AN EXPERIMENTAL STUDY OF CONVERSION OF CARBON DIOXIDE INTO HYDROCARBON FUEL BY USING PHOTOCATALYTIC METHOD

MOHAMAD REDZUAN BIN BUJANG

UNIVERSITI MALAYSIA PAHANG

BORANG PENGESAHAN STATUS TESIS		
JUDUL:	AN EXPERI DIOXIDE PHOTOCAT	MENTAL STUDY OF CONVERSION OF CARBON INTO HYDROCARBON FUEL BY USING ALYTIC METHOD
		SESI PENGAJIAN: 2009/2010
Saya		MOHAMAD REDZUAN BIN BUJANG (HURUF BESAR)
mengaku me Malaysia Pal	mbenarkan tesis Proje hang dengan syarat-sya	k Sarjana Muda (PSM) ini disimpan di Perpustakaan Universiti arat kegunaan seperti berikut:
1.	Hakmilik kertas proje projek bersama dan d	ek adalah di bawah nama penulis melainkan penulisan sebagai ibiayai oleh UMP, hakmiliknya adalah kepunyaan UMP.
2.	Naskah salinan di dal bertulis daripada penu	am bentuk kertas atau mikro hanya boleh dibuat dengan kebenaran 11is.
3.	Perpustakaan Universi pengajian mereka.	siti Malaysia Pahang dibenarkan membuat salinan untuk tujuan
4.	Kertas projek hanya l	boleh diterbitkan dengan kebenaran penulis. Bayaran royalti adalah
 5. *Saya membenarkan/tidak membenarkan Perpustakaan membuat salinan kertas projek ni sebagai bahan pertukaran di antara institusi pengajian tinggi. 6. **Sila tandakan (✓) 		
	SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)
	TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
	✓ TIDAK TERI	HAD
		Disahkan oleh
(TANDATA	ANGAN PENULIS)	(TANDATANGAN PENYELIA)
Alamat Tetaj	p: Lot 272,Lrg 4, Jl Salim, 96000, Sibu, Sarawak	n Sentosa, Dr. Iqbal Ahmed ^ Nama Penyelia
Tarikh:	30April 2010	Tarikh:
CA	TATAN:* Jika tesi	is ini SULIT atau TERHAD , sila lampirkan surat daripada pihak

ATAN:* Jika tesis ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasiberkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT atau TERHAD. "I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the qualities and requirements for the award of Bachelor's Degree of Chemical Engineering (Gas Technology)".

Signature	:
Supervisor's Name	: Dr. Iqbal Ahmed
Date	:

AN EXPERIMENTAL STUDY OF CONVERSION OF CARBON DIOXIDE INTO HYDROCARBON FUEL BY USING PHOTOCATALYTIC METHOD

MOHAMAD REDZUAN BIN BUJANG

A thesis submitted in fulfilment for the award of the Degree of Bachelor in Chemical Engineering (Gas Technology)

> Faculty of Chemical and Natural Resources Engineering Universiti Malaysia Pahang

> > **APRIL 2010**

DECLARATION

I declare that this thesis entitled "An Experimental Study of Conversion of Carbon Dioxide into Hydrocarbon Fuel by using Photocatalytic Method" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	:
Name	: Mohamad Redzuan Bin Bujang
Date	: 30 April 2010

Dedicated, in thankful appreciation for support, encouragement and understanding to my beloved family and friends.

ACNOWLEDGEMENT

First of all, I would like to express my heartily gratitude to my research supervisor, Dr. Iqbal Ahmed for his guidance, advices, efforts, supervision and enthusiasm given throughout for the progress of this research.

I would also like to thank Mr. Mohd Anuar Hj Ramli, Khairil Izwan Ahmad Tarmidzi, Kishore a/l Kannan, Aizuddin Abd. Malek and all of my friends for their cooperation, sharing of knowledge and experience during my research.

Also I would like to express my sincere appreciation to my parents, brother and sisters for continuously support me all these years. Without them, I would not be able to complete this research. Unfortunately, it is not possible to list all of them in this limited space. I am grateful to all. Only Allah S.W.T. can repay all your kindness. Insyaallah.

ABSTRACT

The production of hydrocarbon fuel, methanol (CH₃OH) from the carbon dioxide (CO₂) has been studied using photosynthesis method. The study conducted in FKKSA lab using existing reactor and modified with addition of photosynthesis lamp. The effect of catalyst influenced the yield of the CH₃OH for the sample. With the presence of a metal oxide catalyst, overall water splitting can be driven by visible light to produce hydrogen and oxygen. After the hydrogen and oxygen splitting process, hydrogen reacts with carbon dioxide to produce hydrocarbon fuel synthetically. The sample obtain from the reaction been tested to define the composition. The functional groups of the product which is CH₃OH are identified by using fourier transform infrared spectrometer (FTIR). From the studies showed that the photocatalytic method that has been use is applicable but need more of enhancement to produce high yield of CH₃OH which can be commercialized.

ABSTRAK

Penghasilan minyak sintetik daripada bahan gas karbon dioksida dengan menggunakan kaedah fotosintesis. Eksperimen di jalankan di makmal FKKSA di mana reactor yang sedia ada digunakan dan membuat sedikit penambahan terhadap reactor tersebut dengan menambah lampu fotosintesis. Bahan pemangkin seperti ferum oksida digunakan untuk menambah kadar reaksi kimia untuk menghasilkan methanol. Dengan menggunakan pemangkin, pemisahan ikatan molekul air di dalam pancaran cahaya berlaku untuk membentuk molekul H dan O. Setelah molekul H dan O dipisahkan, reaksi dengan gas karbon dioksida akan menghasilkan hidrokarbon sintetik. FTIR digunakan untuk mengetahui kumpulan berfungsi. Dalam analisis ini, kaedah fotosintesis boleh digunakan untuk memperoleh hasil yang efektif yang boleh dikomersilkan.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	ABSTRACT	i
	ABSTRAK	ii
	TABLE OF CONTENT	iii
	LIST OF TABLES	vi
	LIST OF FIGURES	vii
	LIST OF SYMBOLS	viii
	LIST OF APPENDICES	ix

1 INTRODUCTION

1.1 Introduction	1
1.2 Carbon dioxide emission	2
1.3 Problem Statement	3
1.4 Objectives Research	4
1.5 Scope Of Works	5
1.6 Rationale Significance	5

2 LITERATURE REVIEW

2.1 Carbon Dioxide and Global Warming	6
2.2 Carbon Sequestration	7
2.3 Utilization of Carbon Dioxide	8
2.4 Production of Chemicals	8
2.5 Production of Fuels	10
2.5.1 Hydrogenation Reactions	11
2.5.2 Electrochemical Reduction of CO ₂	11
2.5.3 Photochemical Reduction of CO ₂	13
2.6 Photosynthesis Process	14
2.7 Artificial photosynthesis	16
2.8 Methanol	17

3 RESEARCH METHODOLOGY

3.1 Introduction	20
3.2 Research Methodology	20
3.3 Materials and Chemicals	21
3.3.1 Carbon Dioxide Gas	22
3.3.2 Photosynthesis Lamp	22
3.3.3 Iron Oxide Catalyst	23
3.3.4 Fourier Transform Infrared Spectrometer	23
3.4 Experimental Procedure	24

4 **RESULTS AND DISCUSSIONS**

4.1 Experimental Result	26
4.2 Physical Characteristic of Sample	27
4.3 FTIR Analysis	27

5 CONCLUSION AND RECCOMENDATION

5.1 Conclusion	30
5.2 Recommendation	30
REFERENCES	32

APPENDICES	35

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Energy for CO ₂ reduction reaction	10
4.1	Summary of Sample Functional Group	28

LIST OF FIGURES

FIGURE NO.	RE NO. TITLE	
1.1	Global CO ₂ emissions	4
2.1	Chemical transformations of CO ₂	9
2.2	Possible pathways for the competing interaction of low- valent catalysts with protons or CO_2	12
3.1	Workflow diagram	21
3.2	Electrical diagram for photosynthesis lamp	22
3.3	Iron Oxide Catalyst	23
3.4	Experimental diagram	24
4.1	Sample after experiment	26
4.2	Sample after cooled	27
4.3	FTIR Analysis for wavenumber 400-1000 (cm-1)	28
4.4	FTIR Analysis for wavenumber 1000-2000 (cm-1)	28
4.5	FTIR Analysis for wavenumber 2000-4000 (cm-1)	29

LIST OF SYMBOLS

mg	-	Milligram
S	-	Second
min	-	Minute
^{0}C	-	degree celcius
atm	-	Pressure
CO_2	-	Carbon Dioxide
CH ₃ OH	-	Methanol
FTIR	-	fourier transform infrared spectrometer

LIST OF APENDICES

APPENDIX	TITLE	PAGE	
٨	Photocatalytic Experimental Picture	35	
A	Photocatalytic Experimental Picture	55	

CHAPTER 1

INTRODUCTION

This chapter discusses brief overview of the study and discussed, the nature of the research, the problem that this paper trying to address, aims and objectives of the work and indication of how will the work progressed. Due to high emission of CO_2 into atmosphere, this research was conducted to minimize the emission by converting CO_2 into useful product such as CH_3OH by using photosynthesis method which is still new and never been claimed successful before.

1.1 Introduction

Renewable energy is growing importance and it relate to the environment and security of energy supply. Ever since environmental concerns over the fossil fuels with respect to their limited reserves emerged, interest in environmental – friendly alternative energy resources that can reduce dependency on fossil fuels has been growing (Hafizi, 2009).

With respect to the global issues of sustainable energy and reduction in greenhouse gases, synthetic fuel is getting increased attention as a potential source of renewable energy. According to the World Energy Assessment report, 80% of the worlds primary energy consumption is contributed by fossil fuel, 14% by renewable energy (out of which biomass contributes 9.5%) and 6% by nuclear energy (Rogner *et al*, 2002).

Combustion of hydrocarbon fuel mostly by power generation plant produced high amount of CO_2 and harmful to be emit to environment. Due to this issue, CO_2 mitigation has been extremely worked out to reduce the problem.

1.2 Carbon dioxide emission

 CO_2 has taken a centre stage in the environmental arena in recent years. One of the most alarming global environmental problems of today is greenhouse effect. This problem is mainly caused by the increased atmospheric CO_2 concentration due to the burning of fossil fuels for power generation. A response strategy, to reduce the problem of a further increasing greenhouse effect, is to decrease anthropogenic CO_2 emissions, from flue and fuel gases produced in combustion and gasification processes in power plants, by efficiency improvement or CO_2 removal. The removal of CO_2 from these gases is not a major technological problem anymore, because many technologies have been developed for this purpose. While CO_2 is certainly not a panacea, it possesses a number of characteristics that suggest the use of CO_2 could provide both environmental and economic benefit (Scibioh, 2006).

A practical study to enhance practical photosynthetic carbon dioxide mitigation had been done. This research focused on the development of a practical photosynthetic system for greenhouse gas control with special focus on application at smaller fossil generation units. The work described here has focused on selection and study of viable thermophilic organisms, design of the growth surfaces within the bioreactor to reduce overall system size, photon collection and delivery via fiber optics to optimize growth and reduce system footprint, and harvesting schemes to facilitate maximum growth rates. Research has also 4 been directed to the application of translating slug flow technology to enhance concentrations of soluble carbon species to increase organism growth rates, which is also used to reduce flue gas temperatures. The ultimate goal is to test a complete pilot scale system to demonstrate process viability (D.J. Bayless et al, 2003).

Converting CO₂ into synthetic hydrocarbons through catalytic hydrogenation is a process invented by M. Fischer and M. Tropsch during the twenties and thirties. As M. Bergius at the same time, they used an iron catalyst to produce hydrocarbons. In 1925, Fischer-Tropsch produced a real industrial synthesis of hydrocarbons and oils under normal pressure with a cobalt catalyst and thorine. These processes were improved in 1930 and during World War 2 using nickel and nickel-cobalt catalysts. The Fischer-Tropsch process was also applied in England by the Synthetic Oil Cy Ltd using cobalt and thorium catalysts. Other companies improved the Fischer-Tropsch process using costly alloy catalysts without succeeding to eliminate problems of instability due to the presence of oxygen, humidity or water vapour in the reactor (G. Robert, 2006).

1.3 Problem Statement

The emission of CO_2 to environment caused a lot of problem regarding safety and health of environment itself. In the global CO_2 cycle of nature, generation and absorption of large amounts of CO_2 are in perfect equilibrium: 200 Gt CO_2 are generated each year by plant and soil respiration and decomposition and the ocean, and they are matched by an equal amount of CO_2 absorbed by plant photosynthesis and by the oceans. Man is disturbing this equilibrium by generating yearly 8 Gt of CO_2 , of which only 4.5 Gt are reabsorbed by nature. 6 of the 8 Gt are caused by electricity generation (1.8 Gt C/yr) and by transportation and industry and domestic use (4.2 Gt C/yr) (Scibioh et al, 2006).

Figure 1.1 in the next page shows the trend of CO_2 emission per year from early 17th century until 20th century. The trend show the increasing amount of CO_2 emit due to several sources. In early 19th century, the emission of CO_2 was considered still low. After 1950, the emission started to amplify due to increasing demand and usage of hydrocarbon fuel which produce CO_2 . Fossil fuel states the highest amount of CO_2 emitted with almost 7 billion metric tons in 2006 and predicted to be increased until 2050.



Figure 1.1: Global CO₂ emissions (Scibioh et al, 2006)

There several method that have been done to lower the level of CO_2 . One that has been studied is photosynthetic carbon dioxide mitigation. In this method CO_2 converted into biomass by reacting CO_2 with organic compound, algae. Algae are organism that found in water. It is difficult to gather large amount of algae in large scale production.

1.4 Objectives Research

The objective of this research is to study:-

- i) The synthesis of hydrocarbon fuel production.
- The capability of carbon dioxide conversion by photocatalytic method
- iii) Development of new green technology.

1.5 Scope of Works

On this research, there are focuses on two main scopes:

- i. Catalytic photosynthesis technique
 - a. Experiment conduct in a reactor with presence of iron oxide catalyst and high intensity photosynthesis lamp.
- ii. Determination of composition
 - a. Analyze product composition by using FTIR.
 - b. Define the characteristic of the product.

1.6 Rationale and Significance

The rationale of this research is CO_2 is one of harmful gas if being emitted to atmosphere in large amount. Instead of emitting the gas to atmosphere, using it as feed stock to produce another valuable product is more preferred. Turning carbon dioxide into a useful feedstock chemical could help to reduce levels of this greenhouse gas in the atmosphere, as well as providing a cheap source of carbon. The transformation of CO_2 into organic substances is a promising long term objective. It could allow the preparation of fuels or chemicals from a cheap and abundant carbon source.

Photocatalytic method is a new method that has not been acclaimed to be effective in converting CO_2 into hydrocarbon fuel. This head start research as an initiative in findings a new method producing hydrocarbon fuel which efficient and cheap and in the same time environmental friendly.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide and Global Warming 33

In the 19th century, scientists realized that composition of gases in the atmosphere cause a greenhouse effect which affects the climate changes. These scientists were interested chiefly in the possibility that a lower level of carbon dioxide gas explain the ice ages of the distant past. At the turn of the century, Svante Arrhenius calculated that emissions from human activity might someday bring a global warming (Arrhenius, 1908). Other scientists dismissed his idea as faulty. In 1938, G.S. Callendar argued that the level of carbon dioxide was climbing and raising global temperature, but most scientists found his arguments questionable. It was almost by chance that a few researchers in the 1950s discovered that global warming truly was possible (Callender, 1939). In the early 1960s, C.D. Keeling measured the level of carbon dioxide in the atmosphere and it was rising fast. Researchers began to take an interest, struggling to understand how the level of carbon dioxide had changed in the past, and how the level was influenced by chemical and biological forces. They found that the gas plays a crucial role in climate change, so that the rising level could gravely affect to the future (Weart, 2009).

As fossil fuels are depleted and global warming becomes critical, renewable energy such as solar electric, wind, hydroelectric, geothermal, solar thermal, biomass and nuclear energy will become prime energy sources. From all these future energy sources, only biomass produces fuels directly. Although biomass derived fuels will without a doubt contribute to meeting future fuel requirements, they will not be able to fulfil future fuel demands. The reduction of CO_2 to methanol, methane, and other carbon-based fuels using renewable energy sources or nuclear energy would provide a future energy distribution system based on high-energy density liquid and gaseous fuels and without any net increase in atmospheric CO_2 . This could have a significant impact on future CO_2 emissions, especially from the transportation sector (Scibioh, 2006).

2.2 Carbon Sequestration

Carbon sequestration is the process through which plant life removes CO2 from the atmosphere and stores it in biomass. Over the course of a year, plants remove and release CO2 and net sequestration results if the rate of removal is higher than the rate of release. Young, fast-growing trees in particular will remove more carbon dioxide from the atmosphere than they will release. Agricultural and forestry practices can enhance the rate of carbon sequestration, or cause net emissions, depending on the overall balance. The term "sink" is a broader term used to describe agricultural and forestry lands or other processes that absorb or sequester CO2, and other chemical processes that remove other greenhouse gases from the atmosphere (Markels, 2002).

Under the critical circumstances of global climate change and hunger for cost-effective and environmentally-friendly energy, carbon sequestration will allow continuous the growth of current fossil fuel-based economy, while facilitating the transition to sustainable energy sources. Carbon sequestration technologies include the capture, storage and long term utilization of CO_2 that have been the cause of the greenhouse emissions associated with global warming (Markels, 2002).

Turning CO_2 into a useful feedstock chemical could help to reduce levels of this greenhouse gas in the atmosphere, as well as providing a cheap source of carbon. The conversion of CO_2 into organic substances is a promising long term objective. It could allow the preparation of fuels or chemicals from a cheap and abundant carbon source (Scibioh, 2006).

Hence, three strategies are available. First, prevention of CO_2 emission. Avoiding the formation of CO_2 by higher efficiencies in electricity generation, transmission and use could reduce amount of CO_2 emitted to atmosphere. Other than that, turning CO_2 as feedstock for commercial use is another alternative to reduce amount of CO_2 emitted. Last but not least, disposal of CO_2 .

2.3 Utilization of Carbon Dioxide

There are several driving forces for producing chemicals from CO_2 whenever possible (Behr, 1988). CO_2 is a cheap, nontoxic feedstock that can replace toxic chemicals such as phosgene or isocyanides. CO_2 is a totally renewable feedstock compared to oil or coal. The production of chemicals from CO_2 can lead to totally new materials such as polymers. New routes to existing chemical intermediates and products could be more efficient and economical than current methods (Scibioh, 2006). The production of chemicals from CO_2 could have a small but significant positive impact on the global carbon balance.

 CO_2 is generally considered to be a green, or environmentally benign, solvent in that it is relatively nontoxic, is non-flammable, and is naturally abundant. As such, CO_2 has been suggested as a sustainable replacement for organic solvents in a number of chemical processes.

2.4 Production of Chemicals

Approximately 110 MT (megatons) of CO_2 are currently used for chemical synthesis annually. The chemicals synthesized include urea, salicylic acid, cyclic carbonates, and polycarbonates. The largest of these uses is urea production, which

reached approximately 90 million metric tons per year in 1997. In addition to these commercial processes using CO₂, there are a number of reactions currently under study in various laboratories that hold promise. These reactions differ in the extent to which CO₂ is reduced during the chemical transformation. The simplest reactions of CO₂ are those in which it is simply inserted into an X-H bond. Figure 2.1 shows the chemical transformation of CO₂. Examples are the insertion of CO₂ into organic amines to afford carbamic acids which may be converted into organic carbamates. More recent examples include the insertion of CO₂ in P-N bonds of P(NR₂)₃ compounds to form P(NR₂)(OCONR₂)₂ compounds and the reaction of ammonium carbamates (derived from CO₂) with alkyl halides in the presence of crown ethers to form useful urethane intermediates (Halmann, 1993).



Figure 2.1: Chemical transformations of CO₂ (Halmann, 1993)

2.5 **Production of Fuels**

Unlike chemicals that derive value from their fundamental chemical and physical properties, the value of fuels is in their energy content and the ease with which they are stored and transported. Currently no fuels are currently commercially made by the reduction of CO_2 . Renewable energy sources and nuclear energy do not produce CO_2 , and therefore, production of fuels from these sources would provide fuels but not contribute to net CO_2 emissions.

The following reactions in Table 2.1 show CO_2 reduction reactions in which energy in the form of electricity or hydrogen, derived from nuclear or renewable resources, is stored as either liquid or gaseous carbon based fuels (ΔE° and ΔG° values are for 298 K). The high energy density of these fuels and their transportability makes them advantageous. However, the energy required to produce these fuels must be minimized to ensure efficient use of renewable and nuclear energy sources. In general, entropy considerations suggest that these energy storage reactions are best carried out at low temperatures to reduce the free energy required. Both hydrogenation reactions and corresponding electrochemical reactions are shown in equations below (Scibioh, 2006). In the electrochemical reactions, CO_2 is reduced at the cathode and O_2 is produced at the anode. These electrochemical reactions may be considered as the sum of the corresponding hydrogenation reactions and the water splitting reaction.

	$\Delta E^{o}(V)$	ΔG^{o} (kcal/mol)
$H_2O \rightarrow H_2 + 0.5O_2$	1.23	56.7
$CO_2 + H_2 \rightarrow HCOOH$	-	5.1
$CO_2 + H_2O \rightarrow HCOOH + 0.5O_2$	1.34	61.8
$CO_2 + H_2 \rightarrow CO + H_2O$	-	4.6
$CO_2 \rightarrow CO + 0.5O_2$	1.33	61.3
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	-	- 4.1
$CO_2 + 4H_2 \rightarrow CH_3OH + 2 H_2O$	-	-31.3
$CO_2 + 2 H_2O \rightarrow CH_3OH + 1.5O_2$	1.20	166
$CO_2 + 2 H_2O \rightarrow CH_4 + 2 O_2$	1.06	195

Table 2.1: Energy for CO₂ reduction reaction (Gattrell et al, 2006)

2.5.1 Hydrogenation Reactions

CO₂ is currently used as an additive in the synthesis of methanol from CO and H₂, and it is believed that reduced forms of CO₂ are kinetically important intermediates in this process. The thermodynamics for methanol production from H₂ and CO₂ are not as favourable as that for production of methanol from H₂ and CO. For instance, at 200 °C the equilibrium yield of methanol from CO₂ is slightly less than 40% while the yield from CO is greater than 80%. The reduction of CO₂ is rendered favourable by the use of hybrid catalysts that dehydrate methanol to form dimethyl ether. Ethanol has also been produced by the hydrogenation of CO₂. This fuel is attractive because it has a slightly higher energy density than methanol and it is not as toxic. However, the selectivity for ethanol production is generally low (<40%). The hydrogenation of CO₂ to methane and higher hydrocarbons is also known. For C₂ and higher hydrocarbons, hybrid catalysts such as Cu-ZnO-Cr₂O₃ and H-Y zeolite are generally used. Catalytic synthesis of formic acid derivatives by CO₂ hydrogenation, together with other substrates, in supercritical CO₂ is also known (Omae, 2006).

2.5.2 Electrochemical Reduction of CO₂

Carbon dioxide reduction at a number of metal electrodes has been investigated, and Cu electrodes were found to catalyze CO₂ reduction to methane in bicarbonate solutions with current efficiencies as high as 65%. Although over potentials are large (1.5 V), this is a remarkable transformation in which eight electrons are transferred to CO₂ with cleavage of two C-O bonds and formation of four C-H bonds. Cu electrodes have been studied extensively to gain insight into the mechanism, which is thought to involve coordinated CO as an intermediate, and to overcome poisoning of the electrode under catalytic conditions. Under slightly different conditions, CO₂ can also be reduced to ethylene at Cu electrodes. Copper oxides on gas diffusion electrodes at large negative potentials have also been reported to reduce CO₂ to ethanol (Sullivan et al, 1993). This selectivity of reduced forms of the catalyst for H^+ versus CO₂ also appears to determine the nature of the CO₂ reduction product observed. If the reduced form of the catalysts reacts with CO₂ to form an M-CO2 complex, protonation yields a metallocarboxylic acid; further reaction can then produce CO by C-O bond cleavage to form hydroxide or water. Thus, reaction of a reduced form of the catalyst with CO₂, as opposed to protons, leads to CO formation. If the reduced form of the catalyst reacts with protons to form a hydride complex, subsequent reaction of the hydride with CO₂ leads to formate production; these two possibilities are illustrated in Figure 2.2 (Scibioh, 2006).

It is unusual for homogeneous catalysts to form reduction products that require more than two electrons. However, it has been reported that the formation of glycolate (HOCH2COO-), glyoxylate (OCHCOO-), formic acid, formaldehyde, and methanol as CO2 reduction products using [Ru(tpy)(bpy)-(CO)]2+ complexes as electrocatalysts (bpy = 2,2'- bipyridine, and tpy = 2,2':6',2"-terpyridine). Figure 2.2 shows possible pathway for the competing interaction of low valent catalyst. Although turnover numbers were not given for these more highly reduced species, their formation raises the exciting possibility that a single-site catalyst can result in multielectron reductions of CO2 and even C-C bond formation.



Figure 2.2: Possible pathways for the competing interaction of low-valent catalysts with protons or CO₂ (Scibioh, 2006)

The relatively mild conditions and low overpotentials required for some of the homogeneous catalysts make them attractive for future studies; however, a number of barriers must be overcome before useful catalysts are available for fuel production (Scibioh, 2006).

2.5.3 Photochemical Reduction of CO₂

Many of the reactions described above rely on energy input either in the form of reactive bonds (alkenes, alkynes, etc.), hydrogen, or electricity. Photochemical systems, been studied in an effort to develop systems capable of directly reducing CO_2 to fuels or chemicals using solar energy. Transition-metal complexes have been used as both catalysts and solar energy converters, since they can absorb a significant portion of the solar spectrum, have long-lived excited states, are able to promote the activation of small molecules, and are robust. Carbon dioxide utilization by artificial photo conversion presents a challenging alternative to thermal hydrogenation reactions which require H_2 (Scibioh, 2006).

The systems studied for photochemical CO₂ reduction studies can be divided into several groups: $Ru(bpy)_3^{2+}$ both as a photosensitizer and a catalyst; $Ru(bpy)_3$ $^{2+}$ as a photosensitizer and another metal complex as a catalyst; ReX(CO)₃(bpy) or a similar complex as a photosensitizer; $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+-}$ type complexes as photosensitizers in microheterogeneous systems; metalloporphyrins both as a photosensitizers and catalysts; and organic photosensitizers and transition-metal complexes as catalysts. Photochemical CO₂ reduction is normally carried out under 1.0 atm CO_2 at room temperature. Therefore, the concentration of dissolved CO_2 in the solution is low (e.g., 0.28 M in CH₃CN, 0.03 M in water). These systems produce formate and CO as products. In the most efficient systems, the total quantum yield for all reduced products reaches 40%. In some cases with Ru or Os colloids, CH₄ is produced with a low quantum yield. Under photochemical conditions, the turnover number and the turnover frequency are dependent on irradiation wavelength, light intensity, irradiation time, and catalyst concentration, and they have not been optimized in most of the photochemical experiments described. Typical turnover frequencies for CO or HCOO- are between 1 and 10 h⁻¹, and turnover numbers are generally 100 or less (Scibioh, 2002).

The aforementioned molecular sensitizers can be replaced with semiconductor electrodes or particles to achieve light harvesting. These systems may use enzymes or catalysts to promote electron transfer from the semiconductor-solution interface to CO_2 or reduce CO_2 directly. Typically these reductions require a potential bias in addition to solar energy input to achieve CO_2 reduction and electrode corrosion is a major concern. This corrosion can sometimes be overcome using high CO_2 pressures.

2.6 Photosynthesis Process

Photosynthesis is a process that converts CO_2 into organic compounds, especially sugars, using the energy from sunlight. Photosynthesis occurs in plants, algae, and many species of Bacteria, but not in Archaea. Photosynthetic organisms are called photoautotroph, since they can create their own food. In plants, algae and cyanobacteria photosynthesis uses CO_2 and water, releasing O_2 as a waste product. Photosynthesis is vital for life on Earth. As well as maintaining the normal level of O_2 in the atmosphere, nearly all life either depends on it directly as a source of energy, or indirectly as the ultimate source of the energy in their food (Bryant et al, 2006).

Photosynthetic organisms are photoautotroph, which means that they are able to synthesize food directly from CO_2 using energy from light. However, not all organisms that use light as a source of energy carry out photosynthesis, since photoheterotrophs use organic compounds, rather than CO_2 , as a source of carbon (Bryant et al, 2006). In plants, algae and cyanobacteria, photosynthesis releases O_2 . This is called oxygenic photosynthesis. Although there are some differences between oxygenic photosynthesis in plants, algae and cyanobacteria, the overall process is quite similar in these organisms. However, there are some types of bacteria that carry out anoxygenic photosynthesis, which consumes CO_2 but does not release O_2 . CO_2 is converted into sugars in a process called carbon fixation. Carbon fixation is a redox reaction, so photosynthesis needs to supply both a source of energy to drive this process, and also the electrons needed to convert CO_2 into carbohydrate, which is a reduction reaction. In general outline, photosynthesis is the opposite of cellular respiration, where glucose and other compounds are oxidized to produce CO_2 , water, and release chemical energy. However, the two processes take place through a different sequence of chemical reactions and in different cellular compartments.

The general equation for photosynthesis is therefore:

$$2n \text{ CO}_2 + 2n \text{ H}_2\text{O} + \text{photons} \rightarrow 2(\text{CH}_2\text{O}) n + n \text{ O}_2 + 2n \text{ A}$$

Carbon dioxide reacts with electron donor with the presence of light energy produced carbohydrate and oxidize electron donor and release oxygen.

Since water is used as the electron donor in oxygenic photosynthesis, the equation for this process is:

 $2n \operatorname{CO}_2 + 2n \operatorname{H}_2\operatorname{O} + \text{photons} \rightarrow 2(\operatorname{CH}_2\operatorname{O}) n + 2n \operatorname{O}_2$ Carbon dioxide + water + light energy \rightarrow carbohydrate + oxygen

Other processes substitute other compounds (such as arsenite) for water in the electron-supply role; the microbes use sunlight to oxidize arsenite to arsenate (Chem Eng News, 2008).

The equation for this reaction is:

 $(AsO_3^{3-}) + CO_2 + photons \rightarrow CO + (AsO_4^{3-})$ (Kulp et al, 2008) Carbon dioxide + arsenite + light energy \rightarrow arsenate + carbon monoxide

Photosynthesis occurs in two stages. In the first stage, light-dependent reactions or light reactions capture the energy of light and use it to make the energy-

storage molecules ATP and NADPH. During the second stage, the light-independent reactions use these products to capture and reduce CO₂.

2.7 Artificial photosynthesis

Photosynthesis, the reduction of carbon dioxide into biomass using energy derived from light, is one of the most important biological processes known to mankind. In oxygenic photosynthesis, light-driven water oxidation provides the redox equivalents necessary to reduce carbon dioxide. In natural photosynthesis water oxidation occurs at Photosystem II (PSII) through the Kok cycle following absorption of four photons that result in activation of the Oxygen Evolving Complex (OEC). Carbon dioxide reduction occurs through the light-independent steps of the Calvin-Benson-Bassham cycle.

Water oxidation and carbon dioxide reduction are also key reactions in artificial photosynthesis. Solar driven water splitting into hydrogen and oxygen, 2 $H_2O \rightarrow O_2 + 2 H_2$, can provide most needed clean, renewable energy, whereas carbon dioxide reduction can diminish excessive amounts of carbon dioxide in the atmosphere.

Artificial photosynthesis is a research field that attempts to replicate the natural process of photosynthesis, converting sunlight, water, and carbon dioxide into carbohydrates and oxygen. Sometimes, splitting water into hydrogen and oxygen by using sunlight energy is also referred to as artificial photosynthesis. The actual process that allows half of the overall photosynthetic reaction to take place is photo-oxidation. This half-reaction is essential in separating water molecules because it releases hydrogen and oxygen ions. These ions are needed to reduce carbon dioxide into a fuel. However, the only known way this is possible is through an external catalyst, one that can react quickly as well as constantly absorb the sun's photons. The general basis behind this theory is the creation of an "artificial plant" type fuel source (Yarris, 2009).

2.8 Methanol

Methanol, also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits, is a chemical with formula CH₃OH (often abbreviated MeOH). It is the simplest alcohol, and is a light, volatile, colorless, flammable, liquid with a distinctive odor that is very similar to but slightly sweeter than ethanol (drinking alcohol) (NIOSH, 2008). At room temperature it is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol. It is also used for producing biodiesel via transesterification reaction.

Methanol is produced naturally in the anaerobic metabolism of many varieties of bacteria, and is ubiquitous in the environment. As a result, there is a small fraction of methanol vapor in the atmosphere. Over the course of several days, atmospheric methanol is oxidized with the help of sunlight to carbon dioxide and water (Galluci, 2007).

Methanol burns in air forming carbon dioxide and water:

 $2 \text{ CH}_3\text{OH} + 3 \text{ O}_2 \rightarrow 2 \text{ CO}_2 + 4 \text{ H}_2\text{O}$

A methanol flame is almost colourless in bright sunlight. Because of its toxic properties, methanol is frequently used as a denaturant additive for ethanol manufactured for industrial use. This addition of methanol exempts industrial ethanol from liquor excise taxation. Methanol is often called wood alcohol because it was once produced chiefly as a by-product of the destructive distillation of wood (Galluci, 2007).

Today, synthesis gas is most commonly produced from the methane component in natural gas rather than from coal. Three processes are commercially practiced. At moderate pressures of 4 MPa (40 atm) and high temperatures (around 850 °C), methane reacts with steam on a nickel catalyst to produce syngas according to the chemical equation:

$$CH_4 + H_2O \rightarrow CO + 3 H_2$$

This reaction, commonly called steam-methane reforming or SMR, is endothermic and the heat transfer limitations place limits on the size of and pressure in the catalytic reactors used. Methane can also undergo partial oxidation with molecular oxygen to produce syngas, as the following equation shows:

$$2 \text{ CH}_4 + \text{O}_2 \rightarrow 2 \text{ CO} + 4 \text{ H}_2$$

This reaction is exothermic and the heat given off can be used in-situ to drive the steam-methane reforming reaction. When the two processes are combined, it is referred to as autothermal reforming. The ratio of CO and H2 can be adjusted to some extent by the water-gas shift reaction, to provide the appropriate stoichiometry for methanol synthesis as shown below:

$$CO + H_2O \rightarrow CO_2 + H_2$$
,

The carbon monoxide and hydrogen then react on a second catalyst to produce methanol. Today, the most widely used catalyst is a mixture of copper, zinc oxide, and alumina first used by ICI in 1966. At 5–10 MPa (50–100 atm) and 250 °C, it can catalyze the production of methanol from carbon monoxide and hydrogen with high selectivity:

$$CO + 2 H_2 \rightarrow CH_3OH$$

It is worth noting that the production of synthesis gas from methane produces 3 moles of hydrogen for every mole of carbon monoxide, while the methanol synthesis consumes only 2 moles of hydrogen for every mole of carbon monoxide. One way of dealing with the excess hydrogen is to inject carbon dioxide into the methanol synthesis reactor, where it, too, reacts to form methanol according to the equation:

$$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O$$

Although natural gas is the most economical and widely used feedstock for methanol production, many other feedstocks can be used to produce syngas via steam reforming. Coal is increasingly being used as a feedstock for methanol production, particularly in China. In addition, mature technologies available for biomass gasification are being utilized for methanol production (Galluci, 2007).

CHAPTER 3

METHODOLOGY

3.1 Introduction

The purposed of this researched is to experimentally define the capability of converting CO_2 into hydrocarbon fuel, CH_3OH . Besides, the study is to analyze the potential of using photocatalytic method in converting green house gas into useful product. The experiment is done by using glass reactor and installed with photosynthesis lamp.

3.2 Research Methodology

Figure 3.1 shows summary of this research workflow. The research was started with finding the related information from the journals. Next was gathering all the material needed to run experiment such as CO_2 gas with 99.97% of purity, quartz glass reaction vessel, photosynthesis lamp and iron catalyst. The conversion of carbon dioxide into hydrocarbon fuel takes place inside the reactor. The reaction will follow the nature of chemical reaction formula as below.

$$CO_2 + 2 H_2O \xrightarrow{photosynthesis lamp} CH_3OH + 1.5O_2$$
Iron oxide

The reaction will be done in present of photo catalytic and iron as catalyst.

Products gain at the bottom of the reactor and analyze by using FTIR.



Figure 3.1: Workflow diagram

3.3 Material and Chemical

In this experiment, several chemical and material required to achieve the objective. CO_2 gas with 99.97% of purity, quartz glass reaction vessel, and photosynthesis lamp and iron catalyst are required.

3.3.1 Carbon Dioxide Gas

Carbon dioxide that will be used must more than 95% of purity. The purity of gas can affect the product composition. Handling this type of chemical must be very cautious because it can cause health hazard. Carbon dioxide is supplied by Linde Industrial Gases (Malaysia) and being pre-odered by FKKSA lab. Dealing with such gas must have certain equipment for safety. Pressure regulator for CO_2 tank must be prepared. Flow meter also required to make sure the flow of CO_2 can be control.

3.3.2 Photosynthesis Lamp

Artificial photosynthesis is required to enhance the photosynthesis process in the experiment. Metal Halide lamp with clear tubular outer bulb with high output is suggested. Higher output of the lamp can increase the rate of conversion. Thus, 1000W E40 Metal Halide Lamp suggested. This type of lamp ordered from D.S Electric (Kuantan) Sdn Bhd. Using high intensity lamp need several devices such as ballast, ignitor and capasitor. Lamp being assembles according to electrical diagram below.



Figure 3.2 Electrical diagram for photosynthesis lamp

3.3.3 Iron oxide Catalyst

Iron oxide catalyst, (Fe_2O^3) used as catalyst for the reaction. Iron oxide that used is not soluble in water or in common organic solvents. This iron oxide used has spesific gravity of 5.30. with purity of 79%. This type of catalyst is available in FKKSA laboratory.



Figure 3.3: Iron Oxide Catalyst

3.3.4 Fourier Transform Infrared Spectrometer

FTIR is being used to analyze the product achieve. Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength (wavenumber) of light. Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule.

3.4 Experimental Procedure

Operating condition: The reaction should be take place in 60 to 120 °C with at least 1 atm pressure. The reactor design should resist the operating condition. Experimental design describe in Figure 3.2 below. Flowrate of gas supplied into the reactor controlled by flowmeter. In the same time water and iron catalyst been injected into the reactor. The reaction runs for 2 hour approximately. The reactor must be installed with an exhaust fan near the lamp to remove heat that produced by lamp.



Figure 3.4: Experimental diagram

Product gained from the reaction analyze by using FTIR spectrometer. Besides that, product also been characterized by several method such as burning test, pH and temperature measurement.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experimental Results

Figure 4.1 shows the sample of product right after experiment conducted and Figure 4.2 shows the samples of produce after being settled down. Product must be left for settling, so that the catalyst that leftover after the reaction will settle down and gives clearer product.



Figure 4.1: Sample after experiment



Figure 4.2: Sample after settling

4.2 Physical Characteristic of Sample

Sample has been tested by using several devices to check pH content, temperature and others. Sample is colourless liquid and have distinctive odour. In ambient temperature, sample has lower temperature than ambient which is 19 °C. The sample also gives pH reading of 6.57. The sample has fewer tendencies to combust. According to methanol safety data sheet, 21% of methanol contains in water is less efficient to be burn. Thus this sample believed to contain less than 21% of methanol.

4.3 FTIR Analysis

Fourier transform infrared (FTIR) was used in this analysis in order to determine the functional of the product. Sample analyze from 3 different part of wavelength as below. In Figure 4.3, graph show several peaks existing within wavenumber 400 to 1000 cm⁻¹. This peak believes to be exist due to the existing of the some inert that contained in the sample such as the leftover of the catalyst.



Figure 4.3: FTIR Analysis for wavenumber 400-1000 (cm-1)

Figure 4.4 show the peak of FTIR of 1000-2000 cm⁻¹ wavenumber. In this graph only one peak existed. From analysis that been done, this peak is in Alkenes functional group stretch.



Figure 4.4: FTIR Analysis for wavenumber 1000-2000 (cm-1)

Figure 4.5 in next page shows FTIR analysis for wavenumber 2000-4000 cm⁻¹. From analysis that been done, this peak is in Alcohol functional group stretch.



Figure 4.5: FTIR Analysis for wavenumber 2000-4000 (cm-1)

The table 4.1 below show the summary of functional group that exists in the sample tested. The stretch of alcohol and alkenes had been found in the sample. Other peaks that existed in range 400 - 1000 cm⁻¹ are defined to be inert that existed while starting the FTIR analysis and inert that contained in sample which is catalyst.

Type of Functional Group	Wave number	Class of Component	Sample Wave number
	(cm ⁻)		(cm ⁻)
O–H stretching	3600–3300	Phenols, alcohols	3392.53
C–H stretching	3000–2800	Alkanes	-
C=O stretching	1750–1650	Ketones, aldehydes,	-
C C		carboxylic acids,	
		esters	
C=C stretching	1675–1575	Alkenes	1639.57
C–H stretching	1460–1350	Alkanes	-
C-O stretching	1300–950	Primary, secondary	-
		and tertiary	
		alcohols, phenols,	
		esters	
C–H bending	900-650	Aromatic	-
		compounds	

Table 4.1: Summary of Sample Functional Group

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

Study of conversion of CO_2 into hydrocarbon fuel has been successfully done. Methanol production can be achieved from CO_2 reduction by using photocatalytic method. Overall the objectives of this research have been fulfilled. Methanol which has been produce is not more than 21% of yield. Although objectives had been fulfilled, the yield of methanol production is still poor. Thus, this research still has further drive before can be acclaimed as 100% successful. From this research, the photocatalytic technique is feasible to be used but still need more enhancements. It is not impossible anymore to recycle CO_2 that produced from combustion process especially from transportation and power generation.

Sample that analyzed shows a good result for a head start experiment. Sample contains alkenes and alcohol functional group. The sample also poses almost similar characteristic with pure methanol, except the sample contain too much of water that influence the burning ability of sample.

5.2 Recommendation

Based on the result and discussion, these recommendations can be taken into consideration to upgrade future studies of conversion of CO_2 into hydrocarbon fuel

using photocatalytic technique. First of all, a proper photocatalytic reactor must be design. The reactor should follow design considerations such as can withstand high pressure and temperature. Besides, installation photosynthesis inside the reactor is recommended to boost the radiation during the reaction.

Selection of catalyst also must be considered. Catalyst selection is very important because it affect the reaction that carried out by CO_2 and water. Different catalysts give different product of each reaction. Furthermore, the yield of production also might be differ. Use different types of catalyst such as copper oxide, zinc oxide, magnesium and etc.

Other than that, parameters such as temperature, pressure and flowrates different must be highlighted. More range of sample gives the best result and analysis can be done accurately. Analyzing using different devices like gas chromatography and liquid chromatography also gives more accurate analysis.

REFERENCES

Arrhenius, Svante (1908). Worlds in the Making. New York: Harper & Brothers. 2008

Behr, Arno (1988). Carbon Dioxide Activation by Metal Complexes. 1988

Callendar, G.S. (1939). "The Composition of the Atmosphere through the Ages." Meteorological Magazine 74 1939, pg: 33-39

Chemical & Engineering News (2008). *Anaerobic Photosynthesis*. August 18, 2008, p. 36

D.A. Bryant & N.-U. Frigaard (2006). *Prokaryotic photosynthesis and phototrophy illuminated*. November 2006

D.J. Bayless, G.G Kremer, M. E. Prudich, B. J. Stuart, M. L. Vis-Shiasson, K. Cooksey, and J. Muhs (2003). *Enhanced Practical Photosynthetic CO2 Mitigation*. 2003

Eds B P Sullivan, K Krist and H E Guard (1993). *Electrochemical and Electrocatalytic Reaction of Carbon Dioxide*. 1993

Gagnon, Robert (2006). *How to convert carbon dioxide into synthetic hydrocarbon through a process of catalytic hydrogenation called CO2 hydrocarbonation*. January 17, 2006

Gallucci, F., Basile, A., Drioli, E (2002., *Methanol as an energy source and/or energy carrier in membrane processes Separation and Purification* Reviews 36 (2). 2002 pp. 175–202

Halmann, M M (1993). *Chemical Fixation of Carbon Dixoide* CRC Boca Raton. 1993

Hafizi, M (2009). Effect of Particle Size on Palm oil Waste for Production of biooil through Batch Pyrolysis Process. 2009

I.Omae (2006), Catalysis Today 115. 2006 pg 33-52

J. K. S. Wan, G. bamwenda, and M. C. Depew (1991). *Microwave Induced Catalytic Reaction of Cabon Dioxide and Water: Mimicry of Photosynthesis*. November 7, 1991

Karthik Shankar, James I. Basham, Nageh K. Allam, Oomman K. Varghese, Gopal K. Mor, Xinjian Feng, Maggie Paulose, Jason A. Seabold, Kyoung-Shin Choi, and Craig A. Grimes (2009). *Recent Advances in the Use of TiO2 Nanotube and Nanowire Arrays for Oxidative Photoelectrochemistry*. 2009

Lynn Yarris (2009). Turning Sunlight Into Liquid Fuels. Mar 2009

M. Gattrell, N. Gupta and A. Co, J (2006). Electroanal Chem. 2006 pg 1-19

Markels M., Jr. and Barber, R.T (2002). *Sequestration of Carbon Dioxide by Ocean Fertilization*. 2002, pg 122.

National Institute for Occupational Safety and Health (2008). *The Emergency Response Safety and Health Database: Methanol.* August 22, 2008 Scibioh, M. Aulice and B.Viswanathan (2002). *Photo/ Electrochemistry & Photobiology for Environment, Energy & Fuel*, 2002, 1-46, ISBN: 81-7736-101-5.

Scibioh, M. Aulice and B.Viswanathan (2006). *Carbon dioxide: Matter of Pollution* or Profit? 2006

Weart, Spencer (2009). The Carbon Dioxide Greenhouse Effect. 2009

APPENDIX A

Photocatalytic Picture



Picture 1: Photosynthesis Lamp



Picture 2: CO₂ cylinder



Picture 3: Oxygen released from the reaction



Picture 7: Valve and Pressure Gauge