PALM OIL WASTE GASIFICATION: THE EFFECT OF OPERATING TEMPERATURE FOR HYDROGEN PRODUCTION

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AHMAD AMIRUL ASRAF BIN MOHD DAUD

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
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SUPERVISOR'S DECLARATION

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

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STUDENT’S DECLARATION

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

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Dedication

Dedicated especially to my beloved parents, siblings, lecturers and friends who gave me inspiration and support that made this work possible.

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ABSTRACT

The production of synthesis gas from the gasification of palm oil waste; Kernel Shell, (KS) and Mesocarp Fibre, (MF) has been studied using a small lab scale gasification unit. The effect of operating temperature on the sample for the products yield and composition were investigated. The sample was collected, cleaned, dried, resized and gone through CHNS analysis prior to be used as the feedstock. Initially, approximately three grams of sample was used. Reactor and condenser were weighted before and after the gasification process in order to know the weight percent of solid, liquid and gas for each sample. Nitrogen gas; N_2 was first purged at 50 ml/min into the reactor as the carrier gas to remove gases in the system for about 20 minutes. It was done to achieve oxygen free atmosphere in order to avoid any explosion. After that, the flowrate was increased to 100 ml/min and the furnace was turned on to the desired temperature. The products which were syngas and bio-liquid from the gasification were firstly flown into the condenser. Then, the uncondensed gases were flew into a 12 L gas sampling bag and analyzed via Gas Chromatography, GC. The liquid product was trapped in the condenser. The gasification process was done in one hour. The effect of operating temperature has influenced the yield of bio oil, syngas and char for the samples (KS and MF). The highest syngas produced from MF and KS was obtained at 900 ^{o}C. As the temperature increased, the product yield of bio-oil and char were decreased. The highest amount of Hydrogen gas produced for both samples was obtained at 900 ^{o}C and it can be deduced that 900 ^{o}C is the optimum temperature for the gasification process. The composition of the syngas produced was identified using Gas Chromatography (GC). The result showed that the Hydrogen composition in MF is higher than KS. The studies on the production of Hydrogen gas from the gasification of KS and MF showed that the Hydrogen obtained from the KS and MF might be a potential valuable source for renewable fuel and for the usage of chemical feed stocks.

ABSTRAK

Pengeluaran gas sintesis dari pengegasan sisa kelapa sawit Isirong Kelapa Sawit, (KS) dan Fiber, (MF) telah dikaji menggunakan unit pengegasan berskala makmal. Kesan suhu operasi ke atas sampel untuk hasil produk dan komposisi telah disiasat. Sampel dikumpul, dibersihkan, dikeringkan, diubah saiz dan menjalani analisa CHNS sebelum digunakan sebagai bahan mentah. Pada mulanya, kira-kira tiga gram sampel telah digunakan. Reaktor dan kondenser ditimbang sebelum dan selepas proses pengegasan untuk mengetahui peratus berat pepejal, cecair dan gas bagi setiap sampel. Nitrogen; N_2 dialirkan dengan kadar 50 ml/min ke dalam reaktor sebagai gas pembawa untuk mengeluarkan gas dalam sistem untuk kira-kira 20 minit. Ia dilakukan untuk mencapai suasana bebas oksigen untuk mengelakkan letupan. Selepas itu, kadar alir ditingkatkan kepada 100 ml/min dan pemanas telah dihidupkan pada suhu yang diingini. Produk-produk gas dan cecair dari pengegasan telah pertamanya melalui kondenser. Kemudian, gas dikumpulkan ke dalam 12 L beg pensampelan gas dan dianalisis melalui Gas Chromatography, GC. Produk cecair dikumpulkan di dalam kondenser. Proses pengegasan dilakukan dalam satu jam. Kesan suhu operasi telah mempengaruhi hasil minyak bio, gas sintesis dan arang. Gas tertinggi dihasilkan daripada MF dan KS telah diperolehi pada 900 ^{o}C. Semakin suhu meningkat, hasil produk minyak bio dan arang telah berkurangan. Jumlah tertinggi gas hidrogen dihasilkan bagi kedua-dua sampel telah diperolehi pada 900 ^{o}C dan ia adalah suhu optimum untuk proses pengegasan. Komposisi sintesis gas yang dihasilkan telah dikenal pasti menggunakan Gas Chromatography (GC). Hasilnya menunjukkan bahawa komposisi hidrogen dalam MF adalah lebih tinggi daripada KS. Kajian ke atas penghasilan gas hidrogen dihasilkan daripada KS dan MF menunjukkan bahawa hidrogen yang diperolehi daripada KS dan MF mungkin menjadi sumber berharga yang berpotensi untuk bahan api yang boleh diperbaharui dan bagi kegunaan stok bahan kimia.

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^{O}C	degree celcius
%	percent

LIST OF ABBREVIATIONS

KS	Kernel Shell
MF	Mesocarp Fiber
C	Carbon
H	Hydrogen
N	Nitrogen
S	Sulphur
H_2	Hydrogen
CO	Carbon Monoxide
CH_4	Methane
CO_2	Carbon Dioxide
TGA	Thermo Gravimetric Analysis
GC	Gas Chromatography
wt.	weight
min^{-1}	per minute
conc.	Concentration

1 INTRODUCTION

1.1 Background of the Research

Until the petroleum has been discovered in the late 1800’s, biomass is known as the main energy sources for heat and power generation. Recently, the demands for heat and energy increase steadily, but the depletion of the global petroleum resources has been observed. Due to the reason, petroleum energy has been estimated to be disappearing in 50 years period (Shuit et al., 2009). Apart from that, scientist and researchers worldwide has introduced several renewable and alternatives source of energy in order to cover the demands of petroleum energy, one of the sources of the energy is gasification of biomass to produce hydrogen. With increasing trend in the awareness of biomass potential as an energy resource, the palm oil industry has emerged to be one of alternative platform for continuous and large biomass supply.

Among all the countries in this globe, Malaysia is one of the largest exporters of palm oil. Examples of biomass from palm oil industry are Palm Oil Mill (POME), Empty Fruit Bunch (EFB), fibers, shells, kernels, trunks and fronds as widely discussed by many researchers like Faizal et al., (2010), Abdullah et al., (2011) and Razuan et al., (2010). However, oil palm frond is not given too much attention for the biomass production and is normally left on the plantation floor as natural fertilizer once pruned or it is being used as nutrient for the cultivation of young oil palm (Haron et al., 2007). Due to large in quantities, the waste from oil palm is now facing a disposal problem, thus the best way to disposed it is with the gasification process which not only give the efficient way but then, it can also produce one source of energy.

Biomass gasification is one of the most promising thermo-chemical conversion routes to recover energy from biomass. During the process occurring, biomass is thermally decomposed to solid charcoal, liquid bio-oil and bio-gases under partial oxidation condition. The yield of the product from biomass is dependent on several parameters which include moisture content, catalyst, biomass species, particle size, equivalence ratio and temperature. As two most important parameters, temperature and equivalence ratio, (ER) (Wang et al., 2008) have been investigated widely in bench scale reactors including fixed beds, (Yang et al., 2004).

In this study, the effect of temperature were analysed for the production of hydrogen from palm oil waste gasification using tubular reactor equipped with furnace in the attempt to improve the performance of biomass conversion to energy with higher yield of Hydrogen (H_2)-rich gas. The biomass gasification technologies were found to present highly interesting possibilities for biomass utilization as a sustainable energy. In more specific, biomass used as an energy source that can reduce the Carbon Dioxide (CO_2) greenhouse effect as well as Sulphur Dioxide (SO_2) atmospheric pollution (McKendry, 2002), due to its characterization of natural carbon, less sulphur and nitrogen contents.

1.2 Problem Statement

Recently, the demands for heat and energy increase steadily, but the depletion of the global petroleum resources has been observed. Due to this reason, a new way to obtain heat and energy is being proposed. Hydrogen economy has become more attractive with the heat and energy crises and environmental issues associated with fossil fuel utilization. With the discovery that hydrogen can be produced from renewable biomass such as palm oil waste, this provides good prospect to Malaysia that generates abundant palm wastes.

Palm oil wastes are the main biomass resources in ASEAN countries. In Malaysia alone, there were 9.66, 5.20 and 17.08 million tons for fibres, shell and empty fruit bunches respectively (Nasrin et al., 2008). Thus, to treat this tremendous amount of wastes, gasification is use in order to solve waste disposal and to gain a renewable energy.

Gasification of palm oil waste to produce hydrogen is found to be an efficient and economically viable technology to convert the energy in biomass into chemical energy in the hydrogen gas (Gil et al., 1999). This process provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security. In particular, conversion of non-edible biomass, such as agriculture residues, wood chips, and fruit bunches, stalks, industrial and municipal wastes, into fuels and useful chemicals would solve waste disposal and energy issues.

Gasification may be defined as a process by which a remnant – biomass, carbon, etc. – is converted into gases by means of a partial oxidization carried out at high temperature (Ganan et. al., 2006). At temperatures of approximately 875–1275 K, solid biomass undergoes thermal decomposition to form gas-phase products that typically include H_2, CO, CO_2, CH_4, H_2O, and other gaseous CHs. In most cases, solid char plus tars that would be liquids under ambient conditions are also formed (Stevens et. al., 2001). The solid phase usually presents a carbon content higher than 76%, which makes it possible to use it directly for industrial purposes (Ganan et. al., 2006). The gaseous products can be burned to generate heat or electricity (Demirbas, 2006) or they can potentially be used in the synthesis of liquid transportation fuels (Boerrigter et. al., 2003), H_2 (Rapagna et. al., 1998), or chemicals (Boerrigter et. al., 2004). On the other hand, the liquid phase can be used as fuel in boilers, gas turbines or diesel engines, both for heat or electric power generation (Ganan et. al., 2006). However, the main purpose of biomass gasification is the production of low- or medium heating value (LHV, MHV) gas which can be used as fuel gas in an IC engine for power production (Morf, 2001).

For the production of hydrogen, Kernel Shell (KS) and Mesocarp Fibre (MF), undergone gasification process in a laboratory scale electrical tubular furnace with stailess steel reactor as shown in Figure 1.1. The main gasfication characteristics components, moisture contents, ash, and volatile matter were analysed by using TGA for both samples. A lower volatile sample will tend to be degraded at lower temperature. The sample which are KS and MF are ground and sieved to get the particle size in a range of lower than one millimetre (mm).

Figure 1.1: Stainless Steel Reactor

1.3 Research Objective

Based on the research background and problem statement described previously, the following are the objectives of this research:

- to study the effect of temperature for the production of hydrogen from various type of palm oil waste via gasification

1.4 Scope of Research

In this study, the samples were prepared by using two types of biomass waste which were Kernel Shell, KS and Mesocarp Fibre, MF. The sample were undergone the preparation stage including of cleaning, drying, and sizing. The gasification processed was carried out in a tubular reactor equipped with electrical furnace. The operating temperatures were varied in a range of 500 ^{o}C to 900 ^{o}C in attempt to get the optimum temperature for the production of Hydrogen, H_2 gas. The pressure for the gasification was maintained at atmospheric and the sample weight of approximately three grams was used. The product gas from the process was analysed by using gas chromatography (GC) to determine the composition of the gas.

2 LITERATURE REVIEW

2.1 Background of Biomass

Biomass energy currently contributes 9–13% of the global energy supply accounting for 45±10 EJ per year or up to 14%. Biomass energy includes both traditional uses such as a ring for cooking and heating and modern uses such as producing electricity and steam, and liquid bio-fuels. Biomass, in the energy production industry, refers to living and recently dead biological material which can be used as fuel or for industrial production.

Most commonly, biomass refers to plant matter grown for use as bio-fuel, but it also includes plant or animal matter used for production of fibres, chemicals or heat. Biomass may also include biodegradable wastes that can be burnt as fuel. It excludes organic material which has been transformed by geological processes into substances such as coal or petroleum.

The term "biomass" encompasses diverse fuels derived from timber, agriculture and food processing wastes or from fuel crops that are specifically grown or reserved for electricity generation. Biomass is a material that contain carbon and hydrogen compound which can be form as a fuel or for production.

2.2 Types of Biomass

Biomass can be categorized into two distinct categories which are waste biomass and energy crops. Waste biomasses are forestry residue, sewage waste, animal farming waste, organic municipal solid waste (MSW), slaughterhouse and fishery. For energy crops are short rotation coppice (SRC), miscanthus, woodchips, straw, residue from fruit processing (e.g. stones, husks) and others. Furthermore, biomass is referring to recently or deadly organic material and it useful in providing renewable source of fixed carbon.

Each will give different range of product either gas, solid or liquid. Physical conversion involved densification; more easily handled such as briquettes particles, palletized fuel and fuel logs. These involve extrusion process of biomass particles with or without binder at higher pressure and later carbonized to obtain charcoal material.

2.3 Palm Oil Biomass

Palm oil, *Elaeis guineensis,* is a tree whose fruits are used for extraction of oil. It was originated from South Africa, it was cultivated in all tropical areas of the world and has become one of the main industrial crops. The fruit is reddish in colour and grows in a large bunches, estimated 10 – 40 kg for each. Inside the fruit, it is a single seed also known as the palm kernel surrounded by the soft pulp. The oil extracted from the pulp is edible oil used for cooking oil, while the extracted oil from the kernel used mainly in the soap manufacturing industries.

Palm oil topped the ranking as number one fruit crops in terms of production for the year of 2007 with 36.90 million tonnes produced or 35.90% of the total edible oil in the world (MPOC, 2007). Palm oil is now one of the major economic crops in a large number of countries, which triggered the expansion of plantation area around the world (Yusoff, 2006). Overall, the palm oil account for 29.04% of the total oil crops production in Asia region and 21.16% for Africa (FAO, 2007).

In Malaysia, total mature areas of palm oil plantation represent 62% of the total forestry land and 11.75% of the country's total land area (MPOC, 2013). The total area of forest for the plantation is shown in Figure 2.1. It can be seen that Malaysia has used a large area of its forest for the plantation in compared to United Kingdom (UK), United States (US), Canada, Indonesia and Colombia.

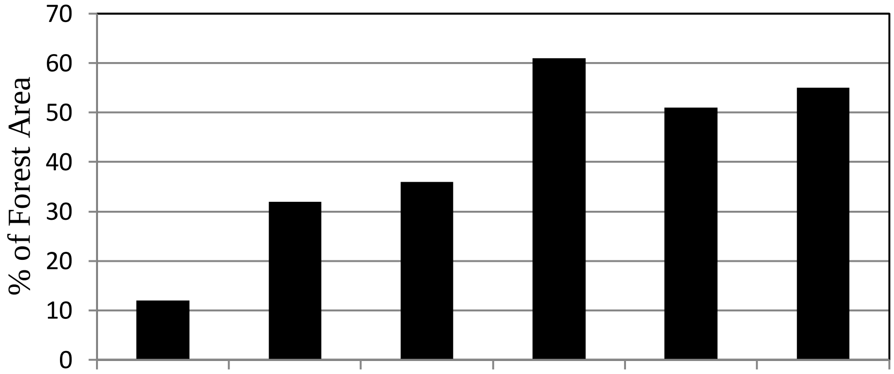

Figure 2.1: Area of forest used for plantation.

With the projected growth in the cultivation of palm oil, the concern is on what should be done with the enormous quantities of waste. Every year, oil palm industries produced more than a hundred million tons of waste worldwide. Currently, palm oil biomass is converted into various types of value-added products via several conversion technologies that are readily available. Among the biomass, fibers from EFB were used to make mattresses, seats, insulations. Ashes produced from incineration of EFB were then used as fertizers/soil conditioner due to its high organic and nutrient content beneficial to crops. In paper making industries, they utilized paper pulp from palm oil biomass for its various end usage purposes. Nevertheless, it had it limitations since the presence of small quantity of oil caused fouling effect to the end product therefore affecting its quality.

Fibre, shells and EFB were generally dumped in an open area or disposed by open burning generating pollutants gases that are harmful to the environment (Yusoff, 2006). In some cases, the palm oil mill generates heat and electricity from the fibre and shell by using combustion reaction (Yusoff, 2006). Unfortunately, this practice was not feasible due to high moisture content in the biomass and huge amount of energy required for complete combustion thus reducing significantly the energy efficiency in the reaction.

Today, hydrogen is mainly produced from natural gas via steam methane reforming, it represents only a modest reduction in vehicle emissions as compared to emissions from current hybrid vehicles, and ultimately only exchanges oil imports for natural gas imports (Turner, 2004). It is clearly not sustainable. Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resources (Kan A., 2009). It will play an important role in the future global energy infrastructure for the generation of power and heat, but also for the production of chemicals and fuels.

2.4 Biomass Technologies

There are some technologies that can convert biomass into energy and higher value-added product. This technology is classified as shown in Figure 2.2. The biochemical process leads to anaerobic digestion to produce gases and alcohol fermentation to produce ethanol. For non-biological process, it refer to thermal conversion which the main of it is converting solid waste into energy and by-product; gasification, combustion, pyrolysis and liquefaction.

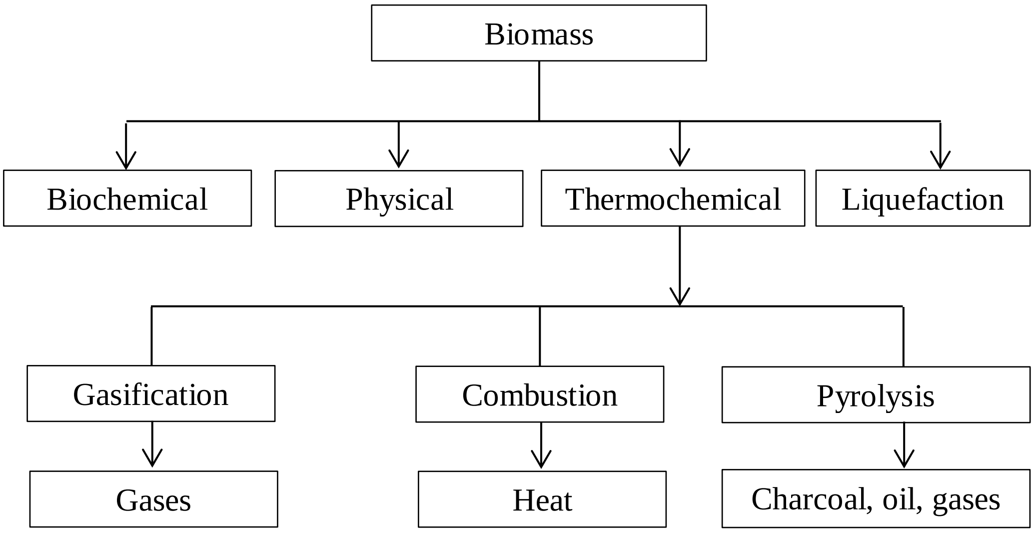

Figure 2.2: Main Type and Process of Biomass

Physical conversion involved densification; more easily handled such as briquettes particles, palletized fuel and fuel logs. These involve extrusion process of biomass particles with or without binder at higher pressure and later carbonized to obtain charcoal material. As for the product of biomass gasification, it is shown in Figure 2.3.

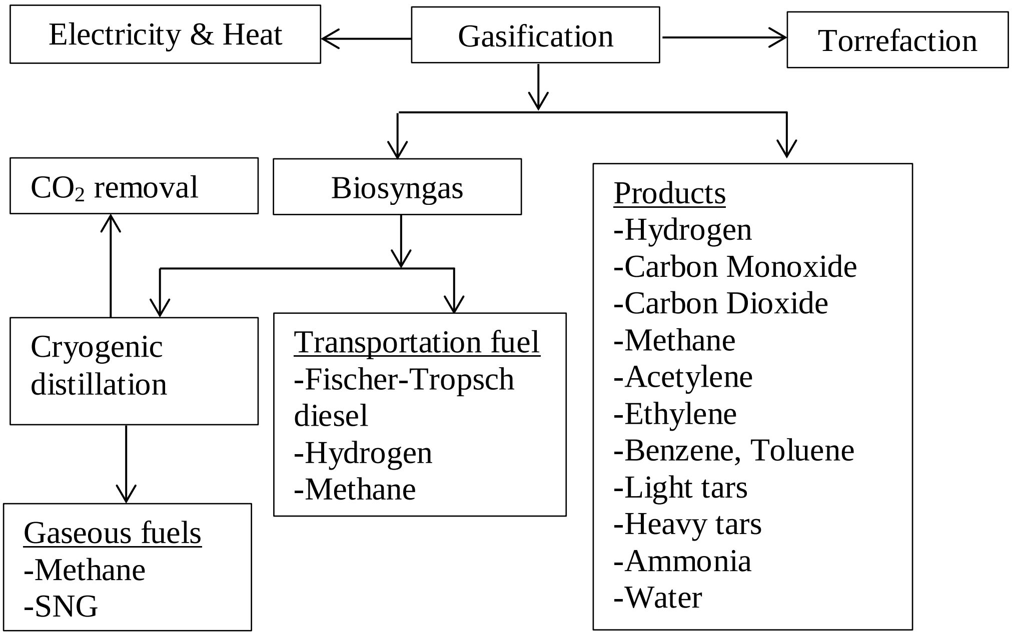

Figure 2.3: Products from Biomass Gasification (Balat et al., 2008)

2.5 Principles of Biomass Gasification

The gasification of biomass is a thermal treatment, which results in a high production of gaseous products and small quantities of char and ash (Demirbas., 2002). It is a well-known technology that can be classified depending on the gasifying agent: air, steam, steam–oxygen, air–steam, oxygen-enriched air, etc. (Gao., 2008). In order to optimize the gas production, it is being carried out at high temperature. The resulting gas, known as producer gas that produced from the reaction, is a mixture of carbin monoxide, hydrogen and methane, also with carbon dioxide and nitrogen (Balat, 2008). Yield a product gas from thermal decomposition composed of CO, CO_2, H_2O, H_2, CH_4, other gaseous hydrocarbons (CHs), tars, char, inorganic constituents, and ash. The composition of the producer gas from biomass gasification are depends heavily on the gasification process, the gasifying agent, and the composition of the feedstock (Balat, 2009). Gasification of biomass is generally observed to follow the reaction:

$$\text{Biomass} + \text{Heat} \rightarrow CO, CO_2, H_2O, H_2, CH_4 + \text{other } CH_S + \text{tar} + \text{char} + \text{ash} \qquad \text{Eq. 1}$$

Results indicate that the mineral (ash) content and composition of the original biomass material, and pyrolysis conditions under which char is formed significantly influence the char gasification reactivity. One of the major problems in biomass gasification is how to deal with the tar formed during the process (Devi et al., 2003). Tar is a complex mixture of condensable hydrogen which includes single ring to five-ring aromatic compounds along with other oxygen containing hydrocarbons and complex the polycyclic aromatic hydrocarbons (PAHs) (Devi et al., 2003). Control technologies of tar production can broadly be divided into two approaches (Cao., 2006): (1) treatments inside the gasifier (primary methods) and (2) hot gas cleaning after the gasifier (secondary methods). Although secondary methods are proven to be effective, treatments inside the gasifier are gaining much attention due to economic analysis. In primary methods, the operating parameters such as temperature, gasifying agent, equivalence ratio, residence time and catalytic additives play important roles in the formation and decomposition of tar.

2.6 *Types of Gasifiers*

The most important types are fixed bed (updraft or downdraft fixed beds) gasifiers, fluidized bed gasifier, and entrained flow gasifier. Fixed-bed gasifier are the most suitable for biomass gasification. Fixed-bed gasifiers involve reactor vessels in which the biomass material is either packed in or moves slowly as a plug, with gases flowing in between the particles (Munzinger et al., 2006). Fixed-bed gasifier usually fed from the top of the reactor and it can be designed whether updraft or downdraft configurations. Fluidized-bed gasifiers are a more recent development that takes advantage of the excellent mixing characteristics and high reaction rates of this method of gas–solid contacting (Warnecke, 2000).

2.7 *Previous Work on Palm Oil Waste*

There are a few researched that has been studied by other researchers before. Some of the researched are listed in Table 2.1.

Table 2.1: Previous work by other researchers

Author, (year)	**Biomass and processed used**	**Parameters studied**	**Comment**
Pooya et. al., 2011	Palm empty fruit bunch. Catalytic Gasification.	Temperature in the range of 700 ^oC to 1000 ^oC.	The total gas yield was enhanced greatly and reached maximum (~ 90 wt. %) at 1000 ^oC with a big portion of H_2 (38.02 vol. %) and CO (36.36 vol. %)
Mohammed et. al., 2012	Oil Palm Frond. Downdraft gasification.	Temperature in the range of 700 ^oC to 1000 ^oC	H_2 hit maximum of 11.29 vol. % at 800 ^oC – 900 ^oC.
Moni and Shaharin, 2013	Palm Empty Fruit Bunch. Fluidized Bed Gasifier	Various bed materials and bed temperature in the range of 650 ^oC to 1050 ^oC.	Increasing the bed temperature from 650 ^oC to 1050 ^oC improved the H_2 content of the producer gas from 7.3 to 12.4 vol. %.

2.8 Mesocarp Fibre

Palm oil fruit is in oval shape with length about five centimetre (cm). It consists of yellowish red oily flesh mesocarp and single seed Palm Kernel Nut. In palm oil mill industry, palm fruit is cook under hot stream and pressed for oil extraction, with mesocarp fibre, MF and palm kernel shell are left over mass. The MF is separated from palm kernel nut by cyclone separator. MF is elongated cellulose with 30 – 50 mm length. It is being used as biomass fuel for steam boiler due to its porous nature. By replacing fossil fuels for steam generation, it basically reduced the cost of operation of steam boiler.

As the palm oil extraction process does not involved any chemical, MF is naturally and non-toxic. It can be used as fertilizers and potting media by mixed it with other material preferably with high nitrogen content to produced composted mass. Due to its loose structure, composting time can be as short as 50 days if the composting parameters are optimum. The mesocarp fibre is shown in Figure 2.4.

Figure 2.4: Mesocarp Fiber

2.9 Kernel Shell

Palm kernel nut which highly contain kernel oil will be cracked down to kernel and kernel shell. However, the kernel is actually will be extracted for kernel oil and kernel shell will be the by-product for this process. Kernel Shell, KS is commonly left unutilized after the process of extraction was done. In fact, KS has become one of the valuable commodities in palm oil industry, much usage or application has been developed. KS has high calorific value that make its commodity has been one of the key biomass material in order to replace fossil fuels for steam power plant.

Carbonize KS can be used as charcoal which can be pressed into bio-fuel briquette; these form of charcoal could be directly sell to consumer especially for family used. Carbonized KS is also processed into activated carbon which use in liquid and gaseous phase filtration or adsorption. The KS was shown in Figure 2.5.

Figure 2.5: Kernel Shell

3 RESEARCH METHODOLOGY

3.1 Overview

Methodology of this researched is shown in the flow diagram showed in Figure 3.1.

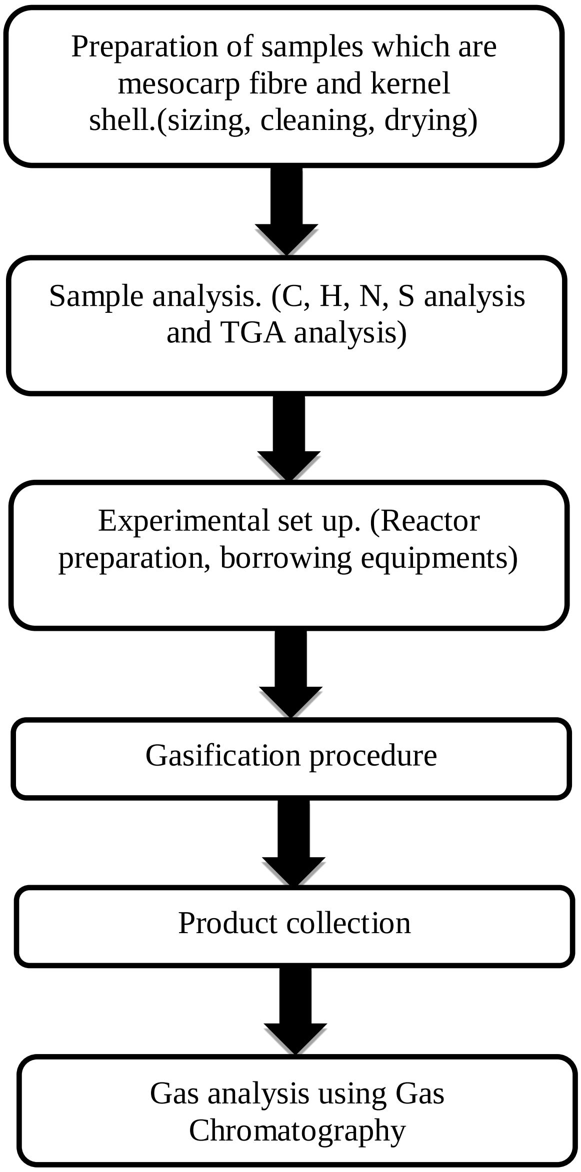

Figure 3.1: Flow diagram of the methodology

3.2 Materials and Chemicals

In this study, biomass sample which were used in this investigation were kernel shell and mesocarp fibre. Nitrogen was used as carrier gas in order to remove all trapped gas in the tubular reactor.

3.3 Preparation of Samples

Mesocarp Fibre, MF and Kernel Shell, KS was collected from Felda Palm Oil Industries Sdn. Bhd., which is located at Felda Lepar Hilir, Kuantan, Pahang. The sample was in solid form. It was firstly exposed to the surrounding atmosphere for one night to reduce the moisture content of the sample. Then, sample was cleaned from any contaminant that may sticks at it as it affected the result for analysis. Then, the cleaned sample was put in an oven which is located at FKKSA lab for overnight at temperature of 45 ^{o}C. The sample was ground by using grinding machine in order to reduce the size of the sample. Lastly, the sample was sieved by using sieve shaker to get the size of sample less than one mm.

3.4 C, H, N, S Analysis

The prepared sample was then analyzed for C, H, N and S contents. The analysis was done by using Elementary C, H, N, S, analysis which is located at Central Laboratory, Universiti Malaysia Pahang. This analysis was done in order to know the composition of C, H, N and S in each sample.

3.5 Thermo Gravimetric Analysis (TGA)

The sample also analyzed by using TGA to determine the moisture contents, volatile matter and ash contents of each sample.

Heating rate used for this analysis was 20 ^{o}C min^{-1}. It was started at room temperature until a final temperature of 900 ^{o}C. Nitrogen gas was used in the analysis. Sample weight of five milligrams (mg) was used and the flow rate of the N_2 gas was 100 ml min^{-1}.

3.6 *Experimental Set Up*

Tubular reactor equipped with electrical furnace operated at atmospheric pressure, was employed for all the runs. The cylindrical configuration reactor used that is made up of stainless steel with 1.5 cm outer diameter and 42 cm in height. The reactor consists of three main systems, namely reactor (a tubular reactor and electrical furnace), condenser and gas storage (gasbag) and is shown in Figure 3.2. Sample were placed into the reactor in between of quartz wool beds.

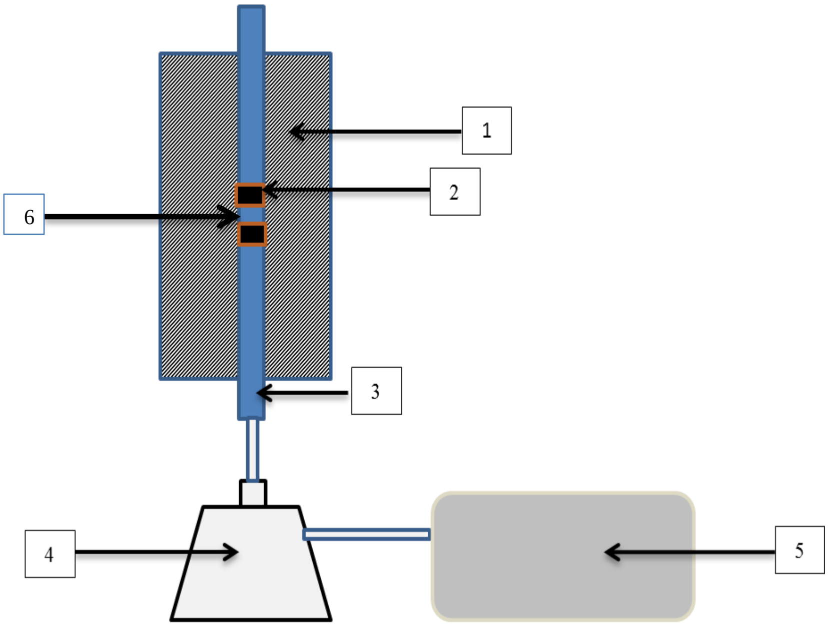

Figure 3.2: Schematic diagram of the tubular reactor with furnace for gasification process. 1, electrical furnace; 2, quartz wool beds; 3, tubular reactor; 4, condenser; 5, gas bag; 6, sample

3.7 *Gasification Procedure*

Initially, approximately three grams (g) of sample was used. Reactor were weighted before and after the gasification process in order to know the weight percent of solid, liquid and gas for each sample. Nitrogen gas; N_2 was first purge with 50 ml/min flowrate into the reactor as the carrier gas to remove gases in the system for about 20 minutes. It was done to achieve oxygen free atmosphere in order to avoid any explosion. After that, the flowrate was increased to 100 ml/min and the furnace was turned on to the desired temperature.

The products which were syngas and bio-liquid from the gasification were firstly flown into the condenser. Then, the uncondensed gases were flew into a 12 L gas sampling bag and analyzed via Gas Chromatography, GC. The liquid product was trapped in the cooling system condenser. The gasification process was done in one hour.

The operating temperature used in this research was 500 ^{o}C, 750 ^{o}C and 900 ^{o}C. All samples will be tested at this operating temperature.

3.8 Gas Analysis

The gas composition was analyzed via gas chromatography, GC. The Agilent GC was equipped with Haysep DB (30 ft x 1/8 in OD x 2 mm ID) and Molecular Shieve 13x (10 ft x 1/8 in OD x 2mm ID). Helium was used as the carrier gas to analyze CO, H_2, CO_2, CH_4 and N_2. The setting pressure 10 psi was used and the oven temperature was at 120 ^{o}C with holding and running time of 20 minutes. The standard gas mixture of 10.0300 volume percent, vol. % H_2, 0.1018 vol. % CO, 0.1017 vol. % CH_4, 0.1017 vol. % of CO_2 and 10.3352 vol. % N_2 was used as a quantitative calibration of GC.

4 RESULTS AND DISCUSSIONS

4.1 Introduction

The goal of this study was to produce H_2 gas from palm oil waste gasification. The experiments were conducted to investigate the effect of operating temperature; 500 ^oC, 750 ^oC, 900 ^oC and different biomass; Kernel Shell, KS and Mesocarp Fibre, MF on the production of H_2 gas.

4.2 C, H, N, S Analysis

The result of the analysis was tabulated in Table 4.1. The composition of O was calculated by different with 53.84 wt % for Mesocarp Fibre, (MF) and 41.14 wt % for Kernel Shell, (KS). It was observed that the composition of H was higher in Kernel Shell compared to Mesocarp Fibre with 11.24 wt % and 6.67 wt % respectively. This might lead to a higher composition of Hydrogen in shell. However, the composition of C are higher in KS which lead to the reaction of H with C to form CH_4 in the gas product. Composition of O is higher in MF with 53.84 wt % which might lead to the reaction of H with this O to form water.

Table 4.1: C, H, N, S analysis of sample

	Ultimate analysis (wt %)				
Biomass	**C**	**H**	**N**	**O[a]**	**S**
Mesocarp fibre	38.12	6.70	1.20	53.84	0.13
Kernel Shell	46.82	11.24	0.476	41.14	0.34

[a] the oxygen (O) content was determined by difference.

4.3 Thermo Gravimetric Analysis, TGA

The moisture contents, volatility and ash contents were determine by using TGA analysis. Table 4.2 shows the result from the analysis. It was observed that Mesocarp fibre, (MF) has more volatiles matter (85.46 volume percent, vol. %) than Kernel Shell, (KS) with 20.81 vol. %. The moisture content in MF was 8.72 wt. % which was higher than KS with only 6.92 wt. %. Meanwhile, the ash content of kernel shell was higher than mesocarp fibre with 22.28 wt. % and 5.82 wt. % respectively.

Table 4.2: TGA analysis of sample

	Proximate analysis (wt %)	
	Kernel Shell	**Mesocarp Fibre**
Moisture	6.92	8.72
Volatiles	70.81	85.46
Ash	22.28	5.82

4.4 The Influence of Operating Temperature on Gasification Yield

The yields of the final products from the biomass gasification at different temperatures for each samples illustrated in Figure 4.1 and 4.2. As the temperature increased from 500 ^{o}C to 900 ^{o}C, the total gas yield increased constantly from 13.67 wt % to 31.10 wt%, but the liquid and solid was found to have constantly reduced for Kernel Shell, KS. Meanwhile, the same trend is observed for Mesocarp Fibre, MF. Total gas yield increased from 39.09 wt % to 49.66 wt % as the temperature increased from 500 ^{o}C to 900 ^{o}C , the liquid and solid yields also constantly reduced at the same condition but the gas product from MF and KS are at the maximum when the operating temperature was at 900 ^{o}C with 49.66 wt % and 31.10 wt % respectively. The solid product in MF gasification, on the other hands, decreased from 44.30 % at 500^{o}C to 39.12 % at 900 ^{o}C. Meanwhile, the KS solid product decreased to 50.84 % at 900 ^{o}C from 61.33 % at 500 ^{o}C. Both results were agreed with Mohammed et. al., (2012) where the same trend studied. These phenomena would be due to various reason namely (i) higher production of gases at initial pyrolysis step whose rate is faster at higher temperature (Franco et al., 2003); (ii) higher gas production caused by endothermic char gasification reactions, which are favored at high temperature in pyrolysis zone; (iii) elevated temperature in gasification zone is favourable for tar and heavy hydrocarbons cracking that result to higher gas production (Tavasoli et al., 2009). Furthermore, increasing of gasification temperature also increases thermal cracking of tar and heavy hydrocarbon into gaseous components (Babu, 1995).

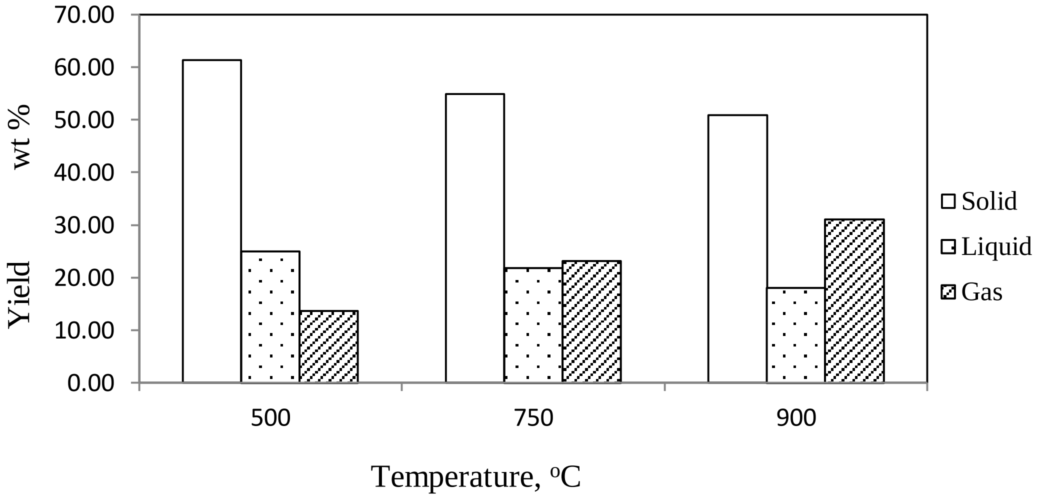

Figure 4.1: Product yields from KS

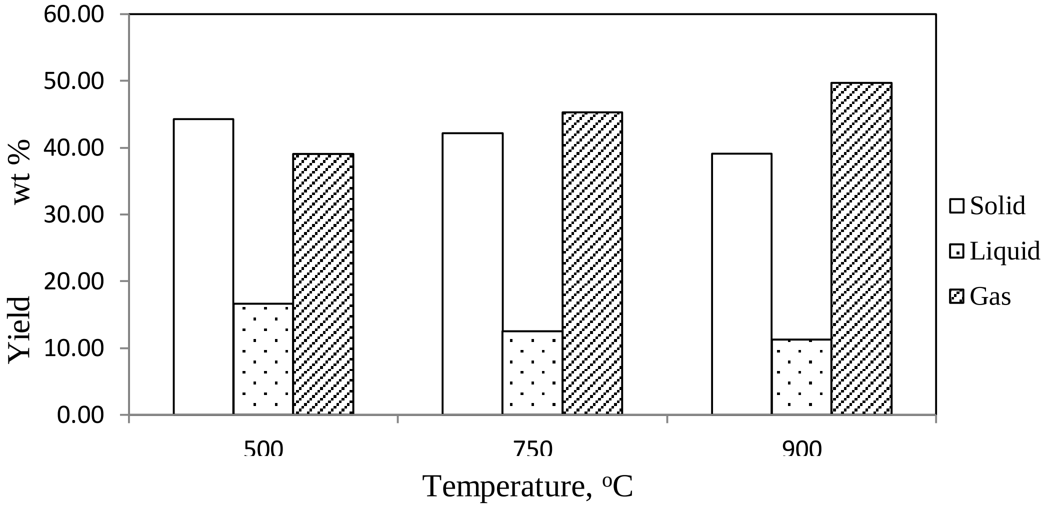

Figure 4.2: Product yields from MF

4.5 Gas Composition of Kernel Shell

As shown in Figure 4.3, the main gas products are H_2, CO, CO_2, and CH_4. It was observed that the amount H_2 content increased steadily from 0 volume percent, (vol. %) to 0.5 vol. % as the temperature rose from 500 ^oC to 900 ^oC. This indicates that water gas shift reaction occur at this temperature and tends to produce higher amount of H_2. It agrees with (Tigabwa et al., 2012) where similar trends was also obtained. Meanwhile, CH_4 vol. % was at most at 750 ^oC with 0.37 vol. % which might resulted from methanation reaction that might be occured at this range of temperature. Nevertheless, the CO_2 gas decreased with the increased of temperature from 500 ^oC to 900 ^oC. The maximum CO produced, 0.47 vol. %, was achieved at 750 ^oC which might be due to

Boudoudard reaction occur at this temperature which decreased the amount of CO_2 produced.

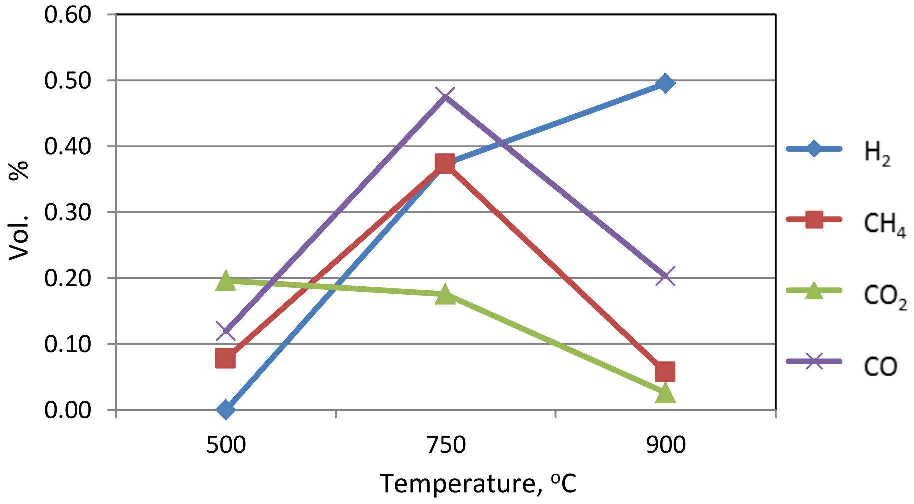

Figure 4.3: Syngas of Kernel Shell

Higher temperature lead to a higher reaction rates and also favor free radical reaction that leads to gas formation (Choy et al., 2012). It shows that hydrogen increases as temperature increases. This might be due to a water shift reaction that occured at higher temperature where CO is converted to H_2 and CO_2. The water shift reaction occurred in any gasification process due to the presence of water inside of fuel and water vapour inside the air. Water vapour and carbon dioxide promote hydrogen production in biomass gasification process (Cao et al., 2006). Methanation reaction is also favored at the higher temperature. However, at temperature of 900 ^{o}C, a reverse methanation might be occurs, leading to an increased of H_2. The same observation was also obtained by Choy et al. (2012) which shows similar trend.

4.6 Gas Composition of Mesocarp Fibre

As shown in Figure 4.4, the main gas products are H_2, CO, CO_2, and CH_4. The optimum H_2 production for MF from the gasification process was at 900 ^{o}C with 0.52 vol. %. The increase of H_2 product might be due to water gas shift reaction occurred at 900 ^{o}C. The lowest CO produced was obtained at 750 ^{o}C with 0.36 vol. %. At 900 ^{o}C, the amount of CH_4 and CO_2 produced is at most with 0.97 vol. % and 1.23 vol. % respectively.

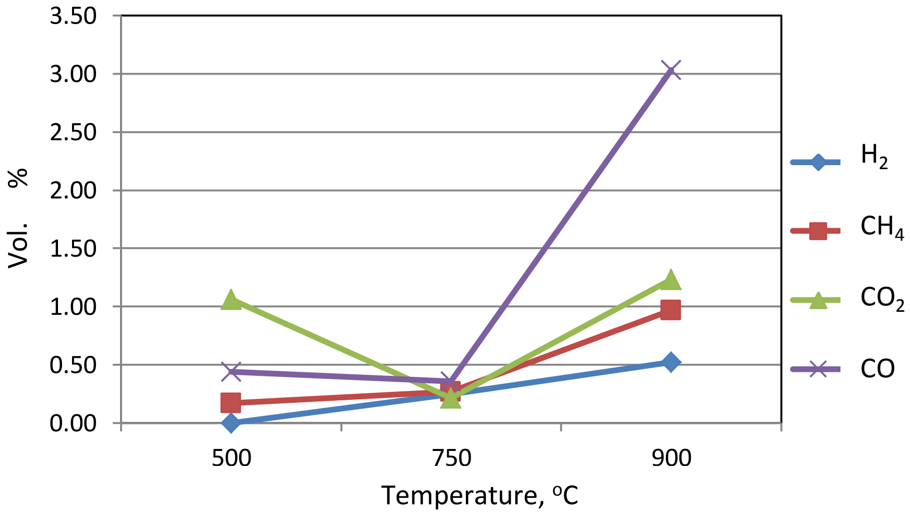

Figure 4.4: Syngas of Mesocarp Fibre

At higher furnace temperature, gas generates from the biomass at pyrolysis zone could undergo further reaction (secondary reaction), such as tar cracking, methanation and shifting reaction, leading to a much more incondensable gases (including H_2) generated. Thus, the total of yield of gas products increasing significantly as temperature increase. The other gas components might increase or decrease with the occurring of secondary reactions. As a result, more H_2 could be obtained when secondary reactions occurred significantly with the same result obtained by Mohammed et al., (2012).

4.7 The Influence of Operating Temperature on Gas Composition

The thermal cracking of gas-phase hydrocarbons at the high temperature might explain the variation of the gas product distribution from the gasification process (Dai et al., 2003). At a high furnace temperature, the gas species generated from the biomass at pyrolysis zone could undergo further reactions (secondary reactions), such as tar cracking and shifting reaction, leading to much more incondensable gases (including H_2) generated. Therefore, the total yield of gas products increased significantly as the temperature increased from 500 to 900 °C.

The main reactions involved could be expressed using equations (2) - (11) (Dai et al., 2003; Demirbas, 2001). Equations (2) – (6) are the principle or heterogenous gasification reactions whilst equations (7) – (11) are homogenous and secondary reactions. In terms of increasing H_2 production, equations (7) to (11) are the main reactions of interest for the biomass gasification at atmospheric pressure and temperature between 500 °C and 900 °C. The other gas components might increase or decrease with the occurring of secondary reactions. As a result, more H_2 could be obtained when secondary reactions occurred significantly.

$C + O_2 \rightarrow CO_2$ Eq. 2

$C + (1/2)O_2 \rightarrow CO$ Eq. 3

$C + CO_2 \rightarrow 2CO$ Eq. 4

$C + H_2O \rightarrow CO + H_2$ Eq. 5

$C + 2H_2 \rightarrow CH_4$ Eq. 6

$CO + H_2O \rightarrow CO_2 + H_2$ Eq. 7

$CH_4 + H_2O(\mathrm{g}) \rightarrow CO + 3H_2$ Eq. 8

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ Eq. 9

$Tar + H_2O(\mathrm{g}) \rightarrow CO + H_2O + CH_4 + H_2 + CmHn$ Eq.10

$CmHn + nH_2O \rightarrow nCO + [n + (m/2)H2]$ Eq.11

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

In this research, the influenced of temperature and type of palm oil biomass were investigated to produced Hydrogen from the gasification. Experiments were conducted in order to know the optimum temperature and also the type of biomass sample that can increase the production of H_2 gas. The main products from the biomass gasification were solid charcoal, bio-oil liquids and gas products. It was shown that the main gas products produced from the gasification was maily consists of H_2, CO, CO_2, and CH_4.

As the temperature increased from 500 ^{o}C to 900 ^{o}C, the gas yields also increased whilst solid and liquid yields decreased constantly. Production of syngases was thermodynamically reactive, which was shown by the fact that gaseous products changed with reaction temperature. A higher temperature were observed to be favourable for higher Hydrogen/syngas production. The optimum operating temperature were found to be 900 ^{0}C for both samples. On the other hand, it was observed that Mesocarp Fibre produced higher H_2 gas compared to Kernel Shell. It can be deduced that palm oil biomass are potential for hydrogen productions as an alternative renewable energy source and partially reduced the landfill problems of agricultural residues.

5.2 Recommendation

As recommendations for future improvement related to the research are as follows:

- For future research, use more sample from palm oil biomass such as Empty Fruit Bunch (EFB), Palm Trunk, Palm Oil Mill Effluent (POME), and Palm Frond in order to know which type of biomass will produce the highest composition of H_2.

- Studied more on gasification performance for optimized gas producer quality (yield, composition, production of CO, CO_2, H_2, and CH_4 and energy content) such as gasifier design and others operating parameters such as static bed height, fluidizing velocity, equivalence ratio, oxidants or catalysts.

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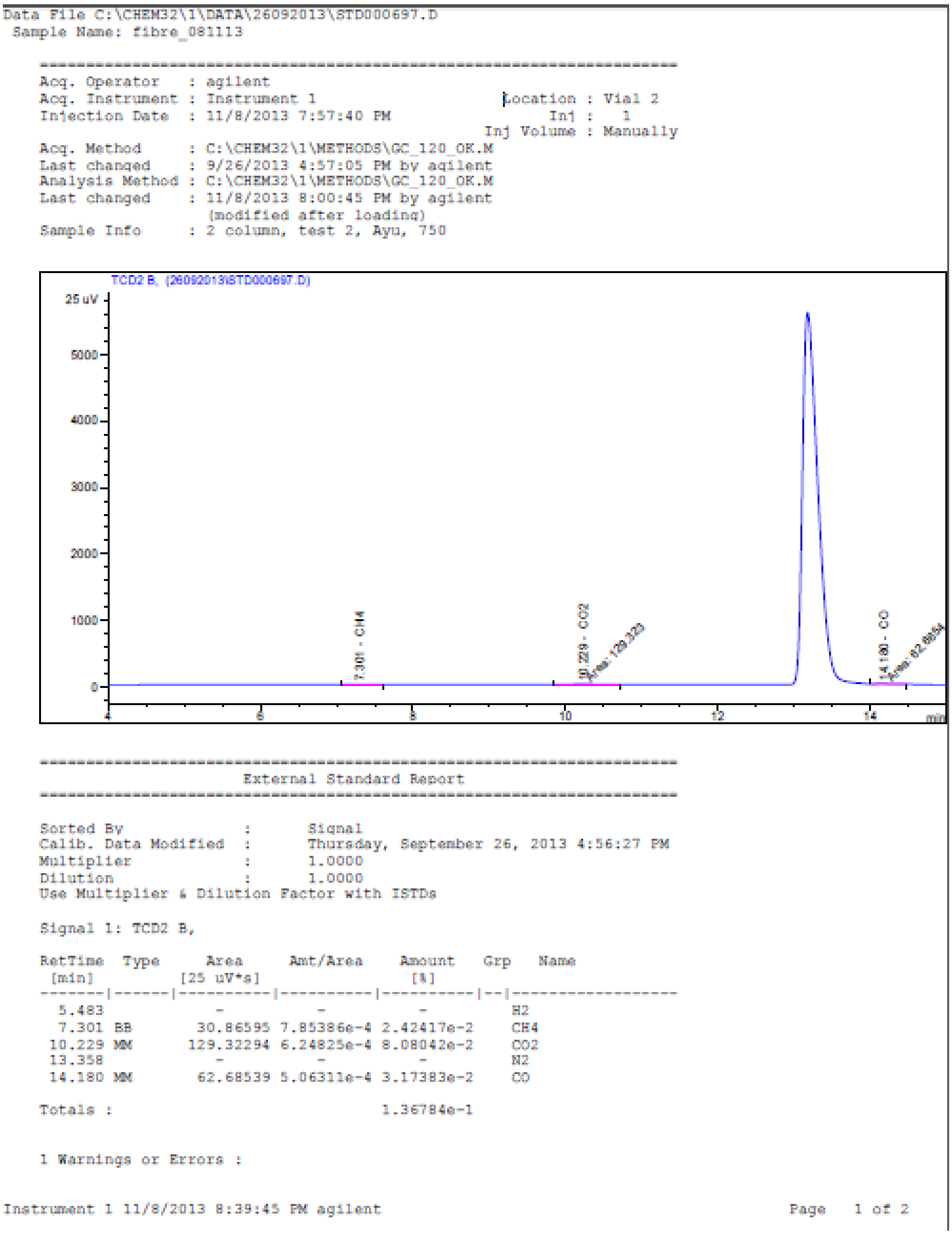
APPENDICES

A1: GC Results

1. Shell at 500 °C



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      7.301 BB      30.86595 7.85386e-4 2.42417e-2   CH4
     10.229 MM     129.32294 6.24825e-4 8.08042e-2   CO2
     13.358           -          -          -        N2
     14.180 MM      62.68539 5.06311e-4 3.17383e-2   CO

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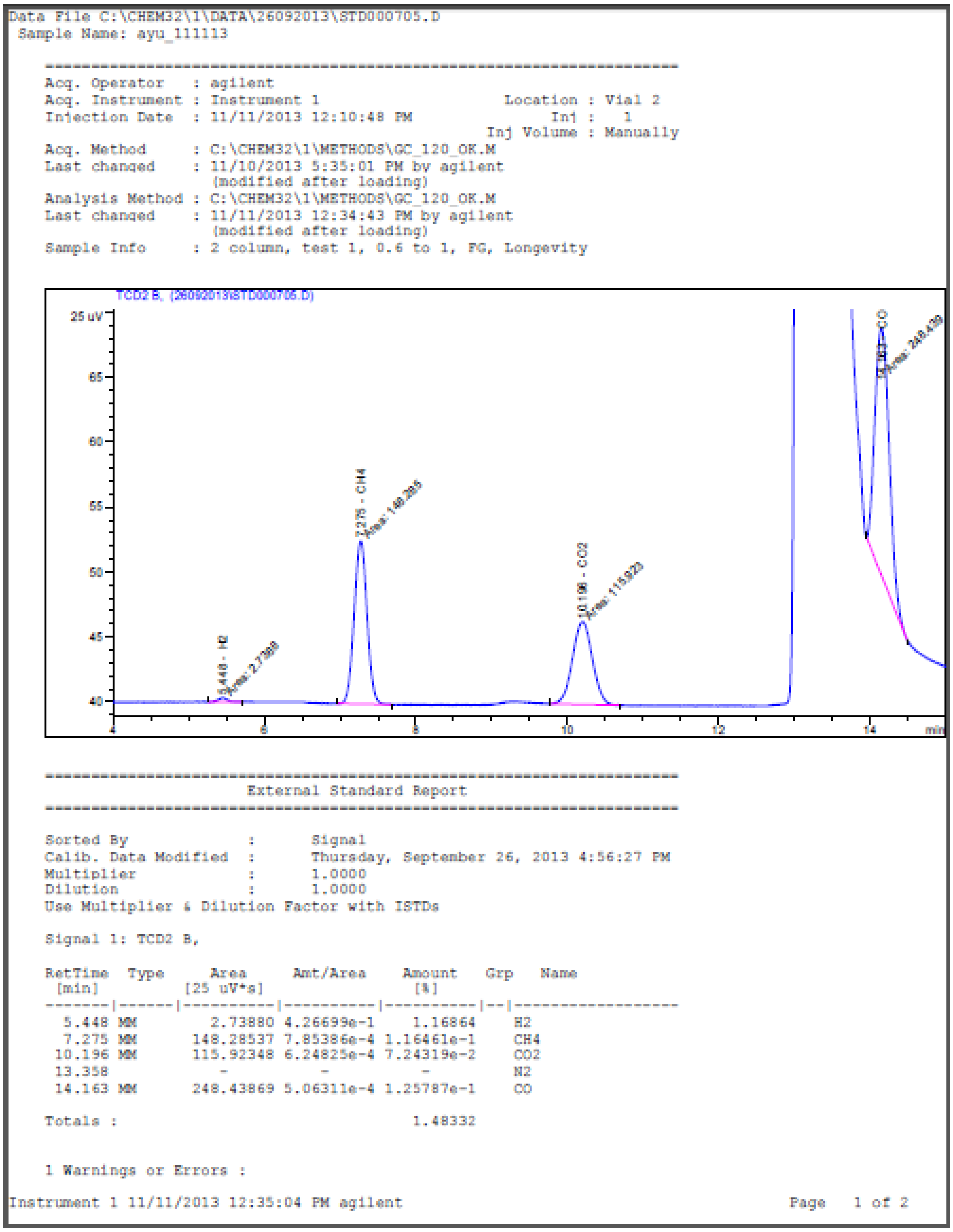

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      7.275 MM     148.28537 7.85386e-4 1.16461e-1     CH4
     10.196 MM     115.92348 6.24825e-4 7.24319e-2     CO2
     13.358             -          -          -        N2
     14.163 MM     248.43869 5.06311e-4 1.25787e-1     CO

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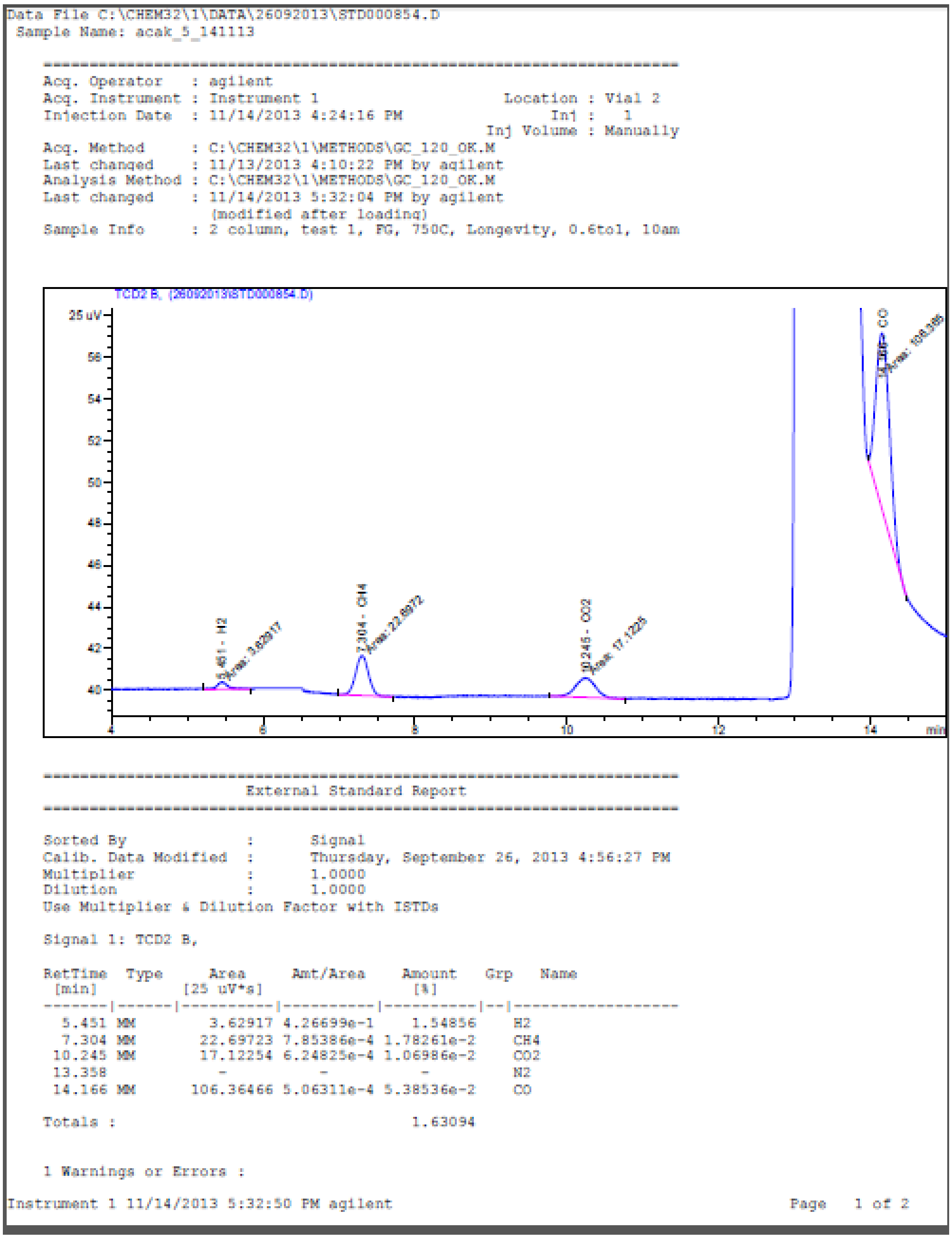
3. Shell at 900 °C



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      7.304 MM       22.69723 7.85386e-4 1.78261e-2    CH4
     10.245 MM       17.12254 6.24825e-4 1.06986e-2    CO2
     13.358              -          -          -       N2
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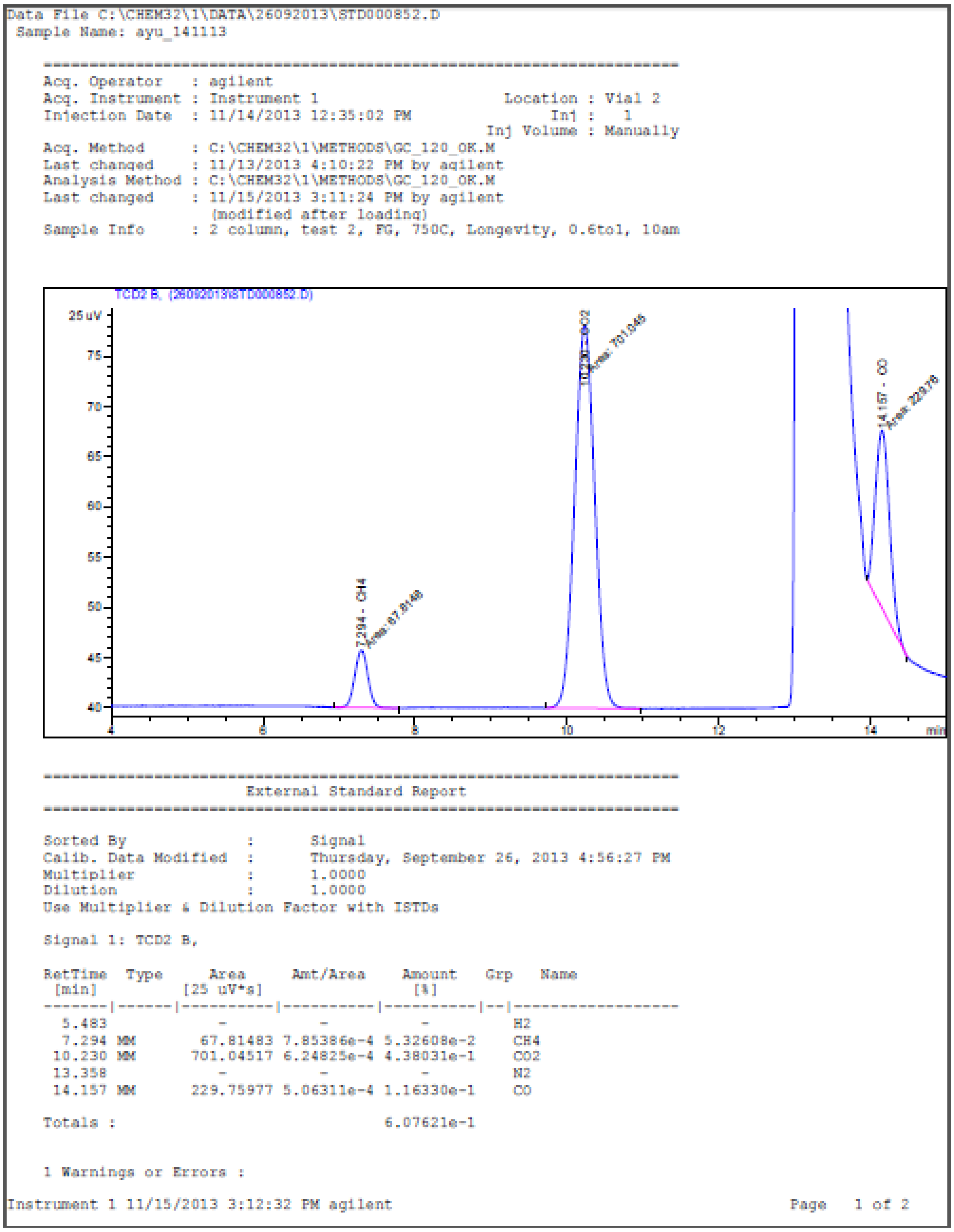
4. Fibre at 500 °C



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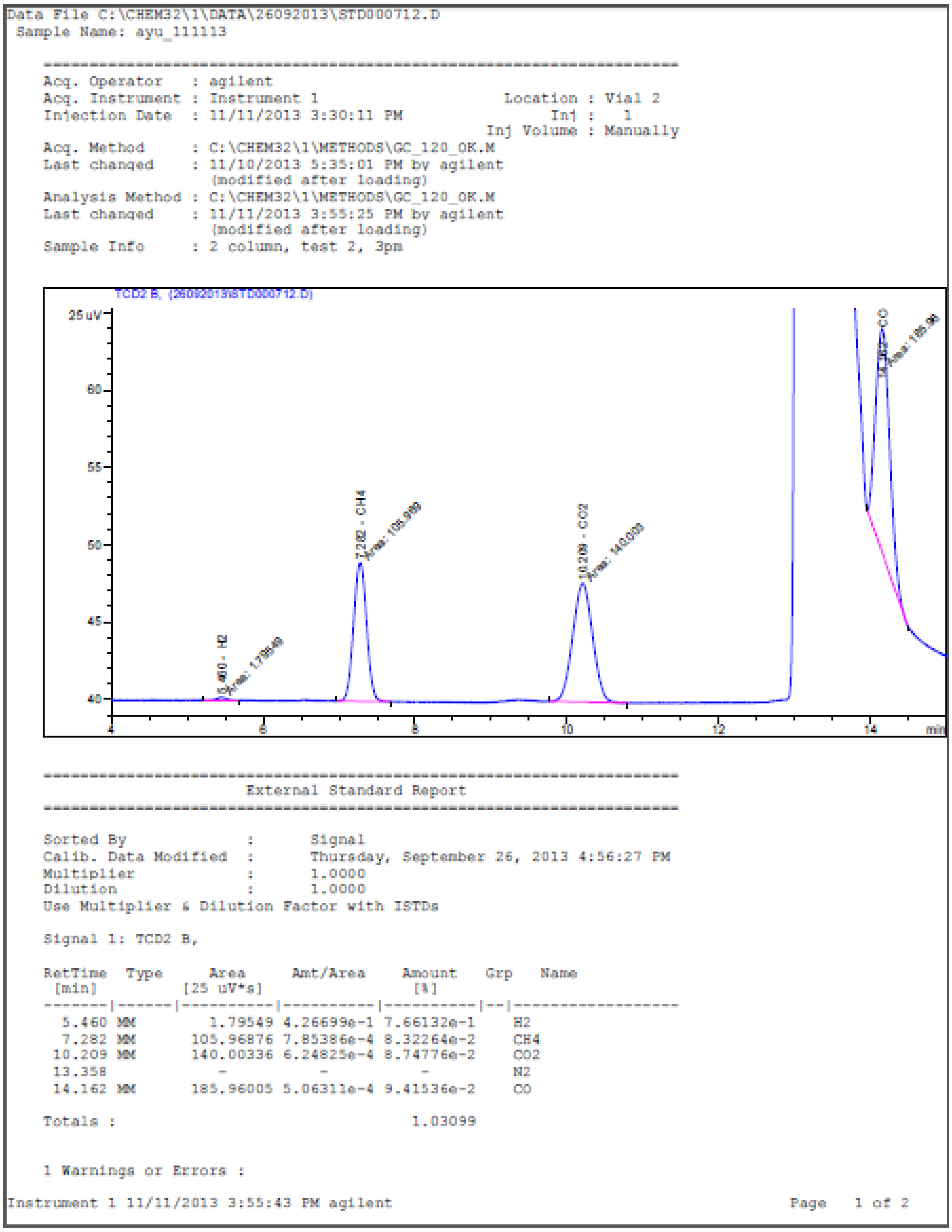
    RetTime  Type     Area      Amt/Area     Amount    Grp   Name
     [min]          [25 uV*s]                 [%]
    -------|------|----------|----------|----------|--|------------------
      5.483            -          -          -          H2
      7.294 MM      67.81483 7.85386e-4 5.32608e-2    CH4
     10.230 MM     701.04517 6.24825e-4 4.38031e-1    CO2
     13.358            -          -          -          N2
     14.157 MM     229.75977 5.06311e-4 1.16330e-1    CO

    Totals :                            6.07621e-1


    1 Warnings or Errors :

Instrument 1 11/15/2013 3:12:32 PM agilent                      Page    1 of 2
```

5. Fibre at 750 °C



```
Data File C:\CHEM32\1\DATA\26092013\STD000712.D
 Sample Name: ayu_111113

    =====================================================================
    Acq. Operator   : agilent
    Acq. Instrument : Instrument 1                    Location : Vial 2
    Injection Date  : 11/11/2013 3:30:11 PM                Inj :   1
                                                   Inj Volume : Manually
    Acq. Method     : C:\CHEM32\1\METHODS\GC_120_OK.M
    Last changed    : 11/10/2013 5:35:01 PM by agilent
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\GC_120_OK.M
    Last changed    : 11/11/2013 3:55:25 PM by agilent
                      (modified after loading)
    Sample Info     : 2 column, test 2, 3pm

    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      Thursday, September 26, 2013 4:56:27 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

    Signal 1: TCD2 B,

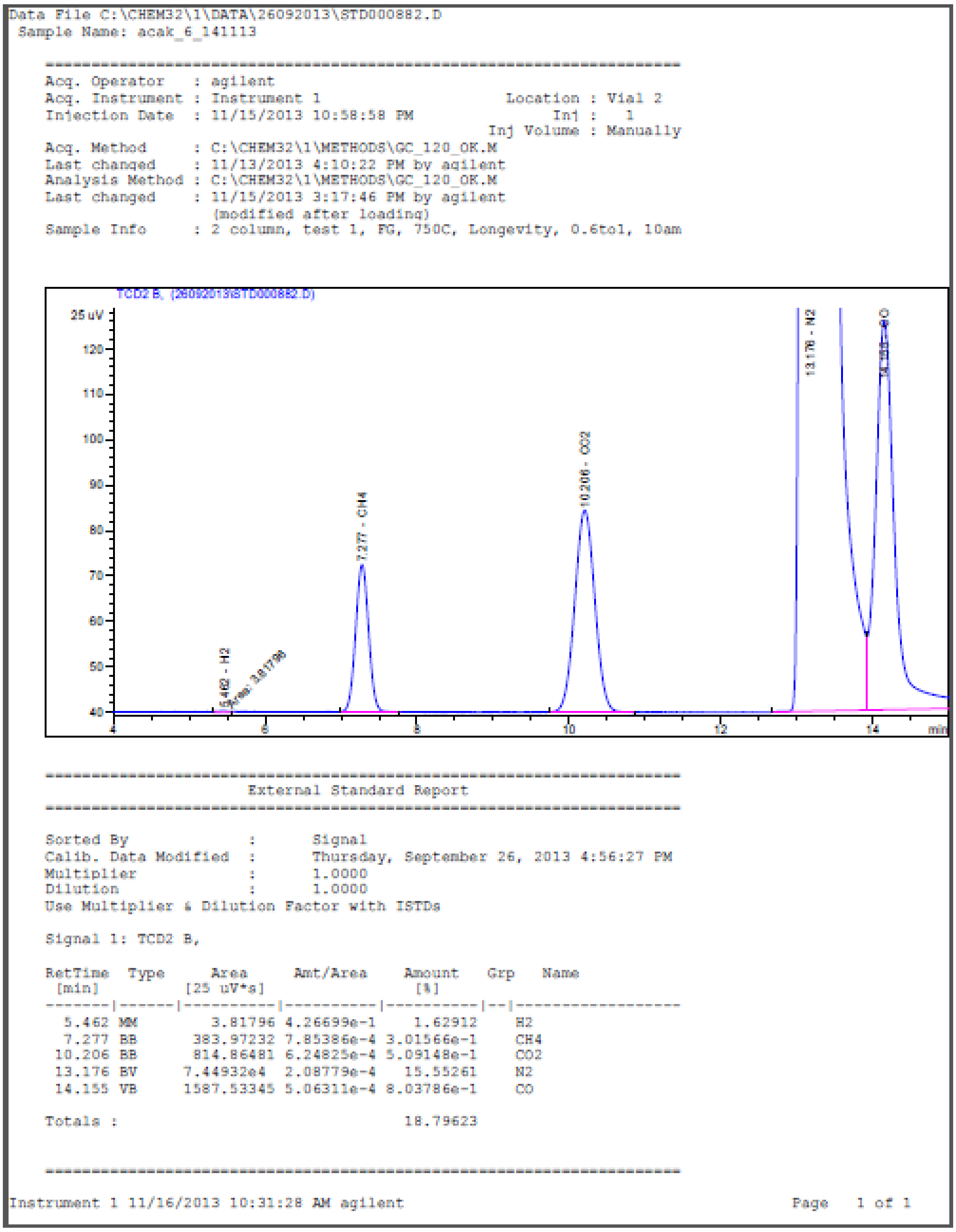
    RetTime  Type     Area      Amt/Area    Amount   Grp   Name
     [min]          [25 uV*s]               [%]
    -------|------|----------|----------|----------|--|------------------
      5.460 MM        1.79549 4.26699e-1 7.66132e-1    H2
      7.282 MM      105.96876 7.85386e-4 8.32264e-2    CH4
     10.209 MM      140.00336 6.24825e-4 8.74776e-2    CO2
     13.358             -          -          -        N2
     14.162 MM      185.96005 5.06311e-4 9.41536e-2    CO

    Totals :                               1.03099


    1 Warnings or Errors :

Instrument 1 11/11/2013 3:55:43 PM agilent                      Page    1 of 2
```

6. Fibre at 900 °C



```
Data File C:\CHEM32\1\DATA\26092013\STD000882.D
 Sample Name: acak_6_141113

    =====================================================================
    Acq. Operator   : agilent
    Acq. Instrument : Instrument 1                Location : Vial 2
    Injection Date  : 11/15/2013 10:58:58 PM           Inj :   1
                                              Inj Volume : Manually
    Acq. Method     : C:\CHEM32\1\METHODS\GC_120_OK.M
    Last changed    : 11/13/2013 4:10:22 PM by agilent
    Analysis Method : C:\CHEM32\1\METHODS\GC_120_OK.M
    Last changed    : 11/15/2013 3:17:46 PM by agilent
                      (modified after loading)
    Sample Info     : 2 column, test 1, FG, 750C, Longevity, 0.6tol, 10am

    =====================================================================
                         External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      Thursday, September 26, 2013 4:56:27 PM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

    Signal 1: TCD2 B,

    RetTime  Type     Area      Amt/Area     Amount    Grp   Name
     [min]          [25 uV*s]                 [%]
    -------|------|----------|----------|----------|--|------------------
      5.462 MM        3.81796 4.26699e-1    1.62912     H2
      7.277 BB      383.97232 7.85386e-4 3.01566e-1     CH4
     10.206 BB      814.86481 6.24825e-4 5.09148e-1     CO2
     13.176 BV     7.44932e4  2.08779e-4   15.55261     N2
     14.155 VB     1587.53345 5.06311e-4 8.03786e-1     CO

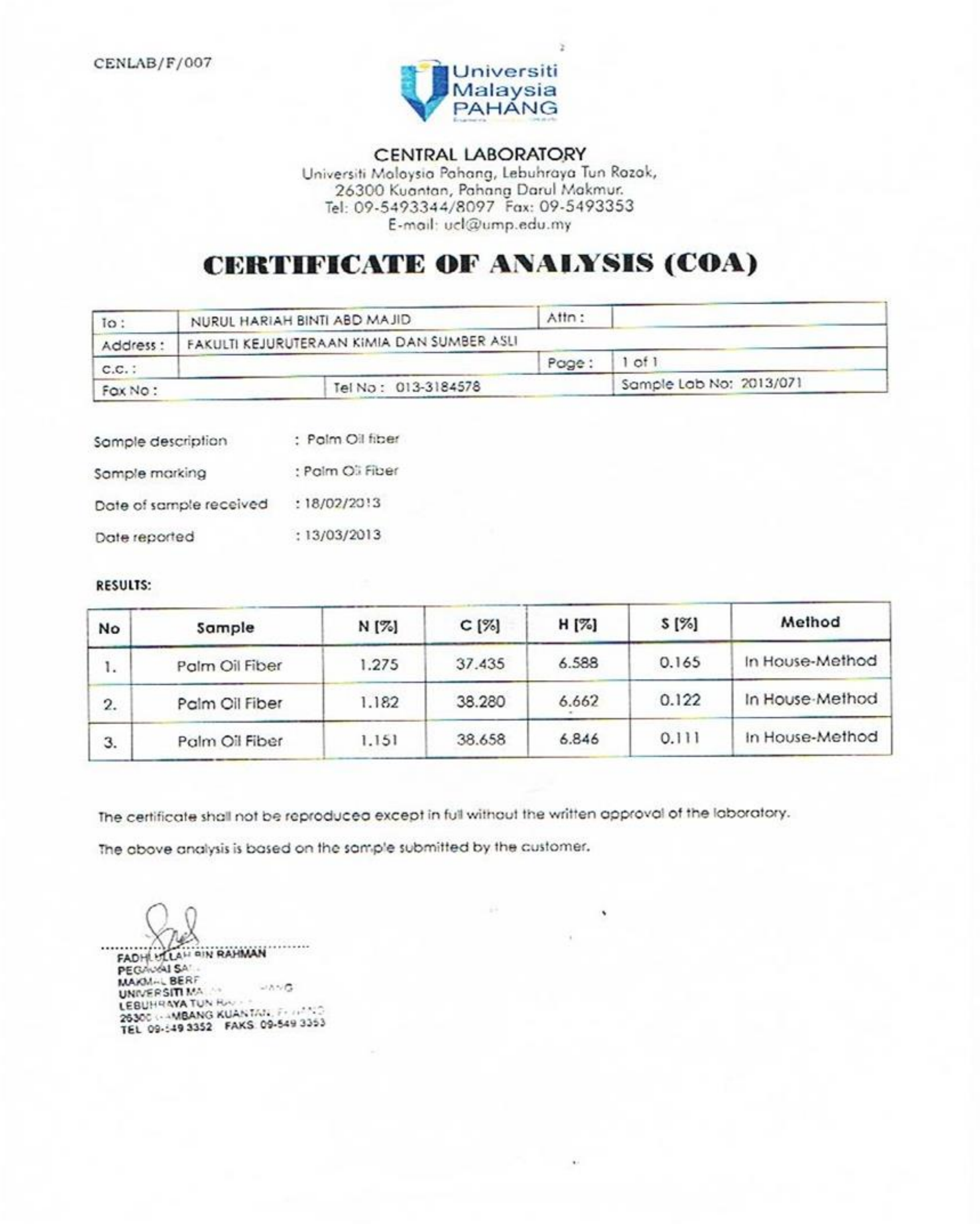
    Totals :                               18.79623


    =====================================================================

Instrument 1 11/16/2013 10:31:28 AM agilent                       Page    1 of 1
```

A2: C, H, N, S Analysis

1. Mesocarp Fibre



CENLAB/F/007

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E-mail: ucl@ump.edu.my

CERTIFICATE OF ANALYSIS (COA)

To :	NURUL HARIAH BINTI ABD MAJID	Attn :	
Address :	FAKULTI KEJURUTERAAN KIMIA DAN SUMBER ASLI		
c.c. :		Page :	1 of 1
Fax No :	Tel No : 013-3184578	Sample Lab No: 2013/071	

Sample description : Palm Oil fiber

Sample marking : Palm Oil Fiber

Date of sample received : 18/02/2013

Date reported : 13/03/2013

RESULTS:

No	Sample	N [%]	C [%]	H [%]	S [%]	Method
1.	Palm Oil Fiber	1.275	37.435	6.588	0.165	In House-Method
2.	Palm Oil Fiber	1.182	38.280	6.662	0.122	In House-Method
3.	Palm Oil Fiber	1.151	38.658	6.846	0.111	In House-Method

The certificate shall not be reproduced except in full without the written approval of the laboratory.

The above analysis is based on the sample submitted by the customer.

....
FADH[illegible]LLAH [illegible]IN RAHMAN
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MAKMAL BERF[illegible]
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26300 [illegible]AMBANG KUANTAN, [illegible]
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2. Kernel Shell.

CENLAB/F/007

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CERTIFICATE OF ANALYSIS (COA)

To :	NOORAHAYU BINTI ARIFFIN	Attn :	
Address :	FKKSA UNIVERSITI MALAYSIA PAHANG		
c.c. :		Page :	1 of 1
Fax No :	Tel No : 013-9725741		Sample Lab No: 2013/441

Sample description	: 2 samples in glass beaker
Sample marking	: EFB and SHELL
Date of sample received	: 24/09/2013
Date reported	: 25/09/2013

RESULTS:

No	Sample	N [%]	C [%]	H [%]	S [%]	Method
1.	EFB	0.712	48.864	6.341	0.153	In House-Method
	EFB	0.753	47.447	5.983	0.221	In House-Method
2.	SHELL	0.453	46.523	10.591	0.318	In House-Method
	SHELL	0.498	47.106	11.874	0.356	In House-Method

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The above analysis is based on the sample submitted by the customer.

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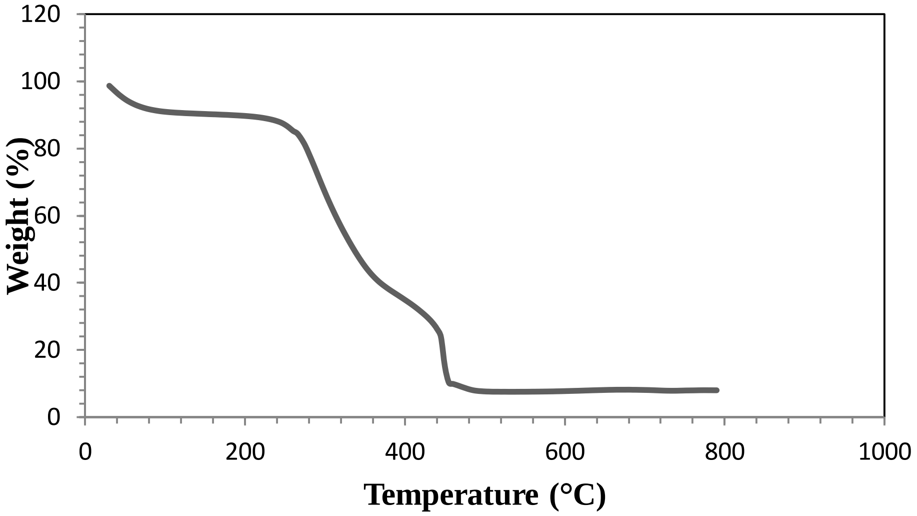
A3: TGA Analysis

1. Fibre



2. Shell