UNIVERSITI PUTRA MALAYSIA

MALAYSIAN DOLOMITE MODIFICATION FOR HYDROGEN PRODUCTION ENHANCEMENT AND CARBON DIOXIDE EMISSION REDUCTION VIA OIL PALM FROND GASIFICATION

NUR FAIZAL BIN ABDUL RAHIM

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By

NUR FAIZAL BIN ABDUL RAHIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Science

May 2014

DEDICATIONS

This thesis I highly dedicated especially to my both lovely parents, Abdul Rahim bin Nayan and Suriati binti Maun for the support that they gave me throughout my study either by morale or financial.

My beloved ones, Shazana binti Zulkifle together with my brother, Nur Farhan and my younger sister, Nur Hidayah for their enormous encouragement with no doubt on my ability for finishing this master study excellently.

Words cannot express alone my gratitude to the people above for their endless and boundless love, and most of all for their ever continuous doa for my life. Hope Allah always gives his guidance and grants them with all the goodness.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Chairman : Professor Taufiq Yap Yun Hin, PhD
Faculty : Science

As the world production of crude oil is expected to be depleted in the near future, many researchers embarked on tremendous kinds of research to find the most propitious replacement for the world current energy and hydrogen is prescribed as renewable energy with zero net greenhouse gases emission and found abundantly as a feedstock. In addition, the feedstock obtained from various source of agricultural wastes provide huge advantage for this kind of energy due to sustainable and renewable aspects. This research aimed to enhance the production of hydrogen by using gasification method by utilizing oil palm fronds as a feedstock in the presence of catalysts.

Firstly, calcined dolomite was undergone mechanochemical treatment under different media (air, ethanol and water) to deform its physical properties like surface area and grain size. The physical and chemical properties of treated dolomites were characterized by using X-ray diffraction (XRD), BET surface area (S_{BET}), thermal gravimetric analysis (TGA), field emission scanning electron microscope attached with energy dispersive X-ray (EDX-FESEM) and the catalytic test is been carried out using temperature programmed gasification (TPG). Results, the treatment improves catalytic activity significantly which can be seen from TPG spectra and H_2 cumulative bar chart. Moreover, the cumulative CO_2 substantially decreased at the end of the reaction. This is mostly due to the treatment effect especially using water as a media in milling process which increased the dolomite catalyst surface area from 13 m^2/g to 22 m^2/g made it became superior for H_2 production as well as reducing CO_2 emission from the gasification reaction.

Secondly, the modification of the dolomite was extended to the introduction of promoters on the calcined dolomite phase. Potassium (K), cerium (Ce), nickel (Ni), iron (Fe) and cobalt (Co) were all been selected for the purpose of this study. All these metals in the form of metal nitrate undergone wet impregnation method with calcined dolomite. The catalysts were denoted as K/CD, Ce/CD, Ni/CD, Fe/CD, Co/CD according to their chemical formula and CD is represented as calcined dolomite. All the catalysts been characterized by aforementioned method with additional gas product ratio (H_2/CH_4) parameter because to find out the most efficient catalyst able to give quality of the product-end. The promoters have been detected on the phase of calcined dolomite and been confirmed with XRD pattern. Meanwhile, from BET surface area result showed the pore size diameter increased which leads to increase in surface area and this confirmed by referring to the transmission electron microscopy. All dopants improved H_2 production significantly which can be seen from TPG profile where potassium dopant showed a promising result including gas product ratio study which it differs five times from the un-promoted ones. Overall, the results confirmed that the order of most active catalysts in the ascending order was CD < Ce/CD < Co/CD < Fe/CD < Ni/CD < K/CD.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PENGUBAHSUAIAN DOLOMIT MALAYSIA UNTUK MENINGKATKAN PENGELUARAN HIDROGEN DAN MENGURANGKAN PELEPASAN KARBON DIOKSIDA MELALUI PENGGASAN PELEPAH KELAPA SAWIT

Oleh

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Pengeluaran dunia minyak mentah dijangka akan habis dalam masa terdekat, ramai penyelidik telah memulakan pelbagai penyelidikan untuk mencari pengganti yang paling sesuai untuk tenaga semasa dunia dan hidrogen dikenali sebagai tenaga boleh diperbaharui dengan sifar pelepasan bersih gas rumah hijau dan boleh didapati dengan banyaknya sebagai bahan mentah. Di samping itu, bahan mentah yang diperolehi daripada pelbagai sumber sisa pertanian memberi kelebihan besar untuk tenaga ini disebabkan aspek mampan dan boleh diperbaharui. Kajian ini bertujuan untuk meningkatkan pengeluaran hidrogen dengan menggunakan kaedah penggasan dengan menggunakan pelepah kelapa sawit sebagai bahan mentah dalam kehadiran pemangkin.

Pertama, kalsin dolomit telah menjalani rawatan mekanokimia di bawah media berbeza (udara, etanol dan air) bagi mengubah bentuk fizikal seperti luas permukaan dan saiz bijian. Sifat-sifat fizikal dan kimia dolomit terawat telah dikenalpasti dengan menggunakan pembelauan sinar-X (XRD), luas permukaan BET (S_{BET}), analisis gravimetrik terma (TGA), bidang pelepasan elektron imbasan mikroskop disertakan dengan tenaga serakan sinar-X (EDX-FESEM) dan ujian pemangkin telah dijalankan dengan menggunakan suhu terprogram penggasan (TPG). Keputusannya, rawatan telah meningkatkan aktiviti pemangkin dengan ketara dan boleh dilihat dari spektra TPG dan H_2 carta bar kumulatif. Tambahan lagi, CO_2 terkumpul menurun dengan ketara pada akhir tindak balas. Ini disebabkan oleh kesan rawatan terutama menggunakan air sebagai media dalam proses pengisaran yang meningkatkan luas permukaan pemangkin dolomit daripada 13 m^2/g kepada 22 m^2/g menjadikan ia unggul untuk pengeluaran H_2 serta mengurangkan pelepasan CO_2 dari tindak balas penggasan.

Kedua, pengubahsuaian dolomit telah dilanjutkan dengan penambahan penggalak atas kalsin dolomit. Kalium (K), serium (Ce), nikel (Ni), besi (Fe) dan kobalt (Co) dipilih untuk tujuan kajian ini. Semua logam dalam bentuk logam nitrat melalui kaedah impregnasi basah bersama kalsin dolomit. Pemangkin dinamakan sebagai K/CD, Ce/CD, Ni/CD, Fe/CD, Co/CD mengikut formula kimia dan CD diwakili sebagai kalsin dolomit. Semua pemangkin telah dicirikan dengan kaedah yang disebutkan dan ditambah nisbah produk gas (H_2/CH_4) parameter bagi mengetahui pemangkin yang paling berkesan memberikan produk akhir berkualiti. Penggalak telah dikesan pada fasa kalsin dolomit dan disahkan dengan corak XRD. Sementara itu, dari hasil luas permukaan BET menunjukkan diameter saiz liang meningkat membawa kepada peningkatan dalam luas permukaan dan ini disahkan dengan merujuk kepada transmisi elektron mikroskop. Semua penggalak menambahbaik pengeluaran H_2 dan dapat dilihat dari profil TPG yang mana penggalak kalium menunjukkan hasil terbaik termasuk kajian nisbah produk gas yang berbeza lima kali dari pemangkin tanpa penggalak. Keseluruhannya, keputusan mengesahkan bahawa pemangkin yang paling aktif dalam susunan menaik adalah CD < Ce/CD < Co/CD < Fe/CD < Ni/CD < K/CD.

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I certify that a Thesis Examination Committee has met on 15 May 2014 to conduct the final examination of Nur Faizal bin Abdul Rahim on his thesis entitled "Malaysian Dolomite Modification for Hydrogen Production Enhancement and Carbon Dioxide Emission Reduction via Oil Palm Frond Gasification" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date:

DECLARATION

Declaration by Graduate Student

I hereby confirm that:

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- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
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This is to confirm that:

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LIST OF ABBREVIATIONS

ATR	Autothermal Reforming of Methane
BET	Brunauer Emmer Teller
BJH	Barret-Joyner-Halenda
CHN	Carbon Hydrogen Nitrogen
CPOM	Catalytic Partial Oxidation of Methane
DRMC	Dry reforming of Methane with Carbon Dioxide
EDX	Energy Dispersive X-ray fluorescent
F-T	Fischer-Tropsch
FWHM	Full-Width at Half Maximum
GC	Gas Chromatography
GHSV	Glass Hourly Space Velocity
GTL	Gas to Liquid
H_2-TPR	Temperature Programmed Reduction in Hydrogen
JCPDS	Joint Committee on Powder Diffraction Standard
POM	Partial Oxidation of Methane
rpm	Round per minute
RWGS	Reversed water gas shif
SEM	Scanning Electron Microscopy
SMSI	Strong Metal Support Interaction
SRM	Steam Reforming of Methane
Syngas	Synthesis gas
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetry Analysis
T_{max}	Temperature at maximum peak
TPD	Temperature Programmed Desorption
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
XRD	X-Ray Diffraction

CHAPTER I

INTRODUCTION

This chapter covers an overview on how to embark such a fascinating research which might help mankind for searching a replacement to our non-renewable fossil fuels as a main source of energy. This chapter also contains problem statements and research objectives.

1.1 Word Energy Crisis

International Energy Agency (IEA) has made a projection on energy demand for 13 different countries from the year 1997 to 2020. From the report, there was a 57% increment of energy demand within the aforementioned periods based on the 2% rate of an annual average. Based on the World Energy Outlook 2000, fossil fuels show dominant based on energy demand followed by gas, coal, nuclear, hydro and other renewable energies. These kinds of energy sources are mainly not renewable and also unsustainable. Besides of having the depletion in reservoir, the negative impact towards environment has embarked substantial researches to find a new replacement for energy; for our future generation utilization. Besides, the increasing price of the non-renewable energy especially petroleum oil refining products has raised the consumer eyebrows and the solution for this issue is crucial for most of the researchers.

1.1.1. Extensive Dependence on Non Renewable Energy

Figure 1.1 (IEA, 2000) shows the projection for energy demand from the year of 1977 up to 2020. Based from the given figure, oil is expected to have a demand up to 96 million barrels per day in the year of 2010 and the number might jump to 115 million barrels per day for the year 2020. Interest in energy saving due to realization of fossil fuels are becoming scarce is the most preferred approach (Banos *et al.*, 2011).

Energy plays a vital role in the development of both industrialization and economic growth which each require huge amount of energy (Monzano *et al.,* 2013). In addition, Xu *et al.*, (2009) stated high activities of human mobilization leads to depletion of the source. Therefore, increasing of fossil fuels consumption to meet our current and future energy demands has generated the interest on energy crisis solution. Several approaches have been used like reducing energy consumption either in industrial (Lee and Chen, 2009) or domestic (Martiskainen and Coburn, 2011) fields. However, this energy saving program which focused on reducing energy demand might not be a good choice since the problem on dependence on fossil fuels is still remains as a major drawback. Therefore, most researchers preferred the second approach which using renewable energy sources like solar energy, wind power, hydropower, bioenergy and geothermal energy. This option might be better due to sustainable in energy supply. Zhou *et al.,* (2010) asserted to achieve the goal; stand-alone systems should be made instead of solely on large-scale energy production. Hence, the development of renewable energy may be crucial for world's future.

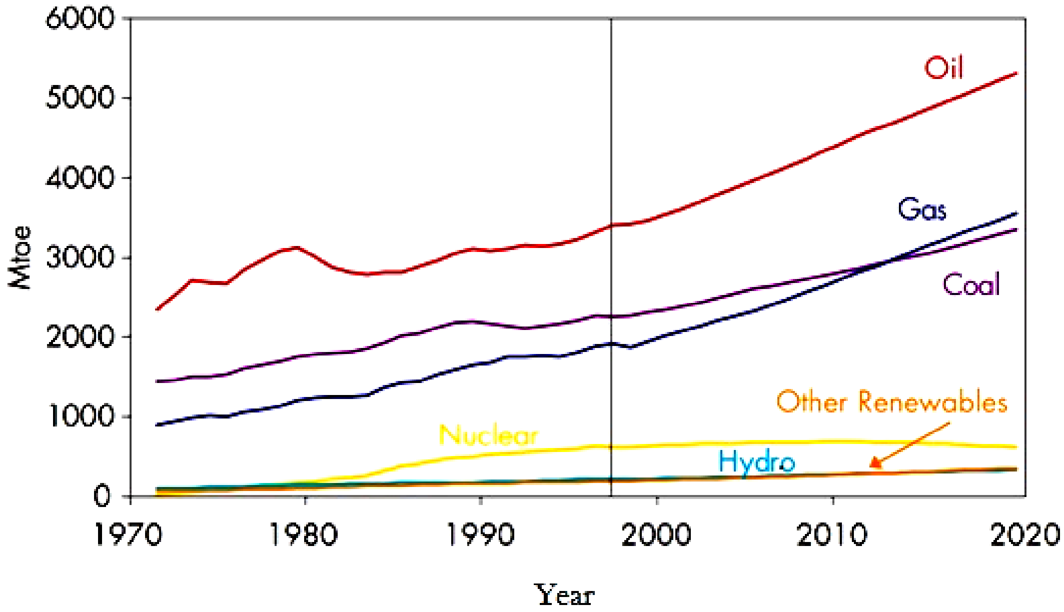

Figure 1.1 World Primary Energy Supply by Fuel, 1977-2020 (Adapted from IEA, 2000)

1.1.2. Tremendous Emission of Greenhouse Gases

Greenhouse gas is defined by gas in an atmosphere which is able to absorbs and emits thermal infrared radiation. Carbon dioxide (CO_2) and methane (CH_4) are the most abundant greenhouse gases in earth's atmosphere. Increasing in the concentration of CO_2 is mainly contributed by fossil fuels usage. According to Table 1.1, the emission of CO_2 has increased from the year 1971 to 2020 where Organization for Economic Co-operation and Development (OCED) contributes the largest portion of the total world emission (IEA, 1998) and they even showed the same increasing pattern in 2013 report (IEA, 2013).

On the other hand, Figure 1.2 reveals an increase of CO_2 concentration since the beginning of Industrial Revolution (NOAA, 2005). This persistent escalation of CO_2 concentration will jeopardize our place of living, by contributing towards global warming. Global warming or also known as climate change occurs when greenhouse gases concentration are as high as its can trap heat radiated from the earth's surface as a result of raising surface temperature of the earth (Dincer, 1998).

Table 1.1 Estimation of CO_2 emissions by region (million tons of CO_2) (Adapted from IEA, 1998)

	1971	1995	2010	2020
OECD	9031	10,763	13,427	14,476
Transition economic	3029	3135	3852	4465
China	875	3051	5322	7081
Rest of the world	1436	4791	8034	11,163
World	14,732	22,150	31,189	37,848

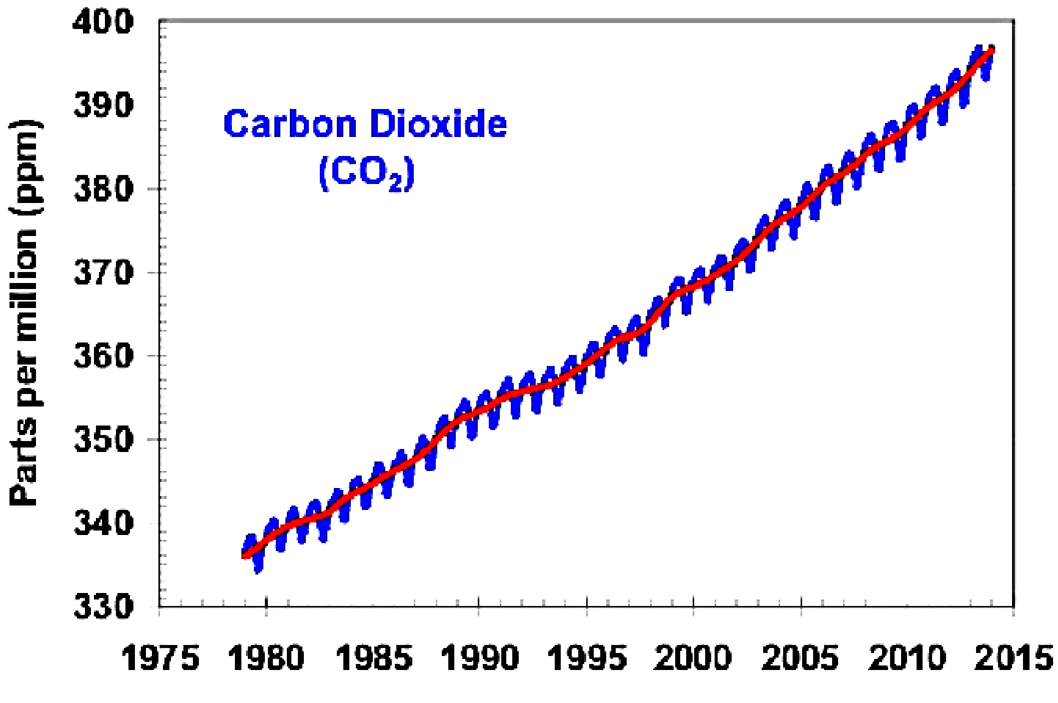

Figure 1.2 Major greenhouse gas trends from 1979 to 2010 (Adapted from NOAA, 2005)

Global warming scenario has become the primary concern for mankind nowadays and finding a solution to reduce the effect will never be imperative than before. The negatively side effect from fossil fuels utilization lead to jeopardize on human health or even life. Although global warming will not produce immediate effect, the risk of disaster and malnutrition will emerge once earth gone through a sequence of pathways like the increment in frequency and intensity of heat wave will lead to an increased in drought and floods then reduction in cold related deaths (Panwar *et al.*, 2011). Overall, this is the price that mankind should be paid due to selfishness in chasing rapid development but on the other side, neglecting our nature which provides the place of living. Table 1.2 shows the contribution made by mankind activities towards the addition of greenhouse gases concentration in the atmospheric (Aebischer *et al.*, 1989).

Table 1.2 The contribution of human activities towards global warming (Adapted from Aebischer *et al.*, 1989)

	Present Concentration	Annual growth rate (%)	Contribution in the greenhouse effect due to human activity (%)	Contribution in the greenhouse increase due to human activity (%)
CO_2	346	0.4	71	50 $\pm$ 5
CH_4	1.65	1.0	8	15 $\pm$ 5
N_2O	0.35	0.2	18	9 $\pm$ 2

1.2 Overview on Renewable Energy Prospect

Nowadays, renewable energy has attracted so much attention from all over the world because of the well known advantages and benefits. With the depletion of fossil fuels as well as its bad impact towards environment, researchers embarked on numerous numbers of studies in order to accomplish the mission. This can clearly be seen from Figure 1.3 where number of scientific publication for renewable energy sources mainly consist by biomass, solar, wind, geothermal and hydropower (Manzano *et al.*, 2013). Moreover, Figure 1.4 shows biomass as a renewable source of energy contributes the highest interest by researchers through its utilization to more valuable product (Manzano *et al.*, 2013) based on many scientific studies published in the ISI database related solely to renewable type of energy from the year 1979 to 2009.

Renewable energy sources are not only sustainable based on their supply but also have many other advantages. Banos *et al.*, (2011) stated by utilizing renewable energy at large scale not only can reduce dependence on fossil fuels but also can reduce carbon emission to the environment. Therefore, renewable energy power plant has become highly desirable (Skolund *et al.*, 2010) due to this advantage. Furthermore, for a large scale production it is safer compared to atomic power plant (Strupczewskim, 2003).

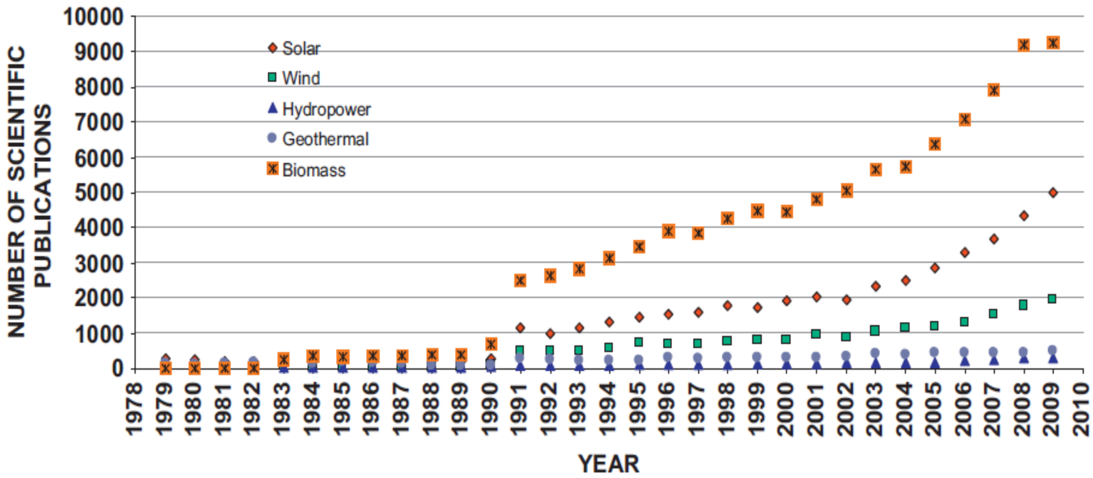

Figure 1.3 Evolution of scientific publication based on renewable energies (Adapted from Manzano *et al.*, 2013)

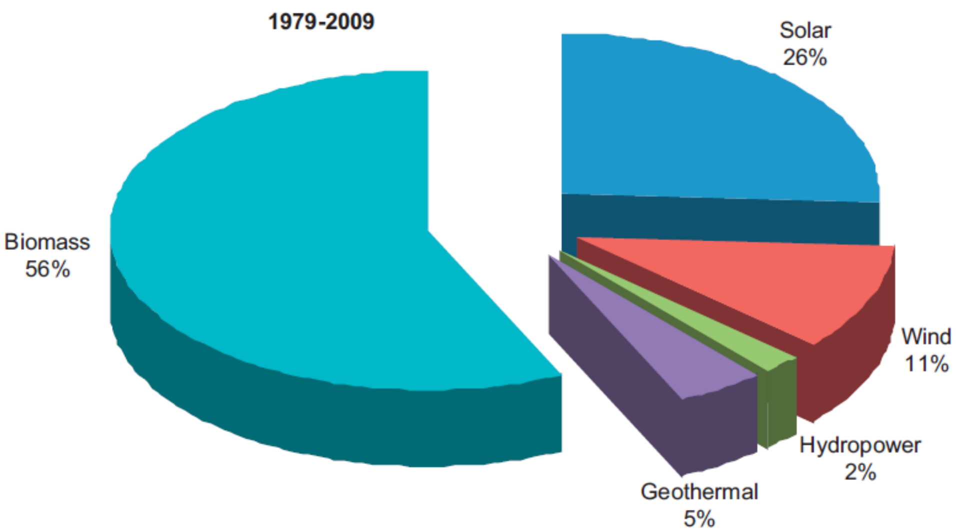

Figure 1.4 Distribution of scientific publication per renewable energy (Adapted from Manzano *et al.*, 2013)

Solar power or solar energy is a radiant energy that is produced by source of light that is the sun. The sun in average emits energy at a rate of 3.8 x 10^{23} kW, but approximately 1.8 x 10^{14} kW is intercepted by the earth (Thirugnanasambandam *et al.*, 2010). Therefore, vast development in solar energy application has been built like cooking, water heating and etc.

There are many ways to convert solar radiation into energy but the most preferred ones are active and passive solar design (Banos *et al.*, 2011). The design for passive solar system usually is built to reduce the need for artificial light and heating by capturing the sun energy. On the other hand, optimal active solar design is base on conventional water heating which use photovoltaic panels and solar cells to convert solar radiation into heat and energy, respectively. Table 1.3 shows the conventional technologies and solar power generation from the aspect of economic and carbon emission (Demirbas, 2007). Even though the cost of employing solar power is quite high, it is worthy to commercialize in the large scale when carbon emission is taking into account.

Table 1.3 Economics and emissions of conventional technologies compared with solar power generation.
(Adapted from Demirbas, 2007)

Electricity generation technology	Carbon emissions (gC/kWh)	Generation cost (US₵/kWh)
Solar thermal and solar PV systems	0	9-40
Pulverized coal-natural gas turbine	100-230	5-7

At present, wind power for electricity is no longer an irrelevant technology to be developed. This kind of energy has been used widely in many areas due to the competitive, mature and virtually pollution-free technology development (Balat, 2009). Wind technologies use wind turbines to convert the motion of the wind into mechanical power or rotational power to drive a generator and is illustrated in Figure 1.5 (Balat, 2005). Ozgener *et al.*, (2004) revealed worldwide wind energy potential is estimated to be 26,000 TWh/yr.

In addition, average wind speed of 4.5 m/s is said to potentially emit lowest CO_2 which is 2194 kg for GM-II model and 5713 kg for SICO model in the case of electricity substitution (Kumar and Kandpal, 2007).

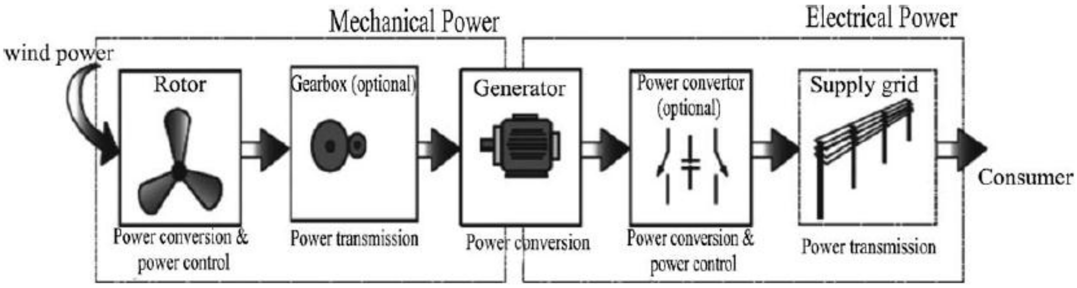

Figure 1.5 Conversion from wind power to electrical power in a wind turbine (Adapted from Balat, 2005)

The other renewable energy which worth to look into a hydropower known as hydraulic power or water power which is the largest contribution based on renewable energy resources (RESs) (Manzano *et al.,* 2013). From its name, this kind of energy source is derived from the force of moving water. Compared to wind power, water is much denser than air. Therefore, even with the slowest flow of water or moderate sea swell, it can provide considerable amounts of energy. It has been a great interest of hydropower either in developing hydropower plant model or its control system in recent decades (Kishor *et al.,* 2007). There are several types of hydropower sources like wave power, tides and stream. These sources have physical advantages and predictability which may be beneficial as an energy supply. Unlike aforementioned sources, ocean waves need to rely on wind current to pass over the open water. In 2010, World Energy Council (WEC) has made a survey regarding major country that contributed in global hydropower production. Among 160 countries, there are five who contribute almost half of the total world production which are Brazil, Canada, China, Russia and the USA.

Next is a geothermal energy that contained as the heat beneath the earth. This source of energy is considered immature from the aspect of development perhaps due to limited potential in only some parts of the world (Manzano *et al.,* 2013) and cost to build a power station is very expensive (Banos *et al.,* 2011). However, compared to solar and wind energy, this renewable energy source can provide energy for even 24 hours a day. Fridleifsson (2001) claimed geothermal energy can make a significant contribution in reducing the greenhouse gases emission. It also can be used to heat greenhouses and to provide fresh water (Mahmoudi *et al.,* 2010).

1.3 Bioenergy

On top of that, there is an energy like no other which has a huge potential to be exploited especially when considering the feedstock comes in abundant and the greener effect to the environment unlike other potential renewable energy. This is bioenergy which is defined as the energy that can be extracted from organic materials that were derived from biological sources. This later called biomass is one of the most promising renewable energy sources due to the abundant amount that can be obtained but yet it needs to prove that utilization of this kind of energy viable both technically and economically. Generally, there are two sources in which biomass can be transformed into energy. One called “First Generation” where the biomass that is suitable for food is used to convert it into energy. However, this kind of technology brings an issue on energy versus food. If this continuously happen, earth's population will suffer from hunger. Unlike above-mentioned source, the second source of biomass seems to fit for long term plan which is called "Second Generation". The second generation technology allows the use of non-food supply which can be found abundantly all over the world. There are two major kind of energy derived from biomass which are biodiesel and biogas which has attracted so much attention as future main future source of energy.

1.3.1 Biodiesel

Rudolf Diesel is a creator of the diesel engine. In 1900, he used peanut vegetable oil to demonstrate his invention in Paris. Diesel has quoted as follow:

> *The use of vegetable oils as engine fuel may seem negligible today. Nevertheless, such oils may become, in the passing years, as important as oil and coal tar presently*

The oil resources are finite and currently the price keep on increased exponentially whereas its reserves are fast depleted (Conceico *et al.*, 2005). Unrefined vegetable oil has high viscosity and usually industry use common approach such as transesterification to reduce the oil viscosity (Bala, 2005). Table 1.4 represents the physical properties of the primary chemical products from transesterification (Kralova and Sjoblom, 2010). Biodiesel is said to be biodegradable, renewable and a clean burning fuel (Panwar *et al.*, 2011). It is also beneficial to human health through reduced of particulate matter released from transportation into atmosphere during burning (Beer *et al.*, 2007).

Table 1.4 Comparison of physical properties of vegetable oil and their methyl ester preparation via transesterification (Adapted from Kralova and Sjoblom, 2010)

Properties	Oil of fat (refined)			Methyl ester		
	Viscosity (mm^2/s at 311K)	Cetane number	Flash Point (K)	Viscosity (mm^2/s at 311K)	Cetane number	Flash Point (K)
Soyabean (US)	33.1	38.1	548	4.08	46	441
Palm (Malaysia)	42.7	65	576	3.94	62	431
Rapeseed (EU)	37.3	37.5	531	4.60	47	453
Sunflower (EU)	34.4	36.7	535	4.16	49	439
Cottonseed (China)	33.7	37.1	524	3.75	42	433
Tallow (US)	32.3	75	525	4.10	58	436
Tall oil (Scandinavia)	51.0	-	485	5.30	50	461

1.3.2 Biogas

On top of that, the most potential source of energy yet not fully utilize and commercialize is a bioenergy gas which so called biogas. Biogas consists mainly of CH_4 (40-70%), CO_2 (30-60%) and other gases (1-5%). On the other hand, its calorific value is about 16-20 MJ m^{-3} (Kurchania *et al.*, 2010). Biogas has so many advantages if we compared to other renewable energy alternatives. It can be processed from feedstock to product when needed and can be stored at ease. Similar to natural gas, biogas can be distributed from the same infrastructure and can be used within the same application similar to natural gas (Nielsen *et al.*, 2009). Berglund and Borjesson, (2006) has made an assessment regarding the energy performance of biogas production from its life cycle. He claimed that biogas as transportation fuels, cooking or even commercial utilization is similar as natural gas and can be also used directly. Figure 1.6 represents the overview of the biogas system (Borjesson and Berglund, 2006). The arrows indicate energy flows, material flows and emission from the system.

In recent years, thermochemical conversion of biomass has attracted special attention due to the foreseen prospect in the near future by utilizing biomass through this method either by gasification or pyrolysis as described in Figure 1.7 (Bulushev *et al.*, 2011). Kalinci *et al.,* (2009) has described pyrolysis is a heating process that used biomass as a feedstock in the absence of air where bio-oils, char and tar can be collected as the end-product. Meanwhile gasification is heating biomass at very high temperature and disengages with combustible gas or gasification agents where in this regard, usually air, steam or water are preferred. Bio-oil is a liquid product from pyrolysis of biomass and it can be converted catalytically to give better end-product that can be used as a fuels or fuels additives. On the other part, gasification approach is considered as a promising method which gives bright prospect from the product-end like hydrogen due to wide application can be used. Plus, the syn-gas can undergo further process for Fischer-Tropsch diesel fuel. Thus, this method will be discussed in the next chapter.

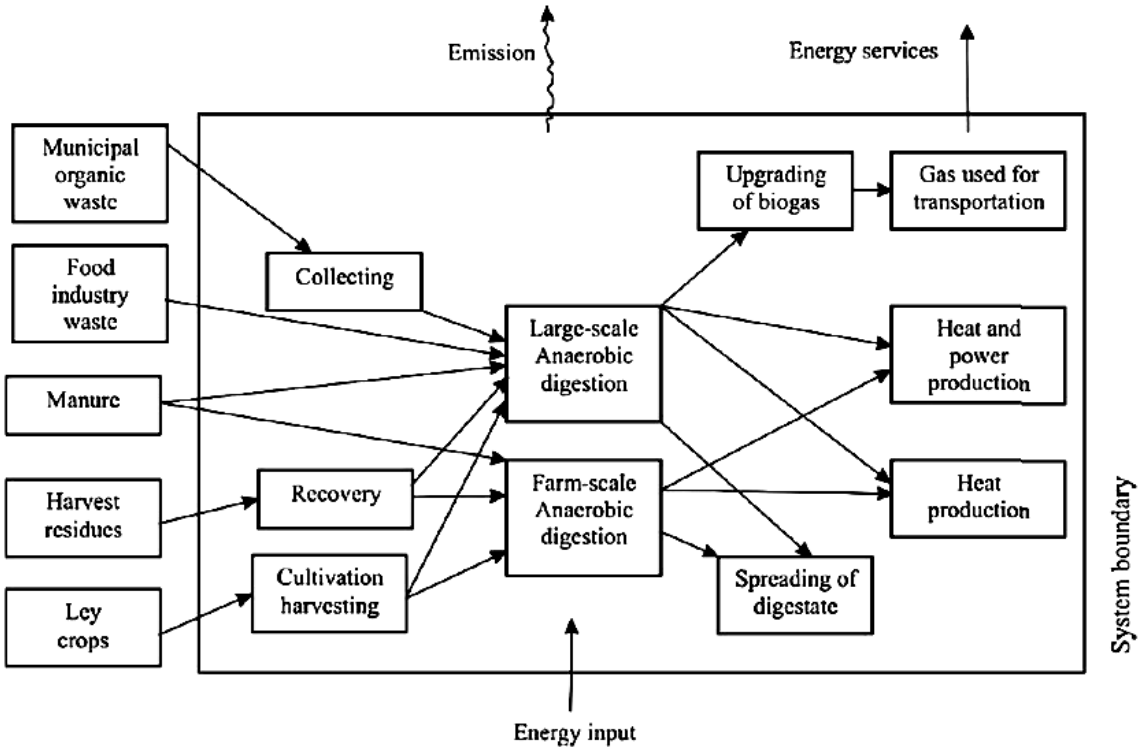

Figure 1.6 Overview of biogas system
(Adapted from Borjesson and Berglund, 2006)

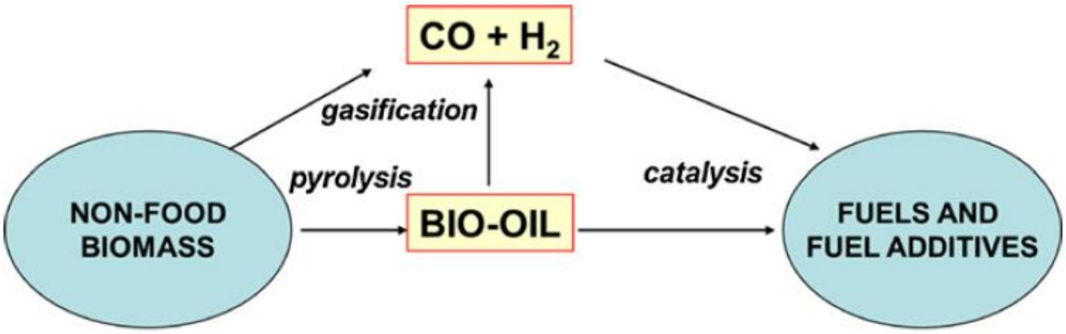

Figure 1.7 Thermochemical catalytic approaches from non-food biomass to fuels additives
(Adapted from Bulushev *et al.*, 2011)

1.4 Development of Catalyst towards Hydrogen Production Enhancement

Ostwald was the first to propose the basic definition of a catalyst in late 1894. The term catalyst carried the meaning of a substance that can hasten or speed up the rate of chemical reaction without itself being consumed. In other words, catalyst can transform the reactants into products without interrupting any part of the cycle in elementary steps and the utmost advantages that can be regenerated prior to its lifetime. Basically, there are three types of catalysts which are homogeneous, heterogeneous and enzymatic. However, this case study emphasized more on the heterogeneous catalysts due to the advantages served during the reaction and the ability of regeneration of the catalysts. Heterogeneous catalysts are defined as those catalysts in the different or separate phase than the reactants. According to Dumesic *et al.,* (2008) the condition of catalysts especially in solid form can easily be separated and recycled whenever the reactants and the products are in neither gas nor liquids phases. There is vary in reported literature about one catalysts compared to another. The researchers tried to find out the most superior catalyst to be commercialized. Fundamentally, there are seven criteria that the catalysts should have which are described in Figure 1.8 (Sutton *et al.,* 2001).

Basically, all the catalysts are grouped under two major types which are primary catalysts and secondary catalysts. These groups are depending on their position in the catalytic reactor relative to the gasifier. Primary catalysts is added either by wet impregnation or dry mixing with the biomass material in order to reduce tar formation and also to have a little effect in C_{2-3} hydrocarbon and methane conversion to syngas. On the other hand, second catalyst was placed in the reactor after the gasifier which purposely to reform hydrocarbon and methane. Sutton *et al.,* (2001) classified catalysts into three distinct groups which are dolomite catalysts, alkali metals and other metal catalysts and nickel catalysts. Moreover, Dayton (2002) grouped the catalysts under three types which are alkali metals, non-metallic oxides and supported metallic oxides. However, most important thing is that the function of the catalysts under certain condition of operation and their effectiveness as catalysts towards formation of desired products.

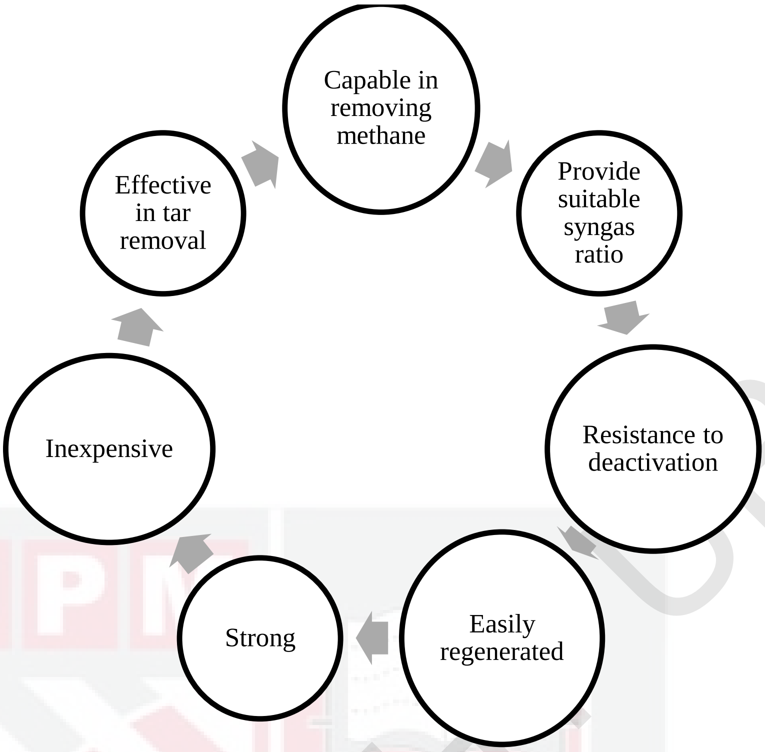

Figure 1.8 Fundamental of catalysts criteria for gasification reaction (Adapted from Sutton *et al.*, 2001)

The most metal that has been exploiting for the gasification purposes is the nickel catalyst either as standalone catalyst or modified with other metal to improve its reactivity and resistant to deactivation. Nickel catalysts took part in the primary bed catalyst in order to reduce the formation of tar. However, nickel catalyst is always limited by its vast deactivation caused by several factors which are chlorine, sulfur and alkali metals that contains in the feedstock which also act as the catalyst poison. On the other hand, catalyst attrition and formation of coke led to reducing the reactivity of nickel catalyst towards tar conversion activity. Thus researchers are improving the reactivity and strength of nickel by promoting it with active metals to overcome the nickel problem related to deactivation of nickel activity towards tar reduction.

The effectiveness of 11 wt. % Ni/Al_2O_3 has been studied compared to activated alumina, dolomite, silica carbide and silica alumina in the activity of tar decomposition by Simell and Bredenberg (1990). Base on the study, tar and light hydrocarbon was almost completely reduced at temperature of 900 ^oC. Moreover, by introducing several supports catalyst like TiO_2, Al_2O_3, SiO_2 and ZrO_2 has clearly improved the activity of nickel where the most effective combination is $5\%Ni/TiO_2$ that led to tar conversion up to 98% at 800 ^oC (Sutton *et al.*, 2003).

On the other hand, Dou *et al.*, (2003) studied tar cracking by using 1-methylnaphthalene as a tar model. All five tested catalysts (alumina supported NiMo, alumina, silica, lime and Y-zeolite) showed impressive result in which NiMo/Al_2O_3 and Y-zeolite were the superior ones decomposing about almost 100% of tar at temperature above 500 ^oC. However, even though the high conversion of NiMo – alumina supported about 100 %, after 9 h on-stream the conversion dropped down to 80 % and most probably due to catalyst deactivation. Thus, the durability of Nickel based catalyst in the long term remained the biggest challenge to be exploited to commercial level.

Beside nickel catalysts, other catalysts such as iron based catalysts are also interesting to be studied such as iron oxide, ankerite, sintered iron ore and pelletized iron ore. Among other iron oxides like FeO, Fe_2O_4, and Fe_3O_4, hematite (Fe_2O_3) show almost 100 % tar decomposition at 900 ^oC by using Swedish birch as a feedstock in fluidized bed (Nordgreen *et al.*, 2006). Meanwhile, according to Leppalahti *et al.*, (1991), the addition of iron into the dolomite (4.6 wt. % of Fe) showed higher activity compared to sintered iron ore (59.2 wt. % of Fe). The difference in the activity is most likely due to the calcium contained in the catalysts where Fe-dolomite has 19.2 wt. % and sintered iron ore has only 5.4 wt. %. The CaO contained in the dolomite is believed to be an active component in tar reduction activity. This will be discussed later in details in the next chapter.

In term of abundant and inexpensive catalysts, there are about three catalysts that could show great success either in increasing the syngas production or reducing tar. Three natural minerals are limestone, olivine and dolomite where each has the advantage over one another prior to their capability in their function during the reaction. Apparently, pretreatment of these natural source catalysts provide better activity in increasing the H_2 gas. The agreement showed from the study made by Hu *et al.*, (2006) where four catalysts (calcined dolomite, un-calcined dolomite, calcined olivine and un-calcined olivine) were tested as a secondary catalyst for gasification of apricot stone. In conclusion, calcined dolomite showed superior in enhancing the product gas amount. However, if tar conversion is taking into the account, the Fe contained in the dolomite somehow influence its activity. According to Orio *et al.*, (1997) the activity in tar conversion increased as the Fe_2O_3 content increased in the catalysts as well as the increased in pore diameter.

1.5 Problem Statements

As described earlier, fossil fuels which meet massive energy demands nowadays will be depleted and the combustion of this energy especially from the transportation sector is the major contribution for global warming. That is the reason of why many researchers come out with several options for future energy resources. Therefore, this study is meant to make a resolve in finding the potential replacement of current energy. Among all the renewable energy resources, biomass looks the most promising ones which the product-end which is hydrogen brings the bright prospect to be developed. Malaysia itself consists of enormous in agricultural waste especially for their oil palm sector. However, there is no complete technology for the commercialization nowadays and the yield of hydrogen is also low. Thus, the source of biomass and the route of the process have been discussed thoroughly in this writing.

There are many methods that can be utilized for the production of hydrogen from biomass and the most attractive ones is gasification. However, the challenges majorly due to presence of the unwanted product, tar. At present, catalytic gasification seems to be the better choice to reduce the tar yield. Therefore, the choice of the catalyst and developing high resistant from any factors of catalyst deactivation is crucial. On the other hand, Malaysian dolomite catalysts seem can provide dual function during gasification reaction as a result, the function is discussed in thorough. This report will provide comprehensive understanding of catalyst role and how to improve the hydrogen yield with two modifications done in order to achieve the goal.

1.6 Objectives

The objectives of this research are:

1. To prepare and carry out mechanochemical treatment and impregnation method to add the promoters as series of modification on Malaysian dolomite catalyst in order to enhance catalytic activity.

2. To characterize and study the physical and chemical properties for each catalysts used throughout the research by using scientific techniques such as thermogravimetry analysis (TGA), X-ray diffraction (XRD), Brunauer-Emmet Teller surface analyzer (BET) and etc.

3. To produce hydrogen from oil palm fronds by using catalytic gasification approaches.

4. To evaluate the effectiveness of modified catalysts by investigating from hydrogen production as well as carbon dioxide emission based on temperature programmed gasification (TPG) profile.

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