Effect of Limestone Catalyst on Production of Synthesis Gas in a Downdraft Co-Gasification of Coconut Frond and Wood Chips

By

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15936

Dissertation submitted in partial fulfillment of the
requirements for the
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CERTIFICATION OF APPROVAL

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Approved by,

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January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

THAM WAI HUNG

ABSTRACT

The global energy demand is increasing rapidly and biomass has been identifying as one of the major renewable resources for energy which meet the growing ‘green’ inspiration. Malaysia is rich in agriculture resources that are suitable to develop into sustainable biomass fuel. Studies on lignocellulosic biomass from the residues of agriculture by product have been conduction for power generation. These studies show the capability of Malaysia’s biomass in reducing environmental pollution and in providing carbon-neutral energy generation. Throughout many years, co-gasification of lignocellulosic biomass and different fuels such as coal have been conducted for reduction of greenhouse gasses emission by coal and to increase the efficiency of the gasification. Currently, there have been studies on co-gasification of two different lignocellulosic biomass however the resulting energy content is low and improvement of the gasification process is needed. In the current work, catalytic co-gasification of coconut frond and wood chips in a laboratory-scale downdraft gasifier by limestone was investigated. The experiments were performed to identify the effects of catalyst to biomass ratio (0:1, 0.3:1, 0.5:1, and 0.7:1) on product composition, gas yield, carbon conversion efficiency and heating value. The feedstock were mixed a constant weight ratio which was 70:30; 70% of wood chips and 30% of coconut frond. The main gas species generated, as identified by the gas analyser were $\mathrm{H_2}$, CO, $\mathrm{CO_2}$ and $\mathrm{CH_4}$. From the result, it was shown that at 50% catalyst addition ratio, maximum hydrogen content of 11.39% v/v, carbon conversion efficiency of 69.49%, gas yield of $1.677\mathrm{Nm^3/kg}$ and higher heating value of $5.11\mathrm{MJ/Nm^3}$. The presence of limestone catalyst was found to improve the higher heating value, carbon conversion efficiency and gas yield due to the increases in $\mathrm{H_2}$, CO, $\mathrm{CO_2}$ and $\mathrm{CH_4}$. In conclusion, limestone catalyst can help facilitating the reaction rate of partial oxidation and water-gas shift reaction, enhancing the quality of synthesis gas.

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CHAPTER 1

INTRODUCTION

According to the Key World Energy statistic, in year 2011 the total global final consumption of energy are 47.8% oil, 20.0% natural gas, 3.4% coal and the remaining 28.8% is non-fossil fuel. Out of the 28.8%, 5.0% is Biofuels and waste which has increases drastically from 3.0% of the total energy consumption at year 1973 to current 5.0% (Ciolkosz, 2010). This shows that the acceptability of biomass by the public has increased and it is a good sign to mitigate the current energy problem associated with the increase of world population.

Biomass is a truly renewable energy resource, whereby agriculture residues, forestry residues, energy crops and municipal wastes is subject to constant depletion through its use as a fuel or feedstock (Chan & Tanksale, 2014). Biomass is any living matter which consist of carbon, hydrogen and also oxygen (Sheth & Babu, 2010). Also, biomass is the only renewable energy can be converted into liquid fuel and used as feedstock in chemical production. There are two technologies to convert solid biomass into liquid and gaseous fuels: biochemical (fermentation) and thermochemical (pyrolysis, gasification) (Basu, 2010). Biomass gasification is one of the thermochemical conversion technologies which offer higher efficiencies compared to pyrolysis (Sheth & Babu, 2010).

Biomass gasification is the partial combustion conversion of solid carbonaceous fuel into useful gases and chemical through a medium of reaction, which can be gas or supercritical water. The syngas produces from biomass gasification are mainly hydrogen, carbon monoxide, methane, carbon dioxide, water vapour and nitrogen (Sheth & Babu, 2010). There are few factors that affecting the performance of gasification process and quality of syngas such as; heating rate, gasification temperature, gasification pressure and equivalent ratio. Besides, the characteristics of the feedstock such as: elemental composition, fixed carbon content, volatile matters, moisture content, heating value and ash content can also influence the outcome of the gasification.

1.1 Background of Study

Biomass gasification is a chemical conversion of carbonaceous materials into useful combustible fuel gas (Basu, 2010). Combustion also manages to turn carbonaceous material into product gases but there are some major differences. For example, product gases from combustion do not contain heating value, but product gas from gasification does. The synthesis gas produced by gasification can be an important resource suitable for direct combustion, it can be applied in prime mover such as engines and turbines, or for the production of synthetic natural gas (SNG) and transportation fuels (e.g. Fischer-Tropsch diesel) (Akudo, 2008).The major objective of biomass gasification is to produce high quality of syngas to meet the basic operation requirement of turbines or internal combustion engines. In order to produce high quality syngas, one of the major obstacle need to be overcome which is the efficient and economic removal of tars and particulate form the syngas.

Downdraft gasifier is a co-current reactor where air enters the gasifier at a certain height below the top. It is attractive for industrial usage due to its simple and roust construction, reliable operation, suitability with various biomass, high conversion rate (90-99%) (Akudo, 2008). The most attractive part is downdraft gasifier able to deal with internal-combustion engines because it produces relatively clean syngas containing low tar content (0.015-3 g/Nm^3) and particulate concentrations (Basu, 2010).

Heating Value, composition and possible contamination are the major concern for syngas in term of energy production. The volume composition of hydrogen (H_2), methane (CH_4), carbon monoxide (CO), and steam in the syngas determines the heating value of the gas (Akudo, 2008). There are few factors that influencing the composition of syngas which include pressure, temperature of the gasifier, steam/biomass ratio, steam flow, feedstock size and the presence of catalyst, tar formation (Gonzalez et al., 2008). Syngas from gasification contains tar and particulates which can cause several problems such as cracking in the proe of filters, forming coke and plugging them, resulting in severe operation interruption (El-Rub et al., 2004).

Currently, tars can be removed via mechanical, catalytic and thermal methods. Catalytic tar removal is consider a technically and economically interesting approach for gas cleaning due to its potential to enhance the efficiency of conversion while simultaneously eliminating the need for the collection and disposal of tars (Anis & Zainal, 2011).

Catalytic gasification is not only used for tar removal however the second motivation of catalytic gasification is removal of methane from the product gas. Reforming of methane is very important for the production of syngas, which cannot tolerate methane and require a precise ratio of CO and H_2in the product gas (Basu, 2010). Since the heating value is the major concern of gasification therefore improving the syngas quality become the major mission for gasification and catalytic gasification can satisfy the situation.

1.2 Problem Statement

Biomass gasification gives a promise outcome for the future energy by producing gases which content energy that can move machines and pumps. However, it produces gases with a low energy content compare to others common fuel like gasoline, natural gas and diesel. Therefore, it is necessary to determine the method to increase the energy content in the syngas.

Generally, gasification can be done by different combination of feedstock and catalyst. As far as concern different combination of feedstock can produces different level of energy content. Not only this, the amount of catalyst used will also affect the result of gasification. Therefore, it is necessary to determine the optimum amount of catalyst for gasification.

There appears to be lack of information with respect to the gasification of CF and WC in a downdraft gasifier with the presence of a catalyst. Attempt was therefore made to fill this gap.

1.3 Objectives

The objective of this study was to investigate the effect of catalyst on co-gasification of coconut frond and wood chips in relation composition of product, gas yield, heating value and carbon conversion efficiency. By using catalyst on gasification the quality of the syngas will expect to increase in terms of higher heating value, and this experiment is done to prove the hypothesis. An experimental study was done using a downdraft gasifier covering a wide range parameters. The producer gas generated in the downdraft gasifier was analysed using a gas analyser. The effects of catalyst on the quality of producer gas were study by performing experiments.

1.4 Scope of Study

The study was only focus on the feedstock combination of coconut frond and wood. The catalyst chosen was limestone. The size of the limestone was fixed from length 2cm to 3cm. This study was done on a base of 100% experimental study and results were based on data gathering and analysis. Downdraft gasifier was used as the major experiment tool to perform the gasification. The variable of the experiment was the amount of catalyst used during gasification. The variable was used to determine the optimum amount of catalyst used to produce the best quality synthesis gas.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass as Fuel

Biomass refer to any organic materials that are derived from plants or animals. According to United Nations Framework Convention on Climate Change: A-non fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and bio-degradable organic fractions of industrial and municipal wastes. Originally biomass are from plant and they are grow through photosynthesis by converting CO_2 from the atmosphere to oxygen. When it burns, it releases the carbon dioxide that the plants had absorbed from the atmosphere only recently (a few years to a few hours). Thus, the burning of biomass does not make any net addition to the earth's carbon dioxide levels. Such release also happens for fossil fuels. So, on a comparative basis, one may consider biomass "carbon-neutral," meaning there is no addition to the CO_2 inventory by the burning of biomass (Loppinet - Serani, et al., 2008).

However, there are some barriers that causes biomass to become a user friendly fuel which are its bulkiness, low energy density and inconvenient form. Biomass are not flexible to handle, store or transport compare to gas or liquid fuels. Therefore, there is a need to convert solid biomass into liquid and gaseous forms which are more energy dense. Currently, there are two routes of conversion: biochemical conversion (fermentation) and thermochemical conversion (pyrolysis, gasification) (Basu, 2010).

In order to use biomass as a fuel, the type of biomass used as feedstock become the major criteria to take into concern because each biomass has its own properties which may influence the performance to be a fuel. The properties include the physical properties, thermodynamic properties and other gasification related properties of biomass.

2.1.1 Agriculture Wastes as Biomass Feedstock in Malaysia

In Malaysia, agricultural wastes seems to be very attractive for power generation due to bio resource sustainability, environmental concerns and economic reflection. Malaysia is a leader as one of the foremost agricultural countries in the world. The main agricultural crops are oil palm, rubber, cocoa, rice and coconut; hence Malaysia government has targeted to generate energy from by-product and residues of 362 palm oil mills in the country. Malaysia, as the first palm oil producer in the world, is processing 71.3 million tonnes/year of fresh fruit bunch. The result is derivation about 19 million tonnes/year of crop residues consist of empty fruit bunch, fiber and shell. Empty fruit bunch (EFB) and mesocarp fiber (MF) are the utmost contributors of oil palm biomass with around 15.8 and 9.6 MnT production/year, respectively (Sumathi et al., 2008). The EFB and MF can be processed under heat and pressure to produce molded oil palm (MOP), which is a distinctive bio-based material extremely useful in furniture, building, electronics, packaging, and automobile industries. Table 2.1 shows the calorific values and moisture content of these residues (Rahman Mohamed & Lee, 2006; Sumathi et al., 2008)

Table 2.1: Calorific values and moisture content of palm oil residues adopted from PTM (Malaysia Energy Center). (2002)

Residue	Calorific Value (kJ/kg)	Moisture Content (%)
Empty Fruit Bunch	6028	60
Fiber	11,344	40
Shell	18,836	20

Despite the decreasing acreage, coconut still plays an important role in the socio-economic position of the Malaysian rural population that involves 80,000 households. About 63% of coconut production, coconut fronds and shells represent the largest amount asresidues (about 8%). Coconut can be used as feedstock in the form of fronds and debris that are generated from the processing and consumption of coconut fruits, and also the wastes that are generated during the replanting of the coconut trees.

2.1.2 Forest Residues as Biomass Feedstock in Malaysia

Malaysia is rich in wood mass products and only 60-65% of them have been harvested for energy. The remaining percentage is left to rot or burn to waste. The wood can be burnt to generate steam or heat for cooking and also use in charcoal manufacture. In Malaysia, there are 4 types of forest residues which are logging residues, saw milling residues, plywood and veneer residues and the secondary processing residues. Although the large potential of wood waste as the energy production, the usage has been reduce from 100 MW in 1997 to less than 50 MW in 1998 because of environmental problems, and also the effort of government to protect forests (PTM, Malaysia Energy Centre, 2002)..

2.2 Gasification Related Properties of Biomass

Biomass made up of large number of organic compound which contain of carbon (C), hydrogen (H), Oxygen (O) and nitrogen (N). Not only this, biomass contain also moisture (M) and a small amount of inorganic impurities known ash. It is critical to determine the composition of the fuel as well as its energy content for a biomass utilization system. There are three basic properties to determine the composition and energy content of biomass: (1) ultimate analysis, (2) proximate analysis, and (3) heating values. These experimental determination of the properties is covered by ASTM standard E-870-06 (Basu, 2010)

2.2.1 Ultimate Analysis

A typical ultimate analysis can show by:

$$C+H+O+N+S+ASH+M = 100\% \tag{2.1}$$

which expresses the composition of the typical hydrocarbon fuel in terms of its basic elements. C, H, O, N, and S are the weight percentages of carbon, hydrogen, oxygen, nitrogen, and sulphur, respectively in the fuel. These contents are important to act as a references when come to the biomass decision. For example, the sulphur content of lingo-cellulosic biomass is exceptionally low, which is a major advantage in its utilization in energy conversion when SO_2 is taken into account. However, not all biomass contain sulphur and it is normally excluded when calculating the high heating value of the fuel. Next ultimate analysis can be used to determine the atomic ratio (H/C) and (O/C) of different fuels (Basu, 2010). According to (Chiang, et, al. 2012) the higher H/C ratio means, there are more possibility on CH_4 reforming in thermal reaction; the higher O/C ratio represents the higher potential on CO production in gasification. In general, the CH_4 heating value is higher than CO. Therfore, the higher H/C exhibits the higher syngas heating value than low H/C ratio. On the other hand, high carbon content is preferable for gasification process as it is an important element in the fuel (Sulaiman, et, al. 2013).

2.2.2 Proximate Analysis

Proximate analysis is used to show the burning characteristic of the biomass, which include the Fixed Carbon (FC), Ash (ASH), Moisture and Volatile Matter (VM). (Sulaiman et al., 2013). It is a simple and inexpensive process. However the fixed carbon shown in proximate analysis is different from the carbon in ultimate analysis: The carbon in proximate analysis is referred to as the char yield after devolatilization and it does not include the carbon in the volatile matter (Basu 2010).

a) Volatile Matter

Volatile matter is refer as the condensable and non-condensable vapour released when the fuel is heated. Biomass contain high level of volatile organic material, there are 70 to 90% for wood (Akudo, 2008). The amount of volatile matter produced is highly dependence on the rate of heating and the temperature to which it is heated. In order to quantify the volatile matter, the fuel is heated at a standard rate and also to a standard temperature in a controlled environment (Basu, 2010).

b) Ash Content

This refer to the inorganic component in biomass and it created after the fuel is completely burned. This property is crucial in high temperature gasification system because melted ash may cause issues to the gasifier (Quaak et al, 1999). However, the ash content of biomass is generally very small but it may be critical in biomass utilization especially if it contains alkali metals which can lead to agglomeration, corrosion and fouling in gasifier (Mettanant et al, 2009). It is difficult to get the exact amount of ash content using proximate analysis because some of the ash constituent can undergo oxidation during burning (Basu, 2010).

c) Moisture

Moisture content of biomass refer to the amount of water content in term of percentage of the material's weight (Quaak et al., 1999). The weight can be on a wet basis or dry basis and on a dry-and-ash basis. Sometimes the moisture percentage can exceed 100% for very wet biomass, therefore the basis of moisture should always be specified (Basu, 2010). Moisture content is an important parameter for assessment of the cost of or energy penalty in drying the biomass due to the high consumption of energy to evaporate the moisture in the biomass. The energy used is not recovered. Not only these, moisture content affects the value of biomass as a fuel, it is also important that the basis be stated whenever moisture content is measured. Besides that, moisture content of the biomass can affect the thermal efficiency of gasifier and led to low gas heating values. Not only this, the difficulty to ignite the high moisture content fuel increases and will reduce the gas quality and yield (Turare, 1997). Figure 2.1 shows the range of moisture content which work well for gasification.

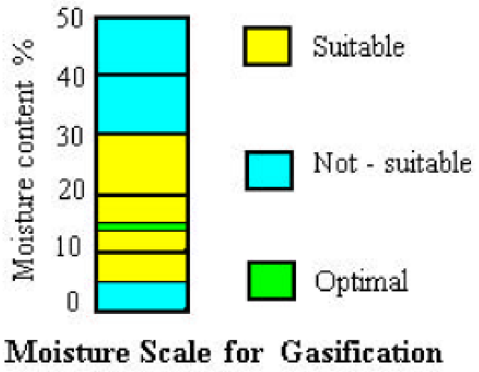


Figure 2.1 Moisture Scale for Gasification adopted from Turare. (1997)

d) Fixed Carbon

Fixed carbon refers to any solid carbon in the biomass that remains in the char in the pyrolysis process after devolatilization (Basu, 2010). Equation 2.2 used to determine the fixed carbon content, where M, VM, and ASH represent moisture, volatile matter and ash respectively.

$$FC = 1 - M - VM - Ash \tag{2.2}$$

In real situation, fixed carbon is not a fixed quantity, but its value, measured under standard conditions, gives a useful evaluation parameter of the fuel. The quantity of fixed carbon is important to determine the efficiency of the gasifier or gasification system in terms of the rate of gasification and also its yield which convert of fixed carbon into gases (Basu, 2010).

2.2.3 Heating Value

Heating Value is the most concerned criteria for biomass gasification because it indicates the total amount energy that can generated from the fuel and normally it is use to determine the quality of syngas. It is mostly a function of the fuel’s chemical composition. Heating Value can be expressed in two forms which are higher heating value (HHV) or the lower heating value (LHV) (Ciolkosz, 2010).

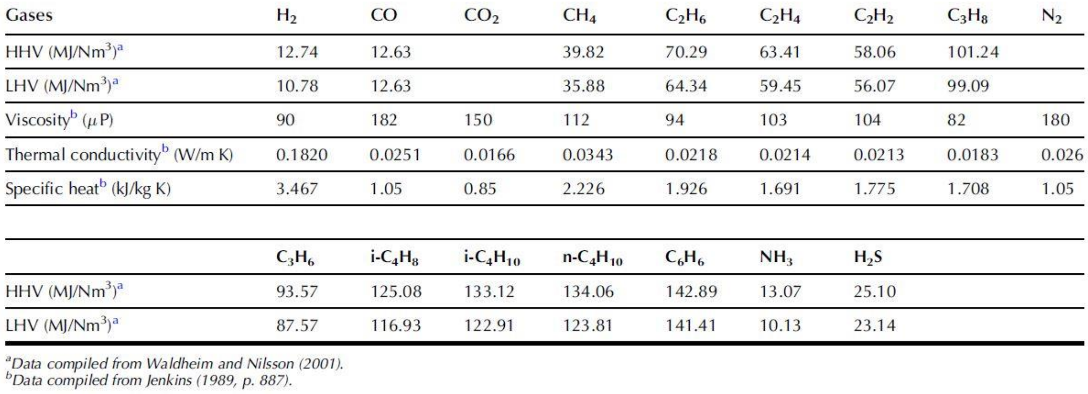
Higher heating value (HHV) is defined as the amount of energy released at initially 25^{o}C by the unit mass once it is combusted and the products have returned to a temperature of 25^{o}C. HHV also including the energy contain in the water vapour or the latent heat of vaporization of water.(Basu, 2010). The lower heating value (LHV) also known as the net calorific value. The difference between HHV and LHV is the energy embodied in the water vapour, for HHV the energy contain included the water vapour however for LHV is defined as the amount of heat produced by fully burn a specified quantity less the heat of vaporization of the water in the combustion product (Ciolkosz, 2010). The heat content of a fuel type is not constant and it is highly depending on the environmental condition which the fuel is grown which include the climate and soil. As a result, the energy content of a biomass fuel should be thought of as a range rather than a fixed value (Ciolkosz, 2010).

The heating value of the syngas can be estimated from the gas composition by following the standard state of 101.3kPa and 273K by using the following Equation 2.3:

$$HHV = (12.75[H_2] + 12.63[CO] + 39.82[CH_4]+63.43[C_2H_4] + \cdot\cdot\cdot)/100 \tag{2.3}$$

The syngas contain are expressed in mol% and their heats of combustion MJ/Nm^3 (Li et al., 2004). This equation is based on the standard heating value of constituents of typical product gas from biomass gasification. Table 2.2 shows the list of standard heating values of some gases.

Table 2.2 List of Standard heating values of product gas from biomass gasification adopted from (Basu, 2010).



Gases	H_2	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	N_2
HHV (MJ/Nm^3)[a]	12.74	12.63		39.82	70.29	63.41	58.06	101.24	
LHV (MJ/Nm^3)[a]	10.78	12.63		35.88	64.34	59.45	56.07	99.09	
Viscosity[b] (μP)	90	182	150	112	94	103	104	82	180
Thermal conductivity[b] (W/m K)	0.1820	0.0251	0.0166	0.0343	0.0218	0.0214	0.0213	0.0183	0.026
Specific heat[b] (kJ/kg K)	3.467	1.05	0.85	2.226	1.926	1.691	1.775	1.708	1.05

	C_3H_6	i-C_4H_8	i-C_4H_{10}	n-C_4H_{10}	C_6H_6	NH_3	H_2S
HHV (MJ/Nm^3)[a]	93.57	125.08	133.12	134.06	142.89	13.07	25.10
LHV (MJ/Nm^3)[a]	87.57	116.93	122.91	123.81	141.41	10.13	23.14

[a] *Data compiled from Waldheim and Nilsson (2001).*
[b] *Data compiled from Jenkins (1989, p. 887).*

2.3 Biomass Gasification

Biomass energy conversion can be categorizing into three main processes which are direct combustion, thermo chemical transformation and biochemical transformation. Gasification is under thermos chemical transformation whereby the solid fuel are turn into useful and convenient gaseous fuel through an chain of chemical reaction and physical transformation (Sharma, 2011). Figure 2.2 shows the summary for the general bioass conversion processes Gasification and combustion are both slightly similar thermochemical process, but there is an obvious difference between them. Gasification gather the energy into chemical bonds in the product gas; in other way combustion breaks those bond to release energy (Basu, 2010). Gasifier is designed to collect the syngas from the incomplete burning process of biomass. Figure 2.4 shows differents zone of thermal processes in downdraft gasification which include drying, pyrolysis, oxidation, and reduction (Akudo, 2008). Among all types of gasifier, fixed bed gasifiers are the simplest gasifiers and suitable for small-scale application (Guangul et al, 2012). Figure 2.3 shows the different types of fixed bed gasifier.

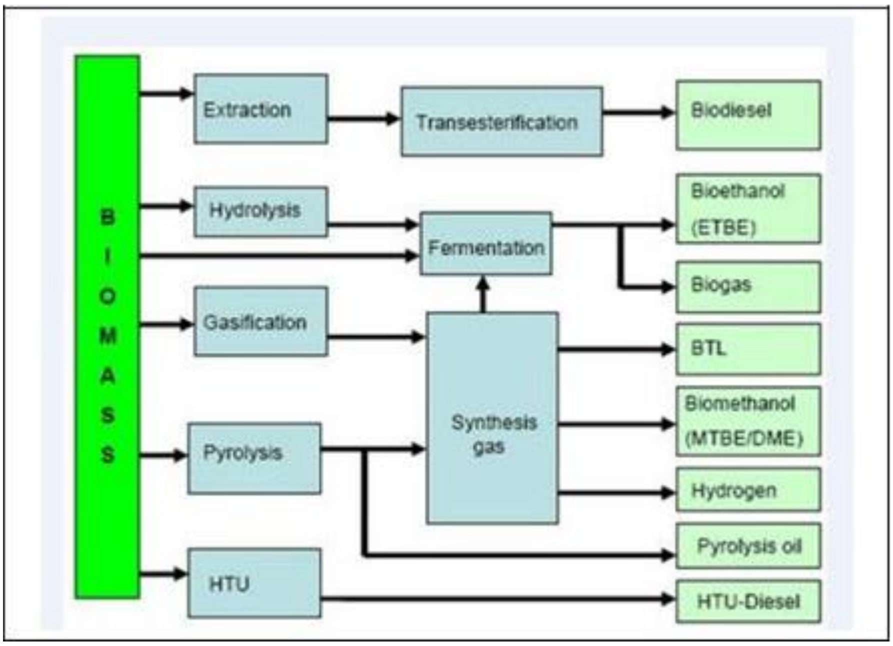


Figure 2.2 General biomass conversion processes

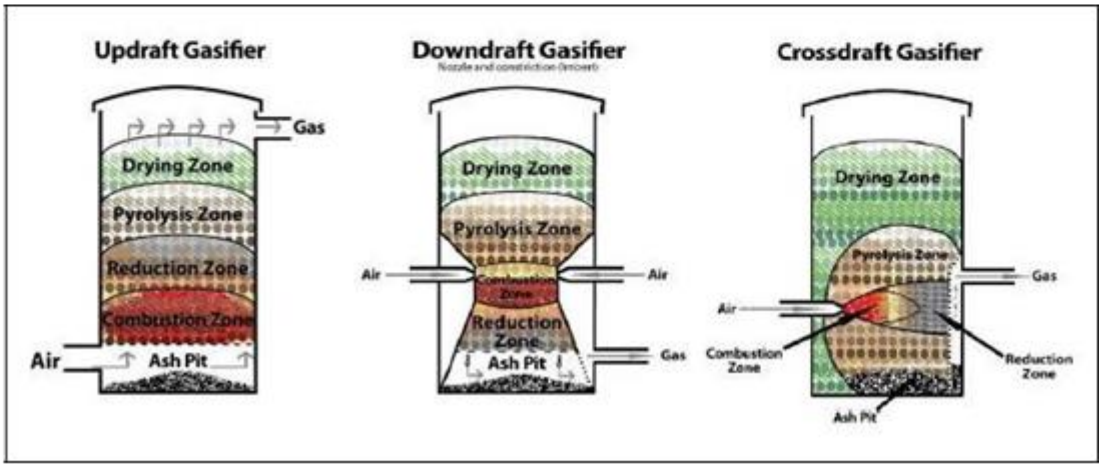


Figure 2.3 Types of fixed-bed gasifier from Guangul et al. (2014)

2.3.1 Drying

Moisture content is a critical parameter in the drying process because for every kilogram of moisture in biomass consume minimum of 2260 kJ of extra energy from the gasifier to vaporized water. Therefore for the energy application, a certain of predrying process is gone through to obtain a optimum level of moisture for gasification process. In order to produce fuel gas with high heating value, most of the gasification use feedstock with a moisture content of 10 to 20% (Basu, 2010).

Drying process occurs at temperature above 100°C and the process continue until a temperature reach 200°C. At 100°C the water vapour evaporates from the surface and the inner pores of the solid fuel. As temperature rises, some of the volatile matter of the fuel may also be released (Sharma, 2011).

2.3.2 Pyrolysis

Pyrolysis defined as a heating of feedstock without oxygen at a specified rate to a maximum temperature and holding it there for a specific time. Pyrolysis is an endothermic process which require heat to initiate the chemical reaction to generate syngas(Sharma, 2011). The quality of the products from pyrolysis is based on several factors including pyrolysis temperature and heating rate (Basu, 2010).

Pyrolysis started when temperature reaches above 200°C (Wei, 2005). The starting products of pyrolysis made up of condensable gases and solid char. The condensable gas may further transform into non condensable gases (CO, CO_2,H_2, and CH_4,), liquid and char. The reactions can be shows as follows.

$$\text{Biomass} \xrightarrow{\text{(Heat)}} C + \text{Tar} + H_2, H_2O, CO, CO_2, CH_4 \text{ etc.} \tag{2.4}$$

The outcome from pyrolysis (gases, liquid and char) is highly dependent on temperature, heating rte, resident time and pressure. In general, a higher temperature and higher heating rate form the lighter hydrocarbons and may crack the tar molecules, thus enhancing the yield of permanent gases. On the other hand, a lower temperature and longer residence time formed the char.

2.3.3 Oxidation

Oxidation reactions starts when air is forced into the gasification chamber from the side. The oxidation zone take place at temperatures ranging from 700 -1000°C (Wei, 2005). Oxidation is an exothermic reaction between the fuel and oxygen with the presence of heat. This process is important to reduce the amount of tars during the combustion process and not present in the syngas however tars cannot be removed completely by one step process. In the downdraft gasifier, the tar gases from the pyrolysis zone will be burn to generate heat for the next process which is the reduction process (Anis & Zainal, 2011). The oxidation reactions are as follow:

$$C + H_2 \leftrightarrow CO_2 \tag{2.5}$$

$$C + H_2O \leftrightarrow H_2 + CO \tag{2.6}$$

2.3.4 Reduction

In downdraft gasifier, the reduction zone is between combustion zone and gas outlet. Reduction reactions contain two different reaction of gasification of char: Boudouard reaction and water-gas reaction model. Boudouard reaction is the gasification of char in carbon dioxide and water-gas reaction is the gasification of char in steam (Turare, 1997). At a temperature of more than 700°C, the products of combustion which are carbon dioxide (CO_2) and water vapour (H_2O) flow across a bed of hot char which is highly reactive with oxygen. The hot char will strip the oxygen off the gasses and redistribute it to as many single bond sites as possible. The reduction stops when there are no more oxide molecules left for bonding. Due to endothermic nature of the reduction reaction syngas temperature decreased around 200-300°C. The principal reactions are as follows (Wei, 2005).

$$CO_2 + \text{C} + \text{Heat} \longrightarrow 2\text{CO} \tag{2. 7}$$

$$C + H_2O + Heat \longrightarrow CO + H_2 \tag{2. 8}$$

$$CO + H_2O + Heat \longrightarrow CO_2 + H_2 \tag{2. 9}$$

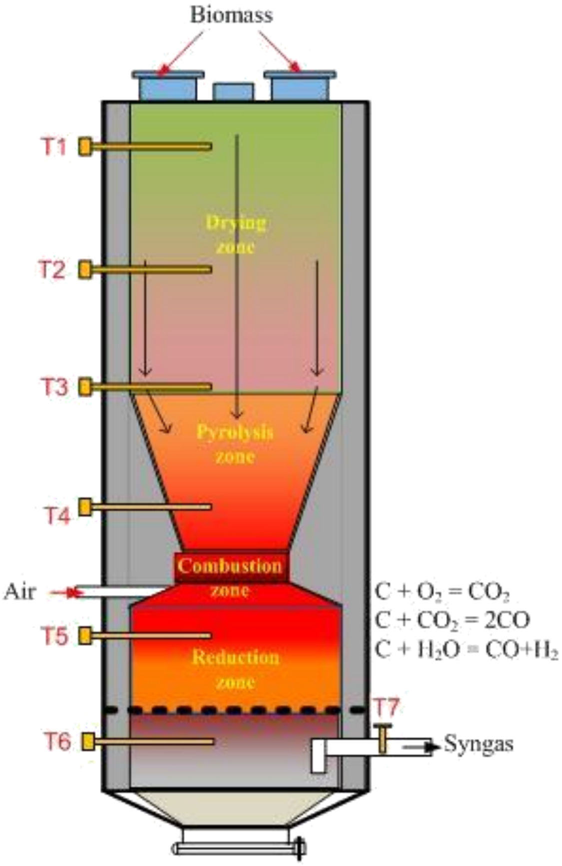


Figure 2.4 Different zones of gasification process in downdraft gasifier

2.4 Past studies on Co-Gasification

According to (Shafie et al., 2012), early co-gasification researches were aimed to reduce the emission of greenhouse gases that produced by the combustion of fossil fuel. Co-gasification literally means using coal and biomass as feedstock for the gasification process due to its renewable character and produces cleaner syngas (Long and Wang, 2011). In return, co-gasification produces gases with low level of hazardous gases such as carbon dioxide and it is the most inexpensive method to efficiently use biomass (Baxter, 2005). Before starting the gasification process, selection of suitable biomass feedstock is important. Proximate and ultimate analyses are normally the first steps in evaluating the feedstock solid fuels. Proximate analysis gives the fuel characteristics in terms of mass percentage of moisture, volatile matters, fixed carbon and ash content in the solid fuel while ultimate analysis gives the elemental constitution of a particular fuel in mass fraction or weight percentage in a dry ash-free basis (Ricketts et al., 2002).

In order to understand the quality and characteristic of the syngas produced by co-gasification of biomass, many researches has been carried out by using different parameters, materials and type of gasifiers. The performance of gasification process and quality of syngas depends upon numerous factors such as gasifying medium (air, steam and oxygen), heating rate, gasification temperature, gasification pressure and equivalence ratio (Inayat et al., 2014). According to (Wongsiriamnuay et al., 2013) by increasing the temperature will decreased the content of $H_2$and CO in the syngas while the content of CO_2 increased. Added steam was found to increase the quality of the syngas showing higher contents of H_2 , CO and LHV.

The result seems to suggest that the overall behaviours of the system’s efficiency are also more significant with suitable biomass blending ratio. The various different amount of coal feedstock with biomass were studied: 100% coal, 100% biomass and various biomass-coal blends composed of 10%, 30% and 50% (wt.) biomass and the better co-gasification performance could be achieve if the blending ratio of the two materials was 50% (Long and Wang, 2011). Although all the studied used the same type of gasifier, the studied did not obtained similar results due to the difference in elemental composition of the material of the specific species.

Dynamic temperature profile along the gasifier bed also studied to understand the performance of the gasification. A downdraft gasifier consists of four distinct zones, which undergo different reaction at different temperatures. According to Sulaiman et al., (2009), average temperature values recorded for drying, pyrolysis, oxidation and reduction zone are 125°C, 324°C, 796°C and 543°C respectively. The combustion zone should be in the range of 750°C to 900°C. Below that temperature range, it will turn the process into pyrolysis, which will produce more tar and charcoal while above that, complete combustion will occur and more carbon dioxide will be produce in the co-gasification product. However, according to Guangul et al., (2012) tar generation of downdraft gasifiers is lower than of fluidized bed gasifiers.

2.5 Past studies on Catalytic Gasification

Biomass Gasification is one of the most promising energy conversion to recover energy from biomass. During gasification, biomass is thermally decomposed into solid charcoal, liquid bio-oil and bio-gases under partial oxidation condition. Gasification temperature is normally classified into three ranges; low (400–600∘C), medium (600–900∘C), and high (>900∘C). According to Wonsiriamnuay et al., (2013) increasing temperature tends to result in increasing H_2, CO, gas heating value, carbon conversion efficiency, and gas yields. The advantage of gasification at low temperatures is due to reduced energy input, low tar yield, and low cost by partial oxidation, but heating value of fuel gas may be low. To increase the heating value of the product gas, steam may be added to the gasifying medium but additional energy input would be needed. This way, the H_2 content in the producer gas can be improved. Steam gasification takes place at high temperatures because the steam reforming reaction is an endothermic process, but catalytic steam gasification at low temperatures was more useful than high temperature with high content of H_2.

Normally, producer gas contains a high content of tar which can cause operational problems by blocking gas cooler, filter elements, and engine components. Most producer gas applications also require the removal of dust and tar before the gas can be used (Abu El-Rub et al., 2004). Tar can be effectively minimized in the producer gas by catalytic cracking. Past studied have shown that a cheap additive such as calcined dolomite (MgO-CaO) was useful in reducing tar, improving gas quality and heating value for biomass gasification (Seshadri & Shamsi, 1998). The destruction of tar is more effective at high temperatures, but increasing temperature may lead to higher tar yield (Sutton et al., 2001). At low temperature of 550∘C, (Asadullah et al. 2002) reported that, with the presence of dolomite, tar conversion was around 63%. At medium temperature, (Yu et al. 2009) found that tar conversion of around 65–75% could be achieved at 700∘C, with the presence of dolomite. Increasing from 700 to 800∘C resulted in a decrease in tar conversion. This was contributed to that fact that more stable compounds of tar were formed, so it was harder to crack. According to

(Chiang et al., 2012) that increasing content of CaO and temperature (600– 900◦C) resulted in an increase of gas heating value and carbon conversion rate. At high temperatures, (Akay et al., 2011) used CaO as an in-bed catalyst in a fixed-bed gasifier at 1,040◦C and obtained minimum tar yields of less than 0.8 g/kg and maximum gas yield of 4Nm3/kg. In addition, the gas produced can be applied into an internal combustion engine and gas burners fixed in the combustion chamber with the downstream process similar to the diesel burner.

2.6 Catalyst

One of the main technical barriers in biomass gasification development is the presence of organic impurities (tars) in the fuel gas. Tar can leads to several serious problems such as blockage of pipe, resulting in serious operational interruptions. Tar is hazardous due to its carcinogenic character. Tar elimination reactions are known to be kinetically limited. Therefore, the reaction rates can be increased by increasing the temperature and/or using a catalyst. However, catalysts can only increase the rate of a reaction that is thermodynamically feasible. There are two classes of catalyst which are synthetic catalysts and minerals shown in Figure 2.5, for the sake of this project only calcined rocks will discussed on the literature reviews. Catalysts are chosen based on their objective and practical used. The criteria for the removal of tar are as follow: (1) Effectiveness, (2) Resistance to deactivation by carbon fouling and sintering, (3) easily regenerated, (4) Strong and resistant to attrition, and (5) Inexpensive.

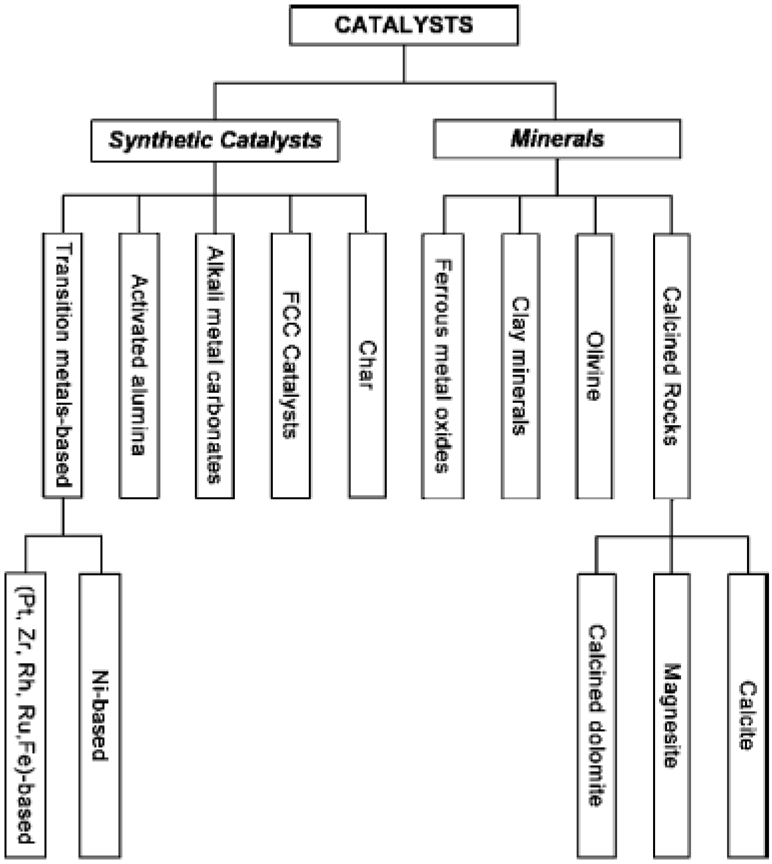


Figure 2.5 Classification and types of catalysts used for tar elimination adopted from (Abu El-Rub et al., 2004)

Calcined rocks include calcites, magnesites, and calcined dolomites. Simell et al. (1992) classified such catalysts according to the CaO/MgO ratio as shown Table 2.3. These catalysts have other names such as alkaline earth oxides, stones, minerals, and naturally occurring catalysts. The uncalcined forms of these materials are called limestone ($CaCO_3$), magnesium carbonate (Mg CO_3), and dolomite (Ca CO_3 Mg CO_3), respectively.

These materials show catalytic activity for tar elimination when calcined. Calcination occurs because of the loss of bound carbon dioxide when the material is heated. The reactions involved in tar elimination over these materials are not well known. Simell et al. (1992) related the catalytic activity for tar elimination of the calcined rocks to several factors such as a large pore size and surface area of the corresponding calcinates and a relatively high alkaline (K, Na) content. Alkaline metals could act as promoters present in commercial steam-reforming catalysts by enhancing the gasification reaction of carbon intermediates deposited on the catalyst surface (Simell et al., 1992). The activity of these rocks can be improved by increasing the Ca/Mg ratio, decreasing the grain size, and increasing the active metal content such as iron. The factors that cause catalytic deactivation of the calcined rocks are related to coke formation and CO_2 partial pressure. Coke causes deactivation of the calcined rocks by covering their active sites and blocking their pores (Deldago et al., 1996). Coke is produced by the catalytic reactions involving tar side reactions that occur on the catalyst surface. The CO_2 partial pressure causes deactivation when it is higher than the equilibrium decomposition pressure of the carbonated form of the material under the same conditions.

The advantages of these materials are that they are inexpensive and abundant. Dolomites can provide relatively high tar conversion (up to 95%). They are often used as guard beds to protect the expensive and sensitive metal catalysts from deactivation caused by tars or other impurities such H_2S. Dolomites are considered the most popular cheap catalysts for tar elimination. The main problem with these materials is their fragility. They are very soft and quickly eroded in fluidized beds with high turbulence (Delgado et al., 1996).

Table 2.3 Classification of Calcined Rocks Based on Ca/MgO Ratio Adopted from Simell et al. (1992).

Type	CaO/MgO
Limestone	➢ 50
Dolomitic Limestone	4 – 50
Calcitic Dolomite	1.5 – 4
Dolomite	1.5

CHAPTER 3

METHODOLOGY

3.1 Project Flow

In order to study the effect of catalyst on the performance of co-gasification of biomass, the project is conducted according to the process flow chart in Figure 3.1. Research also conducted to identify optimum amount of catalyst used to improve the quality of syngas in order to relate with the problem statement of the project, which is to increase the energy content of the syngas. Other than that, the feedstock were choose to suite the specification of the downdraft gasifier used which could not support small sized feedstock and the identification and selection of the feedstock was done by literature review based on past researches. The chosen feedstock will be cut up to size range from 2 to 3 cm and then place in the oven at 105°C for 24 hours until the moisture content was below 15% to ensure the suitability for use in downdraft gasifier for the experiment (ASTM International, 2007), (Agbor et al., 2011).

Elemental analysis were conducted for each of the feedstock to identify their chemical and physical properties, chemical and physical properties. Five trials of co-gasification were done using different weight ratios of biomass to catalyst with the air flow rate at 350 litres per minute.

Six thermocouples were fixed at different spots inside the downdraft gasifier to determine the temperature in order to determine the drying, pyrolysis, combustion and reduction zones. The product gas produced from the gasifier are analyse by a gas analyser and the readings needs to be recorded for comparisons.

The timeline of the Final Year Project 1 and 2 are shown by using Gantt chart and Key Milestone in Figure 3.2 and 3.3.The time allocated to complete the catalytic co-gasification is seven weeks. However, some of the experiment need to repeat due to some problems such as bridging and inappropriate set up.

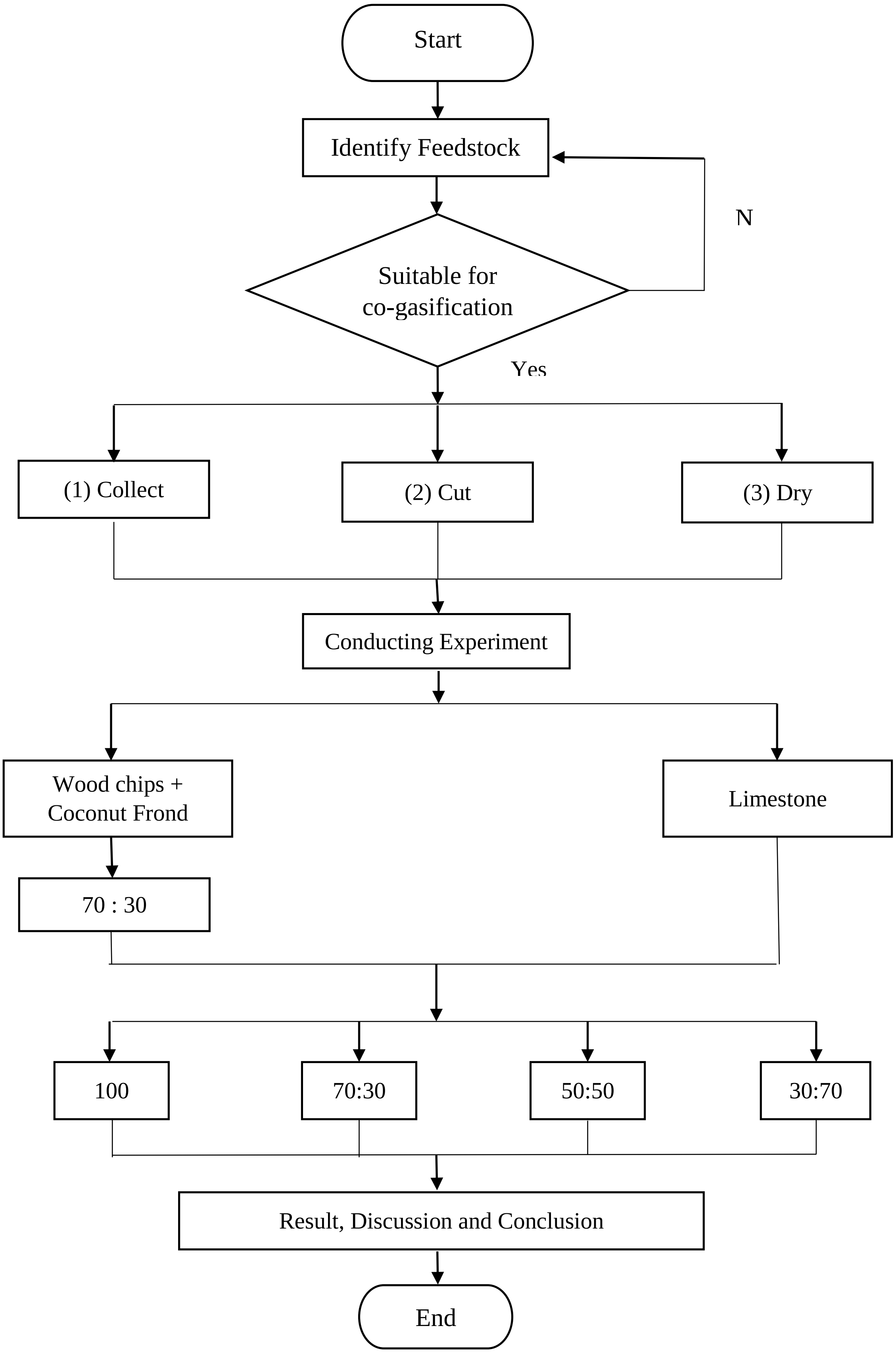
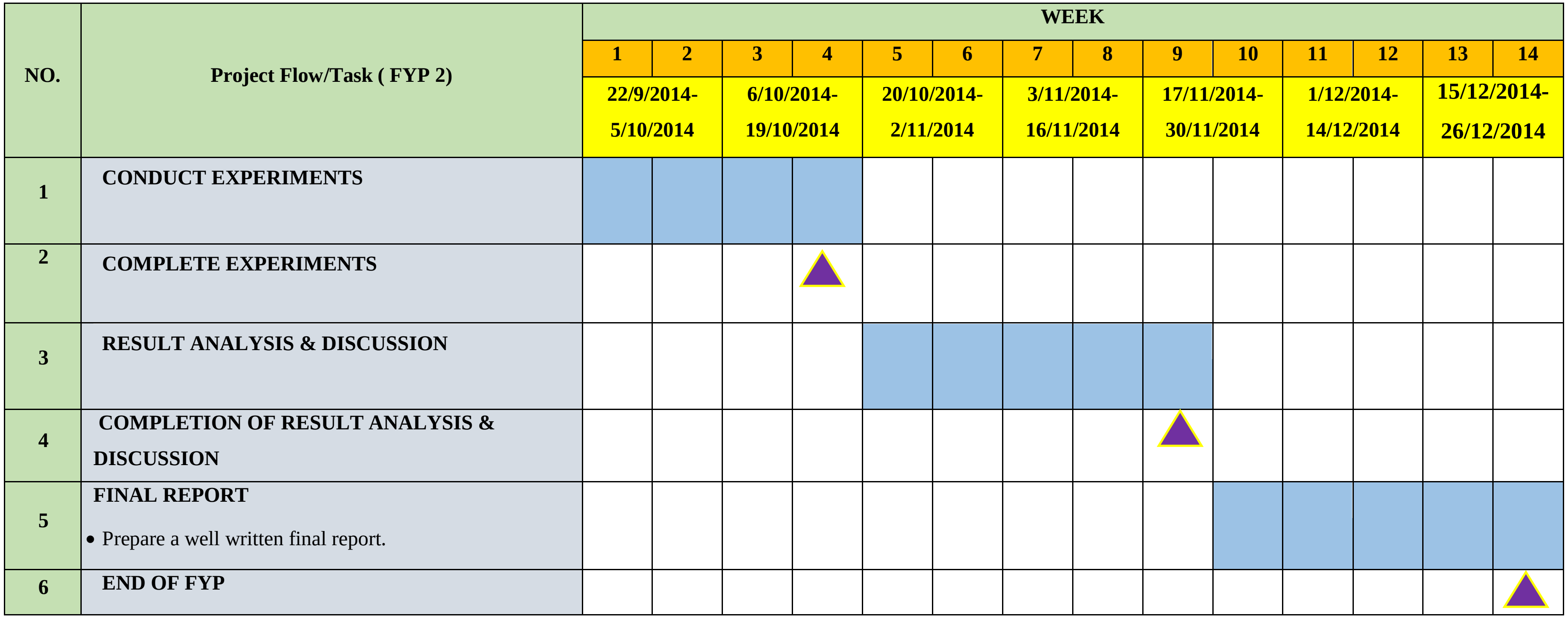


Figure 3.1 Process flow chart

NO.	Project Flow/Task (FYP 1)	WEEK													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
		22/9/2014-5/10/2014		6/10/2014-19/10/2014		20/10/2014-2/11/2014		3/11/2014-16/11/2014		17/11/2014-30/11/2014		1/12/2014-14/12/2014		15/12/2014-26/12/2014	
1	**CONFIRMATION OF PROJECT TITLE** • Consultation with UTP supervisor.	■													
2	**PRELIMINARY RESEARCH WORKS** • Reading and study on related journals.	■	■												
3	**LITERATURE REVIEW** • Review other researchers' works and findings.		■	■	■										
4	**SURVEY FOR TOOLS & EQUIPMENT** • Understand the functions of tools and equipment required.				■	■									
5	**SURVEY FOR FEEDSTOCK AND CATALYST** • Study deeply about the properties of each type of feedstock and catalyst				■	■									
6	**STUDY THE EXPERIMENT SETUP** • Study deeply into the procedures and method of experiments.					■	■								
7	**UNDERSTAND THE EXPERIMENT SETUP**						▲								
8	**OBTAINING EXPERIMENT MATERIALS** • Collect feedstock and buy catalyst							■	■	■	■	■			
9	**PROPOSAL DEFENCE**											■			
10	**CONDUCT EXPERIMENT**											■	■	■	■
11	**INTERIM REPORT**											■	■	■	
12	**END OF FYP 1**														▲

▲ **Key Milestones**

Figure 3.2 FYP I Gantt chart



NO.	Project Flow/Task (FYP 2)	WEEK													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
		22/9/2014-5/10/2014		6/10/2014-19/10/2014		20/10/2014-2/11/2014		3/11/2014-16/11/2014		17/11/2014-30/11/2014		1/12/2014-14/12/2014		15/12/2014-26/12/2014	
1	**CONDUCT EXPERIMENTS**	▨	▨	▨	▨										
2	**COMPLETE EXPERIMENTS**				▲										
3	**RESULT ANALYSIS & DISCUSSION**					▨	▨	▨	▨	▨					
4	**COMPLETION OF RESULT ANALYSIS & DISCUSSION**									▲					
5	**FINAL REPORT** • Prepare a well written final report.										▨	▨	▨	▨	▨
6	**END OF FYP**														▲

▲ **Key Milestones**

Figure 3.3: FYP 2 Gantt Chart

3.2 Gasifier Type and Specification

A downdraft biomass gasifier was used to conduct all the experiments at Universiti Teknologi Petronas. The gasifier had a thermal power output of 50 kW, was assembled as shown in Figures 3.4. The gasifier was produced in a local workshop based on the specification. The internal lining and insulation were built from 50 mm thickness. There are two openings on the top for feeding the fuel. The gasifer also has a easily dismantle grate and ash box. Air is supply into the gasifier by a 250 W vortex blower and the flow rate of the air is controlled using a ball valve and a bypass point and monitored using a pitot tube and a water manometer. The full load of the gasifier is 18 kg for 2.5 - 5.0cm^3 feedstock with 70% compact factor (Sulaiman et al., 2013).

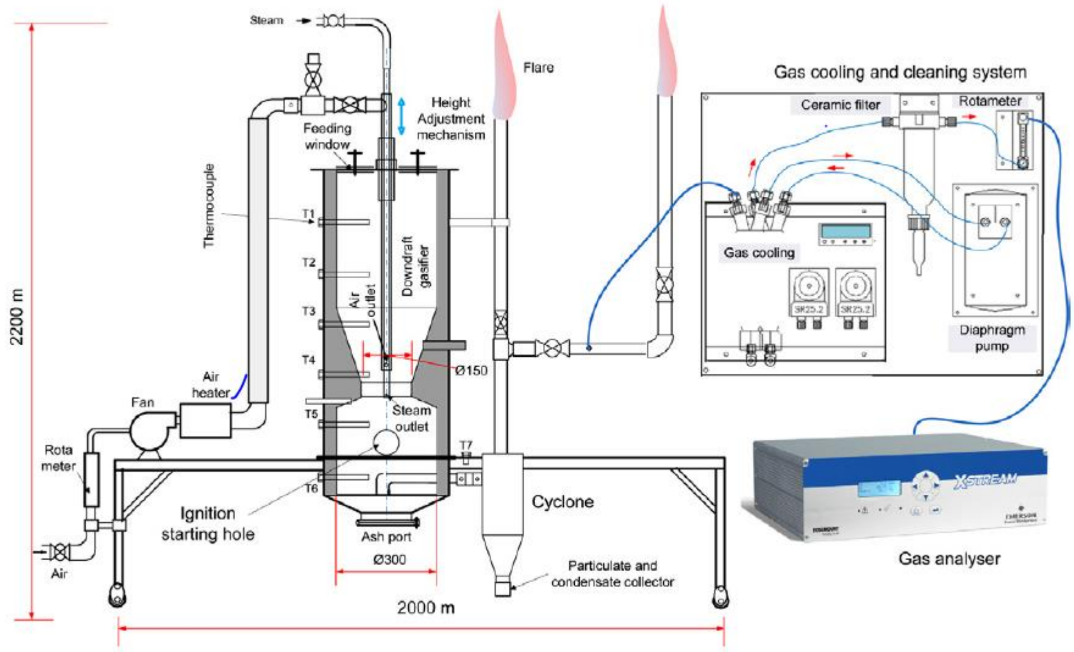


Figure 3.4 Completed gasifier and semi-finished part adopted from (Guangul et al., 2012)

3.3 Measuring Instruments

3.3.1 Thermocouples

There are six type-N thermocouples were connected on the gasifier body at 200 mm interval for monitoring the gasifier temperature profile as shown in figure 3.4. The temperature readings were collected using a USB (Universal serial bus) based temperature data logger at every 30 seconds. The accuracy of the thermocouples used was ± 2.5 °C. The function of the thermocouple are as shown in Table 3.1.

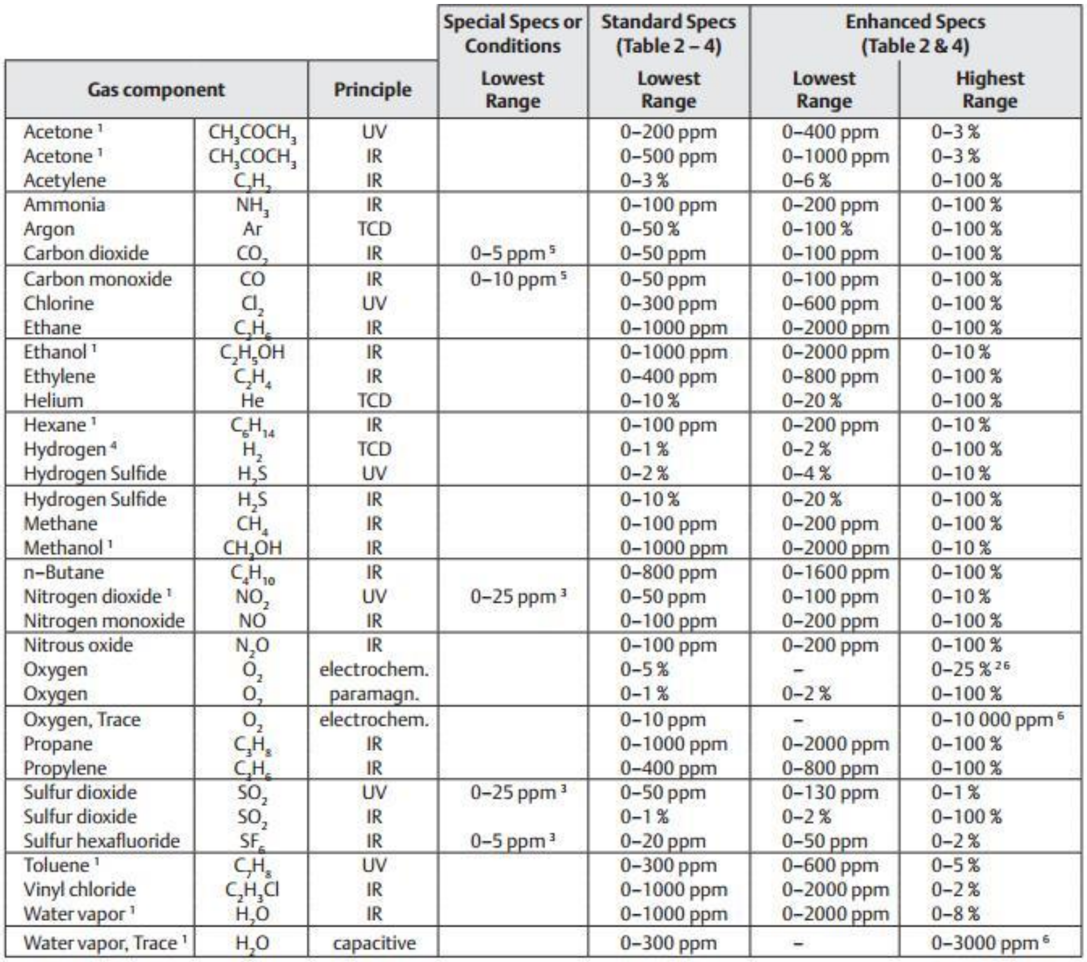
Table 3.1 Function of thermocouples Guangul et al. (2012)

Thermocouple	Position (mm)	Functions
T1	1190	Drying
T2	975	Drying
T3	760	Drying
T4	545	Pyrolysis
T5	330	Combustion
T6	130	Reduction
T7	160	Syngas Temperature

3.3.2 Online gas analyser

X-Stream XE is an online gas analyser, which widely used in exhaust measurement for burner efficiency, biogas and landfill, automotive emissions, natural gas production etc. In total this gas analyser can able to detect more than 60 gases which shown in Table 3.2. For the purpose of the project, this gas analyser is connected to the outlet pipe of the gasifier and it is able to trace CO, CO_2, H_2, N_2 and CH_4. The analyser able to trace the syngas continously in a real time bases and the composition of the syngas are show in the computer for recording and monitoring shown in Figures 3.5 and 3.6

Table 3.2 Gas Components and Measuring ranges Emerson (2011)



			Special Specs or Conditions	Standard Specs (Table 2 – 4)	Enhanced Specs (Table 2 & 4)	
Gas component		Principle	Lowest Range	Lowest Range	Lowest Range	Highest Range
Acetone[1]	CH_3COCH_3	UV		0–200 ppm	0–400 ppm	0–3 %
Acetone[1]	CH_3COCH_3	IR		0–500 ppm	0–1000 ppm	0–3 %
Acetylene	C_2H_2	IR		0–3 %	0–6 %	0–100 %
Ammonia	NH_3	IR		0–100 ppm	0–200 ppm	0–100 %
Argon	Ar	TCD		0–50 %	0–100 %	0–100 %
Carbon dioxide	CO_2	IR	0–5 ppm[5]	0–50 ppm	0–100 ppm	0–100 %
Carbon monoxide	CO	IR	0–10 ppm[5]	0–50 ppm	0–100 ppm	0–100 %
Chlorine	Cl_2	UV		0–300 ppm	0–600 ppm	0–100 %
Ethane	C_2H_6	IR		0–1000 ppm	0–2000 ppm	0–100 %
Ethanol[1]	C_2H_5OH	IR		0–1000 ppm	0–2000 ppm	0–10 %
Ethylene	C_2H_4	IR		0–400 ppm	0–800 ppm	0–100 %
Helium	He	TCD		0–10 %	0–20 %	0–100 %
Hexane[1]	C_6H_{14}	IR		0–100 ppm	0–200 ppm	0–10 %
Hydrogen[4]	H_2	TCD		0–1 %	0–2 %	0–100 %
Hydrogen Sulfide	H_2S	UV		0–2 %	0–4 %	0–10 %
Hydrogen Sulfide	H_2S	IR		0–10 %	0–20 %	0–100 %
Methane	CH_4	IR		0–100 ppm	0–200 ppm	0–100 %
Methanol[1]	CH_3OH	IR		0–1000 ppm	0–2000 ppm	0–10 %
n–Butane	C_4H_{10}	IR		0–800 ppm	0–1600 ppm	0–100 %
Nitrogen dioxide[1]	NO_2	UV	0–25 ppm[3]	0–50 ppm	0–100 ppm	0–10 %
Nitrogen monoxide	NO	IR		0–100 ppm	0–200 ppm	0–100 %
Nitrous oxide	N_2O	IR		0–100 ppm	0–200 ppm	0–100 %
Oxygen	O_2	electrochem.		0–5 %	–	0–25 %[2,6]
Oxygen	O_2	paramagn.		0–1 %	0–2 %	0–100 %
Oxygen, Trace	O_2	electrochem.		0–10 ppm	–	0–10 000 ppm[6]
Propane	C_3H_8	IR		0–1000 ppm	0–2000 ppm	0–100 %
Propylene	C_3H_6	IR		0–400 ppm	0–800 ppm	0–100 %
Sulfur dioxide	SO_2	UV	0–25 ppm[3]	0–50 ppm	0–130 ppm	0–1 %
Sulfur dioxide	SO_2	IR		0–1 %	0–2 %	0–100 %
Sulfur hexafluoride	SF_6	IR	0–5 ppm[3]	0–20 ppm	0–50 ppm	0–2 %
Toluene[1]	C_7H_8	UV		0–300 ppm	0–600 ppm	0–5 %
Vinyl chloride	C_2H_3Cl	IR		0–1000 ppm	0–2000 ppm	0–2 %
Water vapor[1]	H_2O	IR		0–1000 ppm	0–2000 ppm	0–8 %
Water vapor, Trace[1]	H_2O	capacitive		0–300 ppm	–	0–3000 ppm[6]

Figure 3.5 Computer and Gas Analyser

Figure 3.6 Front View of the X-Stream provides measurement and status information with plain text and symbol

3.4 Characterization of Feedstock and Preparation

The feedstocks used for this project are wood chips and coconut frond. This combination is chosen based on two reasons (a) their availability in Malaysia and (b) their size. There are lots of biomass sources possesed high potential to generate energy available in this country such as rice, oil palm fronds, sugarcane, municipal waste, coconut frond and wood waste. The downdraft gasifier could not handle feedstock which is smaller that 2cm as it would block the syngas path and the moisture content was important since it would correspond to one of the main criteria for the selection of energy conversion process. The optimum moisture content for biomass fuels which can operate in the gasifier is 15 to 17%

on dry basis. Therefore, coconut frond and wood chips were chosen as they matched with all the factors stated above and the proximate analysis of wood and coconut fronds are shown in Table 3.3.

Table 3.3 Proximate analysis of wood and coconut fronds

Proximate Analysis				
Biomass	Moisture Content (%)	Volatile Matter (%)	Fixed Carbon (%)	Ash Content (%)
CF	11.95	62.37	17.76	7.92
Wood	11.40	88.07	10.77	1.16

3.4.1 Coconut Fronds

The coconut fronds were collected in Teluk Intan, Perak, Malaysia. There were about 60 stems of coconut fronds to be used for this project. The fronds were cut by using the cutting machine as shown in Figure 3.7 . As the fronds has different size quantity, the outcome for the size was slightly smaller for top and middle part compared with the basal part as shown in Figure 3.8. The feedstock were dried using an oven at 105°C for 24 hours as shown in Figure 3.9.

3.4.2 Wood Chips

Wood branches were collected from UTP's (Universiti Teknologi PETRONAS) landscape maintenance during their tree trimming activities. Acacia Mangium tree were chosen for the experiment to ensure the same chemical and physical properties were obtained from the feedstock. These branches were chipped at a wood factory using a chipper machine to the maximum of 3 cm in length as shown in Figure 3.8. It was dried using an oven at 105°C for 24 hours as shown in Figure 3.9.

Figure 3.7 Cutting feedstock using power saw

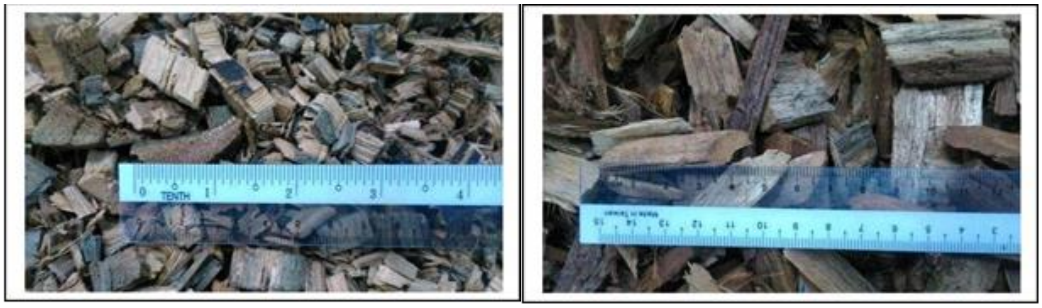


Figure 3.8 Size of feedstock after cutting Cocont frond (left) and wood (right)

Figure 3.9 Drying Processed

3.5 Catalyst Preparation

Natural limestone were collected from Ipoh, Perak, Malaysia. Table 3.4 shows the elemental analysis of the Ipoh's limestone with a CaO as high as 70.91% (Salleh et al., 2006). In catalyst preparation, the limestone was heated and decarboxylated at 900°C for 1 hour.

Table 3.4 Chemical Composition of limestone adopted from (Salleh et al., 2006)

Content	Composition Percentage (%)
CaO	70.91
MgO	16.80
SiO_2	2.19
Al_2O_3	4.43

3.6 Mixing Procedure

After the preparation of feedstocks both of these materials need to be mixed homogenously to achieve a better outcome. The mixing ratio betweeen two biomass is fixed which is 70:30 which means total 14 kg of biomass and further divide into 9.8 kg of wood and 4.2 kg of coconut frond. After the cutting process, the biomass were shieved into suitable sizes before mixing as shown in Figure 3.10. In order to perform homogenous mixing, a big container is used as shown in Figure 3.11, two biomass are pour simulataneously into the container and stir with a stick.

Figure 3.10 Raw CF and Wood Chips before mixing

Figure 3.11 Raw CF and wood chips after mixing

3.7 Catalyst to Biomass Ratio

Since the mixing ratio of both biomass is fixed which is 70:30, therefore the only varible left will be the biomass to catalyst ratio. There are total 3 mass ratio that will be used to conduct the experiment which are catalyst to biomass ratios 0.3:1, 0.5:1 and 1:1. The ratio will base on the mass for example 0.3:1 since there are total 14kg of biomass will be used therefore the mass of catalyst will be 30% of the mass of biomass which is 4.2 kg. . The experiment consisted of two trial with each weight ratios of biomass with catalyst. The mixture ratios for each trial are shown in Table 3.5.

Table 3.5 Ratios of Biomass and Catalyst for experiment

Trials	**Biomass : Catalyst**
1	0.3:1
2	0.5:1
3	0.7:1

CHAPTER 4

RESULT AND DISCUSSION

4.1 Elemental Analysis

Elemental analysis was performed to determine the proximate, ultimate analysis, calorific value and moisture content of coconut frond and wood chips as shown in Table 4.1. The values for coal were extracted from (Alzate et al., 2008) to compare the amount of each lignocellulosic component with coal.

Table 4.1 Physical and chemical characteristics of CF, wood chips and coal

(% dry basis)	**CF**	**Wood Chips**	**Coal**
Proximate Analysis			
Volatile matter	62.37	88.07	38.20
Fixed carbon	17.76	10.77	38.40
Ash	7.92	1.16	14.40
Ultimate Analysia			
Carbon	40.02	43.54	58.67
Hydrogen	6.03	3.59	5.11
Nitrogen	0.14	1.00	0.68
Sulphur	0.54	0.16	0.37
Calorific Value (HHV) (Mj/kg)	15.22 MJ/kg	18.09 MJ/kg	17.28 MJ/kg
Moisture content (%)	11.95	11.40	9.00

Based on the results of the analyses, the amount of volatile matter for both lignocellulosic biomasses show a higher value of up to 50% more compared to coal. The amount of volatile matter represents the ease to start the ignition of the fuel. Wood chips show the highest volatile matter content and trials that contained higher wood ratio should have a higher co-gasification rate for the same volume of feedstock. The low amount of fixed carbon and ashes compared to coal shows that the co-gasification between the lignocellulosic biomasses produce less charcoal and ashes at the end of the co-gasification experiment. Slightly lower amount of carbon and hydrogen present in coconut fronds and wood chips show that there are small differences for gases produced. On the other hand, the low nitrogen and sulphur content in the lignocellulosic biomasses produced very low amount of hazardous gases. Moisture content was a controlled variable set below 15%.

4.2 Steady Operation

Experimental results for batch fed operation of a downdraft gasifier are presented in this paper. Figure 4.1 shows the gas composition on volume percent at different catalyst addition 0%, 30%, 50% and 70%. Unlike continuous feed operation the results for syngas composition show variation with operation duration for the case of batch fed operation due to sharp increase during startup and decrease near the end of the operation due to depletion of the feedstock. From Fig. 4.1(b) it can be seen that CO increased from 0% to 20% within the first 10 minutes. After the 10th minute of operation it had been observed that the gas composition of the gasification found to stabilize till the 30th minute. The decrease in gas composition after the 30th minute of operation was caused due to the batch fed operation, whereby most of the feedstock will be consumed near the end of the experimental run. Therefore the time interval between 10th and 30th minutes of operation could be taken as the stable duration of operation. Similar approach was followed in the work of (Plis & Wilk, 2011). Hence the results from the current study could be reasonably extended to approximate the case of continuous feed operation.

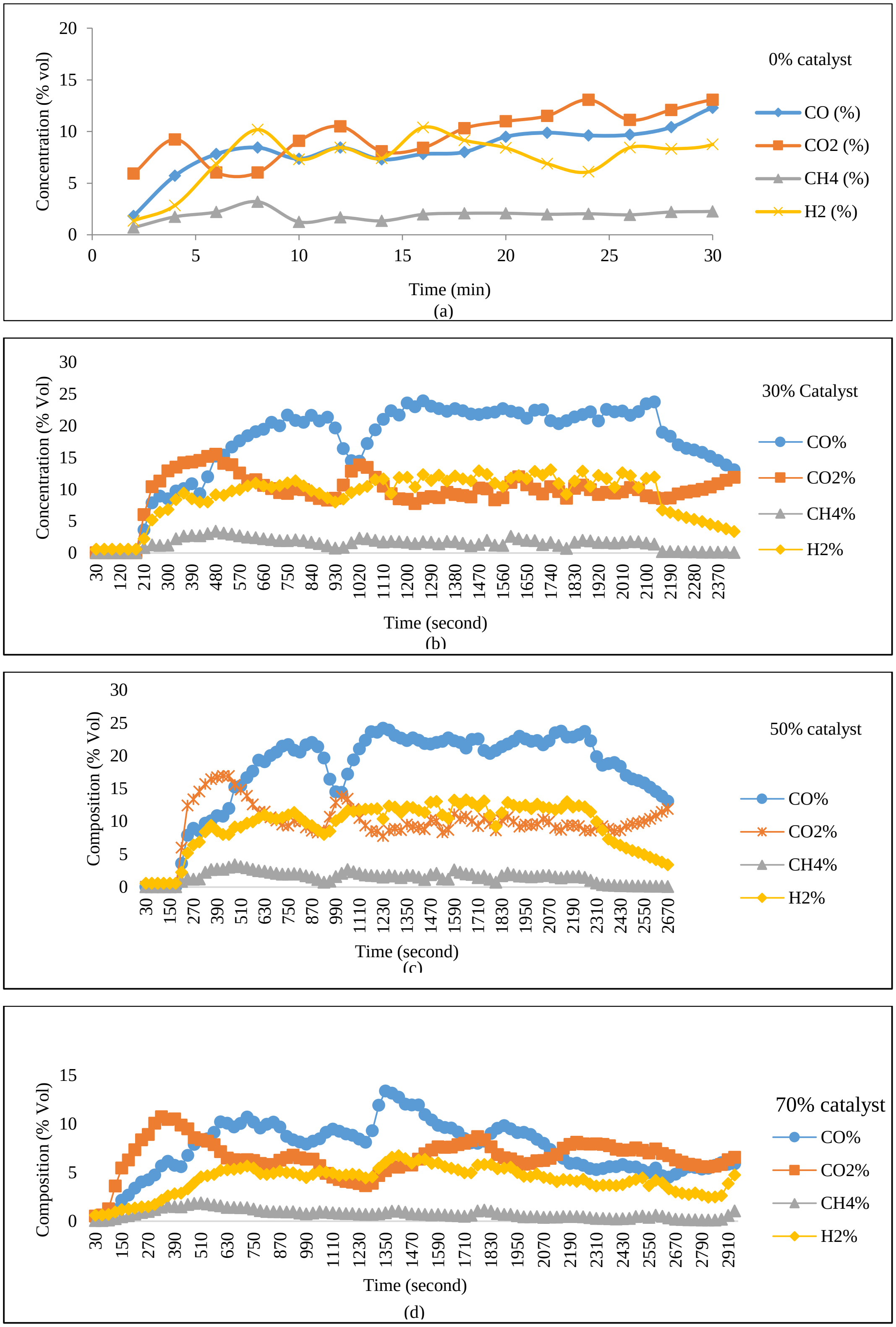


Figure 4.1 Gas composition at various catalyst to biomass ratio (a) 0%, (b)30%, (c) 50%, and (d) 70%.

4.3 Dynamic Temperature Profile

Only one set of data of the optimum result will discuss for the dynamic temperature profile in this report. Co-gasification trials for CF and wood chips mixture with catalyst were conducted for 33 minutes for 70:30 wood to CF ratio and 50% of limestone catalyst. The temperature variation for different zones inside the gasifier for blend of WC (70%) and CF (30%) with time is presented in Figure 4.2. T_1-T_3 are drying zone temperatures where T_4-T_7 are pyrolysis, oxidation, reduction zone and syngas out temperatures respectively and T_5 is the combustion zone.

Figure 4.2 shows the temperature profile for 70:30 woods to CF mix. The operation time lasted for only 33 minutes before the feedstock was completely combusted. Although the operation was conducted in a shorter time, major peaks were observed indicating more bridging problems had occurred with the increase in wood ratio. Combustion temperature increased rapidly from room temperature of 29.7°C at the beginning of the experiment to the maximum temperature of 765.11°C in 5 minutes. This proved that CF was combusted rapidly before first bridging occurred during the 5^{th} to 10^{th} minute of the operation. The combustion zone temperature then started decreasing at 17^{th} minute where the feedstock was completely combusted. The temperature at other zone also showed unstable readings with the average temperatures recorded for T1 to T7 over the total operation as shown in Table 4.2.

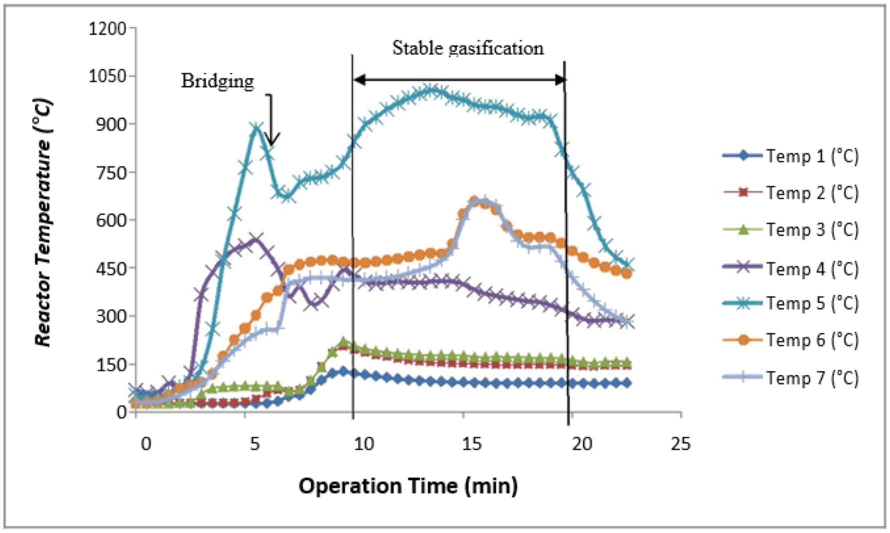


Figure 4.2 Temperature profile for 70% wood and 30% CF with 50% catalyst

Table 4.2 Average reactor temperature for 70% wood and 30% CF with 50% catalyst

Thermocouple	Reactor Temperature (°C)
1	74.9
2	114.9
3	133.4
4	347.3
5	689.
6	402.4
7	357.2

4.4 Effect of Limestone Catalyst on Gas Composition

In this work limestone was used as catalyst for gasification. The effect of the catalyst was studied for the air flow rate at 350 liter per minute and air as the gasifying medium. It can be seen the gas composition of each component were higher when catalyst was used. This observation was in line with (Chiang et al., 2011; Demirbaş, 2002; Encinar et al., 1998; Lv et al., 2007). Figure 4.3 indicates that the presence of limestone clearly encourage the production of H_2 and CO, while the content of CH_4 and CO_2 slightly decreased with increasing catalyst to biomass ratio (Moghtaderi, 2007).

At 0% catalyst, H_2 was amounted to 7.315% and CO was about 9.353%. When 30% catalyst was introduced, H_2 content was amounted to 9.044% and CO was about 17.383%. The optimum amount of H_2 produced when 50% catalyst was added to the gasification which amounted to 9.391% and CO was 17.878%. At 70% catalyst, H_2 and CO content were low due to the improper air flow as too much of limestone had blocked the air flow passage. The H_2 content has increased 28.3% from the non-catalytic gasification. The quantity of CO_2 was found to be higher than that obtained from the uncatalyzed case. With increased catalyst to biomass ratio from 0 to 0.5, higher content of CO_2 was obtained due to the released of CO_2 from limestone. The reforming reaction of tar on a limestone surface by capturing carbon to produce more H_2 and CO, according to reaction (4.1) (Basu, 2010). Besides, figure 4.4 shows that with addition of catalyst favored the gas yield. Gas yield from the gasification was calculated by the following equation (4.2).

$$C_nH_m + nCO_2 \xleftrightarrow{\text{Limestone}} 2nCO + \left(\frac{m}{2}\right) H_2 \tag{4.1}$$

$$Y = \frac{Q_a \text{x } 79\%}{W_b(1 - X_{ash})N_2\%} \ (Nm^3/kg) \tag{4.2}$$

where Y is the gas yield (Nm^3/kg), Q_a is the flow rate of air (Nm^3/hr), W_b is the flow rate of biomass (kg/hr), X_{ash} is ash content in biomass (wt. %) and N_2% is the volumetric percentage of nitrogen in the dry syngas. It was assumed that, air composition consisted only 21% oxygen and 79% nitrogen, furthermore all oxygen in air reacts with feedstock during gasification process. In addition, syngas was consisted only CO, H_2, CO_2, CH_4 and N_2, contents where N_2 was determined by difference method. Gas yield indicates the ability of feedstock converted into gaseous products. Generally gas yield shows the amount of gas in normal meter cube produced by one kilogram of biomass. At non catalytic gasification gas yield was 1.377 Nm^3/kg and has increased 21.78% up to 1.677 Nm^3/kg at 50% of catalyst addition.

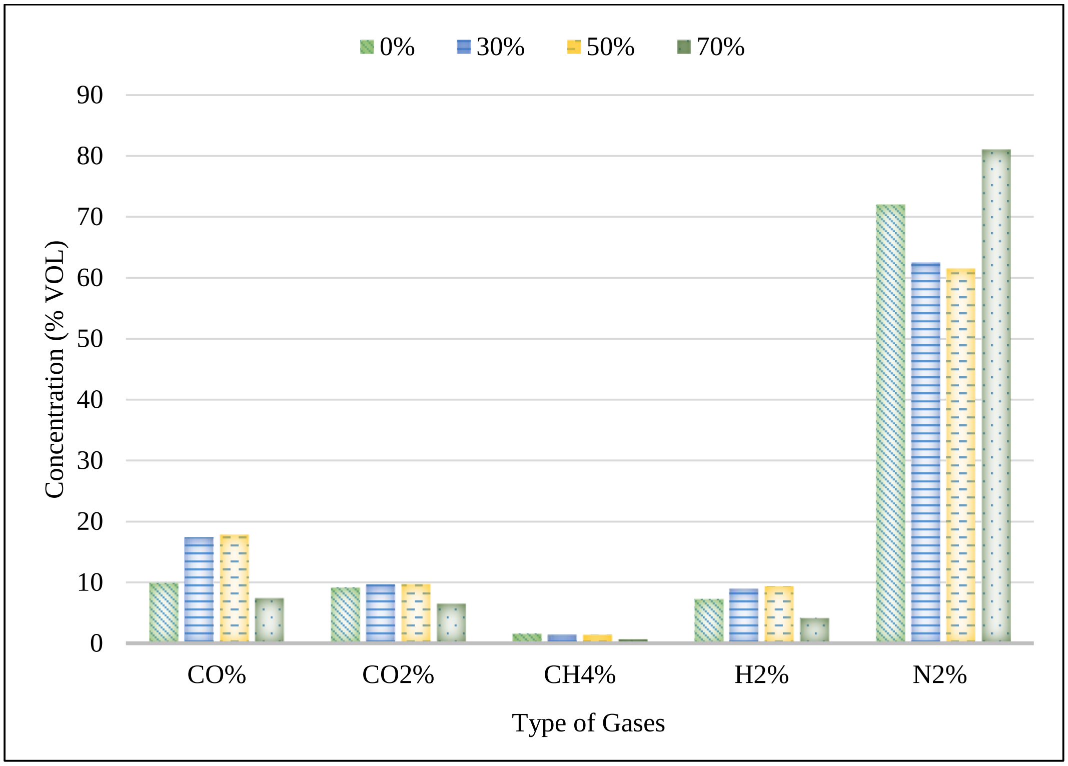


Figure 4.3: Average gas composition at various catalyst percentages 0%, 30%, 50% and 70%.

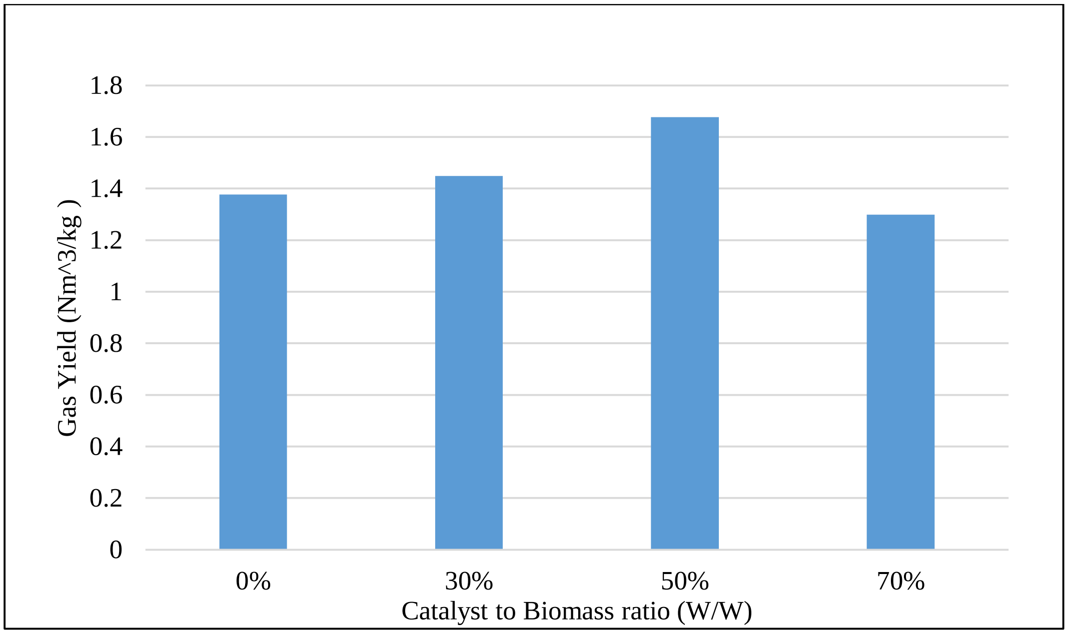


Figure 4.4 Gas yield at various catalyst to biomass ratio

4.5 Evaluation of Energy Efficiency on Catalytic Gasification of CF and WC

Syngas heating value and energy density are used to evaluate the energy efficiency on this study. The energy density defined as the higher heating value of synthesis gas compared with caloric value of tested CF and WC. The targeted indexed were calculated using the empirical formula (4.2) and (4.3) as given as follow:

$$\mathrm{HHV_{Syngas}} = 12.63 \text{ x } \mathrm{X_{co}} + 12.74 \text{ x } \mathrm{X_{H_2}} + 39.82 \text{ x } \mathrm{X_{CH_4}} \tag{4.2}$$

where, the$\mathrm{X_{co}}$, $\mathrm{X_{H_2}}$, and $\mathrm{X_{CH_4}}$: volume percent of gas yield.

$$\text{Energy density} = \left(\mathrm{HHV_{Syngas}} \text{ x } \mathrm{V_t}\right)/(\mathrm{HHV_{Biomass}} \text{ x } \mathrm{W}) \tag{4.3}$$

where, $\mathrm{V_t}$: Syngas yield $(\mathrm{Nm^3, N_2}$ free$)$, $\mathrm{HHV_{Syngas}}$: Higher heating value of syngas $(\mathrm{MJ/Nm^3})$, $\mathrm{HHV_{Biomass}}$: Higher heating value of biomass $(\mathrm{MJ/Kg})$, W: weight of tested biomass (kg).

4.5.1 Heating Values of Syngas

To eliminate the nitrogen effect on the heating value calculation of syngas, the basis of the syngas heating value is nitrogen free. As shown in figure 4.5, the syngas heating value is 2.82 MJ/Nm^3 at non catalytic gasification and the syngas heating value is between 1.96 MJ/N m^3 and 5.11 MJ/N m^3 at catalytic gasification similar to other studies (4 – 6 MJ/Nm^3) derived from bamboo biomass gasification (Chiang et al., 2012). The syngas heating value has increased 81% at catalytic gasification. Again at 70% catalyst added, syngas heating value was low due to the improper air flow rate, whereby the huge amount of catalyst has blocked the air passage. The syngas heating value significantly enhanced by limestone additions, which related to the higher reaction rate of water-gas shift reaction and hydrocarbon reforming (Han et al., 2011).

However, the chemical composition of feedstock could influence the syngas fraction and heating value in biomass gasification. That is the H and O elements might compete to react with C on biomass matrix to form the $\mathrm{CH_4}$ or CO. In general, the $\mathrm{CH_4}$ heating value is higher than CO. Therefore the higher H exhibits the higher syngas heating value.

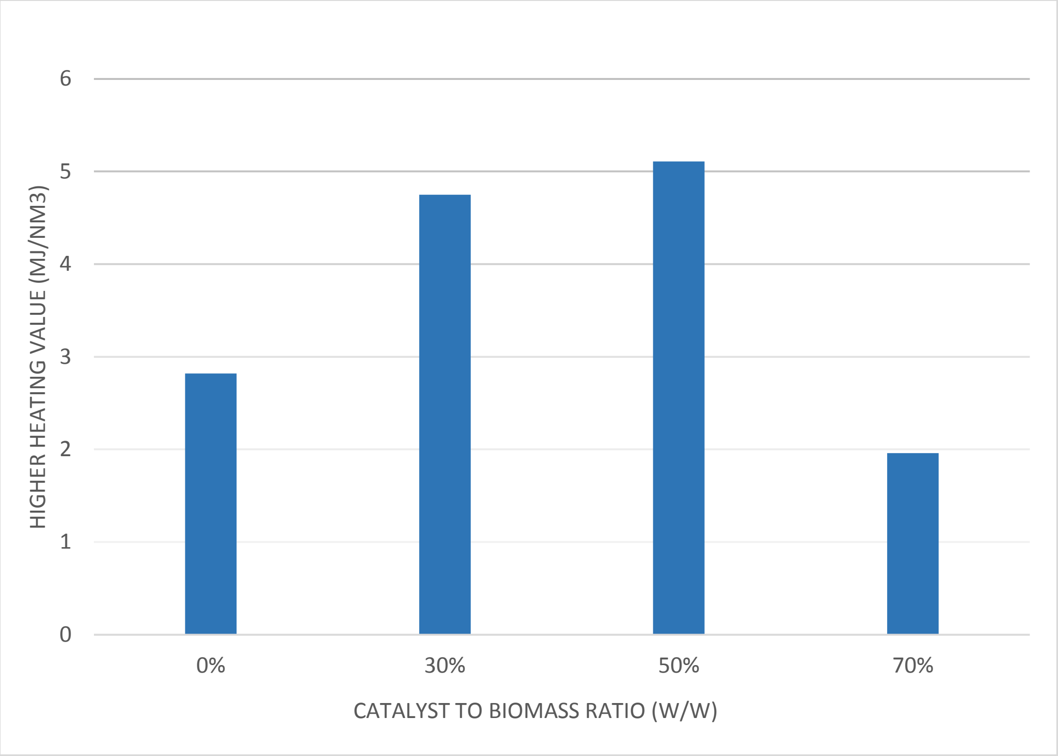


Figure 4.5 Higher Heating Value At various catalyst to biomass ratio

4.5.2 Energy Density of Co-gasification

Energy density (ED) was applied to evaluate the energy efficiency in gasification on energy utilization. Figure 4.6 is the energy density of CF and WC co- gasification. According to the result of the ED on non-catalytic the ED was 0.26. In catalytic gasification the ED was 0.41 at 30% catalyst. ED reached the optimum at 50% catalyst which was 0.5. However a dropped on ED value at 70% catalyst due to the improper air flow was 0.15.

This study showed the similar result as the ED of bamboo gasification, the ED were between 0.54 and 1.05 at 0% to 15% CaO addition (Chiang et al., 2012). However, with respect to the energy density, there are more efforts need to be accomplished on energy transformation like feedstock pre-treatment, gasifying agent adjustment and syngas condition to improve the total energy efficiency.

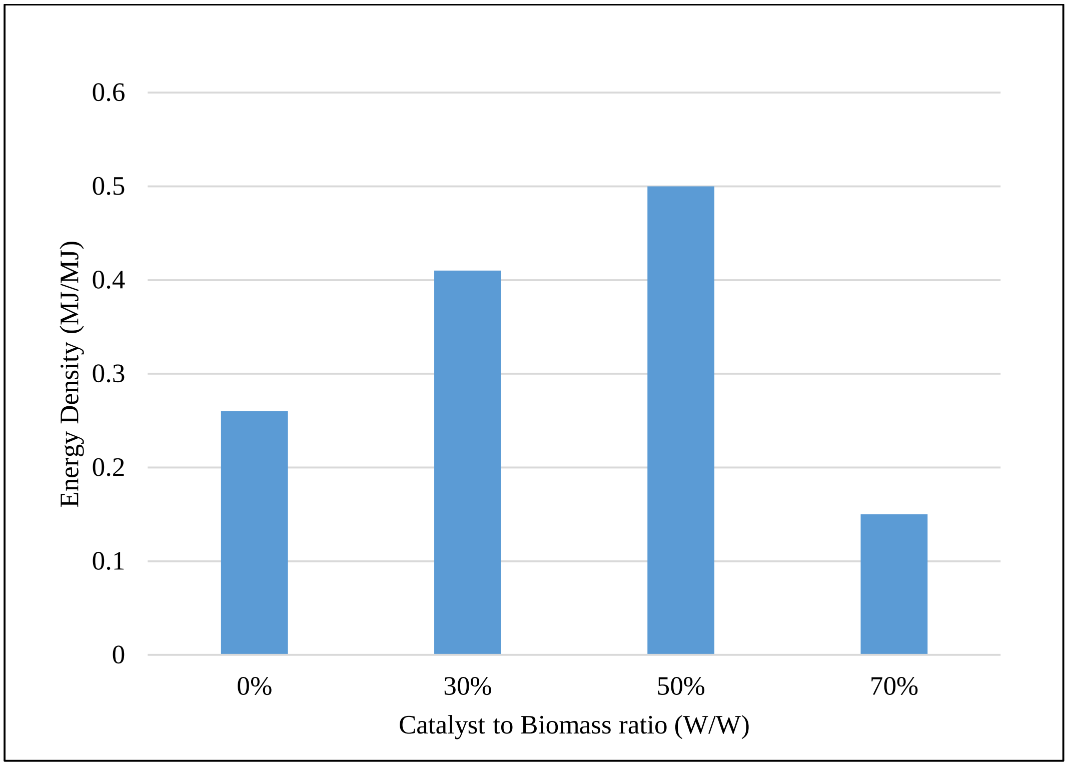


Figure 4.6 Energy Density at various catalyst to biomass ratio

4.6 Effect of Limestone Catalyst on Carbon Conversion Efficiencies

Mass conversion efficiencies is an important parameter that determines the amount of solid feed in percentage converted to permanent gases. High mass conversion efficiency means low generation of unwanted products like tar, char and ash. Carbon conversion efficiencies indicates how much of the initial carbon content of fuel is converted to gaseous product, and thus affecting the amount of unconverted carbon in char and tar by products from gasification.

Figure 4.7 shows the variation of carbon conversion efficiencies with different catalyst to biomass ratio. At non-catalytic gasification the carbon conversion efficiencies was 35.20% and increase sharply up to 59.69% when 30% of catalyst was introduced to the gasification process. The maximum value of carbon conversion efficiencies observed for 50% of catalyst addition, with 69.49% at this condition. The minimal value of carbon conversion efficiencies occurred at 70% of catalyst addition around 24.72% could be attributed to the blockage of catalyst at the gasifier’s grate. Air flow rate was disrupted thus most of the feedstock were not burnt completely therefore the conversion efficiencies is low.

These values of carbon conversion efficiencies obtained for CF and WC were found to be comparable with the results for gasification of rice husk which were reported to be 55-81% (Mansaray et al., 1999). The high mass and carbon conversion efficiencies of CF and WC which could be mainly due to its low ash and fixed carbon composition showed its high potential as a fuel for thermal conversion processes.

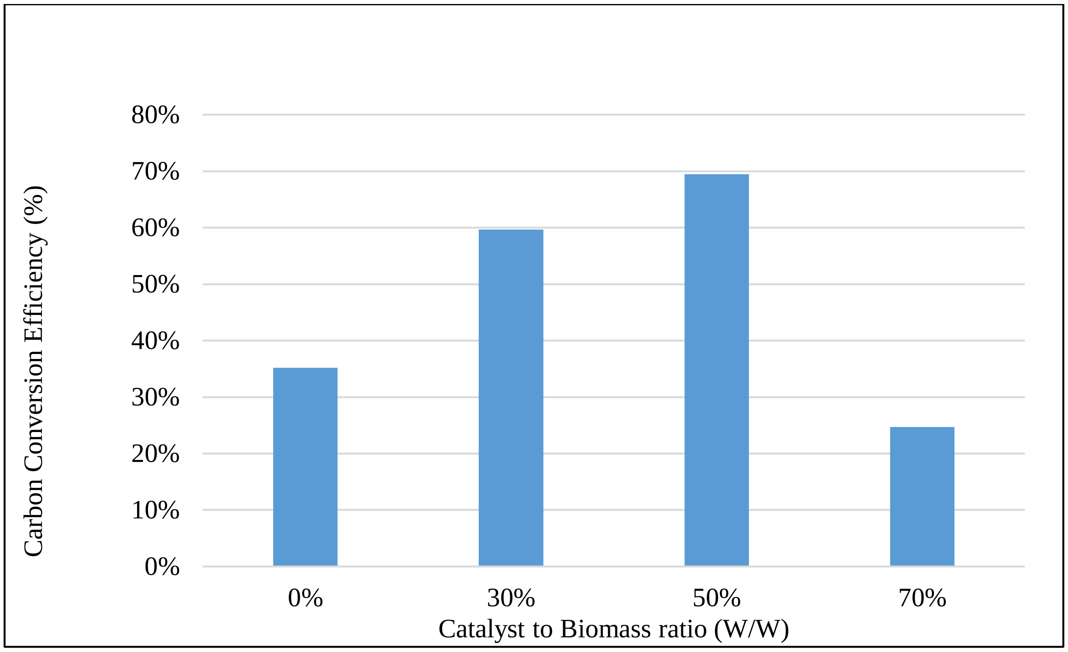


Figure 4.7 Carbon conversion efficiency at various catalyst to biomass ratio

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The main purpose of this project was mainly to study the effect of limestone catalyst on co-gasification with wood chips and CF by using the downdraft gasifier. The focus was to evaluate the quality of syngas obtained from the catalytic co-gasification of selected biomass. Ultimate, proximate and calorific value analyses that were conducted for CF and Acacia Mangium wood showed that these biomasses had high potential to produce syngas for power generation. The results showed better physical, chemical characteristics were present in feedstocks as compared with coal, and the following conclusion can be made.

The study showed that the optimum range of operation in terms of catalyst to biomass ratio is 0.3:1 to 0.5:1. At the optimum catalyst to biomass ratio of 0.5:1 is favourable for high concentration of the fuel components of syngas CO, H_2 and CH_4. The optimum amount of H_2 produced when 50% catalyst was added to the gasification which amounted to 9.391% and CO was 17.878%. The optimum catalyst to biomass ratio also resulted in average syngas heating value of 5.11 MJ/Nm^3 and the carbon conversion efficiencies of 69.49%. The results obtained in the current study for catalytic co-gasification of CF and WC were found to be comparable with result of other studies for downdraft gasification of woody biomass. The results showed that CF and WC have a high potential as a fuel for gasification.

5.2 Recommendations for Future Work

- **Co-gasification of biomass with varying air flow rate**

The current co-gasification studies of different biomass materials were done based on the optimum air flow rate obtained in the previous gasification studies for pure OPF. These results could be improved by varying the air flow rate and determining the optimum air flow rate for different blends of biomass feedstock in order to obtain better quality of syngas and performance of gasification operation.

- **Co-gasification of biomass with different particles size**

Particles size is an important parameter, which has influence on gasification. In the current co-gasification study particles size was varied between 10-25 mm and did not test with bigger or smaller than that size. Hence, study of the effect of particle size on the output syngas could be considered as future research topic in co-gasification of different biomass and catalyst.

- **Co-gasification of biomass with different catalyst**

There are few groups of catalyst can be used for gasification for example synthetic catalyst which included transition metal based catalyst and minerals like calcined rocks. Calcium based catalyst was chosen for this study based on past literature review due to its economically and efficiency. Currently Nickel based catalyst is widely used in chemical industrial and is proven as one of the most effective transition metal catalyst in biomass gasification for tar cracking and reforming (Chan & Tanksale, 2014). Hence study of the effect of different catalyst on the performance of gasification could be considered as future research topic.

- **Redesign the downdraft gasifier**

Current design of the downdraft gasifier is able to accommodate catalyst with an optimum performance up to 7kg. More than 7kg catalyst will cause blockage of air passage, there was no proper air flow when the catalyst have fully covered at the grate. Therefore in order to determine the effect of catalyst which more than 7kg on the gasification, the gasifier should modified to accommodate more catalyst.

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