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METHAN( )N DIOXIDE BY PH( )ROCESS

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ABSTRACT

The large scale of carbon dioxide emission to the atmosphere is one of the most interesting problems in the industry. The primary contributor to the greenhouse phenomenon is carbon dioxide emissions from fossil fuels of combustion. The current innovations to decrease the amounts of CO_2 in atmosphere are photocatalytic processes that also use of solar energy for reaction. This study was mainly focusing on the effect of different catalysts and medium solution on the methanol's performance. There are three types of commercial catalysts used which were titanium dioxide, zinc oxide and zeolite. The different medium of the solution are sodium hydroxide (NaOH) and water (H_2O). The characterization of morphology of catalyst is conducted by using Scanning Electron Microscope. The methanol performance is determined by using High Performance Liquid Chromatography (HPLC). From the characterization of catalyst, TiO_2 have small spherical uniform shapes are the criteria to enhance it light absorption which might be beneficial for its photocatalytic activity enhancement compared to ZnO and zeolite. TiO_2 should be selected and NaOH solution is most suitable medium of solution for the future photocatalytic reduction process of CO_2. The maximum concentration of methanol in NaOH solution was produced at 15.813×10^{-3} g/L compared to ZnO and zeolite only produced at 8.616×10^{-3} g/L and 8.557×10^{-3} g/L, respectively.

ABSTRAK

Pelepasan karbon dioksida dengan kuantiti yang banyak ke atmosfera merupakan salah satu masalah yang besar dalam industri. Karbon dioksida dari bahan bakar fosil merupakan peyumbang utama kepada fenomena rumah hijau. Inovasi semasa untuk mengurangkan jumlah karbon dioksida di atmosfera ialah dengan proses fotopemangkin yang menggunakan tenaga solar untuk berlaku reaksi. Kajian ini menekankan terutamanya kepada kesan pemangkin yang berbeza dan medium larutan yang berbeza untuk mendapatkan prestasi metanol. Terdapat tiga jenis komersial pemangkin yand digunakan iaitu titanium dioksida, zink oksida dan zeolit. Medium yang berbeza larutan iaitu natrium hidroksida dan air. Pencirian morfologi pemangkin dijalankan menggunakan Electron Microscopy Mengimbas. Prestasi metanol pula ditentukan menggunakan Kromatografi Cecair Prestasi Tinggi. Dari proses pencirian pemangkin, titanium dioksida mempunyai bentuk sfera ynag kecil adalah sesuai untuk meningkatkan penyerapan cahaya yang mungkin bermanfaat untuk peningkatan aktiviti fotopemangkin berbanding zink oksida dan zeolit. Titanium dioksida dan medium larutan natrium hidroksida perlu dipilih untuk proses pengurangan fotopemangkinan karbon dioksida pada masa hadapan. Kepekatan yang maksimum metanol boleh dihasilkan dalam natrium hidroksida ialah 15.813×10^{-3} g/L berbanding dengan zink oksida dan zeolite hanya menghasilkan 8.616×10^{-3} g/L dan 8.557×10^{-3} g/L masing-masing.

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminum Oxide
BET	Brunauer Emmett Teller
CB	Conduction Band
CFC	Chlorofluorocarbon
CH_3OH	Methanol
CH_4	Methane
CFC	Chlorofluorocarbon
CO	Carbon Monoxide
CO_2	Carbon Dioxide
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
H_2O	Water
HCHO	Formaldehyde
HCOOH	Formic acid
Hg	Mercury
HPLC	High Performance Liquid Chromatography
IPCC	Intergovernmental Panel on Climate Change
MSDS	Material Safety Data Sheet
NaOH	Sodium Hydroxide
PPM	Part Per Million
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TiO_2	Titanium Dioxide
UV	Ultraviolet
VB	Valence band
ZnO	Zinc Oxide
ZnS	Zinc Sulphate
ZrO_2	Zirconium Dioxide

LIST OF SYMBOLS

°C	Degree Celsius
°K	Degree Kelvin
H	hour
kPa	kilo Pascal
L	Liter
g	Gram
%	percentage
mm	millimeter
M	Molarity

CHAPTER 1

INTRODUCTION

1.1 Overview of Research

Carbon dioxide is the product of mineralization of organic carbon compounds in the soil. The oxidation of organic substance contained in the soil is the source of energy for soil organisms and the product of their respiration where the carbon dioxide is emitted to the atmosphere. The large scale of carbon dioxide emission to the atmosphere is one of the most critical problems of industry.

From pre-industrial the concentration of atmospheric CO_2 are increased from 280 ppm to 379 ppm in 2005. The primary contributor to the greenhouse phenomenon is CO_2 emissions from fossil fuels of combustion. The concentration of CO_2 has increased during the past year century as shown in Figure 1.1.

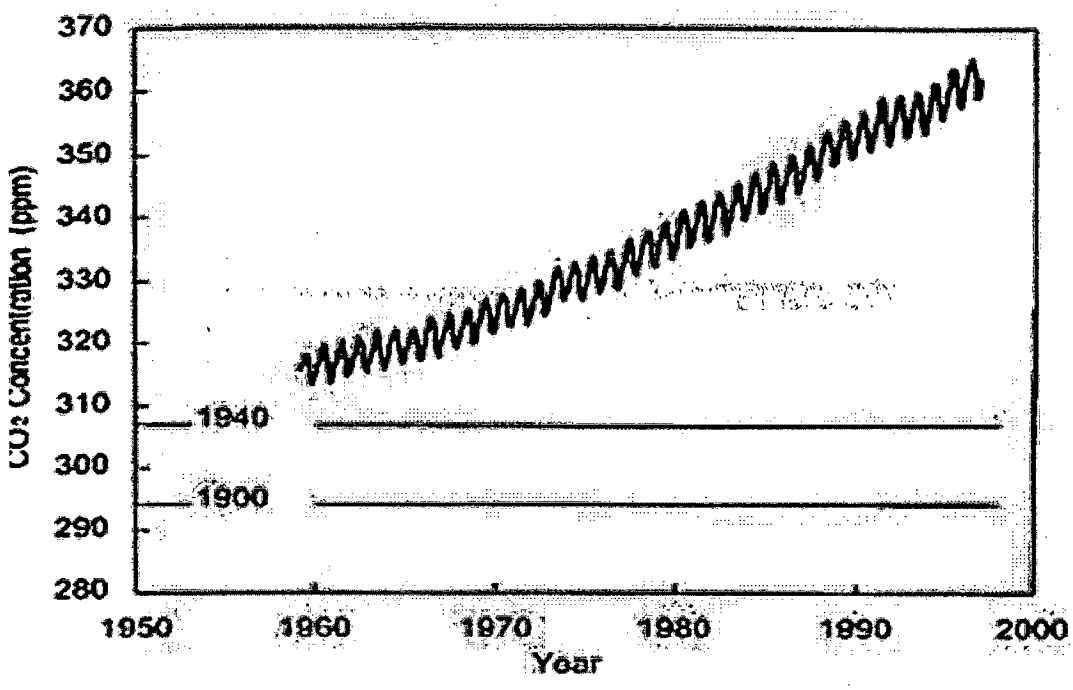

Figure 1.1 The CO_2 Concentration in Parts per Million by Year at Mauna Loa, Hawaii

(Source: Cybula et. al., 2011)

The greenhouse effect is the phenomenon where water vapour, carbon dioxide, methane and other atmospheric gases absorb outgoing infrared radiation resulting in the raising of the temperature. In its turn, CO_2 is essentially blamed to be the main factor causing the greenhouse effect because it is the most important greenhouse gas (IPCC, 2007).

In addition, reduction of CO_2 to hydrocarbons is not only desirable to weaken the greenhouse effect but also to create a renewable energy source. The energy source should be provided without producing more CO_2 such as solar energy, tidal power, wind power, biomass and nuclear energy. The best alternatives to modified CO_2 are to transform it to hydrocarbon via photocatalytic reduction within solar energy is transformed and stored as chemical energy (Ganesh, 2011).

Table 1.1 CO_2 Emissions in 2011 (million tonnes CO_2)

(Source: Ganesh, 2011)

COUNTRY	EMISSIONS 2011	PER CAPITA EMISSIONS			
		1990	2000	2010	2011
United States	5420	19.7	20.8	17.8	17.3
EU27	3790	9.2	8.4	7.8	7.5
Germany	810	12.9	10.5	10.2	9.9
United Kingdom	470	10.3	9.3	8.1	7.5
Italy	410	7.5	8.1	6.9	6.7
France	360	6.9	6.9	6.1	5.7
Poland	350	5.9	7.6	6.3	6.4
Spain	300	5.9	7.6	6.3	6.4
Netherlands	160	10.8	10.9	10.5	9.8
Russian	1830	16.5	11.3	12.4	12.8
Japan	1240	9.5	10.1	10	9.8
Canada	560	16.2	17.9	16	16.2
Australia	430	16	18.6	17.9	19
Ukraine	320	14.9	7.2	6.7	7.1
China	9700	2.2	2.8	6.6	7.2
India	1970	0.8	1	1.5	1.6
South Korea	610	5.9	9.7	12.2	12.4
Indonesia	490	0.9	1.4	2	1.1
Saudi Arabia	460	10.2	13	15.8	16.5
Brazil	450	1.5	2	2.2	2.3

The current innovations to decrease the amounts of CO_2 in atmosphere are photocatalytic processes that also use of solar energy for reaction. The used of solar energy as an energy input because it be supplied naturally and due to its abundant. The photocatalytic reduction CO_2 conversion offers for clean, low cost and environmentally friendly production of fuels by solar energy (Cybula et. al., 2011). The photocatalytic reduction of CO_2 recently as an important research in chemical technology not only for solving the problems resulting of environmental pollution but also for finding ways to maintain carbon resources (Cybula et. al., 2011).

Photocatalytic reduction of CO_2 with water over photocatalysts such as TiO_2, SiC, CdS and ZnS has been studied for the direct conversion of CO_2 into organic compounds such as CH_4, HCHO, HCOOH and CH_3OH. When the composite catalyst was used under concentrated sunlight, CH_3OH was successfully formed According to the Zhang et. al., (2009) the photocatalytic reactions could be carried out in the presence of pure TiO_2.

Carbon dioxide needs to change to the valuable product that is methanol. In this study, the effect of operating temperature, irradiation time and medium solution has been studied. Medium of solution is solution that used to dissolve the catalysts during photocatalytic reduction of CO_2 process. The performances of different type's catalysts were studied in photocatalytic reduction process. Two parameters that affect the reduction process there are effect of different medium solution and irradiation time were studied (Ganesh, 2011).

1.2 Problem Statement

This research need to be conducted due to the undeniable evidence of increasing carbon dioxide emissions. As stated by Intergovernmental Panel on Climate Change (IPCC), the earth's surface temperature has risen by approximately 0.6 K in the past century with significant warming trends over the past decades (IPCC, 2007). The primary contributor to this phenomenon is CO_2 emissions from fossil fuel combustion.

Carbon dioxide is the primary greenhouse gas that causes global warming. Moreover, the atmospheric concentration of CO_2 is continuously increasing owing to human activities. So, it is importance to reduce the emission level of carbon dioxide as well as to convert carbon dioxide to useful substances. The photocatalytic reduction of carbon dioxide to reusable hydrocarbons using water as reductant is very attractive. According to past research, the carbon dioxide could be photocatalytically reduced by water to methane, methanol or ethanol at room temperature.

The latest measurements confirm that the world's oil and natural gas supplies are running out too fast. At some time between 2010 and 2020 the world's supply of oil and gas will fall below the level required to meet international demand. Mean, the methane will run out. To overcome this problem is by creating alternatives to generate energy such as tidal power, biomass, nuclear, solar energy and wind energy. The photocatalytic reduction process is also the alternatives to convert the waste to valuable product.

1.3 Objectives

Based on overview of the research and problem statement described previously, the objectives of this research are as follows:

- To characterize the catalysts.
- To determine the performance of methanol production using different types of commercial catalysts in photocatalytic reduction of CO_2.
- To study the effect of different medium of solution between water (H_2O) and sodium hydroxide (NaOH).

1.4 Scopes of Study

In order to accomplish the objectives of this research, the following scope were drawn:

- Characterizing the catalysts by using Scanning-Electron-Microscope (SEM) method.
- To performances different types of catalysts in photocatalytic reduction process using two different parameters that affect the reaction process: effect of different medium solution and irradiation time (0-5 hours).
- Analyzing the main product (methanol) by using High Performance Liquid Chromatography (HPLC) analyzer.

1.5 Rationale and Significance

The main rationale and significance of this research includes:

- Methanol from carbon dioxide has potential to be commercialized because it is abundant supply and low cost.
- This research applies the concept of 'waste and wealth' due to abundant supply of carbon dioxide as a reactant.
- Another alternative to overcome depleting source of petroleum and fossil fuels.

CHAPTER 2

LITERATURE REVIEW

2.1 Background Study of Methanol

Methanol is the simplest of alcohol compound and is a light, volatile, colorless, flammable and slightly sweeter than ethanol (drinking alcohol). It is also referred as wood alcohol, methyl alcohol, carbinol, hydroxymethane and methylol. In 1997, 86 % of methanol was produced from natural gas, 33 % of produced methanol used in the fuel sector and 67 % by chemical industry (Yank et. al., 1931). By Methanol Institute, methanol is produced naturally in the anaerobic metabolism of many varieties of bacteria. Methanol is the most grade photó-reduced product of CO_2 because it can be transformed into another useful chemical such as gasoline by using conventional chemical technologies (Traynor & Jensen, 2002).

2.1.1 Properties of Methanol

Methanol is a hydrocarbon that made up from one carbon, four of hydrogen and one of oxygen (CH_3OH). It is a colorless liquid with a boiling point of 65 °C. The details properties of methanol are shown in Table 2.1. Methanol will mix with a variety of organic liquids as well as water and often used as solvent in industrial applications. Methanol of the raw material for many types of chemical such as formaldehyde, dimethyl terephphalate, methylamines, methyl halides, methyl methacrylate, acetic acid and gasoline ("Energy-D-Methanol"). The conversion of CO_2 into more useful organic fuels (methanol) using energy that is not produced from fossil fuels is an alternative method (Ganesh, 2011).

Table 2.1 Physical and Chemical Properties of Methanol (Source: MSDS)

Property	Value
Melting Point (°F)	-144
Boiling Point (°F)	148.3
Vapor Pressure (mmHg)	96.0
Vapor Density	1.11
Solubility in Water	Soluble
Appearance	Colorless
Odor	Alcohol smell
Flash Point (°F)	54
Specific Gravity	0.792
Percent Volatile by Volume (%)	100
Evaporation Rate	2.0
Evaporation Standard	Butyl acetate = 1
Auto Ignition Temperature	Not applicable

The inhalation of methanol vapors will cause the central nervous system depression. The symptoms of such exposure can include headaches, nausea, dizziness, drowsiness, confusion and unconsciousness. The nose, throat and other tissues of the upper respiratory system may occur irritation. Methanol has the lowest heating value of all the alcohols because it contains a higher percentage of oxygen by mass. Its heating value per gallon is approximately half of gasoline (Cassady, 1887).

2.1.2 Application of Methanol

Methanol occupies a key position in the chemical industry and the uses of methanol can divided into as a feedstock, fuel for vehicles and others. By far, the largest used of methanol is in manufacture of other chemicals. About 40 percent of methanol of converted to formaldehyde ("Thechemicalcompany," 2005). The initial step ethanol is dehydrogenated and shown in Eq. (2.1).

$$CH_3OH \Leftrightarrow HCHO + H_2 \quad (H = +84\ kJ) \qquad (2.1)$$

Hydrogen can be combusted exothermically on addition of air, resulting in the following formal equation for the oxidative dehydrogenation and shown in Eq. (2.2).

$$CH_3OH + \frac{1}{2} O_2 \rightarrow HCHO + H_2O \quad (H = -159\ kJ/mol) \qquad (2.2)$$

Methanol also can use as fuel for vehicles. The internal combustion engines within used methanol on a limited basis because it is not nearly as flammable as gasoline. Methanol is more difficult to ignite than gasoline and only can produces 1/8

of the heat. Many racing including drag racers and mud racers use methanol as their primary fuel. Methanol is also used as solvent and as antifreeze in pipelines and windshield washer fluid (Cassady, 1887).

A small amount of methanol is added to wastewater to provide a food source of carbon for the denitrifying bacteria. Through a bacteria degration process this ammonia is converted into nitrated. In the process of making biodiesel fuel, methanol is used as a component in process trans esterification. In this process, methanol is used to convert the triglycerides in different types of oils into usable biodiesel fuel (Ganesh, 2011).

2.2 Background of Carbon Dioxide (CO_2)

A Scottish chemist and physician, Joseph Black was the first identify the CO_2 in the 1750 s. He was known for his discoveries on latent heat, specific heat and CO_2. He was professor of Medicine at University of Glasgow. At room temperatures between 20-25 °C, carbon dioxide is an odorless, colorless gas which is nonflammable. The molecular formula of carbon dioxide is CO_2. The carbon is doubly bonded with oxygen atoms, O=C=O. Mainly, carbon dioxide exists in the gaseous form and it also has liquid and solid form. It can be solid at temperature below -78 °C and liquid carbon dioxide forms when carbon dioxide is dissolved in water ("Chemical Business," 2010).

The increased of atmospheric CO_2 concentration is considered as the driving factor that can causes phenomenon of global warming. After carbon dioxide, methane has the second greatest radioactive forcing among the long lived greenhouse gases and effect for 14.3 % of the global greenhouse emissions (Olivier et. al., 2006). Moreover, the data show that CO_2 content in the atmosphere is at minimum in this geological aeon. According to Georgies et. al., (2009), the understanding of the functioning of Earth complex climate system is still poor and scientific knowledge is not at a level to give definite answers for the causes of global warming.

During the last decades, global warming has been a "hot" phenomenon concerning the scientific and not only community. According to the Intergovernmental Panel on Climate Change (IPCC), it is phenomenon that experienced in recent decades where the average temperature of the Earth's near surface air and oceans increases. As stated by IPCC, the increase in globally averaged temperatures since the mid-20th century is very likely to have occurred due to increase in greenhouse concentration that leads to the warming of the Earth's surface and lower atmosphere. The greenhouse effect occurred when water vapors, carbon dioxide, methane and other atmospheric gases absorb outgoing infrared radiation resulting the increase of the temperature. The carbon dioxide is essentially blamed to be the main factor causing the greenhouse effect because it is most important greenhouse gas (IPCC, 2007).

2.2.1 Properties of CO_2

Table 2.2 Physical Properties of Carbon Dioxide

Property	Value
Molecular weight	44.01
Specific gravity (21 °C)	1.53
Critical density (kg/m^3)	468
Concentration in air (ppm)	$370,3 * 10^7$
Stability	High
Liquid	Pressure < 415.8 kPa
Solid	Temperature < -78 °C
Henry constant for solubility (mol/ kg * bar)	298.15
Water solubility (vol/vol at 20 °C)	0.9

The liquid carbon dioxide only forms at pressures above 5.1 atm. The triple point of carbon dioxide is about 518 kPa. The others forms of solid carbon dioxide at high pressure an amorphous glass like solid (Santoro et. al., 2008). There are several physical properties belong to carbon dioxide and was shown in Table 2.2.

2.2.2 Effect of CO_2 in Environment

As stated by Chemical Business, CO_2 is one of the abundant gasses in the atmosphere and plays an important role in vital plant and animal process such as photosynthesis and respiration. Due to human activities the amount of CO_2 in air has been rising extensively during the last 150 years. As a result, it has exceeded the amount in biomass, the oceans and other sinks. The troposphere is the lower layer of the atmosphere about 10-15 kilometers thick. Within the troposphere there are gasses called greenhouse gasses. When the sunlight reaches to the earth, some of it is converted to heat. The amount of heat trapped in the troposphere determines the

temperatures on earth. The most important greenhouse gasses are carbon dioxide, nitrogen oxides and methane ("Chemical Business," 2010).

According to Marta, since the industrial revolution in 1850s began human processes have been causing emissions of greenhouse gasses such as CFC's and carbon dioxide. It can affect environmental problem due to high amounts of greenhouse gasses that the earth's climate is changing because the temperatures are rising. The unnatural effect of greenhouse effect is global warming. As stated by Svante, who is the first person predicted that emission of CO_2 from the burning of fossil fuels would cause global warming. Most of CO_2 emission are derive from industrial processes in develop countries such as in the United States and Europe (Svante, n.d). Moreover, CO_2 emissions from developing countries are rising and are expected to double and affect problems.

2.2.3 Carbon Dioxide and Health

Carbon dioxide is essential for internal respiration in a human body which is oxygen is transported to body and CO_2 is carried away. CO_2 is a guardian of the pH of the blood which is essential for the survival. The primary health dangers of carbon dioxide are asphyxiation, frostbite and kidney damage. The asphyxiation is caused by the released of carbon dioxide in a confined or invented area. By this, it can lower the concentration of oxygen in the body to a level that is immediately dangerous for human health (Ganesh, 2011).