PYROLYSIS OF AGRICULTURAL WASTE: EFFECT OF CATALYST APPLICATION

NUR FARHANIM BINTI MUSTAFFA

BACHELOR OF CHEMICAL ENGINEERING (GAS TECHNOLOGY)
UNIVERSITI MALAYSIA PAHANG

Thesis Access Form

No____________________________Location______________________________

Author : NUR FARHANIM BINTI MUSTAFFA

Title : PYROLYSIS OF AGRICULTURAL WASTE : EFFECT OF CATALYST
APPLICATION

Status of access :OPEN / RESTRICTED / CONFIDENTIAL

Moratorium period:______________ years, ending___________/_______200____

Conditions of access proved by (CAPITALS): DR RUZINAH ISHA

Supervisor (Signature)………………………………………………

Faculty: FKKSA

Author’s Declaration: *I agree the following conditions:*

OPEN access work shall be made available (in the University and externally) and reproduced as necessary at the discretion of the University Librarian or Head of Department. It may also be copied by the British Library in microfilm or other form for supply to requesting libraries or individuals, subject to an indication of intended use for non-publishing purposes in the following form, placed on the copy and on any covering document or label.

The statement itself shall apply to ***ALL*** *copies:*

This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

Restricted/confidential work: All access and any photocopying shall be strictly subject to written permission from the University Head of Department and any external sponsor, if any.

Author's signature……………………………………….Date: ………………………………

users declaration: for signature during any Moratorium period (Not Open work):
I undertake to uphold the above conditions:

Date	Name (CAPITALS)	Signature	Address

PYROLYSIS OF AGRICULTURAL WASTE: EFFECT OF CATALYST APPLICATION

NUR FARHANIM BINTI MUSTAFFA

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JUNE 2013

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

Signature :
Name of main supervisor : DR. RUZINAH ISHA
Position : SENIOR LECTURER
Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : NUR FARHANIM BINTI MUSTAFFA
ID Number : KC09060
Date : JUNE 2013

Dedication

To my beloved parents,

Mustaffa bin Ahmad
Siti Rahani binti Abu Bakar

ACKNOWLEDGEMENT

Assalamualaikum wbt…

First and foremost, thank you Almighty Allah S.W.T for giving me strength, health and guidance so that I am able to complete this research project. The most appreciated person would be my supervisor Dr. Ruzinah Isha for her patience, help, support and guidance through the process. Without her help, it is impossible to carry out this research from scrap until it is finally complete.

I also would like show my appreciations to all my friends in University Malaysia Pahang especially to those who have always believe in me, pushing me to the limits and never allow me to give up. For Noor Hana Yusof , Nur Sakinah Saad and Wan Norain Awang Long, thank you so much and I would never forget your deeds. My friends who always supports me from far and always being with me through thick and thin, thank you so much for the supports and motivations.

Not forgotten, I would also like to thanks the technical staffs in Chemical & Natural Resourcess Engineering Laboratory, especially En. Masri, En. Razak, En. Firdaus, En. Marzuki and Madam Fadhilah for their help in term of apparatus, equipments, times, experiences and advices.

Last but not least, to my family especially my parents, En. Mustaffa Ahmad and Pn. Siti Rahani Abu Bakar for their advices, supports and loves.

ABSTRACT

Fuel gas can be produced from the pyrolysis process of biomass. Fuel gas is a clean and renewable energy thus becoming a very suitable energy that can replace the fossil fuels for example hydrogen and methane. The abundant quantity of agricultural waste in Malaysia especial palm oil waste made this process even more promising. This research is aimed to produce high yield of fuel gas with a coke resistance catalyst. Palm oil wastes were used as samples in this research which are empty fruit bunch (EFB) and palm oil fibre (POF). The catalysts used were nickel alumina, doped with Cerium, $Ni/Ce/Al_2O_3$ and Aluminium Oxide doped with Calcium, Ca/Al_2O_3. The reactor used was tubular reactor type; quartz reactor which was then placed in tubular furnace for heating purposes. The temperature for the pyrolysis to take place efficiently is at 700 ^oC. At higher temperature, the gas produced is higher. Pre-test of pyrolysis by using Thermo gravimetric Analysis (TGA) was done first prior to experimental lab scale was carried out. The production of gas can be determined from the pre-test. From the analysis, POF has lower solid residue content with only 18.33 wt% than 22.78 wt% of EFB. It seems that POF has better performances than EFB due the low content of char. Thus, the experimental lab scale was carried out by using POF samples. The production of fuel gas from this process was recorded and analysed by using portable gas analyzer and thermo gravimetric analysis (TGA). The result was analysed based on the fuel gas produced. From the analysis, Ca/Al_2O_3 produces high CO_2 and has higher percent of solid content compared to $Ni/Ce/Al_2O_3$. In the experiment, $Ni/Ce/Al_2O_3$ produces more fuel gas compared to Ca/Al_2O_3. It can be deduced that the application of $Ni/Ce/Al_2O_3$ produces more gas than non-catalytic process.

ABSTRAK

Gas bahan api boleh dihasilkan daripada proses pirolisis bio jisim. Gas bahan api adalah tenaga bersih dan boleh diperbaharui oleh sebab itu, ia menjadi tenaga yang sangat sesuai yang boleh menggantikan bahan api fosil sebagai contoh hidrogen dan metana. Kuantiti sisa pertanian yang banyak terutamanya di Malaysia seperti sisa kelapa sawit menjadikan proses ini lebih menarik untuk dikaji. Kajian ini bertujuan untuk menghasilkan gas bahan api yang tinggi dengan pemangkin rintangan kok. Sisa kelapa sawit digunakan sebagai sampel dalam kajian ini iaitu tandan kosong (EFB) dan serat kelapa sawit (POF). Pemangkin yang digunakan adalah alumina nikel, disalutkan dengan Serium, $Ni/Ce/Al_2O_3$ dan Aluminium Oksida disalutkan dengan Kalsium, Ca/Al_2O_3. Reaktor yang digunakan adalah jenis reaktor tiub; reaktor kuarza yang akan ditempatkan di dalam relau tiub untuk tujuan pemanasan. Julat suhu pirolisis yang efisien adalah pada 700 ^{o}C. Pada suhu yang lebih tinggi, gas yang dihasilkan adalah lebih tinggi. Ujian pra pirolisis dengan menggunakan Thermo gravimetrik Analisis (TGA) dilakukan terlebih dahulu sebelum eksperimen berskala makmal telah dijalankan. Dengan cara itu, pengeluaran gas boleh diramal dari ujian pra ini. Daripada analisis, POF mempunyai kandungan sisa pepejal yang lebih rendah dengan hanya 18.33 % berat daripada 22.78 % berat EFB. Didapati POF mempunyai prestasi yang lebih baik daripada EFB kerana mengandungi arang yang rendah. Oleh itu, skala makmal eksperimen telah dijalankan dengan menggunakan sampel POF. Pengeluaran gas bahan api dari proses ini direkodkan dan dianalisis dengan menggunakan gas penganalisis dan termo gravimetrik analisis (TGA). Produk eksperimen telah dianalisis berdasarkan gas bahan api yang telah dihasilkan. Berdasarkan analisis, Ca/Al_2O_3 menghasilkan CO_2 dan kandungan arang yang lebih tinggi berbanding dengan $Ni/Ce/Al_2O_3$. Dalam eksperimen ini, $Ni/Ce/Al_2O_3$ menghasilkan lebih gas bahan api berbanding Ca/Al_2O_3. Kesimpulannya, penggunaan $Ni/Ce/Al_2O_3$ menghasilkan lebih gas daripada proses bukan pemangkin.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

%	Percent
<	Less than
>	More than
µ	Micro
cm	Centimetre
g	Gram
min	Minute
MJ/m^3	Mega Joule per metre cube
ml/min	Millilitre per minute
mm	Millimetre
^oC	Degree celcius
$^oC/min$	Degree celcius per minute
psi	Unit of pressure
wt%	Weight percent
$Ca(OH)_2$	Calcium hydroxide
Ca/Al_2O_3	Calcium aluminium oxide
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
CeO_2/SiO_2	Cerium oxide with silicon oxide
CH_4	Methane
CO_2	Carbon dioxide
H_2O	Water
Ni	Nickel
Ni/Al_2O_3	Nickel aluminium oxide
$Ni/Ce/Al_2O_3$	Nickel cerium aluminium oxide
Pt	Platinum
Pd	Palladium
Ru	Ruthenium
$Ru/CeO_2/SiO_2$	Ruthenium cerium oxide silicon oxide

LIST OF ABBREVIATIONS

EFB	Empty Fruit Bunch
FFB	Fresh Fruit Bunch
MPOB	Malaysian Palm Oil Board
MSW	Municipal Solid Waste
POF	Palm Oil Fibre
POME	Palm Oil Mill Effluent
TGA	Thermo gravimetric Analysis
WGS	Water Gas Shift

1 INTRODUCTION

1.1 Motivation and statement of problem

Fuels that we used nowadays come from the hydrocarbon that is formed for hundreds of years ago. This energy resource is not renewable and is depleting. Hydrocarbons are also causing green house effect and bad environmental issue. Emissions from fossil fuel usage significantly degrade air quality all over the world. The resulting carbon byproducts are substantially changing the world's climate.

Unfortunately, the demand for energy is growing but the raw materials for the fossil fuel economy are diminishing. If oil, coal, and natural gas supplies are not replenished as it is consumed, so an alternative must be found. Because of that, people have been searching for new energy source that is renewable, clean for the environment, free and have the same promising quality as fossil fuels.

Hydrogen and methane are one type of fuel gas. It is a type of energy that is renewable, clean, safe and economically competitive with gasoline or diesel .Hydrogen also can help prevent the depletion of fossil fuel reserves .Hydrogen production plays a very important role in the development of hydrogen economy. One of the promising fuel gas production approaches is conversion from biomass, which is abundant, clean and renewable. Alternative thermo chemical (pyrolysis and gasification) and biological (biophotolysis, water–gas shift reaction and fermentation) processes can be practically applied to produce fuel gas. (Ni et al, 2006)

Pyrolysis is a process where oil and gas are produced from biomass. In Malaysia for instance, has a big agricultural industry and resulted to come with a lot of issue with the waste. Thus, pyrolysis of agricultural waste is able to create a new renewable energy that is safe, environmental friendly and economic. It also helps to reuse the agricultural waste. In this study, the sample is used based on the waste product from the palm oil agricultural industries.

To upgrade pyrolysis, catalyst can be added to enhance the production of the gas. But unfortunately, catalysts are exposed to problem of coking and tar formation. Tar formation can decrease the function of the catalyst thus causing the production of gas or oil to be less. To overcome this problem, catalysts are doped with metal transition to avoid the formation of tar thus creating a good coking resistant metal.

Production of fuel gas by using catalytic pyrolysis has been done for a long time. Fuel gas production of pyrolysis is always being compared with other production by using steam reforming and gasification. A review on hydrogen production of steam reforming and pyrolysis shows more hydrogen yield using pyrolysis compared to steam reforming. (Mann et al, 1997) And the review of hydrogen production technologies in Malaysia shows, biomass pyrolysis has the lowest cost in the production of fuel gas energy. (Khan et al, 2010).

1.2 Objectives

The objective of this research is to study the effect of catalyst on fuel gas production.

1.3 Scope of this research

This pyrolysis was carried out by using palm oil fibre and EFB as the feedstock. This was because both of it are low priced and abandoned material from palm oil milling process (Azizan, et.al, 2009). The catalyst used was $NiCeAl_2O_3$ and $CaAl_2O_3$. To avoid the coke formation on the catalyst, two metal transition are going to be use to test for their performances with the catalyst which are Calcium and Cerium. The gaseous product from the pyrolysis was analyzed by using gas analyzer. The element of composition of the gaseous was identified. The best coke resistance metal and the high yield of fuel gas produced is the main target in this research.

1.4 Significant and Rationale

As the fossil fuel prices has risen day by day due to the depleting resources, it is best to find another fuel sources that can replace the non renewable energy. By producing fuel gas using pyrolysis process, biomass waste can be turned from pollution problem into energy supply. This type of energy will have lower cost compared to the fossil fuels due to the abundant availability of the raw material which is agricultural waste. This study also can help to identify the potential catalyst to be used in pyrolysis that able to produce fuel gas.

2 LITERATURE REVIEW

2.1 Overview

This thesis presents the experimental study of catalytic pyrolysis using agricultural waste. In this topic, the study is focusing on the effects of catalyst type towards the production of fuel gas.

2.2 Introduction

Hydrogen is an attractive clean energy carrier. Production of hydrogen by steam reforming of natural gas is the most widely used in industrial process because of its economic feasibility. However, reforming process produces significant amount of carbon dioxide and thereby contributes to the global warming. The inter-related problems between energy and environmental issues are among the biggest challenges today, in particular energy sustainability and carbon emission from fossil fuels. For this reason, renewable biomass becomes an attractive alternative energy resource. There is abundant biomass on the earth, such as energy crops, agricultural residues, forestry residues, industrial and municipal wastes, etc. Since biomass absorbs the same amount of carbon during its grow-up as it consumed as fuel, production of hydrogen from biomass could be critical for the energy and environmental sustainability. Extensive investigations of hydrogen production from biomass have been carried out in the past decades .There are several technologies available for the production of hydrogen from biomass, such as syngas from gasification, hydrogen, bio-oils and char from pyrolysis, and hydrolysis of cellulose for sugar monomer. (Qinglan et al, 2010)

2.3 Renewable Energy

Fossil fuels have become the source of energy for a long time. Either natural gas or even crude oil, engineers have been fought to find more gas wells around the world to ensure the sustainability of fossil fuels. However, sooner or later, there will be no more gas wells. Fossil fuel is one type of non renewable energy which is the energy that cannot be reuse or reproduce due to its limited quantity and will vanish fifty to sixty years from now. Other types of non renewable energy are coal and nuclear. Apart from not being able to regenerate in a short time, these types of energy are not environmental friendly. Non-renewable sources release toxic gases in the air when burnt which are the major cause for global warming. Last but not least, since the non-renewable energy will be depleted, the prices for the energy are increasing throughout the days.

On the other hand, renewable energy is easily regenerated. This is unlike fossil fuels which are perishable once used. The sun, water, wind and biomass are available in the abundant quantity and free to use. The non-renewable sources of energy that we are using are limited and are bound to expire one day. Renewable sources have low carbon emissions, therefore they are considered as green and environment friendly. Renewable helps in stimulating the economy and creating job opportunities. Nowadays, a lot party has shown interests in the renewable energy including the private company and the government bodies. There are a lot of incentives givens to any party that try to come out with new renewable technology such as solar panel or hydrogen energy.

2.4 Biomass

Biomass is biological material derived from living or in the context of energy it is often used to mean plant based material. Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, oxygen, nitrogen and also small quantities of other atoms. Biomass contains stored energy. That's because plants absorb energy from the sun through the process of photosynthesis. When biomass is burned, this stored energy is released as heat. Burning biomass releases carbon dioxide. However, plants also take carbon dioxide out of the atmosphere and use it to grow their leaves, flowers, branches, and stems. That same carbon dioxide is returned to the air when the plants are burned.

2.4.1 Biomass in Malaysia

The main sources of biomass in Malaysia are domestic wastes (MSW), agricultural residues, animal wastes, effluent sludge which is waste water and wood chip. Figure 2-1 shows the overall biomass in Malaysia. Based from the figure, it is shown that agricultural wastes are the biggest biomass source in Malaysia compared to municipal waste.

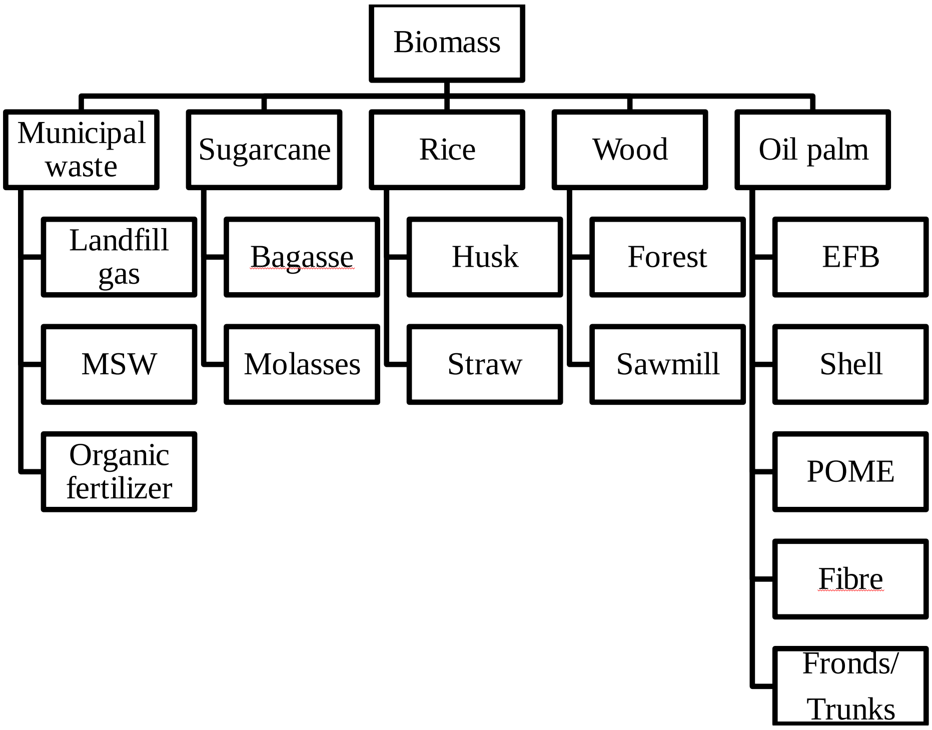

Figure 2-1 : Biomass in Malaysia
(Source: STAR Graphic 2012)

Agricultural waste is one form of biomass which is readily available but unfortunately it is largely not utilized in energy recovery schemes. (William and Nugranad, 1999). Most of the wastes are usually used for other purposes. For example, Oil Palm Fibres are used to make various fibre composites such as furnitures, infrastructures, and mattress. According to MPOB (2009), Malaysia produced 17.86 million tonnes of crude palm oil in year 2009 alone. This data derived from 100 million tonnes of EFB which produce 25 million tonnes of oil palm fibre (Hoong Chan Trading, 2009). It would be such a waste if these wastes are not tested for energy recovery process. The potential of agricultural residues for energy production has been investigated by many researchers (Perez and Cortez, 1997; Natarajan et al., 1998; Liet al., 1999; Di Blasi et al., 1999; Sensoz et al., 2001) and the results are very encouraging

Empty Fruit Bunch (EFB) is the waste component come after Fresh fruit Bunch (FFB) which were thrown away from palm oil mill. In the palm oil milling process, one tonne of FFB produce about 0.22 tonne of EFB (Wingkis, 1998).

Table 2-1 : Availability of EFB in Sabah

(Source: Malaysia Oil Palm Statistics 2008)

Year	FFB*	EFB*
2003	24,200,332	5,324,073
2004	24,939,817	5,486,760
2005	27,803,370	6,116,741
2006	28,632,381	6,299,124
2007	29,425,177	6,473,539
2008	30,698,689	6,753,712

*in unit of tonnes

According to the table above, the increment of EFB occurs each year by approximately 3%. The utilization of fresh EFBs as much has increased extensively, especially in oil palm, rubber and cocoa estates. The practice of placing EFBs on the soil surface has brought economic benefits as it enhances vegetative growth and increased production (Yeow et al., 1985).

EFB from oil palm were initially utilized as fuel. It has a moisture content of 60 - 65%. Before it can be used as a fuel for the boilers, the moisture has to be reduced to 40% or less. This is achieved through the use of a special screw press, which presses out the moisture from the EFB. According to Lim and Ratnalingam (1980), EFB can produce total energy as much as 2 568 calorie/kg (screw pressed EFB), if used as a fuel.

2.4.2 Biomass Utilization

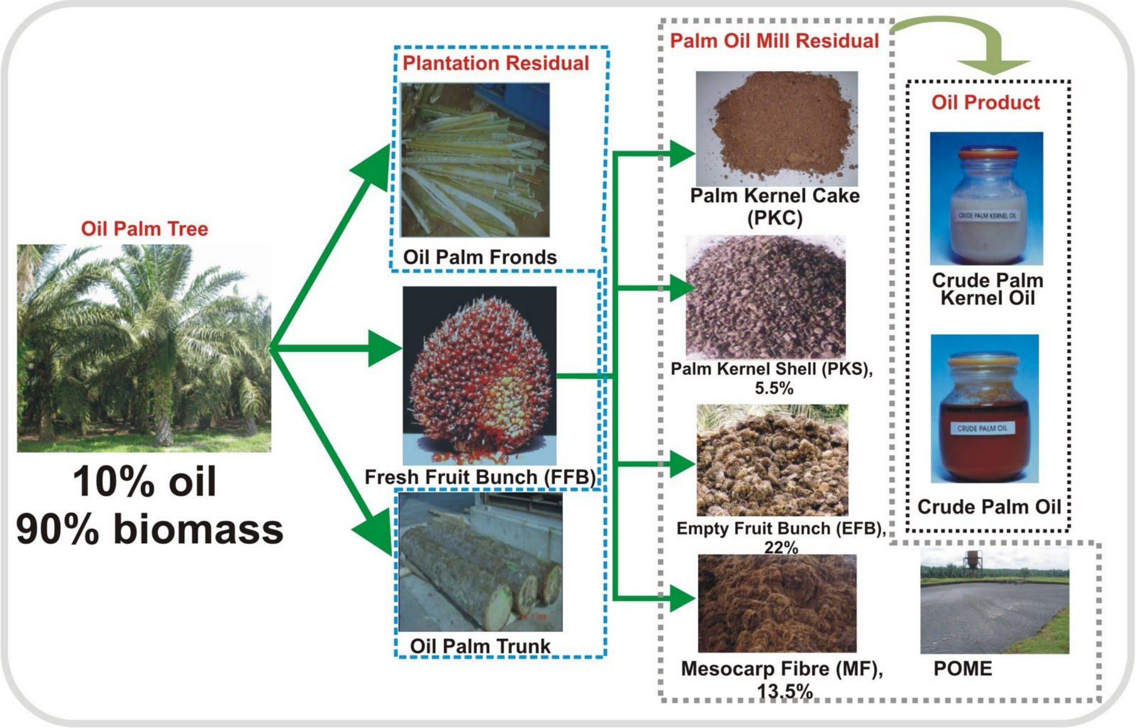

Figure 2-2: Utilization of Biomass

http://jfe-project.blogspot.com/2010_04_01_archive.html (Adopted 2012)

Figure 2-2 shows the production and the usage of the oil palm tree from the plant until oil product. It is stated that only 10% oil can be produced from an oil palm trees but up to 90% of biomass is not economically and fully utilized. Thus, it would be such a waste to not using this waste to make a more productivity use.

2.5 *Thermal Conversion*

2.5.1 Production of Fuel Gas

Figure 2-8 illustrates the different routes which can be adopted to produce hydrogen from biomass, including gasification to produce syn-gas, pyrolysis to produce bio oils and hydrolysis of cellulose to produce sugar.

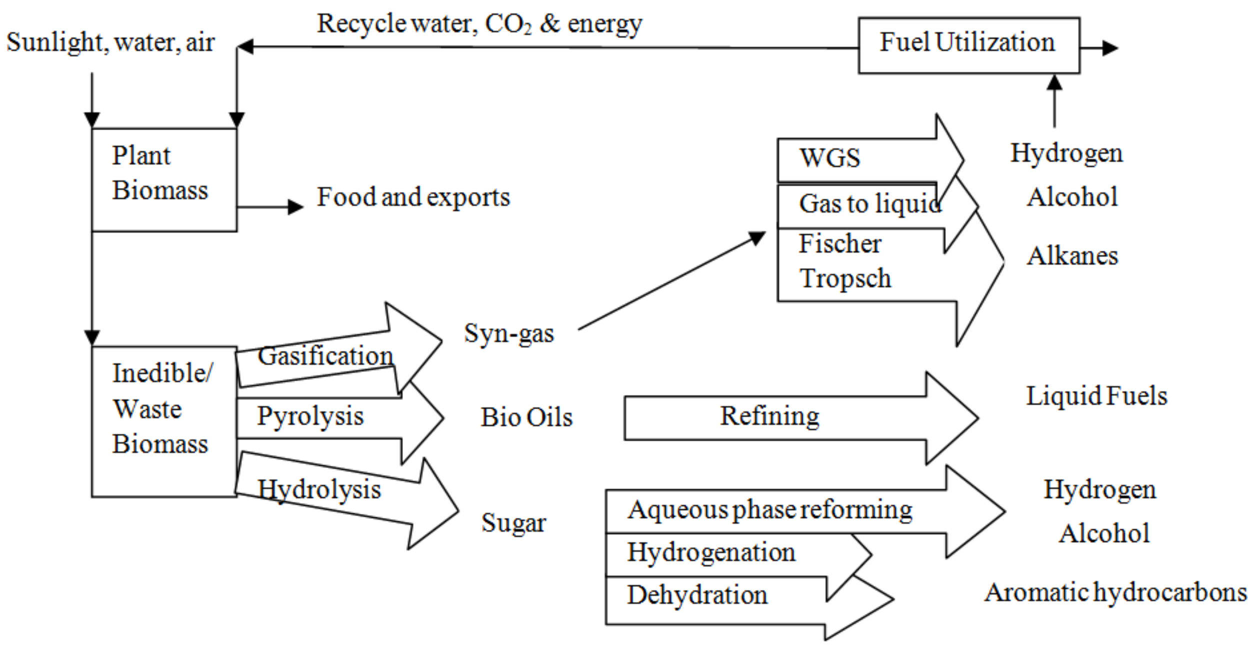

Figure 2-3 : Hydrogen and liquid fuels production from biomass sources. (Huber and Dumesic, 2006)

Syn-gas can be converted to hydrogen by water gas shift (WGS) reaction; however, any remaining CO must be removed from the gas stream. This can be achieved by preferential oxidation of CO. Pyrolysis bio-oil can be converted to liquid fuel but the processes are complex and the conversion is low. Hydrogen can be produced from the bio-oil by auto thermal reforming with high conversion efficiency, especially with the use of catalytic membrane reactors. Aqueous phase reforming can be used to convert sugars and sugar alcohols, such as sorbitol, to produce hydrogen.

2.5.2 Pyrolysis

Pyrolysis is the devolatilization of volatile matter in inert medium to produce pyrolytic liquids, solid char and gaseous fuel. In simple words, it can also be said that pyrolysis is a process which can generate a char, oil and gas product from anything that have a potential end use. (William and Nugranad ,1999) So it means that, pyrolysis process enables biomass or non-biomass waste to be processed into oil, gases and char. But this product may vary depending on the types of samples used.

The catalytic pyrolysis is the pyrolysis using the help of catalyst. Most pyrolysis is designed for biofuels production. However, hydrogen can be produced directly through fast or flash pyrolysis if high temperature and sufficient volatile phase residence time are allowed. The pyrolysis products can be divided into a volatile fraction, which consists of gases, vapors, tar components and a carbon rich solid residue (Demirbas, 2002).

Some research has proved that by adding catalyst onto the process, the production of oil and gas yield can increase far more compared to non-catalytic pyrolysis and also enables the oil to be upgraded thus having the same quality with petroleum fuel. (William and Nugranad, 1999). Catalyst can be upgraded in many ways. Using catalyst can upgrade production of pyrolysis liquid by using fast pyrolysis which can produce up to 75% of bio-oil liquid(Czernik et al., 2003). One of it is by using zeolite type catalysts at atmospheric pressure to dehydrate and decarboxylate the oil (Brown and Holmgren, 2009). But zeolites also have all sorts of type and the main zeolite catalyst used for upgrading biomass pyrolysis is the hydrogen form of the zeolite, ZSM-5. This is because it has a strong acidity, high activities and shape selectivity which can convert the oxygenated oil to a hydrocarbon mixture in the C1 to C10 range which resulting a highly aromatic compounds similar in composition to gas (William and Horne, 1997).

Table 2-2: Hydrogen yields and energy ratios obtained from various processes (Demirbas, 2001)

Processes	H_2 yield	Energy ratio
Pyrolysis + steam reforming	12.6	91
Gasification +WGS	11.5	83
Biomass + steam + heat	17.1	124

Table 2-2 illustrates the H_2 yields that can be obtained from biomass using various processes and the theoretical maximum including the ratios of heating values of the product hydrogen with respect to the biomass feed (Demirbas, 2001)

2.5.3 Type of Pyrolysis

There are four types of pyrolytic reactions, which are differentiated by temperature and the processing of residence time of the biomass.

I. Slow Pyrolysis

Conventional or slow pyrolysis is characterized by slow biomass heating rates, low temperatures and lengthy gas and solids residence times. Depending on the system, heating rates are about 0.1 to 2.0 ^{o}C per second and prevailing temperatures are around 500 ^{o}C. Gas residence time may be greater than five seconds. During conventional pyrolysis, the biomass is slowly devolatillized, hence tar and char are the main products.

II. Flash Pyrolysis

Flash Pyrolysis is characterized by moderate temperatures exist 400-600 ^{o}C and rapid heating rates >2 ^{o}C/s. Vapor residence times are usually less than two seconds.

III. Fast Pyrolysis

The only difference between flash and fast pyrolysis is heating rates. Heating rates are between 200 and 10 ^{o}C per second and the prevailing temperatures are usually higher than 550 ^{o}C. Due to the short vapor residence time, products are high quality, ethylene rich gases that could subsequently be used to produce alcohols or gasoline. The production of char and tar is considerable less during this process.

IV. Catalytic Pyrolysis

Pyrolysis oil consists of a complex mixture of aliphatic and aromatic oxygenates and particulates. It is very viscous, acidic and unstable liquid with relatively low-energy density compared to conventional fossil oil. Such poor quality of the bio oil requires costly post treatment and makes complete process economically less attractive.

2.5.4 Type of Reactor

There are several types of pyrolysis reactor. The most common types are bubbling fluidized bed, circulating fluidized bed, rotating cone pyrolyzer and ablative pyrolyzer. Each type has their own design and applications.

I. Bubbling fluidized bed

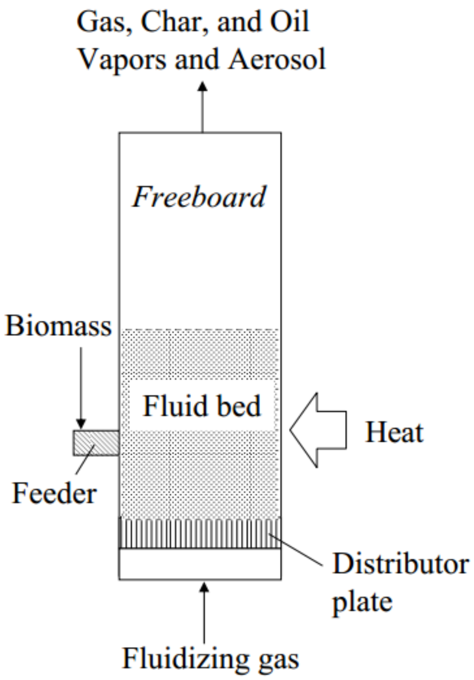

Figure 2-4 : Bubbling Fluidized Bed

Bubbling fluid beds, as shown in Figure 2-3, usually referred to as just fluid beds as opposed to circulating fluid beds. It have the advantages of a well understood technology that is simple in construction and operation, good temperature control and very efficient heat transfer to biomass particles due to high solids density. Heating can be achieved in a variety of ways .However, heat transfer to bed at large-scales of operation has to be considered carefully due to scale-up limitations of different methods of heat transfer.

II. Circulating fluidized beds/transport reactor

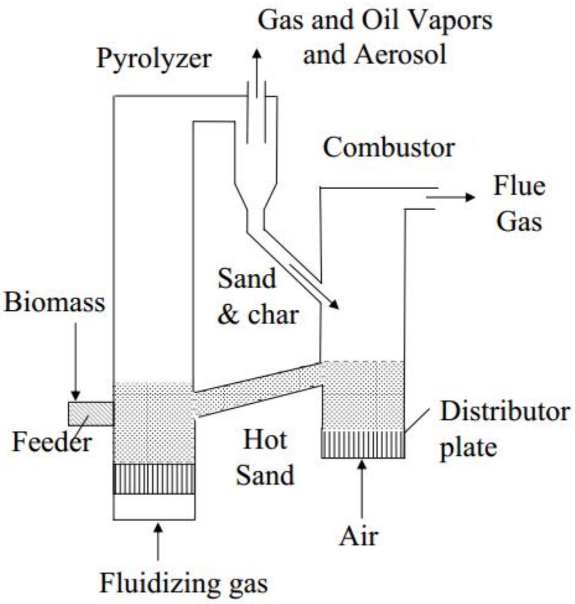

Figure 2-5 : Circulating fluidized beds

Figure 2-4 is a circulating fluidized bed pyrolyzer. This type is similar to bubbling fluidized bed reactors but have shorter residence times for chars and vapors. The short residence times encountered in the reactor result in higher gas velocities, faster vapor and char escape and higher char content in the bio-oil than bubbling fluidized beds. However, they have higher processing capacity, better gas-solid contact and improved ability to handle solids that are more diffi-cult to fluidize but are less commonly used. The heat supply typically comes from a secondary char combustor.

III. Rotating cone pyrolyzer

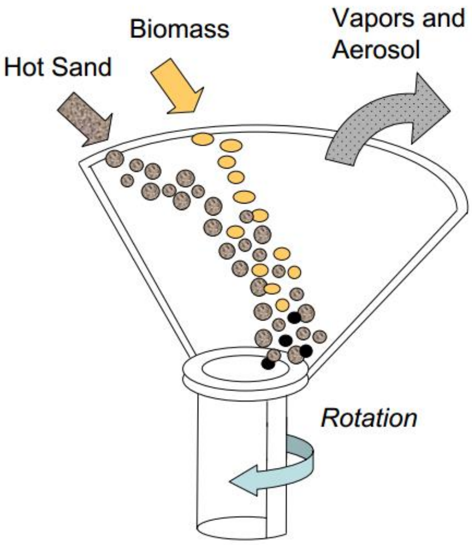

Figure 2-6 : Rotating cone pyrolyzer

In a rotating cone pyrolysis reactor, biomass particles at room temperature and hot sand are introduced near the bottom of a cone at the same time. They are mixed and transported upwards by the rotation of the cone as shown in Figure 2-5. Rapid heating and short gas phase residence times can be easily achieved in this reactor.

IV. Ablative pyrolyzer

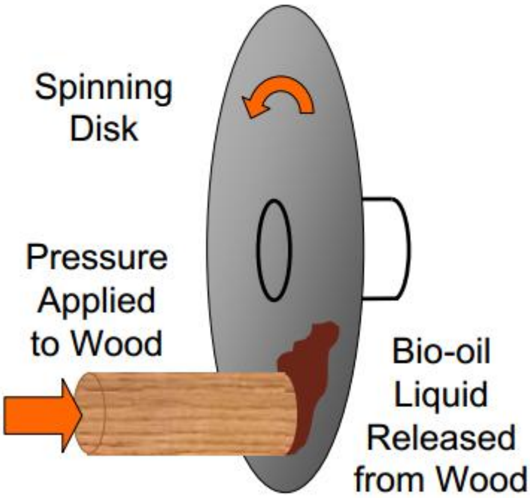

Figure 2-7 : Ablative pyrolyzer

Ablative pyrolysis (Figure 2-6) is different in concept compared to the other methods of fast pyrolysis. In other methods, the rate of reaction is limited by the rate of heat transfer through a biomass particle, which is why small particles are required. In ablative pyrolysis heat is transferred from the hot reactor wall to "melt" wood that is in contact with it under pressure. As the wood is mechanically moved away, the residual oil film both provides lubrication for successive biomass particles and also rapidly evaporates to give pyrolysis vapors for collection in the same way as other processes. The rate of reaction is strongly influenced by pressure, the relative velocity of wood on the heat exchange surface and the reactor surface temperature.

2.6 Catalyst

One of the methods to increase the H_2 yield is to apply catalytic pyrolysis. (Chen et al., 2003) Hydrogen can be effectively produced from biomass pyrolysis with the assistance of catalysts at wide ranges of temperatures. High temperature favour total gas yield containing hydrogen. Catalyst load has an obvious influence on the hydrogen containing gas yield. (Chen et al., 2003) The usage of catalysts in the pyrolysis helps in improving the yield and quality of gas. It has been proven that the highest yield of hydrogen 12.65 wt% and 91 % energy conversion efficiency were obtained from biomass pyrolysis with adding of catalyst. Although hydrogen yield from the direct pyrolysis of biomass is quite low, it was known that the gas yield, could be highly improved by adding catalyst. (Yang et al., 2006)

2.6.1 Coking Problem

One of the major issues in biomass pyrolysis is the formation of tar, soot, coke and other carbon compounds in the reactor (Figure 2-7). Depending on the process conditions, like pressure and temperature, different forms of coke may appear, some of which are more hazardous to the process than others. To ensure trouble free operation of the reformer, it is essential to control the soot formation in all process conditions including process shut-downs, start-ups and disturbances.

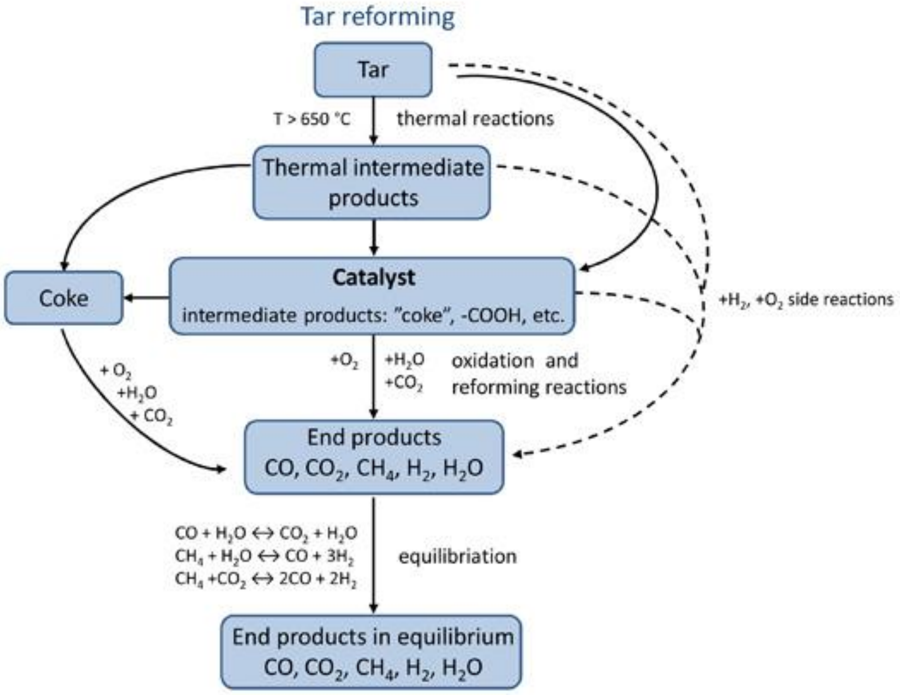

Figure 2-8 : Tar reforming reactions, adapted from Bridger and Chinchen (1970)

Carbon deposition on catalyst can reduce the catalyst performances, coke deposits may not uniformly distributes in the catalyst pellet (Forzatti and Lietti, 1999). It can accumulate within the catalyst effective pores, leading to an increase in the resistance to transport of reactant and products in the pores. High concentration of coke on pore wall initiates a pore blockage to occur (Fogler, 2005). The rate of coke encapsulating formation is enhanced by low temperatures and high final boiling point of the hydrocarbon mixtures. It causes the blockage of equipments and fouling of down-stream application processes, and reduces the thermal efficiency.

By using catalysts in the pyrolysis, it can be an effective method to eliminate tar and improve hydrogen content in the gas products (Qinglan et al., 2010). Nickel catalysts have frequently been investigated for gasification of biomass and bio-oil because of their comparatively low price and high activity. They are normally used in a supported form. By using addition of metal-inorganic particles, the composite can lead obtaining special properties of coatings such as good hardness and wear corrosion resistance, and metal-organic particles can determine new characteristics such as self-lubricating coatings. This can help in producing a better catalyst that is able to resist coking problem.

Moreover, dolomite and CeO_2/SiO_2supported Ni, Pt, Pd, Ru and alkaline metal oxides can be used to catalyse the gasification process to reduce tar formation and improve the product gas purity and conversion efficiency. Although $Rh/CeO_2/SiO_2$ has been reported to be the most effective catalyst to reduce tar formation, Ni based catalysts are also highly active for tar destruction. Since Ni based catalysts are industrially used for steam reforming of methane and naphtha, they are also expected to catalyse the steam reforming of tars as well as WGS reaction to produce H_2.

2.7 Fuel Gas Production

2.7.1 Application of Hydrogen

Hydrogen is one type of fuel gas. There are several applications of hydrogen in our daily life. Hydrogen economy has been promoted due to large number of hydrogen applications in petroleum and chemical sectors such as upgrading crude oil and synthesizing of methanol and ammonia. Besides this, hydrogen has been upgraded as an alternative to fossil fuel products due to its environmental friendly, high energy capacity and potentially gives high efficient processes such as in fuel cell application. Currently, about 98% of hydrogen comes from fossil fuel. However, fast depleting rate and other competing usage of fossil fuels has becoming a serious concern and the search for alternative feedstock for hydrogen production has been intensified. Hydrogen as an energy carriers comprised numerous advantages over other conventional energy carriers. (Z. Khan., 2010)

Hydrogen has a variety of applications and in all sorts of field, up to metals production, ceramics, electronics, food and even energy. For metals, hydrogen can be mixed with inert gases to obtain a reducing atmosphere, which is required for many applications in the metallurgical industry, such as heat treating steel and welding. It is often used in annealing stainless steel alloys, magnetic steel alloys, sintering and copper brazing. For chemicals, hydrogen is used as a raw material in the chemical synthesis of hydrogen peroxide, polymers, and solvents. In pharmaceutical, hydrogen is used to manufacture vitamins and other pharmaceutical products. In float glass manufacturing, hydrogen is required to prevent oxidation of the large tin bath. While for electronics, hydrogen is used as a carrier gas for such active trace elements as arsine and phospine, in the manufacture of semi-conducting layers in integrated circuits. And even for food, it is used to hydrogenate unsaturated fatty acids in animal and vegetable oils, producing solid fats for margarine and other food products.

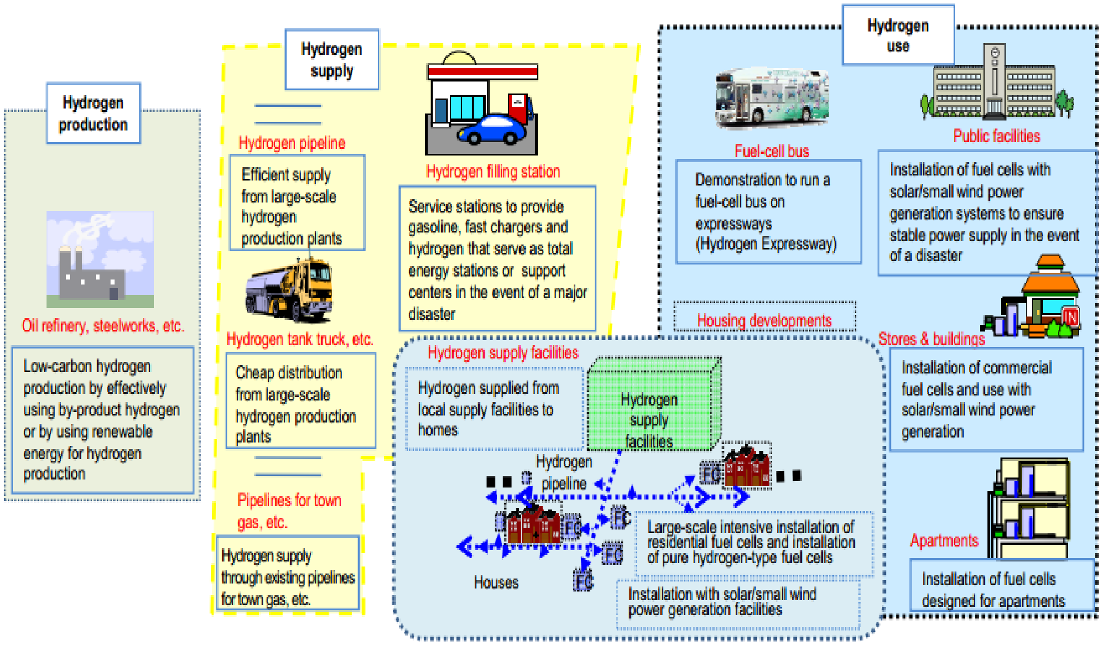

Figure 2-9 : Adapted from Ministry of Economy, Trade and Industry Japan. (September, 2009)

Figure 2-9 illustrate the Japan’s first large-scale field trials of hydrogen-based social systems program that was conducted for the purpose of establishing a hydrogen society. The project aimed to produce hydrogen production with fewer carbon dioxide emissions, efficient transport and storage of hydrogen, and efficient hydrogen use. From this figure, it also shows the application of hydrogen that varies to all rounds of use and it is possible to replace the usage of fossil fuels in daily life.

In today’s energy, hydrogen is used by the industry for the transportation, electric power and also heating. In transportation, hydrogen is used increasingly in oil refining to make fuels. The heavier and higher sulfur crudes make it requires more hydrogen input. But for electric power and heating purposes, hydrogen is used as a component of the singes. It is used either in gasification based electric generation system or for process heat. (Ogden, 2004).

2.8 Summary

There are several types of non-renewable energy. One of the energy is by using biomass. By using pyrolysis or gasification process, biomass can be converted into energy rather than being left on dumpsite and causing pollutions. Since Malaysia is the largest producer for palm oil waste, the availability of the biomass is high. The energy produces can be used to generate power for so many things. However, tar formation on catalyst causing the fuel gas produced to be low. Thus it is important to find the suitable catalyst that can solve this problem.

3 MATERIALS AND METHODS

3.1 Overview

This chapter presents the experimental procedure of catalytic pyrolysis in lab scale by in order to enhance production of hydrogen from biomass namely oil palm waste. The research start the process right after the title of the research study was being chosen. From there, reading of multiple journals to enlighten the understanding of the research was done. The concept, literature review and method were learnt and discovered by reading through the past researchers study. At the same time, chemicals and equipment that was going to be used are prepared for the experiment set up. The catalysts also need to go through the TGA (thermogravimetic analysis). Parameters were set up and experiments were carried out. After the findings, analysis was done and the process will be repeated if the result does not reach the required value. Lastly, discussion and conclusion of the report were done. Figure 3-1 shows the work flow of this research process.

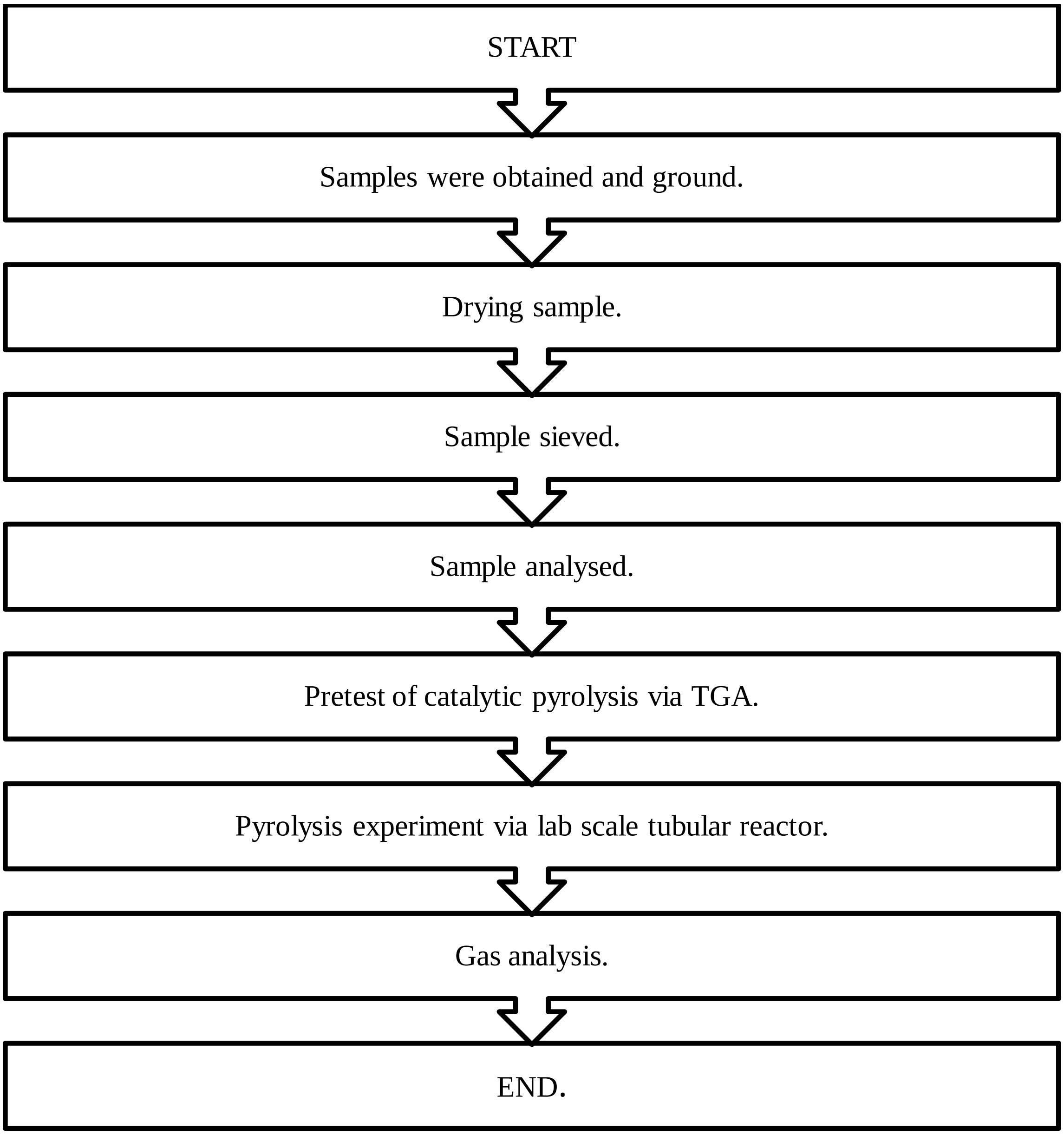

Figure 3-1 : Work Flow.

3.2 Materials and Equipments

3.2.1 Biomass

Biomass used was the palm oil agricultural waste samples which were empty fruit bunch (EFB) and palm oil fiber (POF). The example of EFB collected is in Figure 3-1. All these samples were collected at the Felda Lepar Hilir 3. Each of these samples were grounded and sieved to the range of 0.63 mm and 1 mm in particle sizes by using sieve shaker which is in Figure 3-2. Then the particles were dried at 80 °C until constant weight so that the sample is 10 % dry. This condition is prior to fast pyrolysis condition which is, the condition of feed need to be 10 % dry, and the size of feed particle is less than 3 mm.

Figure 3-2 : Empty Fruit Bunch obtained from Felda Lepar Hilir.

Figure 3-3 : Sieve Shaker used.

3.2.2 Reactor

The experiment was using tubular reactor; quartz reactor having 1 cm of diameter, 52 cm of height and 25.6 g of weight. Figure 3-4 shows the quartz glass reactor used. The sample was filled in the reactor and placed in the tubular furnace for heating purpose. Figure 3-5 shows the reactor in the tubular furnace. The gas used was nitrogen and were preheated prior to its entry into the reactor. Nitrogen was also used for purging and as carrier gas.

Figure 3-4 : Glass quartz reactor.

Figure 3-5 : Quartz reactor in tubular furnace.

3.2.3 Pyrolysis Unit

Pyrolysis unit is the most important part in this experiment. One of the major components in this pyrolysis unit is the tubular furnace. It provides heat to the reactor by using electrical energy. The temperature of the furnace was controlled by using the control panel. Desired temperature, ramping time and heating rate of the tubular furnace was set by using the controller. Pyrolysis unit also consisted of piping systems complete with flow meter to ease the flow of gas to the reactor. Figure 3-6 shows the pyrolysis unit in the Gas Lab section of Chemical & Natural Resources Engineering Lab.

Figure 3-6 : Pyrolysis Unit.

3.2.4 Catalyst

The catalysts used were Ni/Ce/Al_2O_3 and Ca/Al_2O_3. The Ni/Ce/Al_2O_3 catalyst consisted of 12 wt% of Ni, 8 wt% of Ce and balance of Al_2O_3. Meanwhile for Ca/Al_2O_3 consisted of 30 wt% of Ca in the catalyst.

3.3 Experimental Set up

The experiment was set up in the Gas Lab section. The schematic diagram of experimental layout of the rig was shown in Figure 3-7 and the real apparatus arrangement is shown in Figure 3-8.

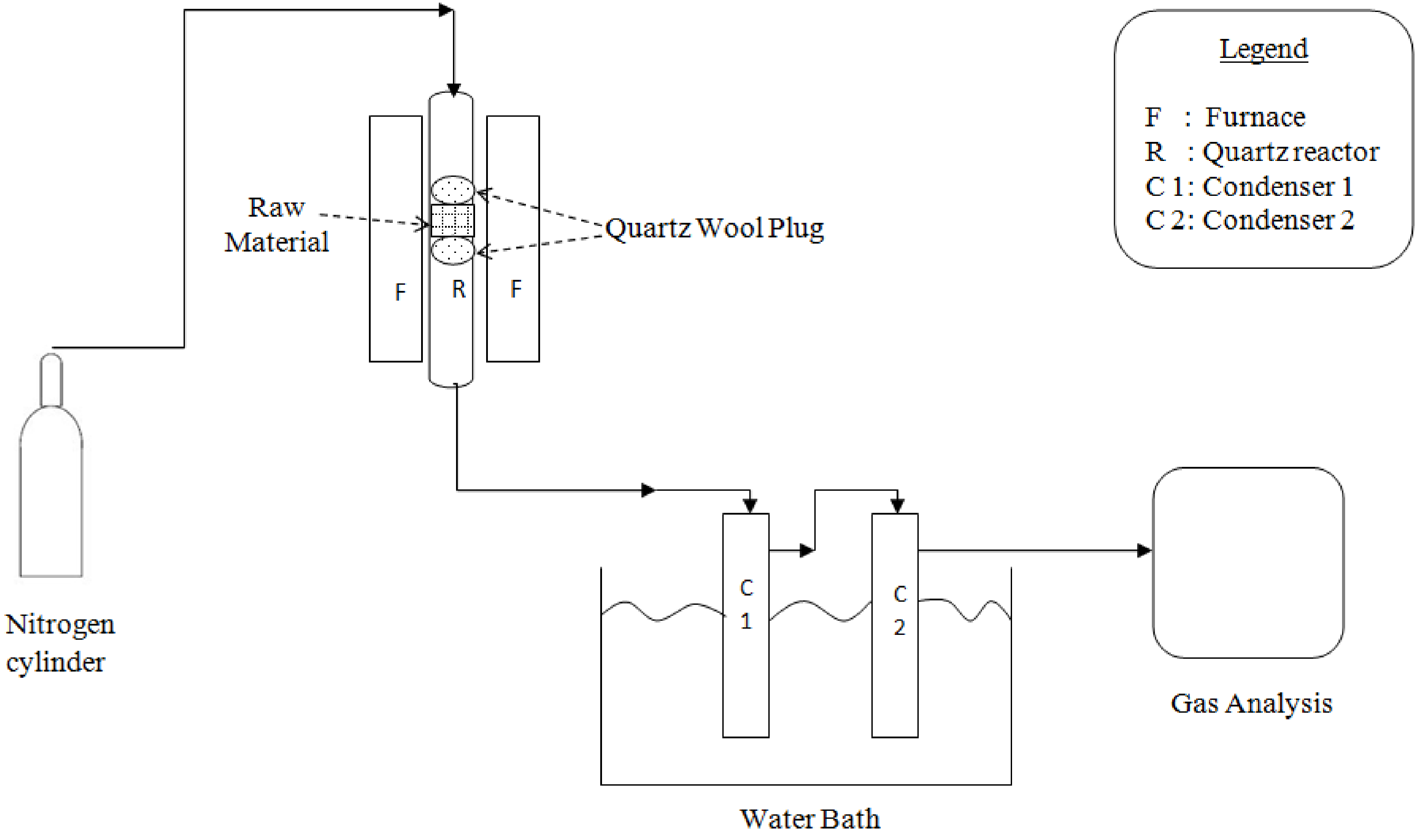

Figure 3-7: Schematic Diagram of Experimental Layout.

Figure 3-8 : Apparatus set up.

3.3.1 Blank Test

The purpose of the blank test is to make sure if there any leakage on any connection that have been made. Nitrogen was used as a carrier gas. In this test, nitrogen was flow through the system for about 15 minutes at 11 psi. Bubble is shown up if any leakage of the set up is determined. There is no leakage if the pressure gauge at the pyrolysis system has same reading with the pressure gauge at the nitrogen regulator. Figure 3-9 shows the nitrogen cylinder used during the experiment.

Figure 3-9 : Nitrogen gas cylinder.

3.3.2 Purging

Purging was the first procedure that must be made before starting the experiment. This is to make sure there in no air in the system. The purging process was done for 10 minutes at 11 psi. The flow of Nitrogen replaced the air in the reactor.

3.4 Experimental Procedures

Pyrolysis experiment was carried out under nitrogen atmosphere at the temperature of 700 ^{o}C because this temperature was found to be an optimum condition for maximum product yield. A quantity of 2 g of EFB was loaded in the reactor with a heating rate of 20 ^{o}C/min up to desired temperature. The gas product was analyzed by using Gas Analyzer.

3.5 Analysis

3.5.1 Thermo gravimetric Analysis (TGA)

This analysis was performed to determine moisture content, volatility and ash content of the sample. Figure 3-10 shows the type of TGA used. There are four types of analysis were done by using TGA.

For the first analysis, the composition of EFB and POF was investigated. Both EFB and POF were cut into <1 mm. The TGA analysis was performed using nitrogen with a flow rate of 100 ml/min. The temperature was increased from ambient temperature to 800 ^oC with a heating rate of 20 ^oC/min.

The characterization of catalyst was carried out by using TGA as well. The catalysts, Ni/Ce/Al_2O_3 and Ca/Al_2O_3 were used in this analysis. For fresh catalyst, the TGA analysis was performed using nitrogen. Meanwhile, for used catalyst of Ni/Ce/Al_2O_3, the analysis was carried out using air flow. However, for used catalyst of Ca/Al_2O_3, the gas flow used was nitrogen gas. The temperature was increased from ambient to 800 ^oC at 20 ^oC/min.

In addition, the catalytic pyrolysis of EFB and POF were also carried out by using TGA. The weight ratio of sample to catalyst are stated in Table 3-1.

Table 3-1: Weight ratio of biomass sample to catalyst.

Sample No.	Biomass Type	Biomass ratio	Ca/Al_2O_3 ratio	Ni/Ce/Al_2O_3 ratio
1	EFB	1	2	-
2	EFB	1	-	1
3	POF	1	2	-
4	POF	1	-	1

Figure 3-10 : Thermo gravimetric Analysis

3.5.2 Percentage of Product Composition

The gas product was measured in percentage by gas analyzer. The calculation for percentage of fuel gas composition is as followed.

$$Fuel\ gas\ composition\ (\%) = \frac{percentage\ of\ fuel\ gas}{total\ percentage\ of\ gas\ product}\ x\ 100$$

3.5.3 Gas Analyzer

Figure 3-11 shows the gas analyzer that was used to detect the gas composition of the fuel gas produced from the pyrolysis process. It is important because pyrolysis is the thermal decomposition under absence or limited supply of air. The gas produced was monitored at 5 minutes intervals for 1 hour.

Figure 3-11 : Portable Gas Analyzer.

4 RESULT

4.1 *Overview*

This chapter discusses the result obtained from the experimental studies. The result was compared with the previous studied to make the conclusions.

4.2 *Components Analysis of Biomass*

4.2.1 Effects of Type of Biomass

The main purpose of this study is to determine moisture content, volatility and solid residue of the sample by using TGA. Figure 4-1 and Table 4-1 illustrate the analysis result of biomass samples, empty fruit bunch (EFB) and palm oil fibre (POF).

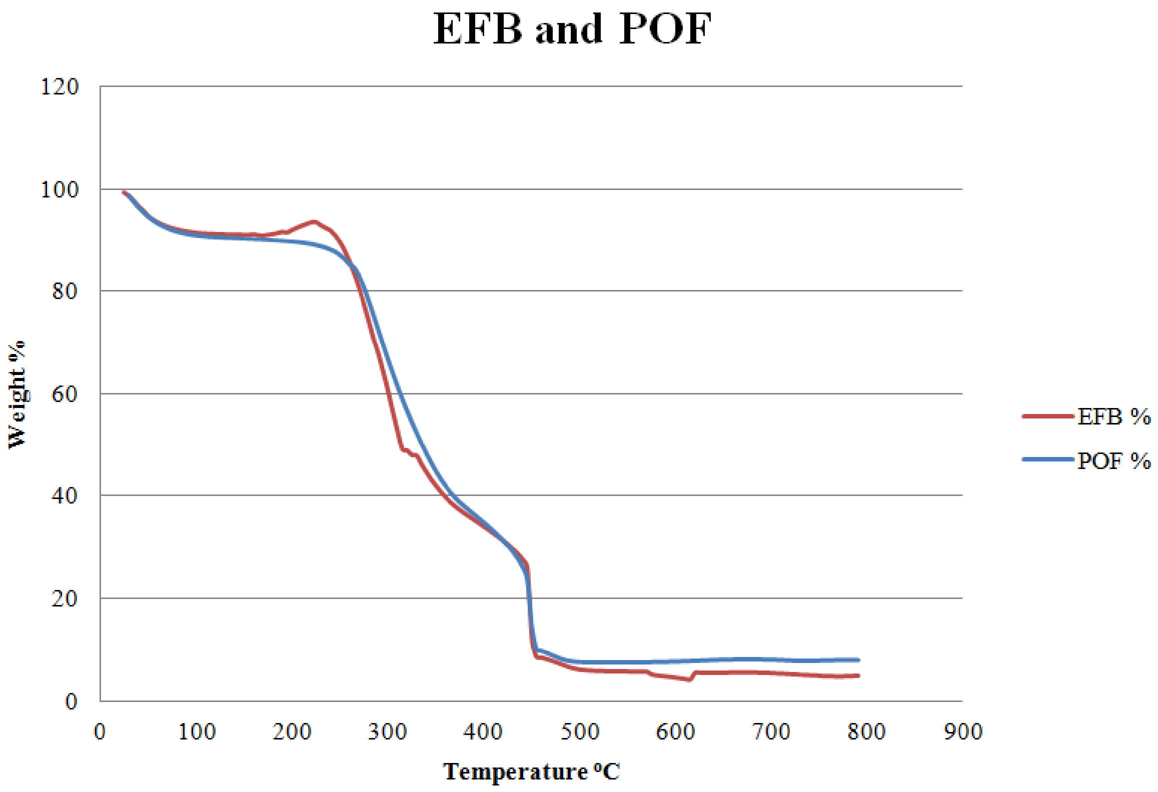

Figure 4-1 : Graph of Weight % against Temperature (^{o}C) for EFB.

Table 4-1 : Components of Biomass

	Moisture content wt%	Volatility wt%	Char Residue wt%
POF	7.00	61.83	18.33
EFB	7.54	64.35	22.78

There are three different stages that can be determined from the analysis result. The first region is at temperature <150 ^{o}C, it indicates the water content of the biomass. It can be seen that EFB has higher moisture content compared to POF which are 7.54 wt% and 7.00 wt% respectively.

The second region is in the range of 200 ^{o}C to 450 ^{o}C. This stage determines the volatility components in biomass. Higher volatile matter might indicate higher production of gas and bio oil. It shows that EFB has higher volatile matter than POF. EFB has 64.35 wt% of volatile matter than POF has 61.83 wt% of volatile matter. This segment also indicates the decomposition of cellulose and hemicelluloses (Azizan et. al,. 2009).

The third segment from 450 ^{o}C until 800 ^{o}C, determines the solid contents or solid residue which indicates the decomposition of lignin for the biomass. It indicates that, EFB has more solid content with 22.78 wt% compared to only 18.33 wt% of solid content in POF.

4.2.2 Effects of Catalysts

The characterization of catalyst is carried out by TGA. The result of investigation is shown in Figure 4-2 and Figure 4-3. The TGA of $Ni/Ce/Al_2O_3$ is shown in Figure 4-2. $Ni/Ce/Al_2O_3$ is maintaining at 100 wt% throughout the various temperatures. This is due to the stability of the catalyst itself to maintain his condition especially at high temperatures.

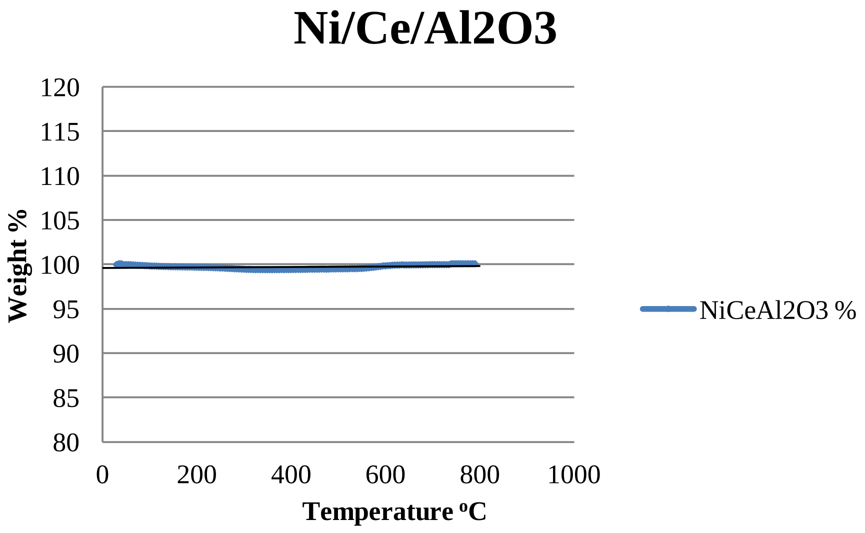

Figure 4-2 : TGA analysis of fresh Ni/Ce/Al_2O_3.

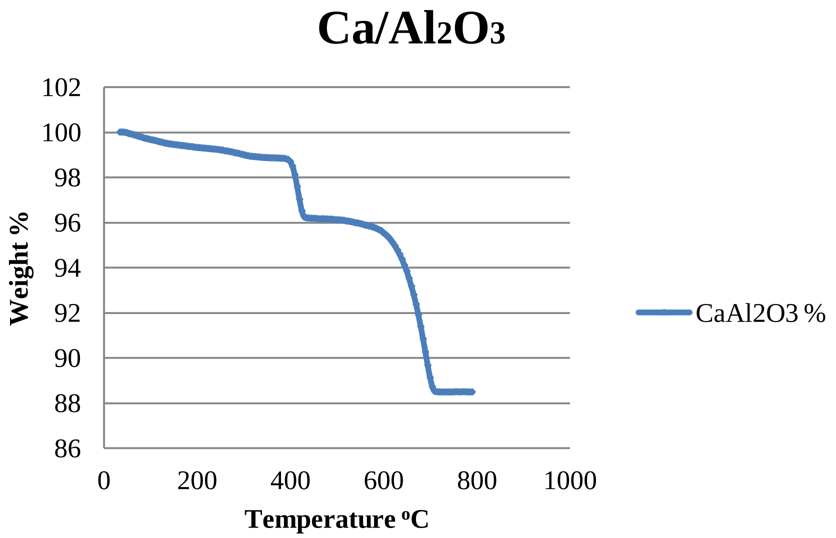

Figure 4-3 : TGA analysis of fresh Ca/Al_2O_3

Figure 4-3 on the other hand, shows the TGA of Ca/Al_2O_3 catalyst. On the first stage of 200 ^{o}C, the lines interpret as the moisture content of the catalyst. By 400 ^{o}C, there is declining of weight % from 98.7 wt% to 96 wt%. This might be because of water were release from $Ca(OH)_2 \rightarrow CaO + H_2O$. While from 400 ^{o}C to 700 ^{o}C, the curves shows that, carbon dioxide was released from $CaCO_3 \rightarrow CaO + CO_2$. At the end of the curve at 700 ^{o}C, is the char content of the catalyst. (Gotoh et. al., 2011)

4.2.3 Effects of Catalytic and Non-Catalytic

Based from the analysis of biomass samples, it was seen that POF has better performances than EFB, therefore POF was further investigated. This is because POF has lower char content compared to EFB. Figure 4-4 shows the catalytic performance with POF compared to non-catalytic of POF. The data calculated from the graph are tabulated in Table 4-2.

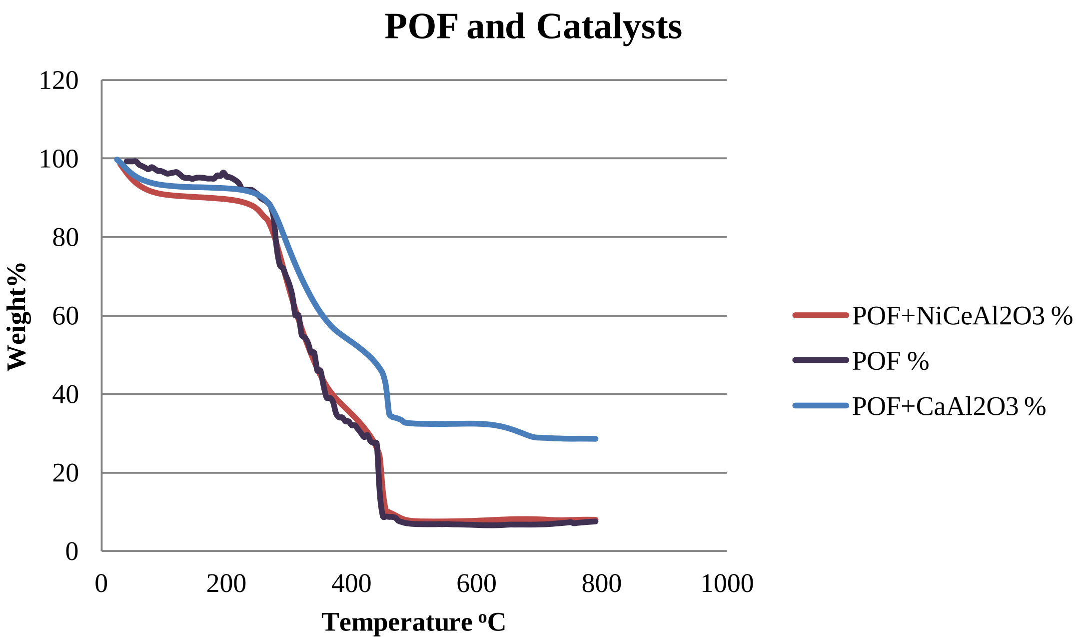

Figure 4-4 : Catalytic pyrolysis of palm oil fibre.

The catalytic performances of catalyst with POF are compared to the non-catalytic of POF which is shown in Figure 4-4. There are three types of components that can be identified from this analysis which are moisture content, volatile matter and char content.

Table 4-2 : Component of Catalytic POF and Non catalytic pyrolysis of POF.

	Moisture content %	**Volatile matter %**	**Solid Residue %**
POF	2.79	43.92	19.89
POF+$NiCeAl_2O_3$	7	61.83	18.33
POF+$CaAl_2O_3$	6.55	41.40	19.06

Moisture content can be determined at temperature <150 ^{o}C. Catalytic performances of catalyst with POF for $NiCeAl_2O_3$ has 7 wt% moisture content compared to 6.55 wt% for $CaAl_2O_3$. Based from data tabulated in Table 4-2, non-catalytic POF has the lowest moisture content.

At temperature 200 ^{o}C to 420 ^{o}C, volatile matter can be identified. This is important because high volatility means high production of gas and bio oil. POF with $NiCeAl_2O_3$ has the highest volatile matter of 61.83 wt% compared to POF with $CaAl_2O_3$ and POF of only at 41.40 wt% and 43.92 wt% respectively. This also means that POF with $NiCeAl_2O_3$ might be able to produce higher yield of gas than $CaAl_2O_3$.

The last component that can be detected is char content. From the graph, it seems that POF with $CaAl_2O_3$ has higher curve line compared to others. This is due to the ratio weight of catalyst to POF. POF with $CaAl_2O_3$ has the ratio of biomass to catalyst of 1:2, while the ratio of POF with $NiCeAl_2O_3$ is 1:1. This is due to the human error while preparing the samples. However, POF has the highest char content of 19.89 wt% compared to others.

4.2.4 Lab scale

This is the results of the experimental pyrolysis process that was carried out on a lab scale. The experimental data collected were compared with the pre-test scale using TGA to see if the results were synchronized.

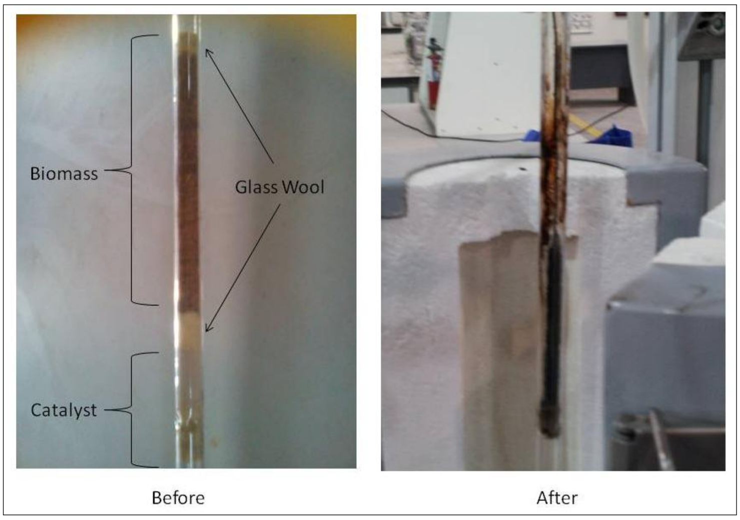

Figure 4-5 : Catalyst conditions in reactor.

Figure 4-5 shows the catalyst condition in the quartz glass reactor before and after the experiments. The experiment was carried out at 700 ^{o}C.

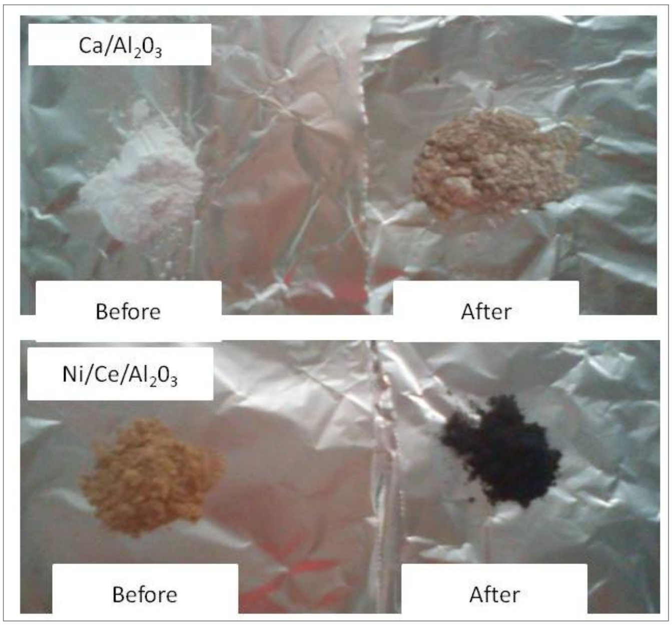

Figure 4-6 : Catalysts colour before and after experiment.

Figure 4-6 shows the differences between the colour of fresh catalyst (labelled as before) and used catalyst (labelled as after). The ratio of catalyst to biomass sample used in the experimental lab scale are 1:1 in weight ratio. The used catalysts were analysed by using TGA to compare their differences with the fresh catalysts which is shown in Figure 4-7 and Figure 4-8.

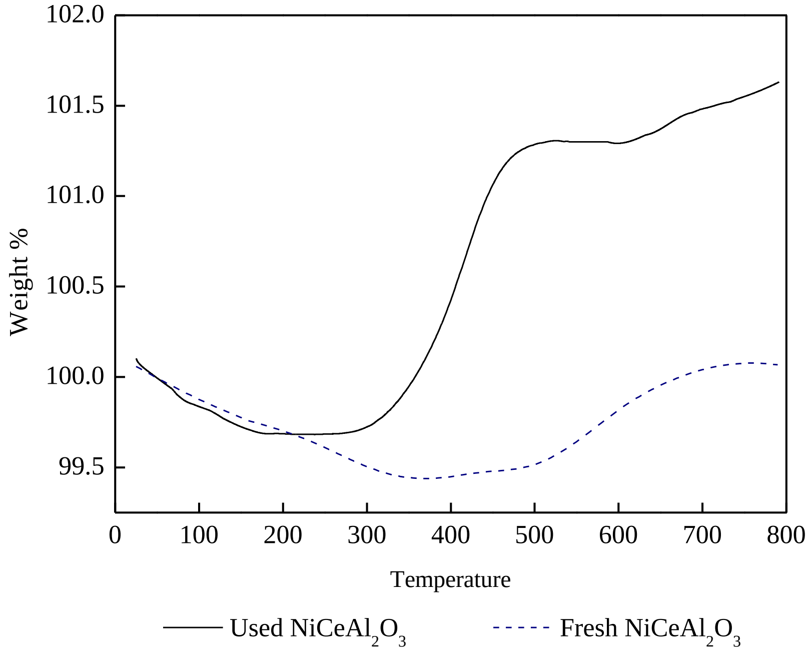

Figure 4-7 : Graph of used and fresh catalyst of $NiCeAl_2O_3$

Figure 4-7 shows the comparisons for used and fresh catalyst of $NiCeAl_2O_3$. The fresh catalyst was using nitrogen flow as carrier gas while the used catalyst was by using oxygen flow. However, both of them were analysed ambient temperature until 800 ^oC at 20 ^oC/min. From this graph, moisture contents can be determined at the temperature of before 100 ^oC.

For the fresh catalyst of $NiCeAl_2O_3$, the curve lines are lower than used catalyst. At 300 ^oC, the fresh catalyst burns to dust causing the particles weight to reduce. Compared to the used catalysts, fresh catalyst has a stable curve through the temperature. This is because the fresh catalyst was analysed under nitrogen flow so there is not much effect on the catalyst.

For the used catalyst of $NiCeAl_2O_3$, the graph shows that used catalyst has two curves lines. The first curve line at 325 ^oC indicates the decomposition of filament carbon. While for the second curve line at 600 ^oC indicates the decomposition of encapsulate carbon (Isha and William, 2011).This also means that encapsulate carbon can only be regenerated at high temperature compare to the filament carbon.

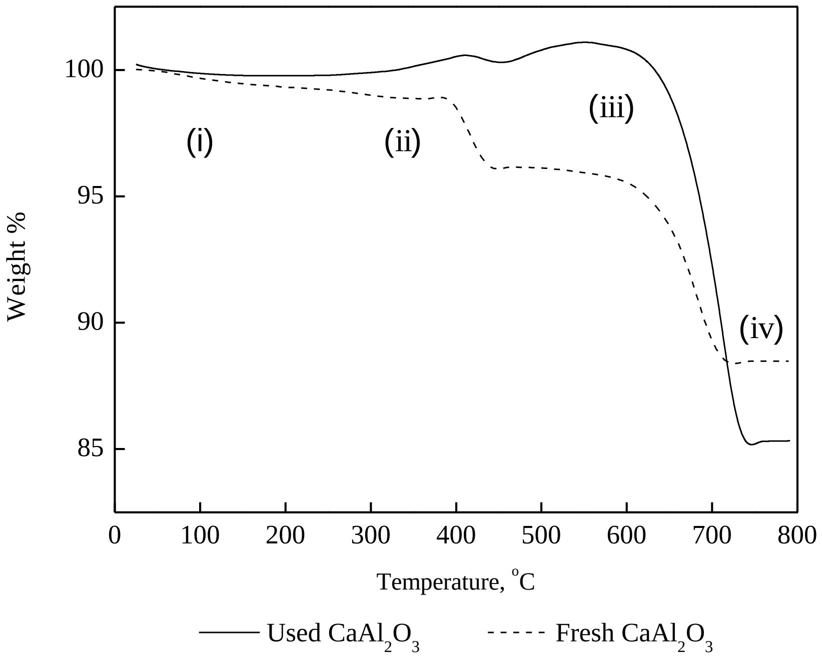

Figure 4-8 : Graph of used and fresh catalyst of $CaAl_2O_3$

Figure 4-8 shows the comparison between used and fresh catalyst of $CaAl_2O_3$ using TGA. These catalysts were analysed from ambient temperature until 800 °C at 20 °C/min. The carrier gas used was nitrogen flow for both catalysts. There are four components that can be identified from this analysis. It is determined by the segments labelled (i), (ii), (iii) and (iv).

The first segment, (i) indicates the moisture contents of the catalyst. At the temperature less than 200 °C, the moisture content of fresh catalyst is about 0.68 wt%. From the graph, it can be seen that fresh catalyst has higher moisture content than used catalyst.

At segment (ii) which is about 420 °C for used catalyst and 400 °C for fresh catalyst, water were release from the equation of $Ca(OH)_2 \rightarrow CaO + H_2O$. Thus, used catalyst might release water at higher temperature compared to fresh catalyst. (Gotoh et. al., 2011)

Segment (iii) at about 600 °C, indicates the release of CO_2 from the equation of $CaCO_3 \rightarrow CaO + CO_2$. Used catalyst release 101 wt% of CO_2 while fresh catalyst release 96 wt% of CO_2. This might also means that used catalyst produced more CO_2 compared to fresh catalyst. (Gotoh et. al., 2011)

Lastly, segment (iv) determines the solid residue of the catalyst. Based from the graph, used catalyst has higher solid content compared to fresh catalyst.

4.2.5 Gas Composition

The gas produced from the experimental pyrolysis are directly analysed by the gas analyzer. There are other flue gas produced, however, this study are focusing on the production of fuel gas. Thus, data of gas collected are tabulated in Table 4-3.

Table 4-3 : Gas production of POF sample at 700 °C

	No catalyst	$Ni/Ce/Al_2O_3$	Ca/Al_2O_3
Pyrolysis Temperature (°C)	700	700	700
Gas Composition (100 %)			
CO	13.2	45.3	15.3
CO_2	12.4	4.5	40.5
CH_4	23.7	33.0	25.0

Table 4-3 shows the gas production of pyrolysis experiment in lab scale by using POF as biomass and both of the catalyst $Ni/Ce/Al_2O_3$ and Ca/Al_2O_3. The gas production of catalytic pyrolysis was higher than non- catalytic. This is parallel to Chen et. al (2003) which is fuel gas production will be higher with addition of the catalyst.

Comparing the both catalyst, $Ni/Ce/Al_2O_3$ produced more fuel gas than Ca/Al_2O_3 and this result is supported by (Koo et, al., 2009) proving that addition of Cerium enhanced the production of fuel gas. According to them, Ni have the strongest effect on fuel gas yield enhancement .With adding of Ni (5 wt %), the total gas yield was improved and gas quality was upgraded greatly, even at lower temperature (600–700 °C).

Table 4-4 : Comparison for $Ni/Ce/Al_2O_3$ with previous research

Gas composition (Vol. %)	Recent Study	Yang et. al., 2006
CO	45.3	41.3
CO_2	4.5	10.78
CH_4	33	33.49

Table 4-4 is the comparison of this study to the previous research of using $Ni/Ce/Al_2O_3$ as the catalyst at 700 ^oC. Yang et. al., (2006) obtain more CO_2 in his findings while in this study only 4.5 vol%. Methane productions are about the same between the studies, but his research was able to obtain more methane. This is supported by Huang et. al., (2000) reported that the presence of Cerium in the Ni/Al_20_3 enhanced the fuel gas production, showed almost 100 % conversion and 104 % of H_2 selectivity achieved at 650 °C.

5 CONCLUSION

5.1 Overview

This chapter covers the conclusion of the research study and also recommendation for planning future work in order to enhance the research topic.

5.2 Conclusion

Production of fuel gas from biomass is a renewable, clean and safe energy that can helps to replace the demand for the fossil fuels energy. By using catalytic pyrolysis, hydrogen can be produces abundantly and with a lower cost. Catalyst was used for upgrading the fuel gas production in the pyrolysis that encounters catalyst coking problem. In this research, it is found EFB has high char content, thus POF was used to be tested with the catalyst. Comparison between catalytic and non catalytic with POF shows that catalytic with POF produces higher gas production than others in the TGA analysis. The gas produced in the experimental lab scale also shows the same results. The TGA predictions and the actual experimental results are synchronized. $Ni/Ce/Al_2O_3$ produces higher fuel gas compared to Ca/Al_2O_3. This is supported by the previous research. These catalysts can be use as coke resistance metal thus research objective is achieved.

5.3 Recommendation

In order to make this research more interesting, a few of suggestions are listed for future research. This would help the technology develop further.

- Varies with other temperature

By using the same catalyst, more temperature ranging would be very interesting since we can differentiate what temperature is the best at fuel gas production.

- Varies with other biomass sample

By adding more ranges of biomass samples, we can see the effects of the same catalyst on other biomass and does the fuel gas productions resulted from the different biomass.

- Varies with other catalyst composition

A study on how different catalyst composition would effect on the same biomass sample would help to aid the research in finding at which compositions the catalyst would act best in producing fuel gas.

REFERENCES

Abdullah, N. and Bridgwater, A.V.(2006*), Pyrolysis Liquid Derived From Oil Palm Empty Fruit Bunche,* Journal of Physical Science, Vol. 17(2), 117–129, 117.

Abdullah, N.,Sulaiman, F., and Gerhauser, H., (2011) *Characterisation of Oil Palm Empty Fruit Bunches for Fuel Application,* Journal of Physical Science, Vol. 22(1), 1–24.

Aho, et. al, *Catalytic Pyrolysis of Biomass in a Fluidized Bed Reactor: Influence of the Acidity of H-Beta Zeolite,* A˚ bo Akademi University, Finland.

Azizan, M. T., Yusup, S., Laziz, F. D. M., Ahmad, M. M. (2009). *Production of Bio-oil from oil palm's fruit empty fruit bunch via pyrolysis*. Proceeding of The 3rd WSEAS International Conferences on Renewable Energy Resources, ISBN, Spain.

Bridgwater, A.V., (2010), *Review of fast pyrolysis of biomass and product upgrading,* Aston University, Bio energy Research Group, UK.

Başak, B. U., and Nuri, S., (2008). *Rapid and catalytic pyrolysis of corn stalks*, Anadolu University, Turkey.

Baker, E. G., Mudge L. K., Brown, M.D. (1987) *Steam gasification of biomass with Nickel secondary catalysts,* Ind Eng Chem Res; 26:1335–9.

Bridger, G.W., and Chinchen, G. C., (1970) *Hydrocarbon reforming catalysts,* in Catalyst Handbook, London, ICI, Wolte Scientific Books.

Bridgwater, A.V., Meier, D.,and Radlein, D. (1999) *An overview of fast pyrolysis of biomass. O*rg Geochem: 30:1479–93.

Chen, G., Andries, J., and Spliethoff, H.(2003) *Catalytic pyrolysis of biomass for Hydrogen rich fuel gas production*. Energy Convers Manage; 44:2289–96.

Chew, T. L., and Bhatia, S., (2007), *Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery,*USM, Penang.

Demirbas, A., (2001) *Yields of hydrogen-rich gaseous products via pyrolysis from selected biomass samples.* Fuel; 80:1885–91.

Demirbas, A., (2002) *Gaseous products from biomass by pyrolysis and gasification: Effects of catalyst on hydrogen yiel*d. Energy Convers Manage;43:897–909.

Demiral, I., and Sensoz, S. (2007), *The effects of different catalysts on the pyrolysis of industrial wastes(olive and hazelnut bagasse),* Eskis_ehir Osmangazi University, Turkey.

Evans, R., Boyd, L., Elam, C., Czernik, S., French, R., Feik, C., et al., (2003) *Hydrogen From biomass - catalytic reforming of pyrolysis vapors. FY 2003 Progress Report*, National Renewable Energy Laboratory, Golden, CO.

Farrauto, R. J., and Bartholomew, C., (1997) *Introduction to Industrial Catalytic Processes, London: Chapman and Hall.*

Forzatti, P., and Lietti, L., (1999) *Catalyst deactivation*. Catalysis today. 52(2-3); p.165-181.

Fogler, H. S., (2005) *Elements of chemical reaction engineering*. 4th ed. Prentice Hall Professional Technical Reference.

Gopakumar S. T., (2012) *Bio-oil Production through Fast Pyrolysis and Upgrading to "Green" Transportation Fuels,* Auburn University, Alabama.

Huber, G. W., and Dumesic, J. A., (2006) *An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery*. Catal

Today; 111:119–32.

Huiyan, Z., Rui, X., He, H., and Gang, X., (2000). *Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor,* Nanjing University of Technology,China.

Khan, Z., Yusup, S., Ahmad, M. M., Chok, V. S., Uemura, Y., and Sabil, K. M., (2010) *Review on Hydrogen Production Technologies in Malaysia* ,International Journal of Engineering & Technology,10.

Patrick, A. H., and Williams, P. T., (1997), *Upgrading of biomass-derived pyrolytic vapours over zeolite ZSM-5 catalyst: effect of catalyst dilution on product yields,* The University of Leeds, UK.

Williams, P. T., and Patrick A. H., (1997), *The influence of catalyst regeneration on the composition of zeolite-upgraded biomass pyrolysis oils, The University of Leeds, UK.*

Rapagna, S. J., Kiennemann, N., and Foscolo, P. U., (2000), *Steam-gasification of biomass in a fluidised-bed of olivine particles. Biomass Bioenergy*, 19:187–97.

Rostrup-Nielsen, J. R., (1975) *Steam Reforming Catalysts: An Investigation of Catalysts for Tubular Steam Reforming of Hydrocarbons*. Copenhagen: Taknisk Forlag.

Robert. C. B., and Holmgren, J., (2009), *Fast Pyrolysis and Bio-Oil Upgrading, Iowa State University.*

Sadaka, S., (2012), *Pyrolysis,*Iowa State University , Nevada.

Tomishige, K., Asadullah, M.,and Kunimori, K., (2004), *Syngas production by biomass gasification using Rh/CeO2/SiO2 catalysts and fluidized bed reactor*. Catal Today, 89:389–403.

Website,

http://www.hoongchan.com/oil_palm_fibre.htm 2009
http://www.vtt.fi/sites/vetaani/vetaani_task2_2_2.jsp?lang=en
http://www.meti.go.jp/english/press/data/20090828_02.html
http://jfeproject.blogspot.com/2010_04_01_archive.html

APPENDICES

A1. TGA Graph Value for Fresh Ca/Al_2O_3

°C	%	°C	%	°C	%	°C	%
35	100	230	99.26	425	96.51	620	95.1
40	100	235	99.25	430	96.25	625	94.95
45	99.99	240	99.24	435	96.2	630	94.77
50	99.97	245	99.23	440	96.19	635	94.58
55	99.93	250	99.21	445	96.18	640	94.36
60	99.91	255	99.2	450	96.18	645	94.1
65	99.88	260	99.17	455	96.17	650	93.84
70	99.85	265	99.16	460	96.16	655	93.51
75	99.81	270	99.14	465	96.15	660	93.17
80	99.79	275	99.12	470	96.16	665	92.79
85	99.75	280	99.09	475	96.15	670	92.37
90	99.72	285	99.07	480	96.15	675	91.9
95	99.7	290	99.05	485	96.14	680	91.38
100	99.67	295	99.02	490	96.14	685	90.83
105	99.65	300	99.02	495	96.12	690	90.25
110	99.63	305	98.97	500	96.11	695	89.66
115	99.6	310	98.95	505	96.11	700	89.12
120	99.57	315	98.93	510	96.1	705	88.71
125	99.55	320	98.92	515	96.09	710	88.51
130	99.52	325	98.91	520	96.06	715	88.49
135	99.5	330	98.9	525	96.05	720	88.48
140	99.48	335	98.89	530	96.03	725	88.48
145	99.47	340	98.88	535	96.01	730	88.48
150	99.45	345	98.87	540	95.98	735	88.48
155	99.44	350	98.87	545	95.97	740	88.48
160	99.43	355	98.86	550	95.94	745	88.48
165	99.41	360	98.86	555	95.92	750	88.48
170	99.4	365	98.86	560	95.88	755	88.49
175	99.39	370	98.85	565	95.86	760	88.49
180	99.37	375	98.85	570	95.83	765	88.48
185	99.36	380	98.84	575	95.81	770	88.49
190	99.35	385	98.84	580	95.77	775	88.49
195	99.33	390	98.82	585	95.73	780	88.48
200	99.32	395	98.79	590	95.68	785	88.48
205	99.31	400	98.7	595	95.63	790	88.48
210	99.3	405	98.49	600	95.54	795	
215	99.29	410	98.11	605	95.46	800	
220	99.28	415	97.59	610	95.36		
225	99.27	420	97.02	615	95.24		

A2. TGA Graph Value for Fresh Ni/Ce/Al_2O_3

°C	%	°C	%	°C	%	°C	%
0		225	99.68	445	99.49	575	99.7
5		230	99.67	450	99.49	580	99.74
10		235	99.66	455	99.49	585	99.78
15		240	99.65	460	99.49	590	99.8
20		245	99.64	465	99.51	595	99.86
25		250	99.62	470	99.5	600	99.86
30	100	255	99.62	475	99.49	605	99.89
35	100.1	260	99.6	480	99.5	610	99.9
40	100.1	265	99.58	485	99.52	615	99.93
45	100	270	99.57	490	99.52	620	99.94
50	100	275	99.56	495	99.52	625	99.95
55	100	280	99.54	500	99.53	630	99.95
60	99.99	285	99.53	505	99.53	635	99.98
65	99.97	290	99.52	510	99.53	640	99.96
70	99.95	295	99.5	515	99.54	645	99.96
75	99.93	300	99.49	520	99.53	650	99.96
80	99.92	305	99.47	525	99.55	655	99.97
85	99.91	310	99.47	530	99.55	660	99.97
90	99.89	315	99.46	535	99.55	665	99.97
95	99.88	320	99.45	540	99.55	670	99.97
100	99.86	325	99.44	545	99.58	675	99.98
110	99.84	330	99.45	550	99.57	680	99.98
115	99.83	335	99.44	555	99.6	685	99.99
120	99.81	340	99.44	560	99.62	690	99.99
125	99.8	345	99.44	565	99.65	695	100
130	99.79	350	99.43	570	99.68	700	100
135	99.79	355	99.44	575	99.7	705	100
140	99.78	360	99.43	580	99.74	710	100
145	99.76	365	99.44	585	99.78	715	100
150	99.76	370	99.44	590	99.8	720	100
155	99.76	375	99.44	595	99.86	725	100
160	99.75	380	99.45	600	99.86	730	100
165	99.75	385	99.44	605	99.89	735	100
170	99.74	390	99.45	610	99.9	740	100.1
175	99.74	395	99.45	615	99.93	745	100.1
180	99.73	400	99.45	620	99.94	750	100.1
185	99.73	405	99.46	625	99.95	755	100.1
190	99.73	410	99.46	630	99.95	760	100.1
195	99.72	415	99.47	635	99.98	765	100.1
200	99.71	420	99.46	550	99.57	770	100.1
205	99.7	425	99.47	555	99.6	775	100.1
210	99.7	430	99.47	560	99.62	780	100.1
215	99.69	435	99.48	565	99.65	785	100.1
220	99.69	440	99.49	570	99.68	790	100.1

A3. TGA Graph Value for EFB

°C	%	°C	%	°C	%	°C	%
5		225	225	325	48	455	8.572
10		230	230	330	47.85	460	8.381
15		235	235	335	46.17	465	8.126
20		240	240	340	44.65	470	7.82
25	99.36	245	245	345	43.25	475	7.491
30	98.73	250	250	350	41.97	480	7.135
35	97.82	255	87.86	355	40.8	485	6.775
40	96.69	260	85.77	360	39.77	490	6.456
45	95.87	265	83.34	365	38.85	495	6.21
50	94.77	270	80.57	370	38.04	500	6.039
55	94.09	275	77.59	375	37.32	505	5.937
60	93.53	280	74.38	380	36.63	510	5.867
65	93.08	285	70.86	385	35.98	515	5.815
70	92.71	290	67.97	390	35.35	520	5.775
75	92.41	295	64.38	395	34.71	525	5.74
80	92.16	300	60.72	400	34.06	530	5.724
85	91.96	305	56.59	405	33.4	535	5.705
90	91.78	310	52.74	410	32.73	540	5.689
95	91.65	315	49.18	415	32.03	545	5.666
100	91.52	320	48.9	420	31.3	550	5.661
105	91.44	205	92.47	425	30.53	555	5.645
110	91.37	210	92.88	430	29.67	560	5.63
115	91.31	215	93.22	435	28.72	455	8.572
120	91.27	220	93.55	440	27.61	460	8.381
125	91.23	225	93.6	445	25.98	465	8.126
130	91.2	230	92.99	450	11.62	470	7.82
135	91.17	235	92.48	455	8.572	475	7.491
140	91.15	240	91.96	460	8.381	480	7.135
145	91.14	245	90.98	465	8.126	485	6.775
150	91.11	250	89.57	470	7.82	490	6.456
155	91.1	255	87.86	475	7.491	495	6.21
160	91.21	260	85.77	480	7.135	500	6.039
165	91.0	265	83.34	395	34.71	505	5.937
170	90.96	270	80.57	400	34.06	510	5.867
175	91.12	275	77.59	405	33.4	515	5.815
180	91.27	280	74.38	410	32.73	520	5.775
185	91.45	285	70.86	415	32.03	525	5.74
190	91.68	290	67.97	420	31.3	530	5.724
195	91.58	295	64.38	425	30.53	535	5.705
200	92.05	300	60.72	430	29.67	540	5.689
205	92.47	305	56.59	435	28.72	545	5.666
210	92.88	310	52.74	440	27.61	550	5.661
215	93.22	315	49.18	445	25.98	555	5.645
220	93.55	320	48.9	450	11.62	560	5.63

A4. TGA Graph Value for POF

°C	%	°C	%	°C	%	°C	%
°C	%	215	89.36	435	27.95	655	8.111
0		220	89.2	440	26.31	660	8.132
5		225	89.00	445	23.9	665	8.151
10		230	88.77	450	15.02	670	8.153
15		235	88.49	455	10.23	675	8.152
20		240	88.14	460	9.897	680	8.16
25		245	87.7	465	9.522	685	8.141
30	98.68	250	87.06	470	9.104	690	8.131
35	97.57	255	86.22	475	8.692	695	8.109
40	96.48	260	85.24	480	8.308	700	8.083
45	95.50	265	84.54	485	8.014	705	8.056
50	94.64	270	82.98	490	7.825	710	8.020
55	93.91	275	80.95	495	7.721	715	7.968
60	93.30	280	78.33	500	7.644	720	7.924
65	92.78	285	75.54	505	7.603	725	7.884
70	92.35	290	72.65	510	7.569	730	7.857
75	91.98	295	69.72	515	7.566	735	7.849
80	91.68	300	66.88	520	7.553	740	7.863
85	91.44	305	64.15	525	7.556	745	7.89
90	91.23	310	61.56	530	7.542	750	7.92
95	91.06	315	59.09	535	7.544	755	7.943
100	90.93	320	56.74	540	7.546	760	7.958
105	90.82	325	54.52	545	7.555	765	7.981
110	90.73	330	52.38	550	7.555	770	8.00
115	90.65	335	50.33	555	7.567	775	8.007
120	90.59	340	48.39	560	7.579	780	8.001
125	90.52	345	46.58	565	7.587	785	7.997
130	90.47	350	44.90	570	7.604	790	7.984
135	90.42	355	43.39	575	7.618	795	
140	90.37	360	42.04	580	7.636	800	
145	90.32	365	40.85	585	7.653	655	8.111
150	90.27	370	39.81	590	7.682	660	8.132
155	90.22	375	38.89	595	7.707	665	8.151
160	90.18	380	38.05	600	7.744	670	8.153
165	90.14	385	37.26	605	7.775	675	8.152
170	90.08	390	36.49	610	7.807	680	8.16
175	90.03	395	35.71	615	7.835	685	8.141
180	89.98	400	34.92	620	7.872	690	8.131
185	89.91	405	34.11	625	7.912	695	8.109
190	89.85	410	33.27	630	7.951	700	8.083
195	89.78	415	32.37	635	7.985	705	8.056
200	89.70	420	31.41	640	8.021	710	8.020
205	89.60	425	30.39	645	8.05	715	7.968
210	89.49	430	29.26	650	8.083	720	7.924

A5. TECHNICAL PAPER

Catalytic Pyrolysis of Agricultural Waste; Effect of Catalyst Composition

Student name: Nur Farhanim binti Mustaffa (KC09060)
Supervisor: Dr. Ruzinah Isha

Faculty of Chemical & Natural Resources Engineering
University Malaysia Pahang, 26300 Kuantan, Pahang, MALAYSIA.
E-mail: aniemah90@gmail.com, Tel: +0135044275

ABSTRACT

Fuel gas can be produced from the pyrolysis process of biomass. Hydrogen energy is an example of fuel gas. It is a clean and renewable thus becoming a suitable energy that can replace the fossil fuels. This research aimed to produce high yield of fuel gas with a coke resistance catalyst. Palm oil wastes were used as samples in this research which were empty fruit bunch (EFB) and palm oil fibre (POF). The catalysts used were nickel alumina, doped with Cerium, $NiCeAl_2O_3$ and Calcium Alumina, $CaAl_2O_3$. The reactor used was tubular reactor type; quartz reactor and then placed in tubular furnace for heating purposes. The temperature range for the pyrolysis to take place efficiently was from 500 ^oC until 800 ^oC. Thus the experiment was carried out on 700 ^oC. The production of fuel gas from this process was recorded and analysed by using gas analyzer and thermo gravimetric analysis (TGA).

Keywords: Catalyst; EFB; Coking resistant; Palm oil waste

INTRODUCTION

Fuels usually come from the hydrocarbon that is formed for hundreds of years ago. This energy resource is not renewable and is depleting. Hydrocarbons are also causing green house effect and bad environmental issue. Emissions from fossil fuel usage significantly degrade air quality all over the world. The resulting carbon byproducts are substantially changing the world's climate. Thus hydrogen has become the new choice of energy that possibly can solve the issue of hydrocarbon fuel. Hydrogen is a type of energy that is renewable, clean, safe and economically competitive with gasoline or diesel .Hydrogen also can help prevent the depletion of fossil fuel reserves .Hydrogen production plays a very important role in the development of hydrogen economy. One of the promising hydrogen production approaches is conversion from biomass, which is abundant, clean and renewable. A review of hydrogen production technologies in Malaysia shows, biomass pyrolysis has the lowest cost in the production of hydrogen energy. (Khan et al, 2010).

In pyrolysis, catalyst can be added to enhance the production of the gas produced. But unfortunately, catalysts are exposed to problem of coking and tar formation which can decrease the function of the catalyst thus causing the production of gas or oil to be less. To overcome this problem, catalysts are doped with metal transition to avoid the formation of tar thus creating a good coking resistant metal. Thus this research is aimed to study for the effect of coke resistance metal catalyst and also the effect of the catalyst composition on the production of hydrogen.

MATERIALS AND METHOD

Sample Preparation

Biomass used was the palm oil agricultural waste samples which were empty fruit bunch (EFB) and palm oil fiber (POF). All these samples were collected at the Felda Lepar Hilir 3. Each of these samples were grounded and sieved to the range of 0.63 mm and 1 mm in particle sizes by using sieve shaker. Then the particles were dried at 80 °C until constant weight so that the sample is 10 % dry. This condition is prior to fast pyrolysis condition which is, the condition of feed need to be 10 % dry, and the size of feed particle is less than 3 mm.

Reactor

The experiment was using tubular reactor; quartz reactor having 1cm of diameter, 25.6 g of weight and 52 cm of height. The sample was filled in the reactor and placed in the tubular furnace for heating purpose. The gas used was nitrogen and were preheated prior to its entry into the reactor. Nitrogen was also used for purging and acts as carrier gas.

Catalyst

The catalysts used were $Ni/Ce/Al_2O_3$ and Ca/Al_2O_3. Both catalysts were obtained from Dr. Ruzinah Isha. The catalysts ratios were $12Ni/8Ce/Al_2O_3$ and $30Ca/Al_2O_{3.}$ For the experiment, 1 g of catalyst was used together with 1g of biomass sample. For TGA, the ratio of catalyst to biomass sample is about 2:1.

Blank Test

The purpose of the blank test was to make sure if there any leakage on any connection that have been made. Nitrogen was used as a medium. In this test, nitrogen was flow through the system for about 15 minutes at 11 psi. Bubble is needed to determine any leakage of the set up. There is no leakage if the pressure gauge at the pyrolysis system has same reading with the pressure gauge at the nitrogen regulator.

Purging

Purging is the first procedure that must be made before starting the experiment. This is to make sure there in no air in the system. The purging process is done for 10 minutes at 11 psi. The flow of Nitrogen will replace the air in the reactor.

Experimental Procedures

Pyrolysis experiment was carried out under nitrogen atmosphere at the temperature 700 ^{o}C because this temperature was found to be the optimum condition for maximum liquid product yield . A quantity of 2 g of EFB was loaded in the reactor with a heating rate 20 ^{o}C/min up to desired temperature. The gas product was analyzed by using gas analyzer.

Analysis

There are two types of analyzer used. First is by using thermo gravimetric analysis, TGA to determine the moisture content of the samples before pyrolysis begins. Secondly is by using gas analyzer to determine the composition of the gas produced.

TGA

This analysis was performed to determine moisture content, volatility and ash content of the sample. Figure 3-10 shows the type of TGA used. There are four types of analysis were done by using TGA.

For the first analysis, the composition of EFB and POF was investigated. Both EFB and POF were cut into <1 mm. The TGA analysis was performed using nitrogen with a flow rate of 100 ml/min. The temperature was increased from ambient temperature to 800 ^{o}C with a heating rate of 20 ^{o}C/min.

The characterization of catalyst was carried out by using TGA as well. The catalysts, Ni/Ce/Al_2O_3 and Ca/Al_2O_3 were used in this analysis. For fresh catalyst, the TGA analysis was performed using nitrogen. Meanwhile, for used catalyst of Ni/Ce/Al_2O_3, the analysis was carried out using air flow. However, for used catalyst of Ca/$Al_2O_{3,}$ the gas flow used was nitrogen gas. The temperature was increased from ambient to 800 ^{o}C at 20 ^{o}C/min. The catalytic pyrolysis of EFB and POF were also analyzed by using TGA.

Gas Analyzer

Figure 3-11 shows the gas analyzer used to detect the gas composition of the fuel gas produced from the pyrolysis process. It was also used to ensure that the gas condition inside the pyrolysis system was nitrogen and not oxygen. It is important because pyrolysis is the thermal decomposition under absence or limited supply of air. The gas produced was monitored at 5 minutes intervals for 1 hour.

RESULTS AND DISCUSSION

Effects of Type of Biomass

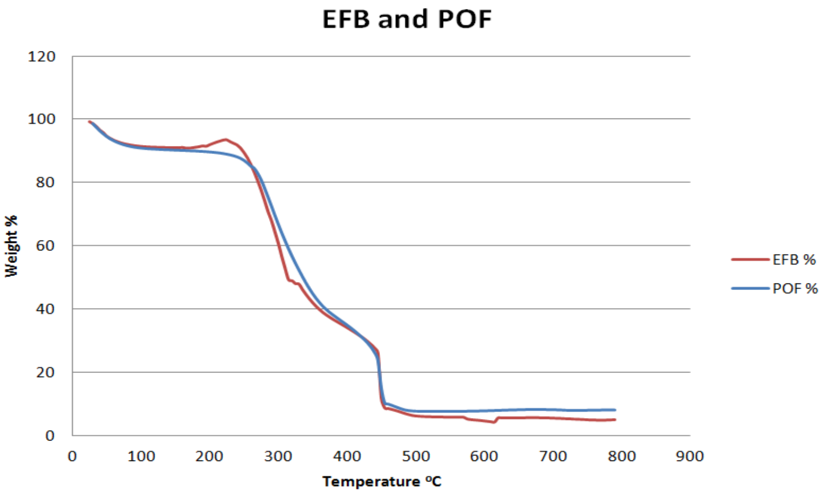

Figure 1 : Graph of Weight % against Temperature (^{o}C) for EFB

There are three different stages that can be determined from the analysis result. The first region at temperature below than 150 ^{o}C, shows the water content of the biomass. EFB has higher moisture content compared to POF which is 7.54 wt% and 7.00 wt% respectively. Moisture content is also use to indicate the oil yield produces.

The second region is the middle part of the graph, from 200 °C until 450 °C. This stage determines the volatility of biomass. Higher volatile matter indicates higher production of gas. For EFB, the temperature is about 240 °C and 220 °C for POF. This means that EFB has higher volatile matter than POF with 64.35 wt% .This segment also indicates the decomposition of cellulose and hemicelluloses.

The last segment after 450 °C until 800 °C, determines the solid contents or char residue which indicates the decomposition of lignin for the biomass. Among the biomass, EFB has more char with 22.78 wt% compared to only 18.33 wt% of POF.

Effects of Catalysts

The characterization of catalyst is carried out by TGA. The result of investigation is shown in Figure 2 and Figure 3. The TGA of $Ni/Ce/Al_2O_3$ is shown in Figure 2. $Ni/Ce/Al_2O_3$ is maintaining at 100 wt% through the temperatures. This is due to the stability of the catalyst itself to maintain his condition especially at high temperatures.

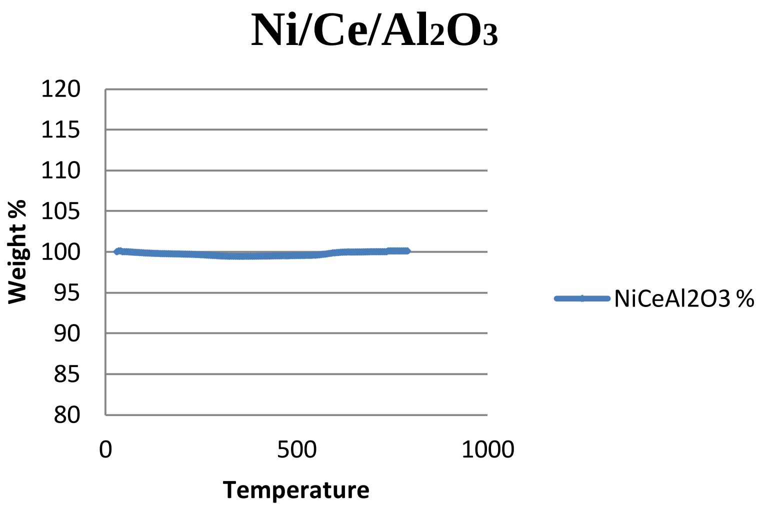

Figure 2 : Graph of Weight % against Temperature (°C) of $Ni/Ce/Al_2O_3$.

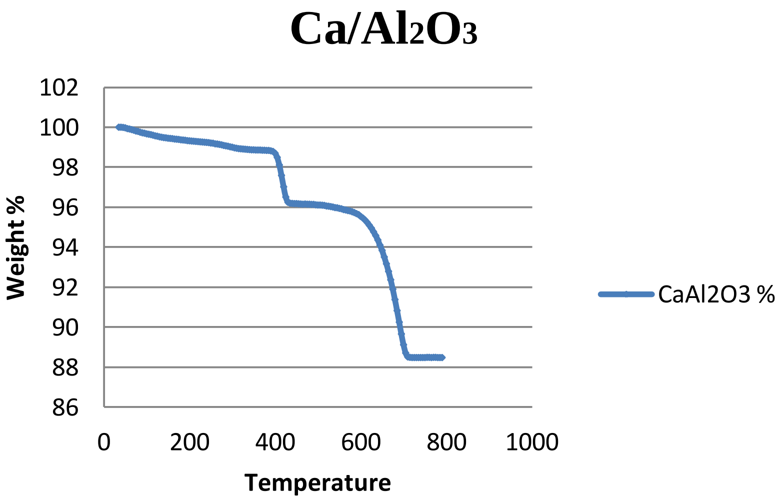

Figure 3 : Graph of Weight % against Temperature (°C) of Ca/Al_2O_3

Figure 3 on the other hand, shows the TGA of Ca/Al_2O_3 catalyst. On the first stage of 200 °C, the lines interpret as the moisture content of the catalyst. By 400 °C, there is declining of weight % from 98.7 wt% to 96 wt%. This might be because of water were release based from the equation $Ca(OH)_2 \rightarrow CaO + H_2O$. (Gotoh et. al., 2011) While from 400 °C to 700 °C, the curves shows that, carbon dioxide was released from the compound based from the equation of $CaCO_3 \rightarrow CaO + CO_2$. At the end of the curve at 700 °C, is the char content of the catalyst.

Effects of Catalytic and Non-Catalytic

Based from the analysis of biomass samples, it was seen that POF has better performances than EFB, therefore POF was analysed. This is because POF has lower char content compared to EFB. Figure 4 shows the catalytic performance with POF compared to non-catalytic of POF.

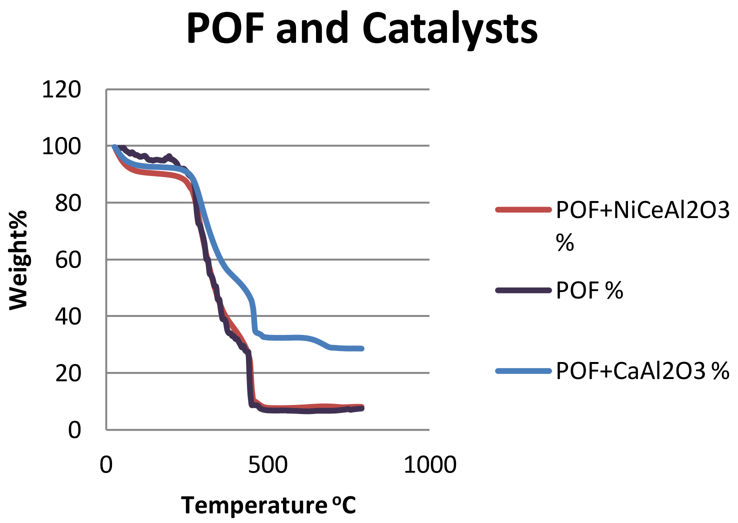

Figure 4 : Graph of Weight % against Temperature (°C) of catalysts mixed with POF.

The catalytic performances of catalyst with POF are compared to the non-catalytic of POF which is shown in Figure 4. There are three types of components that can be identified from this analysis which are moisture content, volatile matter and char content. Moisture content can be determined at temperature of 0 °C until 200 °C. Catalytic performances of catalyst with POF for $NiCeAl_2O_3$ has 7 wt% moisture content compared to 6.55 wt% for $CaAl_2O_3$.

At temperature 230 °C to 420 °C, volatility can be identified. This is important because high volatility means high production of gas. POF with $NiCeAl_2O_3$ has the highest volatile matter of 61.83 wt% compared to POF with $CaAl_2O_3$ and POF of only at 41.40 wt% and 43.92 wt% respectively. This also means that POF with $NiCeAl_2O_3$ might be able to produce high yield of gas.

The last component that can be detected is char content. From the graph, it seems that POF with $CaAl_2O_3$ has higher curve line compared to others. This is due to the ratio weight of catalyst to POF. POF with $CaAl_2O_3$ has the ration of biomass to catalyst of 1:2, while the ratio of POF with $NiCeAl_2O_3$ is 1:1. This is due to the human error while preparing the samples. However, POF has the highest char content of 19.89 wt% compared to others.

Lab scale

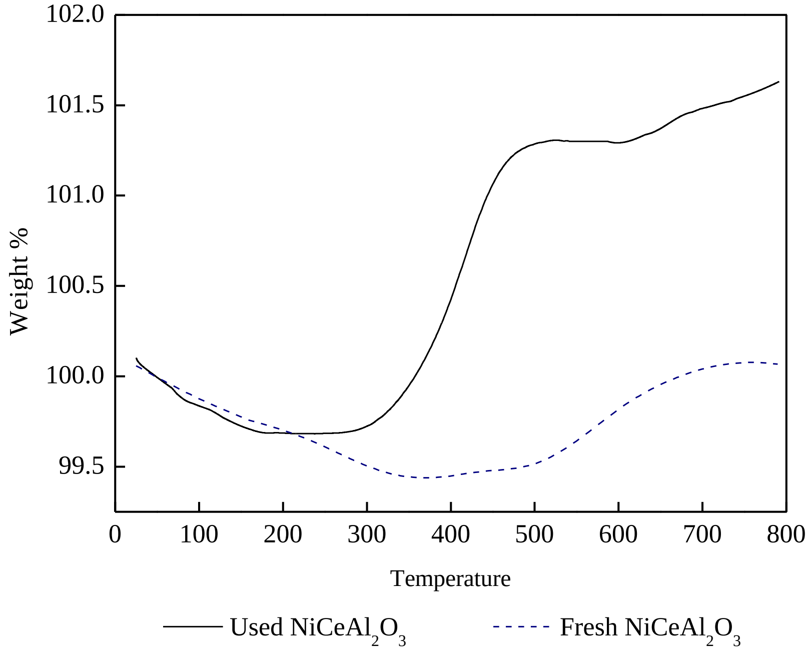

Figure 5: Graph of used and fresh catalyst of $NiCeAl_2O_3$

Figure 5 shows the comparisons for used and fresh catalyst of $NiCeAl_2O_3$. The fresh catalyst was using nitrogen flow as carrier gas while the used catalyst was by using oxygen flow. However, both of them were analysed ambient temperature until 800 ^oC at 20 ^oC/min. From this graph, moisture contents can be determined at the temperature of before 100 ^oC.

For the fresh catalyst of $NiCeAl_2O_3$, the curve lines are lower than used catalyst. At 300 ^oC, the fresh catalyst burns to dust causing the particles weight to reduce. Compared to the used catalysts, fresh catalyst has a stable curve through the temperature. This is because the fresh catalyst was analysed under nitrogen flow so there is not much effect on the catalyst.

For the used catalyst of $NiCeAl_2O_3$, the graph shows that used catalyst has two curves lines. The first curve line at 325 ^oC indicates the decomposition of filament carbon. While for the second curve line at 600 ^oC indicates the decomposition of encapsulate carbon. (Isha and William, 2011) This also means that encapsulate carbon can only be regenerated at high temperature compare to the filament carbon.

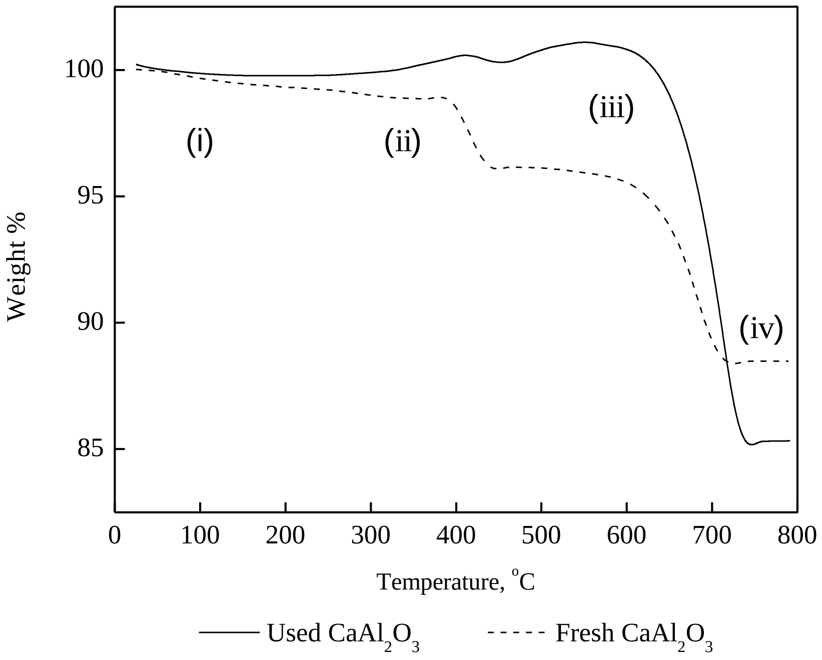

Figure 6: Graph of used and fresh catalyst of $CaAl_2O_3$

Figure 6 shows the comparison between used and fresh catalyst of $CaAl_2O_3$ using TGA. These catalysts were analysed from ambient temperature until 800 °C at 20 °C/min. The carrier gas used was nitrogen flow for both catalysts. There are four components that can be identified from this analysis. It is determined by the segments labelled (i), (ii), (iii) and (iv) in the graph.

The first segment, (i) indicates the moisture contents of the catalyst. At the temperature less than 200 °C, the moisture content of fresh catalyst is about 0.68 wt%. From the graph, it can be seen that fresh catalyst has higher moisture content than used catalyst.

At segment (ii) which is about 420 °C for used catalyst and 400 °C for fresh catalyst, water were release based from the equation of $Ca(OH)_2 \rightarrow CaO + H_2O$. (Gotoh et. al., 2011) Thus, used catalyst release water at higher temperature compared to fresh catalyst.

Segment (iii) at about 600 °C, indicates the release of CO_2 based from the equation of $CaCO_3 \rightarrow CaO+CO_2$. Used catalyst release 101 wt% of CO_2 while fresh catalyst release 96 wt% of CO_2. This also means that used catalyst produced more CO_2 compared to fresh catalyst. Lastly, segment (iv) determines the solid residue of the catalyst. Based from the graph, used catalyst has higher char content compared to fresh catalyst.

Gas Composition

Table 1 : Gas production of POF sample at 700°C

	No catalyst	Ni/Ce/Al_2O_3	Ca/Al_2O_3
Pyrolysis Temperature °C	700	700	700
Gas Composition			
CO	13.2	45.3	15.3
CO_2	12.4	4.5	40.5
CH_4	23.7	33	25

Table 1 shows the gas production of pyrolysis experiment in lab scale by using POF as biomass and both of the catalyst Ni/Ce/Al_2O_3 and Ca/Al_2O_3. The gas production for catalytic pyrolysis were higher than non- catalytic. This is parallel to (Chen et al., 2003) which is fuel gas production will be higher with addition of the catalyst.

Comparing the both catalyst, Ni/Ce/Al_2O_3 produced more fuel gas than Ca/Al_2O_3 and this result is supported by (Koo et, al., 2009) proving that addition of Cerium enhanced the production of fuel gas. According to him, Ni have the strongest effect on fuel gas yield enhancement .With adding Ni (5 wt %), the total gas yield was improved and gas quality was upgraded greatly, even at lower temperature 600–700 °C.

Table 2 : Comparison for Ni/Ce/Al_2O_3 with previous research

Gas composition (Vol. %)	Recent Study	Yang et. al., 2006
CO	45.3	41.3
CO_2	4.5	10.78
CH_4	33	33.49

Table 2 is the comparison of this study to the previous research of using Ni/Ce/Al_2O_3 as the catalyst at 700 °C. Yang et. al., obtain more CO_2 in his findings while in this study only 4.5 vol%. Methane productions are about the same between the studies, but his research was able to obtain more methane. This is supported by Huang et. al., in 2000 reported that the presence of Cerium in the Ni/Al_20_3 enhanced the fuel gas production. His catalyst showed almost 100 % conversion and 104 % of H_2 selectivity achieved at 650 °C.

CONCLUSION

Production of fuel gas from biomass is a renewable, clean and safe energy that can helps to replace the demand for the fossil fuels energy. By using catalytic pyrolysis, hydrogen can be produces abundantly and with a lower cost. Catalyst was used for upgrading the fuel gas production in the pyrolysis that encounters catalyst coking problem. In this research, it is found EFB has high char content, thus POF was used to be tested with the catalyst. Comparison between catalytic and non catalytic with POF shows that catalytic with POF produces higher gas production than others in the TGA analysis. The gas produced in the experimental lab scale also shows the same results. The TGA predictions and the actual experimental results are synchronized. Ni/Ce/Al_2O_3 produces higher fuel gas compared to Ca/Al_2O_3. This is supported by the previous research. These catalysts can be use as coke resistance metal thus research objective is achieved.

Acknowledgement: The authors thank University Malaysia Pahang for the help of completing Undergraduate Research Project.

REFERENCES

Chen G, Andries J, Spliethoff H. *Catalytic pyrolysis of biomass for hydrogen rich fuel gas production*. Energy Convers Manage 2003;44:2289–96.

Patrick A. Horne and Paul T. Williams(1997), *Upgrading of biomass-derived pyrolytic vapours over zeolite ZSM-5 catalyst: effect of catalyst dilution on product yields,* The University of Leeds, UK.

Z. Khan, S. Yusup, M.M. Ahmad, V.S. Chok, Y. Uemura, K. M. Sabil, *Review on Hydrogen Production Technologies in Malaysia* ,International Journal of Engineering & Technology 2010,10