THE EFFECT OF CATALYST COMPOSITION FOR PALM OIL WASTE GASIFICATION: THERMAL GRAVIMETRIC ANALYSIS

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ABSTRACT

Fossil fuels demand is increasing rapidly because of the growth of population and industrialization. However, the conventional energy source is depleted. Biomass is abundant but inefficiently utilized. Gasification of biomass is the one of the alternative ways to encounter this problem. This research aims to study the effect of catalyst composition for palm oil waste gasification and to synthesis and characterize the catalyst. Empty Fruit Bunch (EFB), Palm Oil Fiber (POF) and Palm Oil Shell (POS) were initially analyzed by using a thermogravimetric analyzer (TGA). It is found that EFB contain more volatile matter in comparison to POF and POS. The high content of volatile matter makes EFB highly volatile, reactive and very suitable for gas fuel production. It can also be deduced that EFB might produce more hydrogen than POF and POS.The catalysts were prepared via a wet impregnation method. The nickel alumina catalyst with various weight percent of the promoter, Ce or Ca, were synthesised and tested with a sample consisted of 1:1 weight percent of catalyst to biomass in the Thermo gravimetric Analysis (TGA). The influence of Ce loading on the $Ni/Ce/Al_2O_3$, the different promoters, (Ce or Ca), loading in the Ni/Al_2O_3 and the different ratio of Nickel loading in the $Ni/Ce/Al_2O_3$ were investigated in the gasification of EFB in the Thermo gravimetric Analysis (TGA). Based on the result, Ce show better performance compared to Ca. The result shows the optimum Ce loading was 10 wt% and Ni loading of 5wt%. The $5Ni/10Ce/Al_2O_3$ catalyst was found to be the best catalyst for the palm oil waste gasification.

ABSTRAK

Permintaan bahan api fosil meningkat dengan cepat kerana pertumbuhan penduduk dan kemajuan perindustrian. Walaubagaimanapun, sumber tenaga konvensional semakin habis. Biojisim yang banyak tetapi tidak digunakan secara keseluruhan. Pengegasan biojisim adalah salah satu cara alternative untuk menghadapi masalah ini. Kajian ini bertujuan untuk mengkaji kesan komposisi pemangkin sisa buangan minyak sawit pengegasan dan untuk sintesis dan mencirikan pemangkin. Tandan buah kelapa sawit kosong (EFB), gentian minyak sawit (POF) dan tempurung minyak sawit (POS) pada mulanya dianalisis dengan menggunakan termogravimetrik analisis (TGA). Ia didapati bahawa EFB mengandungi bahan meruap yang lebih berbanding dengan POF dan POS. Kandungan bahan meruap yang tinggi menjadikan EFB cepat meruap dan reaktif malah sangat sesuai untuk pengeluaran bahan api gas. Ia juga boleh dikatakan bahawa EFB mungkin menghasilkan lebih banyak hydrogen berbanding POF dan POS. Pemangkin telah disediakan melalui kaedah pengisitepuan basah. Nikel alumina, pemangkin dengan pelbagai peratus berat, (Ce atau Ca), telah disintesis dan diuji dengan sampel terdiri 1:1 nisbah peratus berat pemangkin kepada biojisim dalam TGA. Pengaruh Ce kepada $Ni/Ce/Al_2O_3$, promoter yang berbeza, Ce atau Ca, memuatkan dalam Ni/Al_2O_3 dan nisbah yang berbeza kandungan Nikel dalam $Ni/Ce/Al_2O_3$ diuji dalam pengegasan EFB dalam TGA. Berdasarkan kepada ujikaji, Ce menunjukkan prestasi yang lebihbaik berbanding Ca. Peratus berat optimum bagi Ce adalah 10% berat dan kandungan Nikel adalah 5% berat. Jadi, $5Ni/10Ce/Al_2O_3$ pemangkin didapati menjadi pemangkin terbaik untuk pengegasan sisa kelapa sawit.

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%	- percentage
°C	- degree Celsius
µm	- micrometer
g	-gram
m	- meter
min	- minute
mm	- millimetre
s	- second
wt %	- weight percentage

LIST OF ABBREVIATIONS

EFB	Empty fruit bunch
POF	Palm oil fiber
POS	Palm oil shell
SEM	Scanning electron microscopy
TGA	Thermo gravimetric analysis

1 INTRODUCTION

1.1 Research Background

Fossil fuel is the most energy demand today. It can make modern life possible. These major sources of energy work to generate electricity and power transportation systems. The demand for energy will never be decreased. The industrial revolution has shown the way and it's still going on. Fossil fuels are the major energy sources but still won over consumption takes place lead to disastrous effects such as air pollution. Burning of fossil fuels releases carbon dioxide, nitrogen monoxide, nitrogen dioxide, sulphur dioxide and carbon monoxide that have severe consequences on the habitats. Furthermore, it also affects human health.

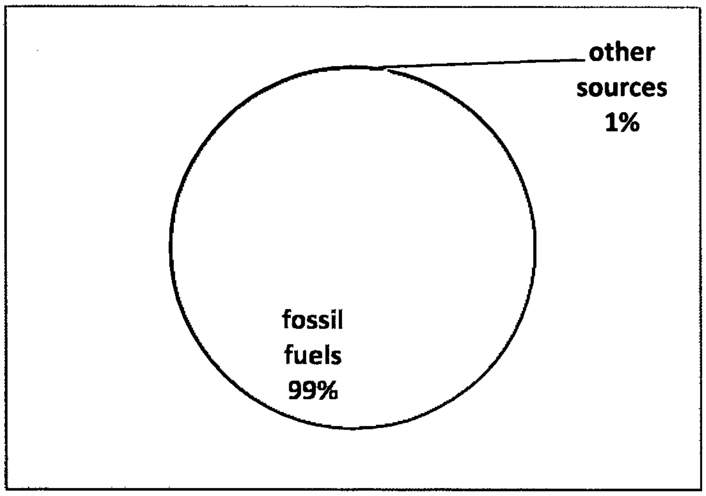

Figure 1-1: Percent of transportation sector consumption.

Sources: Energy information administration, monthly energy review, April (2013)

Because of the depletion of fossil fuels and the growing adverse impact on the environment that caused by the utilization of fossil fuels, researchers are investigating fuels which are renewable and environmentally compatible (Vezirlu and Barbir., 1992). However, among all the fuels considered, hydrogen stands out as the best. Hydrogen stands apart as an alternative fuel. The benefits of hydrogen in the emerging energy environment scene as a promising alternative for simultaneously solving the two problems concerning the protection of the environment and optimum energy utilization.

Nevertheless, while considering hydrogen for automotive applications, the factors must be carefully viewed is the fuel metering system should be capable of supplying the desired quantity of fuel to the engine at the appropriate point in the engine cycle to ensure sustained engine operation without any symptoms of undesirable combustion. Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. Palm oil is a one of the versatile vegetable oil which is used as a raw material for both food and non food industries.

Currently, Malaysia is the largest producers and exporter of palm oil in the world's (Sumathi et al., 2007). Therefore, huge quantities of oil palm waste such as empty fruit bunch (EFB) fibers, shells, fronds, and trunk are also produced. Besides producing oils, at present there is a continuous interest in palm oil waste treatment. To treat this tremendous of waste, introducing a renewable energy feed like biomass for waste into energy conversion is highly recommended.

Biomass is the fourth largest source of energy in the world, accounting for about 15 % of the world's primary energy consumption and about 38 % of the primary energy consumption in the developing countries (Yildiz et al., 2009). Among all biomass conversion processes, biomass gasification for hydrogen production is one of the promising ones (Jianfen et al., 2009).

Table 1-1: Analyses of Biomass Samples (Haiping et al., 2004)

Waste	Proximate Analysis (weight%)			
	Moisture	**Volatile matter**	**Ash**	**Fixed carbon**
	M_{ad}	V_{ad}	A_d	FC_{ad}
Shell	5.73	73.74	2.21	18.37
Fiber	6.56	75.99	5.33	12.39
EFB	8.75	79.67	3.02	8.65

In addition, catalytic cracking is recognized as the most efficient method to diminish the tar formation in the gas mixture (Jianfen et al., 2009). There are different type of catalysts available in the market, but the only common catalyst is Ni due to the characteristics of being able to be reduced and reoxidised easily, and they show a high conversion efficiency to hydrogen reforming reaction. The main obstacle in the commercialisation of Ni catalysts is their stability. The Ni catalysts are easily deactivated from 'free' NiO on the Ni catalyst (Wang et al., 2009). Furthermore, increasing the Ni content leads to decreasing H_2 yield. In this work, the effect of catalyst precursor loading ; Ca and Ce, in the production of hydrogen from palm oil waste gasification were investigated.

1.2 *Motivation*

Presently, fossil fuels are the main source of world hydrogen production. With demand increasing and supply decreasing, there is certain to be a significant gap in the not too distant future. Fossil fuels are close to depletion since it is non-renewable sources and limited. Besides that, the main environmental challenge of our time is to avoid or reduce the impacts of global warming. When oil and coal is burnt, it emitslarge amounts of carbon dioxide and other harmful gases, that have a negative effect on the environment, like sulfur dioxide. Carbon dioxide traps in the sunlight as it only lets light in, it does not allow it to leave the atmosphere which causes temperatures to rise up. The utilization of biomass is environmentally friendly and can be produced domestically. It is also a renewable and economical alternative fuel besides it is the most abundant element on the earth.

1.3 *Problem Statement*

Nowadays, it has been widely accepted worldwide that global warming is the greatest threat and challenge. In order to stop global warming and to promote sustainable development, renewable energy is a perfect solution to achieve both targets (Shuit et al., 2009). The palm oil industry produces large amounts of solid waste from empty fruit bunch (EFB) fibers, shells, fronds, and trunk. If not well-managed, the waste creates a disposal problem.

According to David et al. (2001), since the mid-1980s, interest has grown on the subject of catalysis for biomass gasification. The use of a catalyst to reform condensible organic compounds and methane can increase the overall efficiency of the biomass conversion process by 10% (David et al.,2001). Isha (2011) finds that Ni catalyst are commonly employed due to the characteristics of being able to be reduce and reoxidised easily and reversibly and they show a high conversion efficiency to hydrogen in reforming reaction. According to Rapagna et al. (2002), the fresh nickel based catalysts are extremely active. For economic reasons, nickel catalyst is the most suitable choice among metals like Co, Fe, Pt, Ru and Rh. Ni on Al_2O_3 or MgO favours syngas production with high H_2/CO molar ratio but, when used at high temperatures, sintering of nickel particles and carbon deposition occurs (Courson et al.,2002).

1.4 Objective

The objectives of this research are:

- to synthesis and characterise the catalyst for palm oil waste gasification.
- to study the effect of catalyst composition for palm oil waste gasification.

1.5 Scope of Study

This research mainly focuses on :

i) the catalytic gasification of biomass that carried out in a Thermogravimetric Analysis (TGA). The Empty Fruit Bunch (EFB), Palm Oil Fiber (POF) and Palm Oil Shell (POS) were used as a sample. The biomass sample was obtained from palm oil mill in Kuantan.

ii) investigating various precursor (Ca and Ce) loading and metal loading (Ni, Ca and Ce) weight ratio in the catalyst that influence the performance of the biomass gasification. The catalyst was prepared via wet impregnation.

iii) the catalyst were tested with a sample of 1:1 weight percent of catalyst to biomass in the TGA.

iv) characterization of fresh catalysts which were analyzed by using Scanning Electron Microscopy (SEM).

2 LITERATURE REVIEW

2.1 Introduction

The presence of high levels of carbon dioxide in the atmosphere results in an increase in the amount of heat on the surface of Earth. This is because carbon dioxide traps heat obtained from sunlight and does not let it dissipate out of the atmosphere, a process known as the greenhouse effect. Since fossil fuels are hydrocarbons (made from hydrogen and carbon), burning fossil fuels releases a large amount of carbon dioxide into the air. When there is a significant rise in the percentage of carbon dioxide in the air, the amount of heat captured by the carbon dioxide gas also increases. This in turn leads to an overall rise in the surface temperature of the earth, which is also known as global warming. Fossil fuels are most energy demand today. Nevertheless, there is a limited amount of them and it also creates environmental problems. Since fossil fuels are non-renewable energy, we must find renewable fuels to use instead. These renewable energy can be made from biomass gasification.

2.2 Fossil Fuel

Fossil fuels are one of the energy resources like coal, oil, and natural gas. They are formed by natural processes such as anaerobic decomposition of buried dead organisms. They were formed many hundreds of millions of years ago before the time of the dinosaurs, hence the name fossil fuels.

The age they were formed is called the Carboniferous Period. It was part of the Palaeozoic Era. "Carboniferous" gets its name from carbon, the basic element in coal and other fossil fuels. Nowadays, fossil fuel energy is relatively cheap to produce and most of the world's technology is geared toward the use of fossil fuels. Nevertheless, fossil fuels are a non-renewable energy source, as their production requires millions of years.

Table 2-1: Fossil fuel reserve depletion times (Shafiee and Topal., 2009)

Model	**Ratio of consumption to reserves**		
	Oil	Coal	Gas
	40	200	70

As we keep on using oil, gas and coal for our energy needs, we're close to run out of fuel sooner. Since, fossil fuels are non-renewable energy sources the production and use of fossil fuels raise environmental concerns. Therefore, hydrogen stands apart as an alternative fuel.

2.3 Hydrogen

Nowadays, the world produces carbon dioxide that is released into the earth's atmosphere. This increased content of Carbon Dioxide increases the warmth of our planet and is the main cause of the so called "Global Warming Effect". One answer to global warming is to replace and retrofit current technologies with alternatives that have comparable, better performance and have no undesired consequences, but do not emit carbon dioxide. Bruce et al., (2004) found that most of the hydrogen supply chain pathways would release significantly less carbon dioxide into the atmosphere than would gasoline used in hybrid electric vehicles; Only coal-based non sequestered production and grid-based electrolysis is comparable to gasoline in this respect. The higher efficiency of fuel cell vehicles compensates for the high carbon dioxide content of the fossil fuels.

2.4 Biomass

Biomass is biological material most often referring to plants or plant-derived materials. As a renewable energy source, biomass can either be used directly, or indirectly once it's converted into another type of energy product such as biofuel. Biomass can be converted to energy in three processes, thermal conversion, chemical conversion, and biochemical conversion. Since, biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth and heavy metals.

Biomass is a renewable source of fuel which can make an important contribution to achieve these targets and it is also a flexible energy source, unlike some other sources of renewable energy such as wind and solar, can be stored and used as a fuel when required. Biomass already play a large role in renewable energy, more than all other types of renewable energies combined. The Figure 2-1 shows the role of renewable energy in the nation's energy supply in 2008.

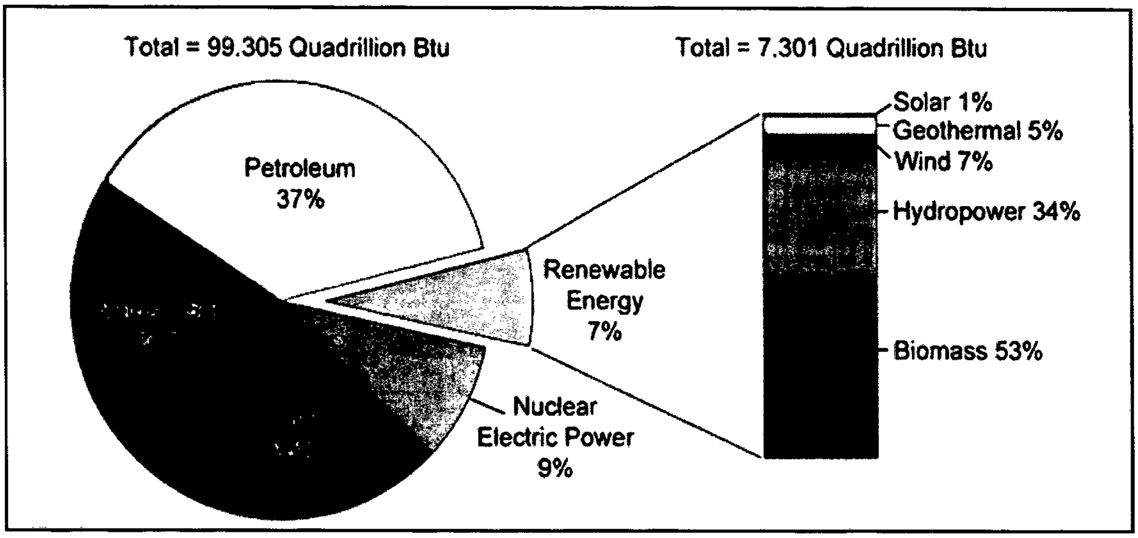

Figure 2-1: The role of renewable energy in the nation's energy supply, 2008. (Source: Energy information administration, renewable energy consumption and electricity preliminary statistics 2008)

2.5 Type of Biomass

Peter, (2001) characterises the various types of biomass in different ways but one simple method is to define four main types, namely;

i) woody plants,

ii) herbaceous plants/grasses,

iii) aquatic plants,

iv) manures.

Plantation that produces energy crops, natural vegetable growth and organic wastes and residues also includes as one of the biomass. According to Panwar et al., (2012) it can be grouped as plantation that produces energy crops, natural vegetable growths and organic waste and residues.

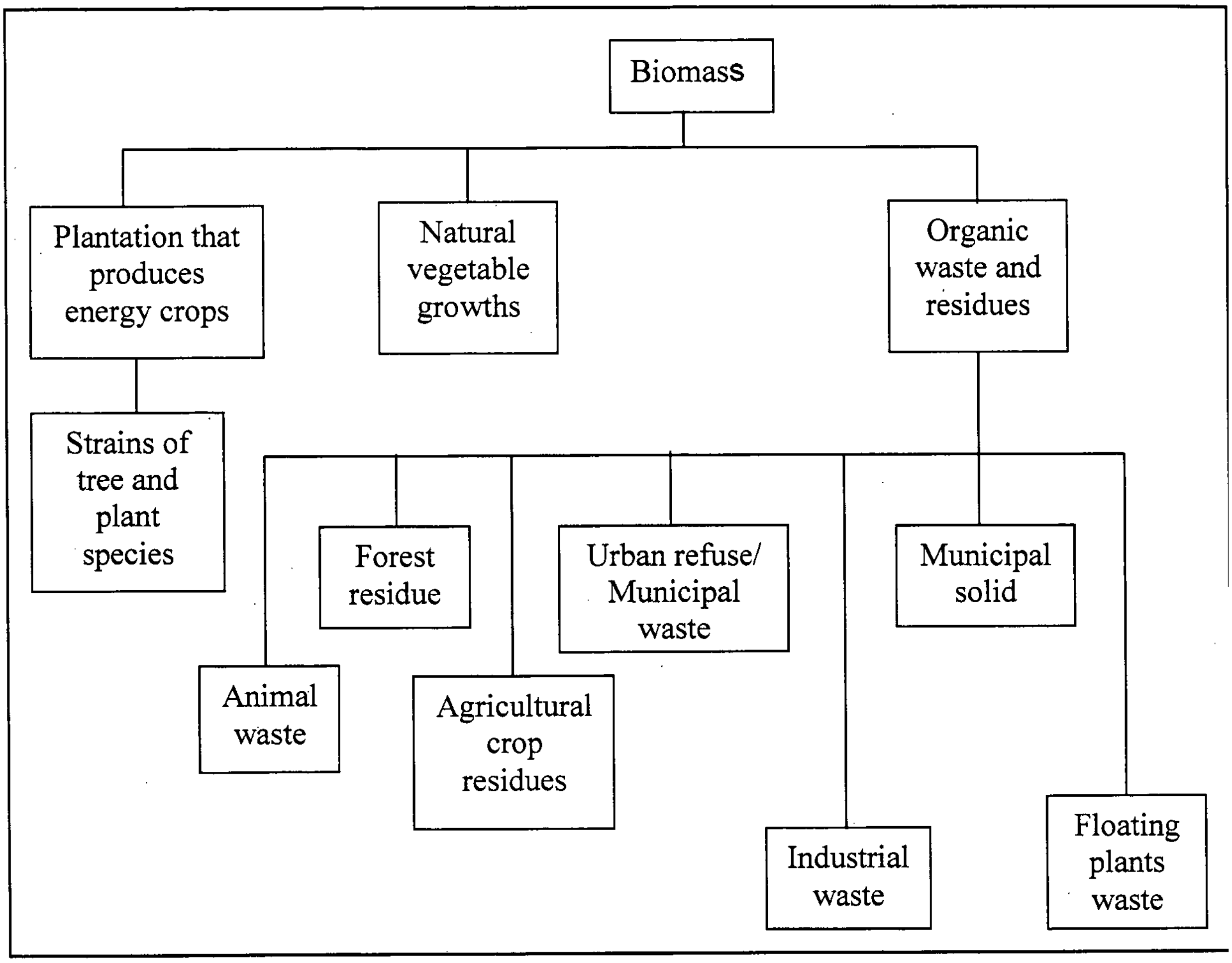

Figure 2-2: Biomass classification (Panwar et al., 2012)

2.6 Resource of Biomass

Demirbas, (2000) claimed that biomass differs from other alternative energy sources in that the resource is varied, and it can be converted to energy through many conversion processes: biomass resources can be divided into three general categories:

i) wastes

ii) standing forests

iii) energy crops

Energy production can used biomass resources to cover a wide range of materials. According to Demirbas., 2005, biomass energy can be separated into two categories, namely modern biomass and traditional biomass.

2.7 Thermo Chemical Conversion of Biomass

Most commonly employed for converting biomass into higher heating value fuels are thermo chemical processes. Major thermal conversion route is include direct combustion to provide heat, liquid fuel and other elements to generate process heat for thermal and electricity generation (Panwar et al., 2012). The Figure 2-3 shows the thermo chemical conversion route of biomass.

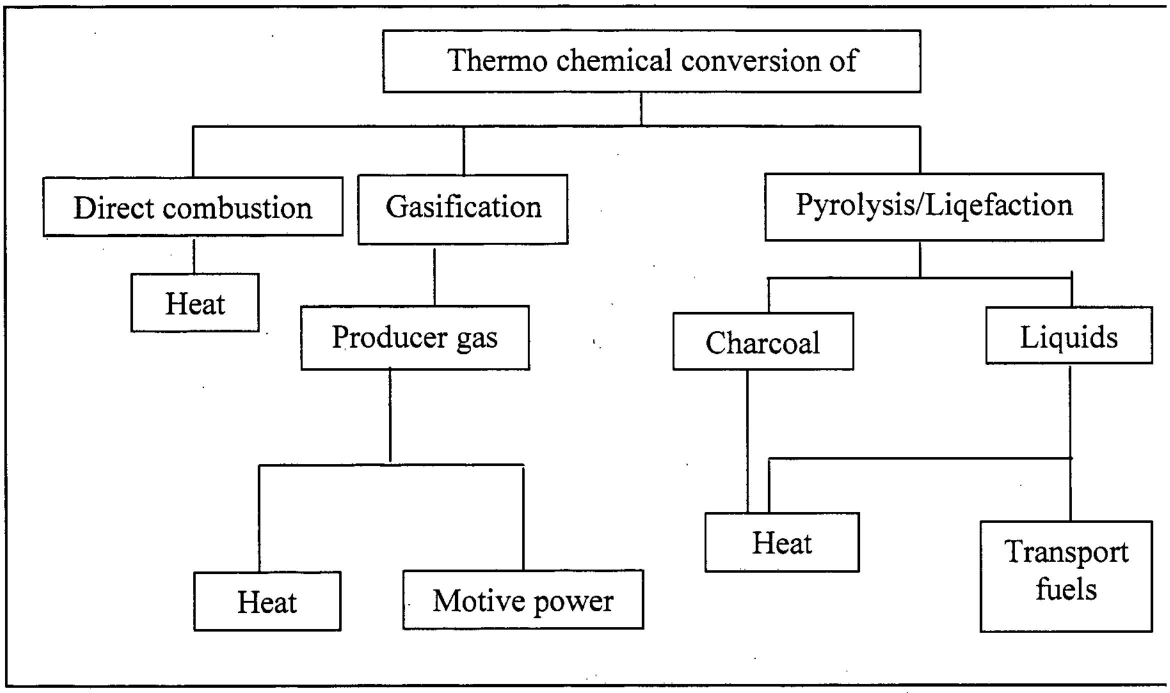

Figure 2-3: The thermo chemical conversion route of biomass. (Panwar et al., 2012)

Biomass may be used to meet a wide variety of energy needs, including generating electricity, providing process heat for industrial facilities, heating homes and fuelling vehicles. The conversion of biomass to such useful forms of energy, also called bio-energy, can be achieved using a number of different technological solutions that can be separated into two basic categories, namely thermochemical processes and biochemical/biological processes (Antonio et al., 2005). A process options classification based on the type of final energy products is tabulated in Table 2-2.

Table 2-2: Thermochemical and biochemical processes classification (Antonio et al., 2005)

Conversion processes	Technological solutions	Final products
Thermochemical processes	Combustion	•Steam •Process heat •Electric energy
	Gasification	•Steam •Process heat •Electric energy •Fuel gas methane
	Pyrolysis	•Charcoal •Bio-coal •Fuel gas
Biochemical processes	Fermentation Anaerobic digestion	•Ethanol •Water for irrigation •Compost •Biogas

2.8 Gasification

Biomass gasification is environmentally friendly way to produce energy. Gasification process is nothing but it is a conversion of solid fuel into gaseous fuel for wide applications. Biomass as a feedstock is more promising than coal for gasification due to its low sulphur content and less reactive character (Panwar et al., 2012). The biomass fuels are suitable for the highly energy efficient power generation cycles based on gasification technology. The combustion in gasifier takes place in limited supply of oxygen it may be called partial combustion of solid fuel (Panwar et al., 2012).

The gasifier design based on the type of fuel used, air introduction in the fuel column and type of combustion bed. Based on Panwar et al., (2012) findings, the fixed bed type gasifier simply consisting of cylindrical reactor in which solid biomass fuel gasifying and produced gas move either upward or downward; these types of gasifier are simple in construction and generally operate with high carbon conversion, long solid residence time; low gas velocity and low ash carry over. Several type of fixed bed gasifiers were operating worldwide and further these can be classified according to the way in which primary air to gasify the biomass enters into the gasifier.

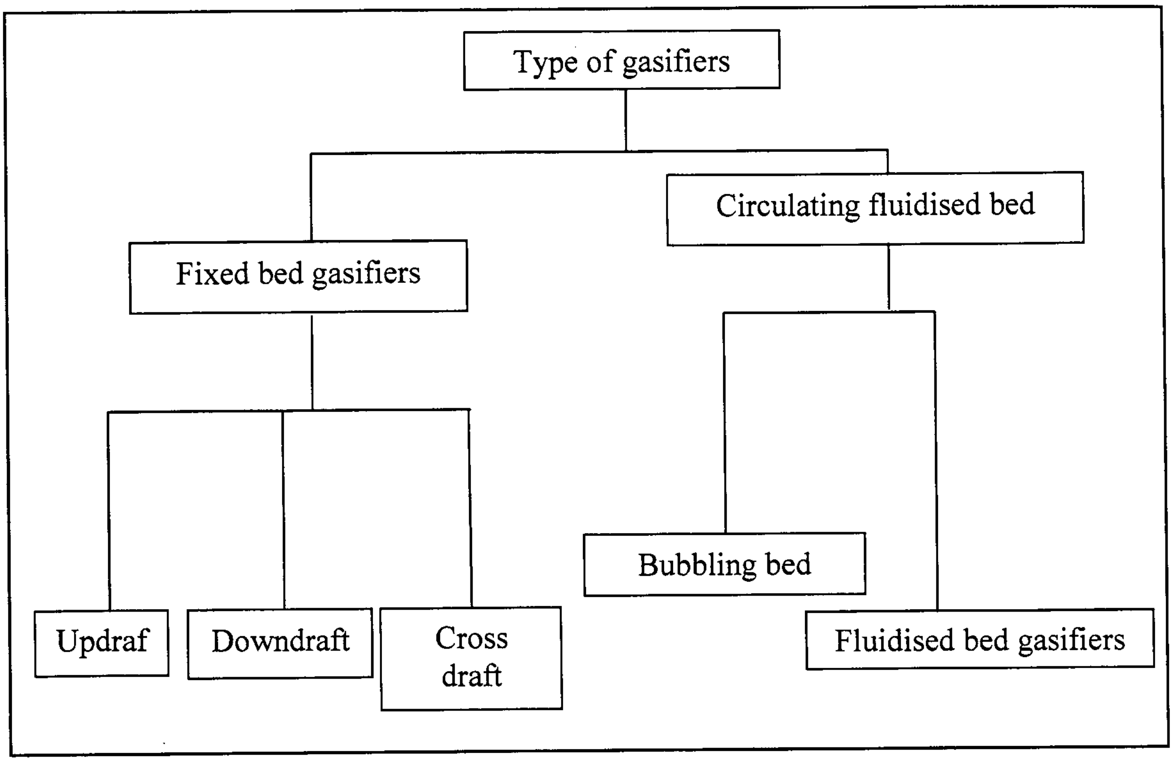

Figure 2-4: The Classification of gasifier. (Panwar et al., 2012)

The Table 2-3 shows the summary of gasification process for previous studies. Based on the previous study, Udormsirichakorn and Salam claimed that the smaller biomass particles which contribute to a larger surface area and hence faster heating rates can allow higher hydrogen production in biomass steam gasification. Furthermore, an increase in the steam/ biomass ratio has a positive effect on the gas fraction composition by increasing the hydrogen content (Erkiaga et al., 2013). According to Kuo.et al., (2013) the higher the sample temperature, the better the syngas yield.

Currently, Malaysia is the largest producer and exporter of palm oil. Malaysia produces about 47% of the world's supply of palm oil (Sumathi et al., 2007). Besides producing oils at present, there are continuous increasing interests concerning oil palm renewable energy. According to Minami (2005) the palm oil biomass residues that can be used for gasification are EFBs, mesocarp fiber, palm kernel shells, palm tree trunks and fronts. Recently, hydrogen production from biomass has become phenomena technology for power generation. Biomass converter also produces bio-fuels, which include methanol, ethanol, bio-oil, and bio-diesel. Biomass energy is the largest source of domestic renewable energy.

Table 2-3: Summary of gasification process for previous studies

Reaction	Biomass	Finding	Author
Steam gasification Of biomass	Pine Holm-oak Eucalyptus	Several aspects of biomass characteristics have significant influence on hydrogen production. Biomass containing higher cellulose and hydrogen to carbon ratio is found to influence higher hydrogen production. Smaller biomass particles which contribute to a larger surface area and hence faster heating rates can allow higher hydrogen production in biomass steam gasification.	Udomsirichakorn and Salam (2014)
Steam gasification Of biomass	Pinewood sawdust	An increase in the steam / biomass ratio has a positive effect on the gas fraction composition by increasing the hydrogen content and the hydrogen / carbon monoxide ratio, which is interesting for the applications of the syngas produced.	Erkiaga et al., (2013)
Gasification in a downdraft fixed bed gasifier using thermodynamic analysis	Raw bamboo (torrefied bamboo)	The higher the torrefaction temperature, the better the syngas yield.	Kuo. et al., (2013)

2.9 Catalyst for Gasification

The Table 2-4 shows the summary of works. Catalytic cracking is recognized as the most efficient method to diminish the tar formation in the gas mixture: Ni-based catalysts are found to be the most popular types and also the very effective ones for hot gas cleaning (Jianfen et al., 2009). Ni catalysts are commonly employed due to the characteristics of being able to be reduced and reoxidised easily and reversibly, and they show high conversion efficiency to hydrogen in reforming reaction (Isha and Williams, 2011). Ni on Al_2O_3 or MgO favours syngas production with high H_2/CO molar ratio but, when used at high temperatures, sintering of nickel particles and carbon deposition occurs (Courson et al., 2002). The support used for the catalyst is important in the development of effective catalyst performance and stability: There are many supports that have been investigated for the reforming reaction: Alumina, Al_2O_3, support is easily available and economical and is the most common support used for the reforming reaction (Watanabe et al., 2005).

Table 2-4: The summary of works.

Biomass	Catalyst	Finding	Author
Almond shells	Nickel	The experimental results show that fresh, nickel based catalysts are extremely active for the elimination of CH_4, and tars: about 2 m^3 of gas (at ambient conditions) are obtained per kg of biomass, with a H, content higher than 60% by volume.	Rapagna et al., 2002
Organic waste	Ni/MgO	The catalytic performance data showed that the carbon yield of gas products increased with increase in Ni metal surface area except 10 wt% Ni/MgO (773 K) catalyst indicating that there is an optimal Ni metal particle size for this reaction. It should be noted that 10 wt% Ni/MgO (873 K) catalyst showed the best performance (carbon yield 30%) under reaction conditions tested.	Takeshi et al., 2006
Palm oil waste	tri-metallic	The experiments demonstrated that the newly developed tri-metallic catalyst in biomass steam gasification was promising, with more than 99% tar removal at 800°C and gas yield and hydrogen yield markedly increased. Especially, the percentage of H in the product gas was obviously enhanced to over 17 vol % due to the presence of catalysts.	Jianfen et al., 2009