of fossil fuels- most effective method

A short review of catalysis for CO2 conversion [45]	Review on the CO_2 cracking	• CH4 reforming • Hydrogenation to methanol • Synthesis of dimethyl carbonate • Reaction with propylene glycol (PG) • Synthesis of cyclic carbonate • Synthesis of cyclic carbonate with ammonium salt	Product: • Methane • Methanol • PG = Zinc oxide modified with potassium salt as catalysts	-	DME synthesis – sensitive to pressure and temperature
Carbon dioxide conversion to fuels and chemicals using a hybrid green Process [46]	Uses bacteria	• Culture propagation and maintenance • Feed gas composition Independent variable estimation • Media, gas mix, bacterium	• Butanol • Butyric Acid • Hexanol • Hexanol Acid	Butanol and Butyric = 4CO2 + 12H2 → C4H9OH + 7H2O 4CO2+10H2 → C3H7COOH + 6H2O	All system will have their own advantages and disadvantages

		factorial experiment • Selection of microbial culture and feed gas composition • Effect of MES buffer		Hexanol Acid $6CO_2 + 18H_2 \rightarrow C_6H_{13}OH + 11H_2O$ $6CO_2 + 16H_2 \rightarrow C_5H_{11}COOH + 10H_2O$	
Carbon dioxide photoconversion. The effect of titanium dioxide immobilization conditions and photocatalyst type [47]	Photoconverted to methane	• Uses TiO_2 to light hydrocarbons • Can replace TiO_2 with gold nanoparticles • Silver and gold nanoparticles can absorb visible light	• Methane is produced	-	Need optimum temperature which is 120oC and the operation of 20 hours produce maximum methane concentration.

APPENDIX II: Properties of Carbon Dioxide at 300^{o}C

Information obtained from Physical Properties calculator: http://www.engineering-4e.com/calc1.htm



Carbon Dioxide

Temperature Range: 273 [K] through 5,000 [K]

Input Values:

Temperature [K] 573	*Pressure [atm]* 1

Output Values:

Temperature [K] 573	*Temperature [F]* 571.73
Pressure [atm] 1	*Pressure [psia]* 14.7
Density [kg/m^3] 0.9361	*Density [lbm/ft^3]* 0.0584
Enthalpy [kJ/kg] -8675.535	*Enthalpy [Btu/lbm]* -3729.809
Internal Energy [kJ/kg] -8783.771	*Internal Energy [Btu/lbm]* -3776.342
Gibbs Free Energy [kJ/kg] -11813.114	*Gibbs Free Energy [Btu/lbm]* -5078.725
*Entropy [kJ/kg*K]* 5.476	*Entropy [Btu/lbm*R]* 1.309

APPENDIX III: Annual solar radiation distribution in Malaysia

Note: The source is obtained from the Malaysian Meteorological Department