ABSTRACT

Bioenergy is now accepted as having the potential to provide the major part of the projected renewable energy provisions of the future. Fast pyrolysis is one of the three main thermal routes, with gasification and combustion, to providing a useful and valuable biofuel. It is strongly believed that the product of the Pyrolysis can be further enhanced by using microwave as a decomposition method. Microwave has a better and cleaner heating distribution during heating as what is explained in the literature review section. The power consumed by the microwave effects the decomposition rate of the biomass. Different decomposition rate will affect in changes in the product distribution. Thus, the objective of this project is to study the characteristic of bio-oil produced by microwave induced Pyrolysis and the results will be compared within the different sizes, power input and also with those from thermal decomposition. Literature reviews on similar experimental works, equipments and devices and simulations are reviewed for better understanding and to improve current ideas on this project. A lot of the experiments conducted previously involve the decomposition of biomass using other form of thermal decomposition are also reviewed. The methodology, which keeps track of the project work, shows the project is completed on time. Experiment setup shows how the microwave reactor is adjusted and reoriented to better distribute the results of the decomposition. The project proceeds with data analysis, where the CHNS analysis, calorific value analysis and also the ash content analysis will be carried out using the CHNS equipment, Bomb Calorie Meter and also Muffle Furnace. Trends are constructed to compare the characteristic of the bio-oil using different input powers and different sizes of biomass. From the results, it is clear that Pyrolysis through microwave is more effective compared to conventional heating, with lower Pyrolysis temperature and higher Bio-oil Quality (Higher calorific value and carbon content). With the best microwave reactor operating condition of 1kW of power input and maintains the temperature at 350^{o}C.

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CHAPTER 1

INTRODUCTION

Chapter 1 presents the project as a whole and identifies the current issues related to it. Identification of the problems leads to the establishment of problem statement which contributes to the objectives of the study.

1.1 Background of Study

For millennia humans have supplemented their own labor with energy from draft animals, sun and wind, and burning wood and whale oil – ancient sources of Bioenergy. Fossil fuels have supplied energy for specialized purposes for many centuries, but the industrial revolution greatly expanded their extraction and use. Fossil fuels have provided immense quantities of inexpensive and high-density energy, they are finite in quantity, are often buried in inconvenient locations, and release large amounts of carbon dioxide into the atmosphere. In recent years, rising petroleum prices linked to higher drilling costs and an inevitable decline of production – as well as concerns for the environment, rural prosperity, and national security – have heightened interest in biomass (renewable organic matter) as a source of fuel and other forms of energy.

1.1.1 Biomass (Lignocellulosic Biomass)

Biomass is the fourth largest source of energy in the world, accounting for about 15% of the world’s primary energy consumption and about 38% of the primary energy consumption in developing countries (Chen, Andries and Spliethoff, 2002). Biomass as an energy source is a system of interdependent components. Economic and technical viability of this system relies on a guaranteed feedstock supply, effective and efficient conversion technologies, guaranteed markets for the energy products, and cost-effective distribution systems. (1) The system begins with biomass harvesting (or biomass collection of non-agricultural waste); (2) this biomass is then prepared as feedstock, (3) which is converted to intermediate products. (4) These intermediate products are converted to final energy and other biobased products; (5) which are finally distributed and (6) used for biofuels, biopower, and biobased products. This system is illustrated in Figure 1.1.

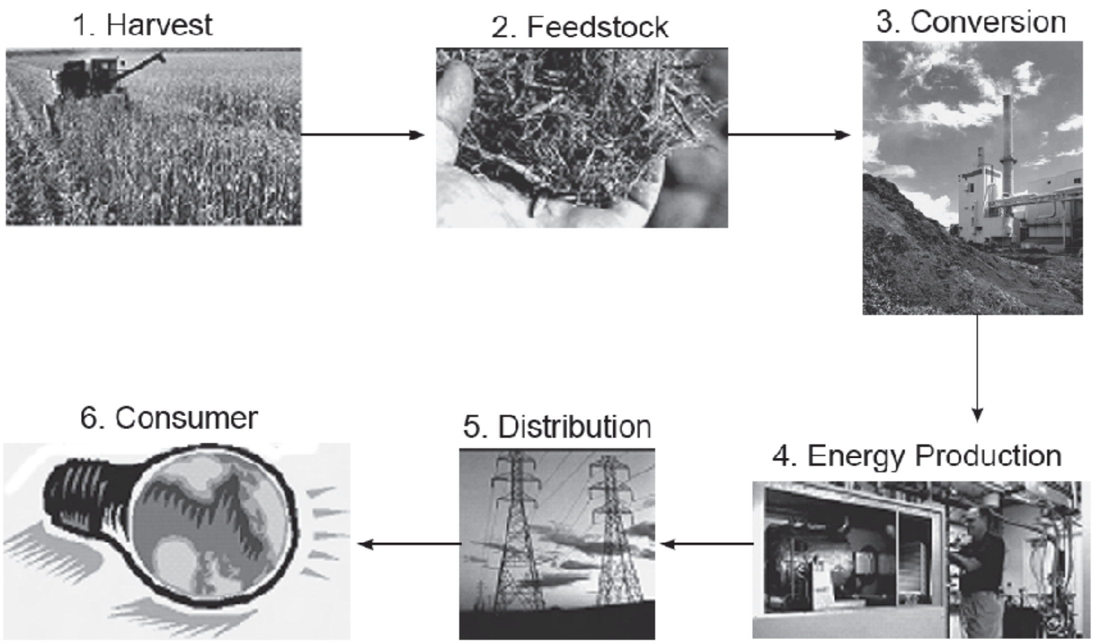


Figure 1.1: System of Biomass as an Energy Source (EPA, 2007)

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Wood and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main renewable energy resources available. These can provide the only source of renewable liquid, gaseous and solid fuels. Biomass is considered the renewable energy source with the highest potential to contribute to the energy needs of modern society for both the developed and developing economies worldwide. Energy from biomass based on short rotation forestry and other energy crops can contribute significantly towards the objectives of the Kyoto Agreement in reducing the green house gases emissions and to the problems related to climate change (Bridgwater, 2004).

This project focuses on the lignocellulosic biomass, which is widely obtained in this country. Lignocellulosic biomass refers to plant biomass that is composed of cellulose, hemicellulose, and lignin. The carbohydrate polymers (cellulose and hemicelluloses) are tightly bound to the lignin. Lignocellulosic biomass can be grouped into four main categories: agricultural residues (including corn stover and sugarcane bagasse), dedicated energy crops, wood residues (including sawmill and paper mill discards), and municipal paper waste. Lignocellulosic materials are the most economical and highly renewable natural resources in the world. It is estimated that the annual production of lignocellulosic materials is over 150 billion tons on the earth and that the annual agricultural wastes only in China are approximately 1 billion tons. The full utilization of this natural resource may be important in maintaining sustainable social development. The most promising approach is to convert these waste products into bio-oil and other useful chemicals. Extensive research has been carried out in this area in last two decades (Zhu, Wu, Yu, Zhang, Li and Gao, 2005).

1.1.2 Conversion Methods

In current time there are several decomposition technologies which are widely used, including (EPA, 2007):

- **Gasification** is a thermochemical decomposition process through which biomass or other organic matter is converted to a gaseous state in the limited presence of oxygen
- **Pyrolysis** (as used in this project) is a thermochemical decomposition process through which biomass or other organic matter is converted to a mixture of oil, gases, and carbon residues in the complete absence of oxygen.
- **Starch and sugar fermentation** is a direct biochemical decomposition process through which glucose-containing material is chemically decomposed in the presence of oxygen using enzymes to form ethanol and carbon dioxide. The method requires no or minimal preprocessing.
- **Lignocellulosic biomass fermentation** is a biochemical decomposition process through which biomass containing lignin, cellulose, and/or hemicellulose is pretreated to break into component sugars, and then is chemically decomposed to form ethanol and carbon dioxide. The method includes the use of a saccharification step, in which calcitrous feedstock is preprocessed into fermentable sugars. Once preprocessed, this type of biomass is fermented as in “Starch and Sugar Fermentation.
- **Transesterification** is a chemical reaction through which alcohol groups from an alcohol catalyst bond to fatty acids from oils, fats, and greases. This process both reduces the viscosity of the fatty acids and converts them to a combustible form. Esterification is a pretreatment process sometimes necessary to prepare the fatty acids for transesterification.

- **Anaerobic digestion** is a biochemical process through which biomass or other organic matter is consumed by bacteria and subsequently released in a gaseous state. This process occurs in the absence of oxygen. Different types of bacteria can be used for this process: psychrophilic, mesophilic or thermophilic processes, depending on bacterial affinity for cool, intermediate or warm temperatures, respectively.
- **Landfill gas collection** is a process through which gaseous effluent is collected from decomposing organic material at a waste disposal site. The waste decomposes under naturally anaerobic or manipulated aerobic conditions, and produces primarily methane and carbon dioxide. Gas is then collected from landfills.

Pyrolysis is thermal decomposition occurring in the absence of oxygen; it is also the first part in combustion and gasification processes where it is followed by total or partial oxidation of the primary products. Based on the previous studies that have been carried out, lower process temperature and longer vapor residence times favors the production of charcoal, while high temperature and longer residence time increase the biomass conversion to gas and moderate temperature and short vapor residence time are optimum for producing liquids (Bridgwater, 2004).

1.1.3 Bio-Oil

Bio-oil is a liquid fuel produced by the decomposition of biomass. The composition and properties of bio-oil depend on the biomass source and decomposition rate (fast or slow) used in its production. Due to its vegetation source, bio-oil is a renewable and greenhouse gas (GHG) neutral fuel when combusted. Considering the great international attention focused on global climate change, these attributes make bio-oil an attractive alternative liquid fuel source for both power generation and transport. At a local level, increased use of biomass resources promotes rural development and full utilization of farmland, while reducing the quantity of material being land filled (Stamatov, Honnery and Soria, 2005).

1.1.4 Microwave Chemistry

Microwave irradiation has been widely used in chemistry because it has high heating efficiency and can, in some cases, increase reaction rate and reduce reaction time (Zhu, Wu, Yu, Zhang, Li and Gao, 2005). Microwave heating has been recognized as a powerful technology for organic synthesis and the processing of polymers (Miura, Kaga, Yoshida and Ando, 2001). Microwave technology for heating has been shown to be more energy efficient than conventional methods in many applications, as microwave irradiation is rapid and volumetric with the whole material heated simultaneously. In contrast, conventional heating is slow and the heat is introduced into the sample from the surface (Yu, Ruan and Steele, 2009). This feature of microwaves is very important for processing poor thermal conducting materials such as wood. Microwave heating can be controlled instantly and the power applied can be accurately regulated. This allows safe and precise control, even when applying very rapid heating rates. Microwaves also promote novel reaction pathways and can greatly accelerate reaction rates as a result of specific interactions. There are many examples of application of microwave irradiation in the field of organic synthesis, chemical catalysis, solid state reactions, polymers and composites, but few have been found in enzymatic engineering, especially for the enzymatic hydrolysis of lignocellulosic materials (EVALUESERVE Microwave Chemistry, 2005).

1.2 Problem Statement

As the world facing a major economic and also energy crisis, we are highly encourage to do study and also research on the substitute of the current energy source. This study would also benefit the environment, as we know that bio-oil is a more environmentally friendly energy source compared to the current energy source. All in all study on biomass (bio-oil) would be able to benefit us in many ways and also for the betterment of the future generations. Fast Pyrolysis decomposition method will be used to decompose the biomass. Fast pyrolysis is a thermal decomposition with the absence of Oxygen. It takes place at moderate temperature, short residence times particularly vapor and based on previous researches, fast pyrolysis has a high liquid product yield. For this project we plan to use microwave as a heating source to decompose Malaysian biomass (lignocelluloses), in order to extract bio oil. The purpose of using a microwave is due to the fact that microwave has a higher heating rate and it also heats up the materials uniformly, which would be able to produce better products as compared to the conventional heating. The bio oil produce can later be enhanced into a conventional energy source.

1.3 Objectives and Scope of Study

1.3.1 Objectives

The objective of this project is to investigate the decomposition behavior and the product distribution for microwave decomposition of Malaysian biomass, using kernel shell. The results will be compared with those from thermal decomposition of the same biomass collected from the references or obtained from research group. The effect of power input t the system will also be observed in order to determine the best Pyrolysis condition in order to obtain the best results The purpose of the decomposition is to obtain the liquid product as much as possible. In the area of biomass thermal decomposition, this technology is called fast-Pyrolysis, and the product is called bio-oil.

1.3.2 Scope of Studies

The scope of study would cover experimental study of the characteristics of biomass (EFB, mesocarp fiber and kernel shell) and also the liquid product (bio-oil) of the experiment, the effects of different sizes of biomass samples and also power input to the microwave will be studied and analyzed as well.

CHAPTER 2

LITERATURE REVIEW AND THEORY

Chapter 2 includes different kinds of literature reviews and theories related to the present research of this project. Some of the literature reviews involve experimental studies, theories, equipment and devices. Section 2.1 on theories refers to all fundamental engineering or general knowledge regarding fast Pyrolysis and the Pyrolysis oil and others. Section 2.2 on experimental studies provides an overview of other experiments conducted previously which contain the elements of interest with respect to this project. The results from these experiments are analyzed for further understanding. Some of the equipment and devices used by others, which are elaborated in Section 2.3, give more ideas on the improvement of the experiment setup.

2.1 Theories

2.2.1 Lignocellulosic Biomass

Lignocellulosic biomass, in the form of wood, has a long history as a source of energy. Since the middle of the 20th century, the interest of biomass as a precursor to liquid fuels has increased. To be specific, the fermentation of lignocellulosic biomass to ethanol (Carroll and Somerville, 2009) is an attractive route to fuels that supplements the fossil fuels. Biomass is a carbon-neutral source of energy: Since it comes from plants, the combustion of lignocellulosic ethanol produces no net carbon dioxide in the earth's atmosphere. Aside from ethanol, many other lignocellulose-derived fuels are of potential interest, including butanol, dimethylfuran, and gamma-Valerolactone (Tokay, 2002).

One barrier to the production of ethanol from biomass is that the sugars necessary for fermentation are trapped inside the lignocellulose. Lignocellulose has evolved to resist degradation and to confer hydrolytic stability and structural robustness to the cell walls of the plants. This robustness or "recalcitrance" is attributable to the cross linking between the polysaccharides (cellulose and hemicellulose) and the lignin via ester and ether linkages (Biofuels Joint Roadmap, 2006). Ester linkages arise between oxidized sugars, the uronic acids, and the phenols and phenylpropanols functionalities of the lignin. To extract the fermentable sugars, one must first disconnect the celluloses from the lignin, and then acidhydrolyze the newly freed celluloses to break them down into simple monosaccharide. Another challenge to biomass fermentation is the high percentage of pentose in the hemicellulose, such as xylose, or wood sugar. Unlike hexoses, like glucose, pentoses are difficult to ferment. The problems presented by the lignin and hemicellulose fractions are the foci of much contemporary research.

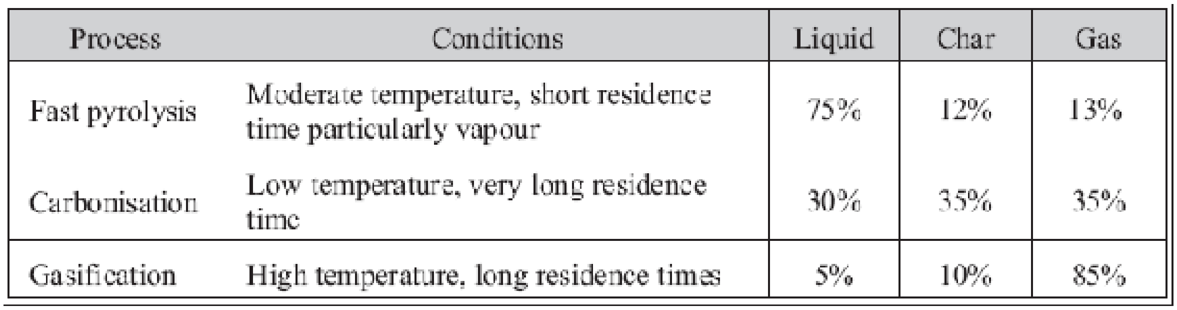
2.2.2 Fast Pyrolysis

Fast Pyrolysis occurs in a time of few seconds or less. According to Bridgwater (2004), in fast Pyrolysis, biomass decomposes to generate mostly vapors’ and aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process, with carefully controlled parameters to give high yields of liquid. The essential features of a fast pyrolysis process for producing liquids are:

- very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed,
- carefully controlled pyrolysis reaction temperature of around 500 ºC and vapor phase temperature of 400-450 ºC,
- Short vapor residence times and rapid cooling of the pyrolysis vapors’ to give the bio-oil product.

The main product, bio-oil, is obtained in yields of up to 75% wt on dry feed basis, together with by-product char and gas which are used within the process so there are no waste streams other than flue gas and ash. A fast pyrolysis process includes drying the feed to typically less than 10% water in order to minimize the water in the product liquid oil (although up to 15% can be accept able), grinding the feed (to around 2 mm in the case of fluid bed reactors), to give sufficiently small particles to en sure rapid re action, pyrolysis reaction, separation of solids (char), and collection of the liquid product (bio-oil).

Any form of bio mass can be considered for fast pyrolysis. While most work has been carried out on wood due to its consistency, and comparability between tests, nearly 100 different biomass types have been tested by many laboratories ranging from agricultural wastes such as straw, olive pits and nut shells to energy crops such as miscanthus and sorghum and solid wastes such as sew age sludge and leather wastes (Bridgwater, 2004).



Process	Conditions	Liquid	Char	Gas
Fast pyrolysis	Moderate temperature, short residence time particularly vapour	75%	12%	13%
Carbonisation	Low temperature, very long residence time	30%	35%	35%
Gasification	High temperature, long residence times	5%	10%	85%

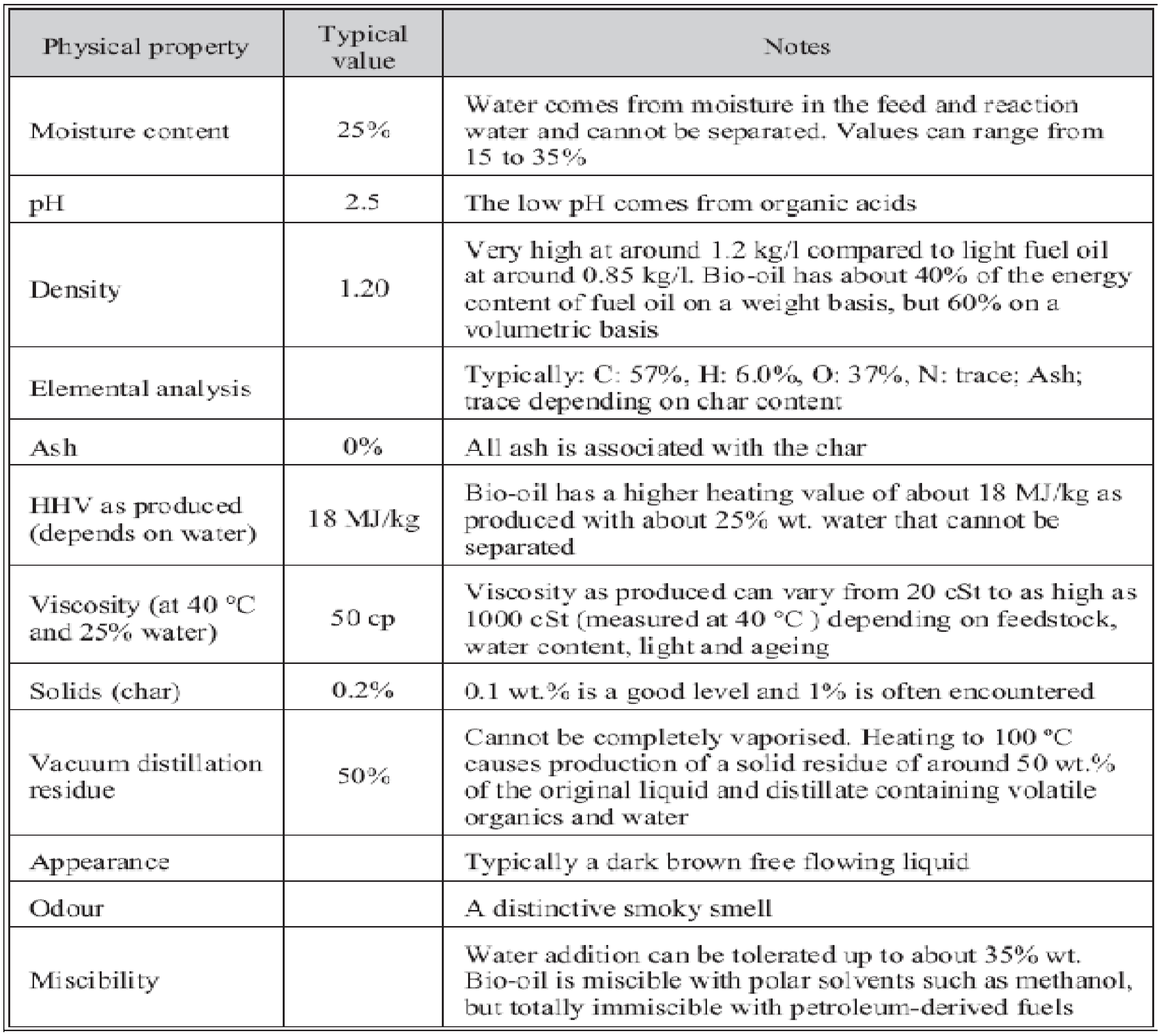
Table 2.1 Typical product yields (dry wood basis) obtained by different modes of Pyrolysis of wood

2.2.3 Pyrolysis Oil

The gaseous products from fast pyrolysis consist of aerosols, true vapors and non-condensable gases. These require rapid cooling to minimize secondary reactions and to condense the true vapors, while the aerosols require coalescence or agglomeration. Pyrolysis liquid is referred to by many names including pyrolysis oil, bio-oil, bio-crude-oil, bio-fuel-oil, wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous tar, pyroligneous acid, and liquid wood. The crude pyrolysis liquid is usually dark brown and free flowing with a distinctive smoky smell. Chemically, it approximates to bio mass in elemental composition and is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product. Solid char may also be present (Bridgwater, 2004).

The physical properties of bio-oils are described in several publications. These properties result from the chemical and physical composition of the oils, which is significantly different from that of petroleum oils. Bio-oils are multi component mixtures comprised of different size molecules derived primarily from depolymerization and fragmentation reactions of three main components blocks which are cellulose, hemicellulose, and lignin. Therefore, the elemental composition of bio-oil produced will resembles that of biomass rather than that of petroleum oils.

The oxygen content of bio-oils is usually 45-50 wt. %. This oxygen is present in most of the more than 300 compounds that have been identified in the oils. The distribution of these compounds mostly depends on the type of biomass used and on the process severity (temperature, residence time, and heating rate profiles). An increase in Pyrolysis severity reduces the organic liquid yield due to cracking of the vapors' and formation of gases but leaves the organic liquid with less oxygen. The single most abundant bio-oil component is water. The other major groups of compounds identified are hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. Most of the phenolic compounds are present as oligomers having a molecular weight ranging from 900 to 2500 (Bridgwater, 2004).



Physical property	Typical value	Notes
Moisture content	25%	Water comes from moisture in the feed and reaction water and cannot be separated. Values can range from 15 to 35%
pH	2.5	The low pH comes from organic acids
Density	1.20	Very high at around 1.2 kg/l compared to light fuel oil at around 0.85 kg/l. Bio-oil has about 40% of the energy content of fuel oil on a weight basis, but 60% on a volumetric basis
Elemental analysis		Typically: C: 57%, H: 6.0%, O: 37%, N: trace; Ash; trace depending on char content
Ash	0%	All ash is associated with the char
HHV as produced (depends on water)	18 MJ/kg	Bio-oil has a higher heating value of about 18 MJ/kg as produced with about 25% wt. water that cannot be separated
Viscosity (at 40 °C and 25% water)	50 cp	Viscosity as produced can vary from 20 cSt to as high as 1000 cSt (measured at 40 °C) depending on feedstock, water content, light and ageing
Solids (char)	0.2%	0.1 wt.% is a good level and 1% is often encountered
Vacuum distillation residue	50%	Cannot be completely vaporised. Heating to 100 °C causes production of a solid residue of around 50 wt.% of the original liquid and distillate containing volatile organics and water
Appearance		Typically a dark brown free flowing liquid
Odour		A distinctive smoky smell
Miscibility		Water addition can be tolerated up to about 35% wt. Bio-oil is miscible with polar solvents such as methanol, but totally immiscible with petroleum-derived fuels

Table 2.2 Summary of typical proper ties and characteristics of wood derived crude bio-oil.

2.2 Experimental Studies

2.2.1 Microwave Pyrolysis of Corn Stover by Yu, Ruan and Steele (2009)

2.2.1.1 Research Background

The objectives of this research was to examine the effects of power input and additives on the product yields, and to characterize the chemical profiles of the gas and bio-oil fractions produced by microwave Pyrolysis of corn Stover. The process yielded bio-oil, gas, and solid charcoal residue. Under experimental conditions, a power input level above 300 W was necessary to initiate thermal Pyrolysis of a 50 g sample of corn Stover.

The yields of gas and bio-oil increased to 46.9 wt % and 30.2 wt %, respectively, when microwave input power increased from 300 to 900 W, and higher power input also favored gas production. Adding 1 wt % pyrolytic charcoal residue to the Pyrolysis of corn Stover increased the bio-oil and gas yields, particularly the bio-oil yield. Addition of NaOH to the Pyrolysis of corn Stover as catalyst increased the gas yield greatly.

2.2.1.2 Apparatus and Process

1. The pyrolysis of the corn stover was carried out in a microwave cavity oven by placing 50 g samples in a quartz flask.
2. The oven was purged with nitrogen gas for 2 min prior to microwave treatment to create an oxygen-free gas background.
3. The time for microwave treatment varied but did not exceed 60 min. A constant power input ranging from 200 to 900 W at the microwave frequency of 2450 MHz was used for each batch.
4. The volatile pyrolyzates were condensed after passing through a water-cooling column and collected in a bottle. This fraction is called bio-oil. The solid char residue was allowed to cool to room temperature before it was weighed.
5. The weight of the gas product was calculated using following equation:

Weight of gas = Initial corn stover mass - Bio-oil mass - Char residue mass

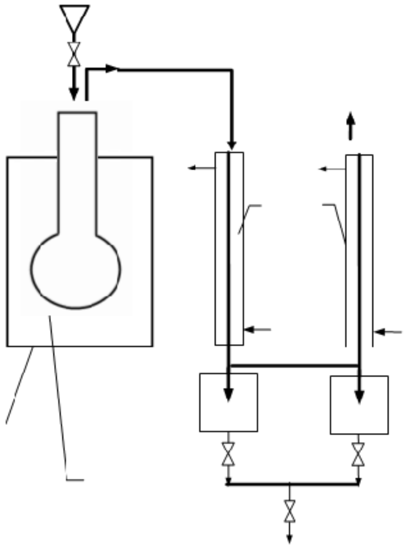


Figure 2.1 Schematic of the microwave pyrolysis apparatus

2.2.1.3 Result and Discussion

At 300 W, the temperature rose to 450°C quickly and then leveled off. Smoke emission was observed at 15 min of heating. A small amount of gas and bio-oil was produced after 40 min of heating. At 900 W, the gas yield had risen to 46.9 wt %. Therefore, a higher input power seems favorable for gas production. In addition, more corn stover was converted to bio-oil at higher input power. Bio-oil yield increased to 25.1 wt % at 600 W and to 30.2 wt % at 900 W.

When the power input level was 600 W, the temperature increased to 800°C in 20 min and then decreased to 605°C. This effect may have been due to lowering of the water content and organic compounds, whose interactions with microwave irradiation are the major contributors to the initial heating of the system.

Charcoal is an excellent microwave absorbent. Therefore, adding pyrolytic charcoal to fresh biomass is a good way to promote rapid pyrolysis and save energy. Alkaline catalysis may reduce the activation energy for the chemical reactions involved in pyrolysis and result in a more efficient process. Gas yield increased from 51 wt % to 57.5 wt % with the increase of input power from 300 to 600 W, while char residue yield decreased, and there was little change in bio-oil yield.

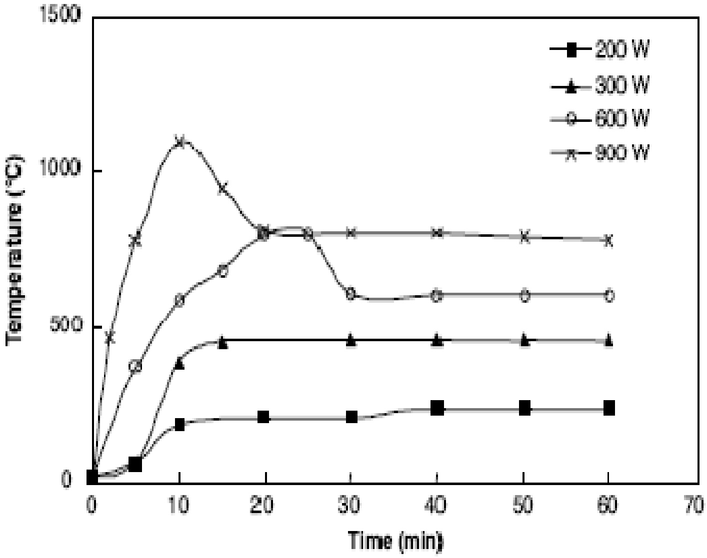


Figure 2.2 Temperature profiles of batches of corn stover

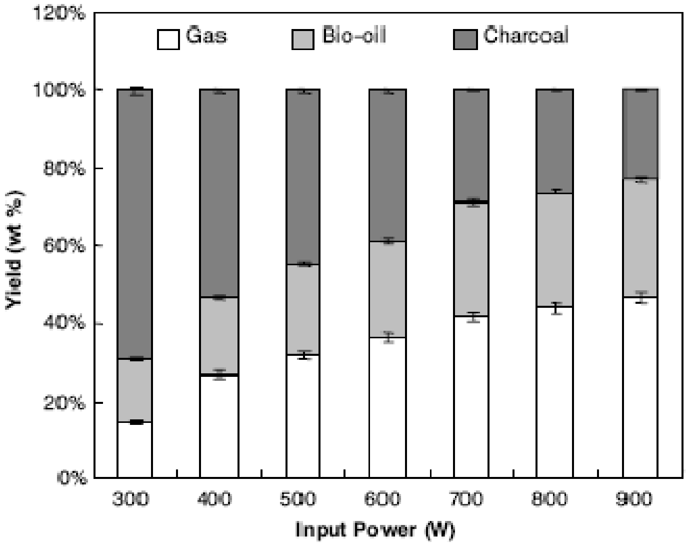


Figure 2.3 Yields of bio-oil, gas, and charcoal from microwave pyrolysis of corn stover from

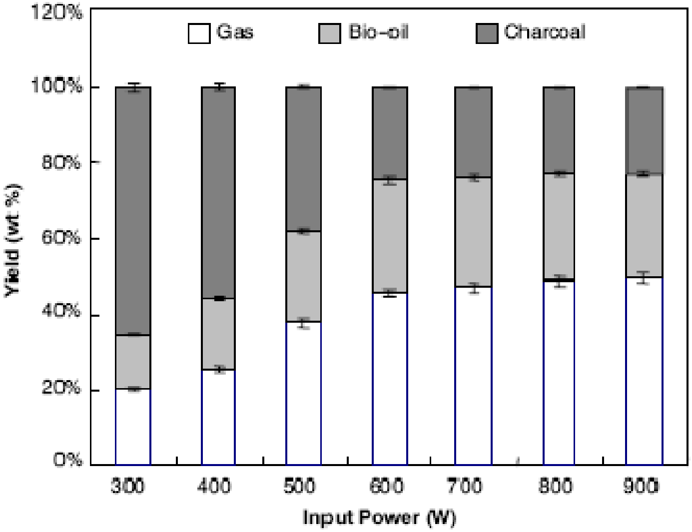


Figure 2.4 Yields of bio-oil, gas, and charcoal from microwave pyrolysis of corn stover with 1 wt %

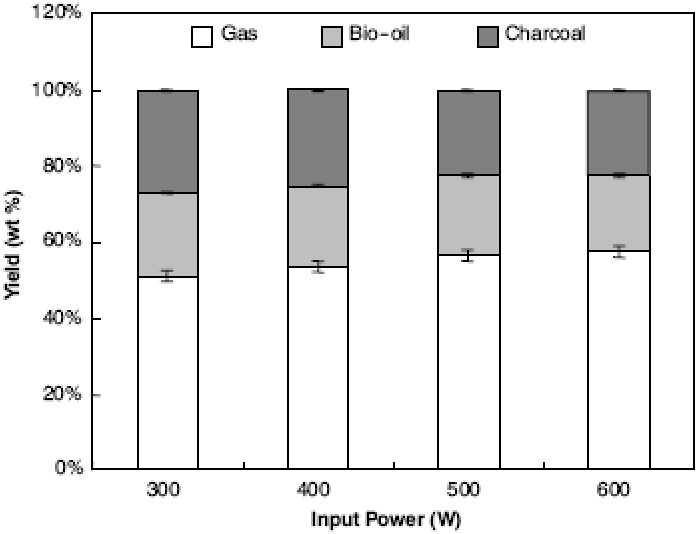


Figure 2.5 Yields of bio-oil, gas, and charcoal from microwave Pyrolysis of corn stover with 5 wt % of NaOH and 1 wt % of charcoal addition at 300 to 600 W

Pyrolytic oils were condensable volatiles, which can be separated into a water-soluble phase and a water-insoluble phase. The water-soluble part contains water and water-soluble organic compounds, while the water insoluble part contains water-insoluble organics. In this research, it was found that the water-insoluble fraction amounts to about 45 wt % of the total oils. The percentage values for all compounds decreased with increasing power input, apparently because fewer oils were produced at higher input power. The percentage of oil decreased and the gas yield increased with the increase in power. It seems that 600 W was sufficient to produce almost complete decomposition of corn stover, due to its extensive high production of bio-oil and low production of char.

Retention Time (min)	Peak Name	Formula	Percentage at 300 W	Percentage at 600 W	Percentage at 900 W
6.021	Furan, 3-Penthyl-	$C_9H_{14}O$	2.59	1.09	1.7
7.857	Styrene	C_8H_8	2.14	2.68	1.95
11.458	Phenol	C_6H_6O	4.29	17.1	17.75
11.718	Benzofuran	C_8H_6O	0.18	0.28	2.67
13.408	Benzene, 1-propynyl-	C_9H_8	2.44	4.54	3.93
14.027	Acetic Acid, 4-methylphenyl Ester	$C_9H_{10}O_2$	0.8	0.53	0.49
14.782	6-Nonynoic Acid, Methy Ester	$C_{10}H_{16}O_2$	0.12	2.26	0
14.839	Phenol, 3-Methyl-	C_7H_8O	2.31	3.35	7.94
14.974	Phenol,2-methoxy	$C_7H_8O_2$	15.9	9.97	3.74
17.727	Phenol, 4-ethyl-	$C_8H_{10}O$	20.51	16.95	19.8
18.135	Naphthalene	$C_{10}H_8$	10.97	16.19	21.4
18.431	Phenol,3,4-dimethyl-	$C_8H_{10}O$	0.5	0.26	0.1
19.397	Benzofuron, 3,4-dimethyl-	$C_{10}H_{10}O$	0	2.94	3.8
19.419	2-Propenoic Acid, 3-(2-hydroxyphenyl)-,(E)-	$C_9H_8O_3$	12.29	1.77	1.6
19.985	Benzeneamine, 2,4-dimethyl-	$C_8H_{11}N$	0.82	0.25	0.69
20.969	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	7.04	6.48	4.25
21.571	1H-indene, 1-ethylidene-	$C_{11}H_{10}$	0.69	0.92	2.05
22.048	Benzeneacethyldehyde	C_8H_8O	6.04	0	0.71
22.091	2-propene, 1-phenoxy-	$C_9H_{10}O_2$	0	1.59	0.68
23.142	Phenol ,3,3-dimethoxy-	$C_8H_{10}O_3$	4.8	3.68	0.32
25.806	Acenaphthylene	$C_{12}H_8$	0	2.49	1.61
32.638	1-Dodecanol, 3,7,11-trimethyl-	$C_{15}H_{32}O$	0.57	0.86	0.81

Table 2.3 Yield (% area) of the main bio-oil compounds obtained from corn stover.

Input Power (W)	Pentane Eluate (wt%)	Benzene Eluate (wt%)	Ethyl Acetate Eluate (wt%)	Methanol Eluate (wt%)
300	11.1	28.8	35.9	23.9
600	11.6	26.9	36.2	24.1
900	12.9	26.1	37.7	23.2

Table 2.4 Chemical fractionation of bio-oil.

2.2.1.4 Conclusion

The effects of microwave input power level, addition of charcoal, and addition of NaOH to the microwave pyrolysis of corn stover were studied. The degradation of corn Stover increased with increasing microwave power. A higher power level favored gas production. The yields of gas, bio-oil, and charcoal residue reached about 46.9 wt %, 30.2 wt %, and 22.9 wt %, respectively, after 60 min of microwave heating at 900 W. Adding 1 wt % pyrolytic charcoal residues to the Pyrolysis of corn stover increased the gas and bio-oil yields, particularly the bio-oil fraction yield. Addition of NaOH to the pyrolysis of corn stover as catalyst increased the gas yield greatly.

2.2.2 Rapid Pyrolysis of Wood Block by Microwave Heating by Miura, Kaga, Sakurai, Kakuchi and Takahashi (2003)

2.2.2.1 Problem Statement

1. Microwave heating has a different temperature distribution, heat transfer and mass transfer compared to conventional heating.
2. Through conventional method, high yield of levoglucosan cannot be obtain, because the escape rate of the volatile products from the wood is very slow, and reducing the size of the wood increases the total cost.
3. Key points of Pyrolysis wood are to prevent undesired secondary reactions of the volatiles and to increase the yield of volatile products.

2.2.2.2 Objective

1. To compare between microwave heating and conventional heating.

2.2.2.3 Apparatus

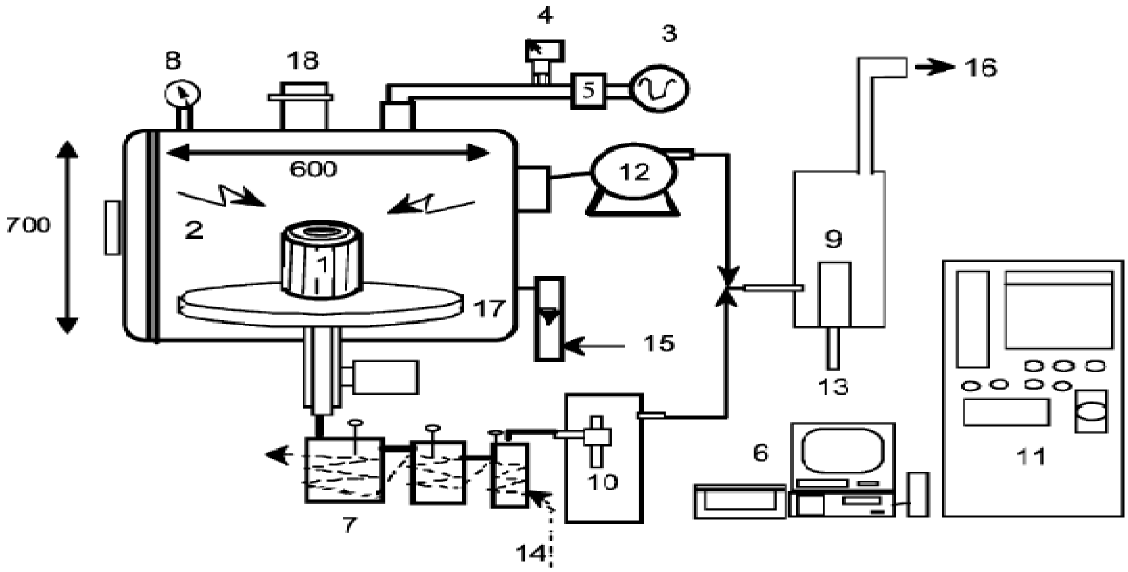


Figure 2.6 : 1: Sample; 2: Reactor (width: 600 mm; depth: 600 mm; height: 700 mm); 3: Microwave power generator; 4: Power monitor; 5: Isolator; 6: Computer; 7: Collection tanks; 8: Pressure gauge; 9: Afterburner; 10: Aspirator pump; 11: Control panel; 12: Blower; 13: Kerosene; 14: Condenser; 15: Nitrogen gas; 16: Exhaust gas; 17: Rotating table; 18: Safety shutoff.

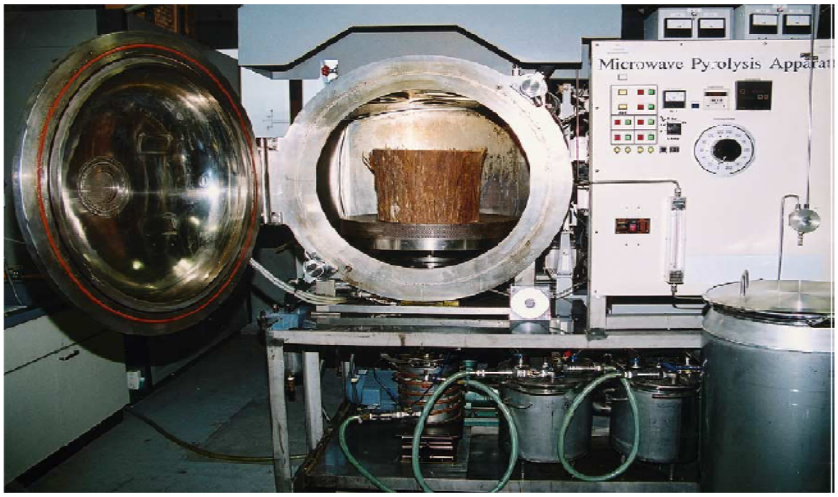


Figure 2.7: Microwave oven

2.2.2.4 Results

After 3 minutes of microwave irradiation, no significant changes on the surface of the wood. The center however changed to black. This shows the core of the wood block was at higher temperature compared to the surface. Carbonization occurs from the center to the surface using microwave. Where primary volatiles of the wood will transfer from the center to the surface indirectly reduces undesired secondary reaction.

Figure 2.8: Cross-section of wood after 3 minutes of microwave irradiation

Using conventional heating, the wood was heated using convective heat transfer and by conduction of heat from the surface to the core. The surface temperature is higher than the core because of the wood's poor thermal conductivity. Therefore it is difficult to prevent undesired secondary reaction, which produces low molecular weight species.

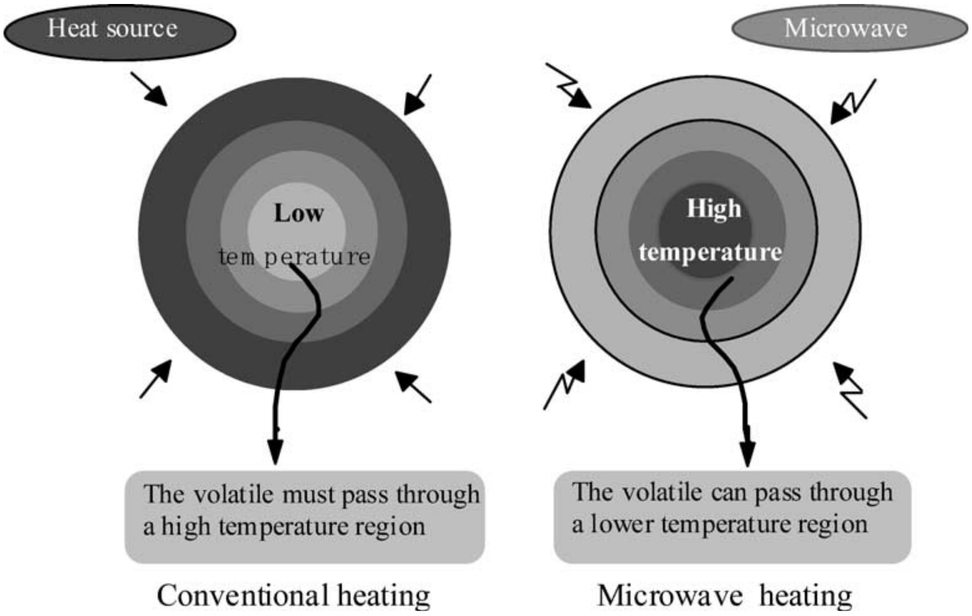


Figure 2.9: Schematic diagram of temperature distribution, heat transfer and mass transfer in the conventional and microwave heating of wood.

For the char produce using conventional heating, the micro pores are filled with large amount of carbon like adhesive. This is due to the deposition of the volatile compound while trying to escape from the wood. For the microwave heating, the micro pores are quite clean and exhibit more open structure as a result of the release of the volatile matter. Specific surface of the char produced by microwave heating is larger than the one produced by conventional heating.

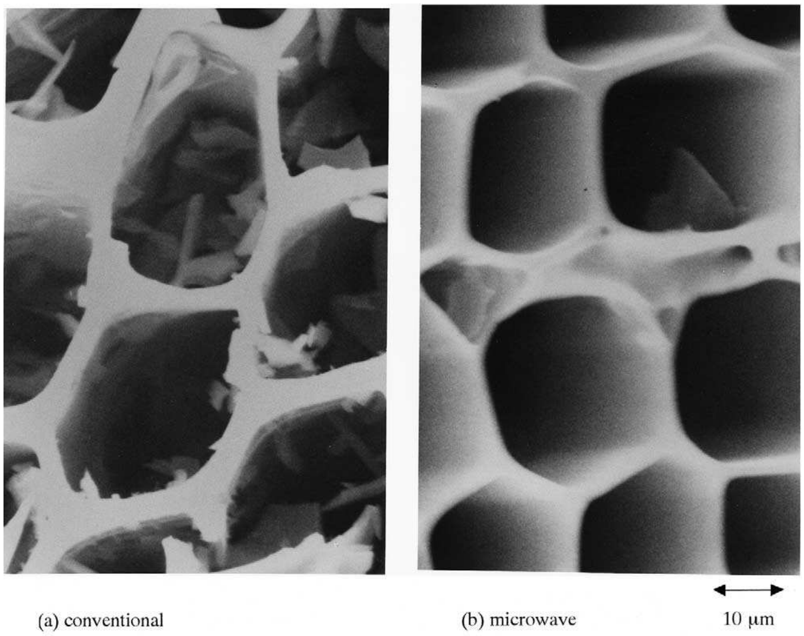


Figure 2.10: Scanning electron microscopy (SEM) of char: (a) prepared by the conventional heating method; (b) prepared by the microwave heating method

2.2.2.5 Conclusion

Microwave heating method has a different heating method compared to the conventional method and it can also prevent secondary reaction. The results from scanning electron microscopy of char demonstrated that the amounts of carbon-like adhesives on the inside of pores are less than those in the conventional methods. The specific surface area of char is larger than that produced by conventional heating.

2.3 Equipment and Devices

2.3.1 Microwave Chemistry (EVALUESERVE Microwave Chemistry, 2005)

Microwave chemistry involves the use of microwave radiation to conduct chemical reactions, and essentially pertains to chemical analysis and chemical synthesis. Microwave radiation has been successfully applied to numerous industrial applications (drying, heating, sintering, etc.). Microwaves lie in the electromagnetic spectrum between infrared waves and radio waves. They have wavelengths between 0.01 and 1 meter, and operate in a frequency range between 0.3 and 30 GHz. However, for their use in laboratory reactions, a frequency of 2.45 GHz is preferred, since this frequency has the right penetration depth for laboratory reaction conditions. Beyond 30 GHz, the microwave frequency range overlaps with the radio frequency range (EVALUESERVE Microwave Chemistry, 2005). The microwave electromagnetic spectrum is divided into sub-bands comprising the following frequency ranges (Table 2.5):

Bands	Frequency
L	1-2 GHz
S	2-4 GHz
C	4-8 GHz
X	8-12 GHz
Ku	12-18 GHz
K	18-26 GHz
Ka	26-40 GHz
Q	30-0 GHz
U	40-60 GHz
V	46-56 GHz
W	56-100 GHz

Table 2.5 Microwave Frequency Bands

While the lower microwave frequency ranges (L band) are used for the purpose of communication, the higher frequency ranges (W band) in the spectrum are used for analytical techniques such as spectroscopy. Microwave RADAR equipment that operate at lower wavelengths (0.01-0.25 m) are used for communication.

2.3.1.1 Fundamentals of Microwave Technology

The fundamental mechanism of microwave heating involves agitation of polar molecules or ions that oscillate under the effect of an oscillating electric or magnetic field. In the presence of an oscillating field, particles try to orient themselves or be in phase with the field. However, the motion of these particles is restricted by resisting forces (inter-particle interaction and electric resistance), which restrict the motion of particles and generate random motion, producing heat. Since the response of various materials to microwave radiation is diverse, not all materials are amenable to microwave heating. Based on their response to microwaves, materials can be broadly classified as follows:

- Materials that are transparent to microwaves, e.g., sulfur
- Materials that reflect microwaves, e.g., copper
- Materials that absorb microwaves, e.g., water

Only materials that absorb microwave radiation are relevant to microwave chemistry. These materials can be categorized according to the three main mechanisms of heating (Figure 2.11), namely:

- Dipolar polarization
- Conduction mechanism
- Interfacial polarizatio

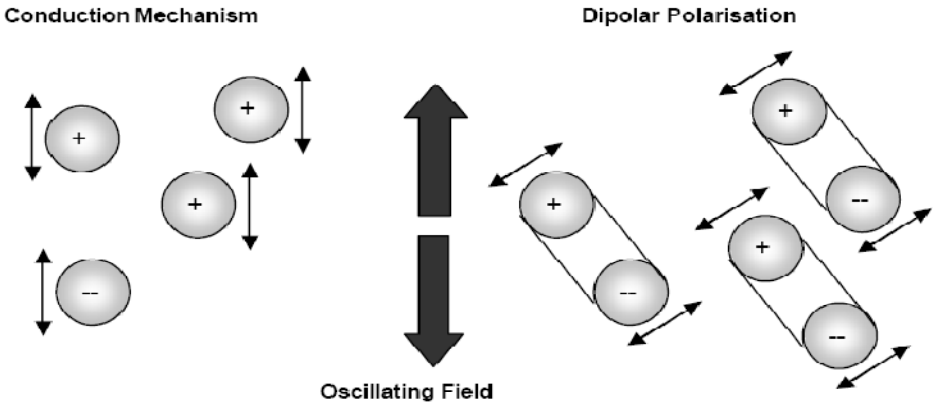


Figure 2.11 Methods of Heating by Microwave Radiation (Pueschner GmBH website (www.pueschner.com/engl/basics/index.html)

2.3.1.2 Evolution of Microwave Chemistry

The use of microwave radiation as a method of heating is over five decades old. Microwave technology originated in 1946, when Dr. Percy Le Baron Spencer, while conducting laboratory tests for a new vacuum tube called a magnetron5, accidentally discovered that a candy bar in his pocket melted on exposure to microwave radiation. Dr. Spencer developed the idea further and established that microwaves could be used as a method of heating. Subsequently, he designed the first microwave oven for domestic use in 19476. Since then, the development of microwave radiation as a source of heating has been very gradual (Table 2.6), (EVALUESERVE Microwave Chemistry, 2005).

1946	Microwave radiation was discovered as a method of heating
1947	First commercial domestic microwave oven was introduced
1978	First microwave laboratory instrument was developed by CEM Corporation to analyse moisture in solids
1980-82	Microwave radiation was developed to dry organic materials
1983-85	Microwave radiation was used for chemical analysis processes such as ashing, digestion and extraction
1986	Robert Gedye, Laurentian University, Canada; George Majetich, University of Georgia, USA; and Raymond Giguere of Mercer University, USA, published papers relating to microwave radiation in chemical synthesis
1990s	Microwave chemistry emerged and developed as a field of study for its applications in chemical reactions
1990	Milestone s.r.l. generated the first high pressure vessel (HPV 80) for performing complete digestion of difficult to digest materials like oxides, oils and pharmaceutical compounds
1992-1996	CEM developed a batch system (MDS 200) reactor, and a single mode cavity system (Star 2) that were used for performing chemical synthesis
1997	Milestone s.r.l and Prof. H.M (Skip) Kingston of Duquesne University culminated a reference book titled “Microwave-Enhanced Chemistry – Fundamentals, Sample Preparation, and Applications”, and edited by H. M. Kingston and S. J. Haswell
2000	First commercial microwave synthesiser was introduced to conduct chemical synthesis

Table 2.6 Evolution of Microwave Chemistry

2.3.1.3 Microwave Chemistry Apparatus

Most pioneering experiments in chemical synthesis using microwaves were carried out in domestic microwave ovens. However, developments in microwave equipment technology have enabled researchers to use dedicated apparatus for organic reactions. The following are the two categories into which microwave chemistry apparatus are classified:

- Single-mode apparatus
- Multi-mode apparatus

Single-mode Apparatus

The differentiating feature of a single-mode apparatus is its ability to create a standing wave pattern, which is generated by the interference of fields that have the same amplitude but different oscillating directions. This interface generates an array of nodes where microwave energy intensity is zero, and an array of antinodes where the magnitude of microwave energy is at its highest (Figure 2.12).

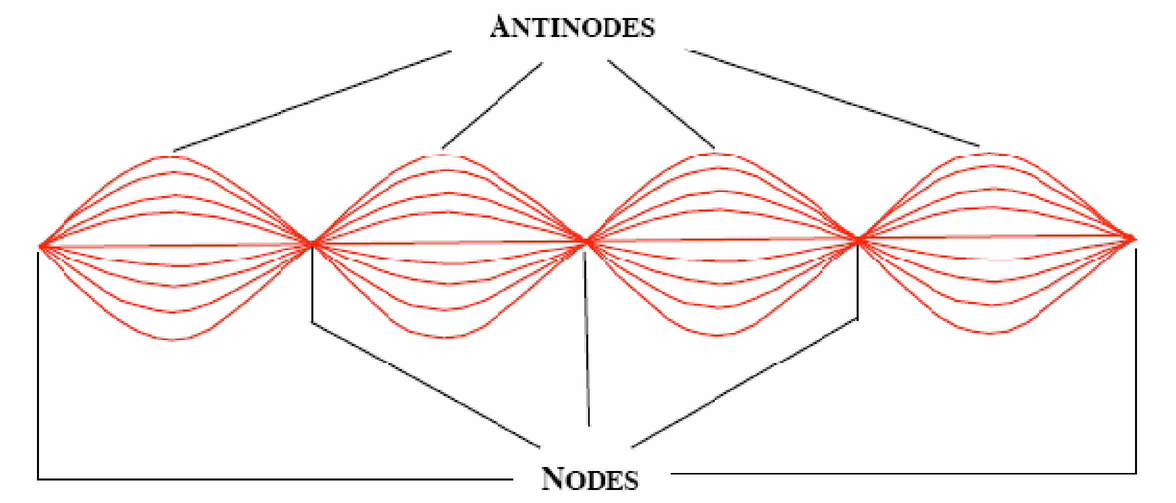


Figure 2.12: Generation of a Standing Wave Pattern

The factor that governs the design of a single-mode apparatus is the distance of the sample from the magnetron. This distance should be appropriate to ensure that the sample is placed at the antinodes of the standing electromagnetic wave pattern (Figure 2.13).

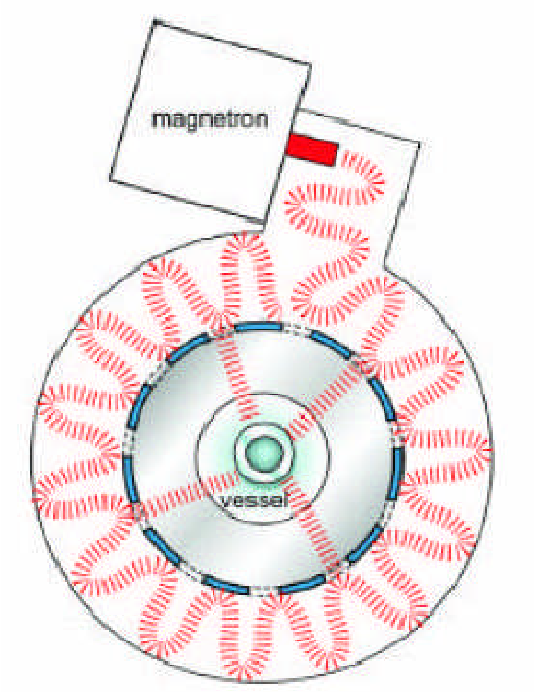


Figure 2.13: Single-mode heating apparatus

One of the limitations of single-mode apparatus is that only one vessel can be irradiated at a time. However, after the completion of the reaction period, the reaction mixture can be rapidly cooled by using compressed air – this is a built-in cooling feature of the apparatus. As a result, the apparatus becomes more user-friendly. Single-mode microwave heating equipment are currently used for small-scale drug discovery, automation and combinatorial chemical applications. An advantage of single-mode apparatus is their high rate of heating. This is because the sample is always placed at the antinodes of the field, where the intensity of microwave radiation is the highest. In contrast, the heating effect is averaged out in a multi-mode apparatus (EVALUESERVE Microwave Chemistry, 2005).

Multi-mode Apparatus

An essential feature of a multi-mode apparatus is the deliberate avoidance of generating a standing wave pattern inside it (Figure 2.14).

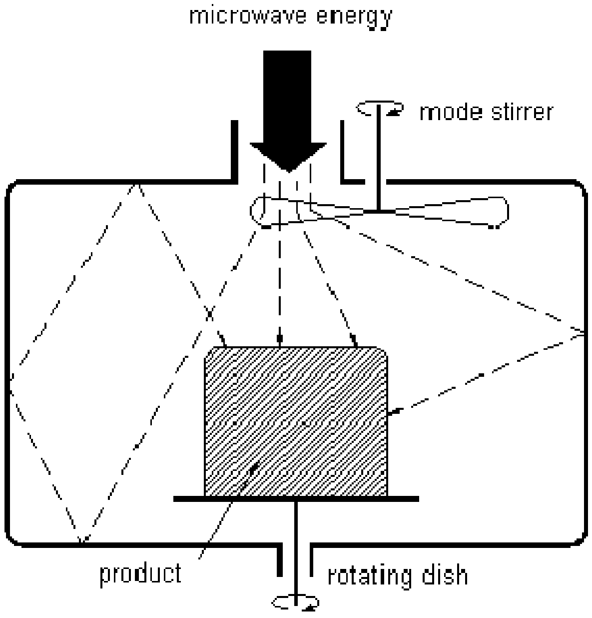


Figure 2.14: Multi-mode Heating Apparatus

(Source: http://www.pueschner.com/engl/basics/index.html)

The goal is to generate as much chaos as possible inside the apparatus. The greater the chaos, the higher is the dispersion of radiation, which increases the area that can cause effective heating inside the apparatus. As a result, a multi-mode microwave heating apparatus can accommodate a number of samples simultaneously for heating, unlike single-mode apparatus where only one sample can be irradiated at a time. Owing to this characteristic, a multi-mode heating apparatus is used for bulk heating and carrying out chemical analysis processes such as ashing, extraction, etc. A major limitation of multi-mode apparatus is that even with radiation distributed around them, heating samples cannot be controlled efficiently. This is largely due to the chaos generated, which makes it difficult to create equal heating conditions for samples that are heated simultaneously (EVALUESERVE Microwave Chemistry, 2005).

CHAPTER 3

METHODOLOGY

This chapter includes a set of methods or procedures which provides the description of the schedule of the project. In Section 3.1, the Gantt chart and project milestones are presented. Project process flow is presented in Section 3.2, which illustrates the work sequence of the project, from the start until the end.

3.1 Gantt Chart and Milestones

The activities or work done during the first semester are listed out and the total period of time involved are fourteen weeks. Selection of project topic and preliminary research work were done within the period planned. Research and literature review are carried out from week 5 until week 14 for more understanding of the project. Literature review was done on variety sources for example journals, articles, researches, conferences, webpages and others. For the first semester I have already gone through a numbered of gathered literature, which are on biomass, fast pyrolysis, expected products, chemistry of microwave and the effects of microwave absorber. Besides that, along with my supervisors, we have planned the set up of the experiment as well as the steps of the experiment that will be use for the current semester's experiment.

Table 3.1 gives a clear illustration on the schedule of this project for activities done in the first semester. Some of the main activities carried out were on literature review, chemical and apparatus selection, experimental setup and experimental steps.

	1	2	3	4	5	6	7	8	9	10	11	12	13
Introduction to FYP and Coordinator	■												
Topic and Proposal Preparation		■											
Literature Review			■	■	■		■	■		■			
Chemical and Apparatus Selection						■							
Seminar and Progress Report Preparation									■				
Experimental Set up Proposal											■		
Experimental Steps												■	
Final Report and Presentation Preparation													■

Table 3.1 Gantt chart and milestone for activities in Semester I

Table 3.2 is an illustration of the progress of the second part of this project. For the second semester I focused on carrying out the microwave induced pyrolysis experiment. Prior to the experiment the biomass samples must first be prepared, which include getting the samples, grinding and also drying it. The preparation steps were carried out during the semester break. The experiment was carried out towards the end of August as the equipment arrived only somewhere towards the end of August. It would take approximately one month to complete the experiment for all the samples, including the product analysis. Once the results are obtained, it will be finalized and tabulated into the final report for evaluation. Below is the expected timeline for the Final Year Project 2, beginning with the sample preparation followed by the experiment and lastly results analysis.

	June	June	July	July	Aug	Aug	Sept	Sept	Oct	Oct
Sample preparation	■	■								
Chemical and Physical Characteristic			■	■						
Microwave Pyrolysis Experiment					■	■	■	■		
Product Analysis						■	■	■	■	
Final Evaluation Preparation									■	■

Table 3.2 Gantt chart and milestone for activities in Semester II

3.2 Experimental Steps

3.2.1 Biomass Preparation

Before beginning the preparation steps, biomass samples must first be collected, for this case we will be using sample from the Malaysian biomass (Palm Oil). The palm oil sample can be obtained either from the palm oil plantation or the palm oil mill. Three types of biomass sample were collected approximately about one kilogram each for Empty Fruit Branch (EFB), Fiber and Kernel Shell.

Once the samples are ready, it was dried using an oven at 105 -110 ^{o}C for 24 hours. After the samples are dried for 24 hours, the water content of the samples was checked every subsequent hour until it reaches a constant value (until the mass of the samples are constant). Once the drying is completed, the samples were grinded. The grinded samples are later sieved into three sizes:-

- 125 – 250 µm
- 250 – 500 µm
- 500 – 1000 µm

Once the sieving is completed the samples should be stored accordingly (air tight) while waiting to proceed with the next procedure.

3.2.2 Biomass Physical and Chemical Characteristic

Once the biomass samples are done with drying, grinding and sieving, the samples are analyzed for its chemical and physical characteristic. Four testing were carried out which are on Carbon, Hydrogen, Nitrogen and Sulfur (CHNS) content testing, using the CHNS Analyzer, the ash content of the samples, using the Muffle Furnace, the moisture content of the samples, using Moisture Analyzer and the calorific value of the samples, using Bomb Calorie Meter. Once all the needed are obtain, the samples are ready to proceed with the microwave Pyrolysis experiment.

3.2.3 Microwave Pyrolysis Experiment

The Pyrolysis experiment should be carried out for one type of sample at a time. For this particular experiment the sample that was used was the kernel shell with the size 500 – 1000 µm.

The Pyrolysis of each sample should be carried out at four different Conditions, which are at 1 kW power supply with temperature 300^{o}C and 350^{o}C and 2 kW power supply with temperature 300^{o}C and 350^{o}C. Time and note down the retention time for each of the samples. Once the Pyrolysis is completed for a particular sample, get the percentage of the bio-oil yield, bio-gas yield and also the char yield.

3.2.4 Product Analysis

Analysis of the bio-oil, bio-gas and char collected need to be carried out once the experiment of each sample is completed. For the bio-oil, the analysis that should be carried out are:

- Test for the calorific value.
- Test for the C, H, N, S content.
- Water Content.
- Gas chromatography-mass spectrometry analysis (to get the detail content of the bio-oil).

Next, for the char, the analysis that should be carried out are:

- Test for the calorific value.
- Test for the C, H, N, S content.
- Moisture content.

Lastly, for the bio-gas, the analysis that should be carried out is the Gas chromatography-mass spectrometry analysis (to get the detail content of the bio-gas).

:

CHAPTER 4

EXPERIMENT SETUP

A description of experiment setup is explained in this chapter in detail. This includes the details of equipments used to conduct experiments, namely Microwave Pyrolysis Oven, Bomb Calorimeter, CHNS Elemental Analyzer and Muffle Furnace. Specification, orientation and illustration are shown in this chapter for every element of the equipments. The Microwave Pyrolysis Oven is explained in detail as it is specifically developed for this research. A trial of experiment using water is also included in this chapter.

4.1 Microwave Pyrolysis Oven

Microwave Pyrolysis Oven, as shown in Figure 4.1, serves the function of decomposing the biomass sample using microwave. The biomass sample will be introduced into the system by putting it in a glass vessel (Figure 4.2) and place it in the oven chamber. The glass vessel is transparent to allow the microwave to penetrate through it and hit the biomass samples. A thermocouple will be placed in the glass vessel to capture the temperature of the samples at all time throughout the experiment. The two hands of the glass vessel will be connected to the two outlet tube within the oven chamber. One of the tube function as the Nitrogen outlet during purging while the other serves as an outlet for the Pyrolysis vapor to flow to the condenser.

Figure 4.1: Microwave Pyrolysis Oven

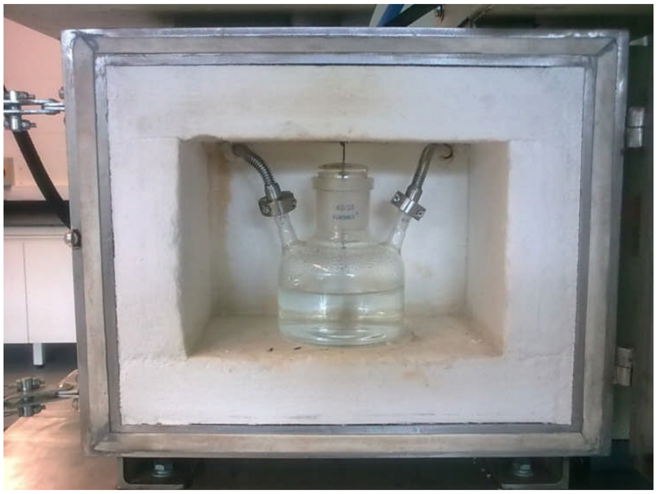


Figure 4.2: Glass Vessel

The schematic diagram of Microwave Pyrolysis Oven is illustrated in Figure 4.3

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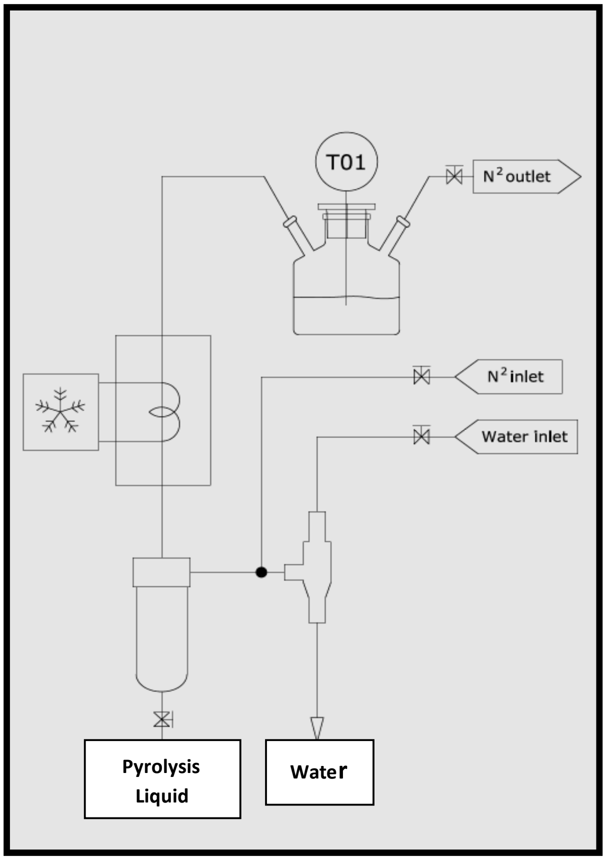

Figure 4.3: Schematic diagram of Microwave Pyrolysis Oven

The oven chamber is a Stainless steel casing with ceramic fiber insulation chamber, air tight seal door. Two Microwave motors are placed on the chamber and function as the source of microwave. Both the Microwave motors can supply up to 1 Kilowatt of microwave and need to be connected to a single phase, 240 V AC power supply.

Before running the experiment, the system should be first purge by Nitrogen for about 15 to 20 minutes. This is to ensure that there is no more air or Oxygen is trapped in the system, as we know Pyrolysis is the decomposition with the absence of Oxygen. Once purging is completed the experiment can be carried out. From the schematic diagram above the water inlet will be supplied to the water aspirator which function as a suction to create a partial vacuum condition within the oven chamber. The suction will enable the flow of Pyrolysis vapor produced during the experiment to the cooling water and also eventually to the collection vessel.

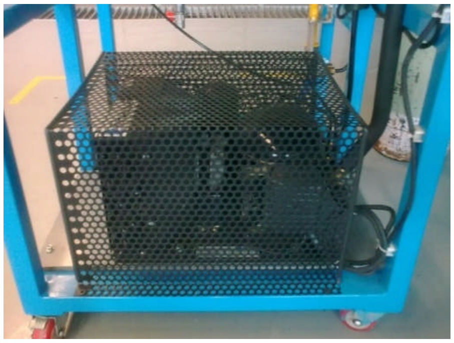

Figure 4.4: ½ HP Refrigerant Chiller.

During the experiment the vapor produced will be flown to the cooling coil which is immersed in the cooling water. The cooling water is placed in the condenser vessel which is a 10 liter water tank with insulation (refer Figure 4.5). The cooling water temperature will be maintained at 16°C using a chiller (refer Figure 4.4). The chiller will absorb the heat from the cooling water using refrigerant. The temperature is set at 16°C to ensure that all the bio oil within the vapor is condensed. The condensed Pyrolysis liquid will be flown to the Pyrolysis liquid collection vessel which is a stainless steel vessel with a drain valve at the bottom (refer Figure 4.5).

Figure 4.5: From top condenser vessel and below Pyrolysis liquid collection vessel.

The balance vapor will be flown to the liquid volume injector, where the vapor product samples can be collected using a gas bag or a syringe. The balance gas will be flown out with the water outlet to the drain.

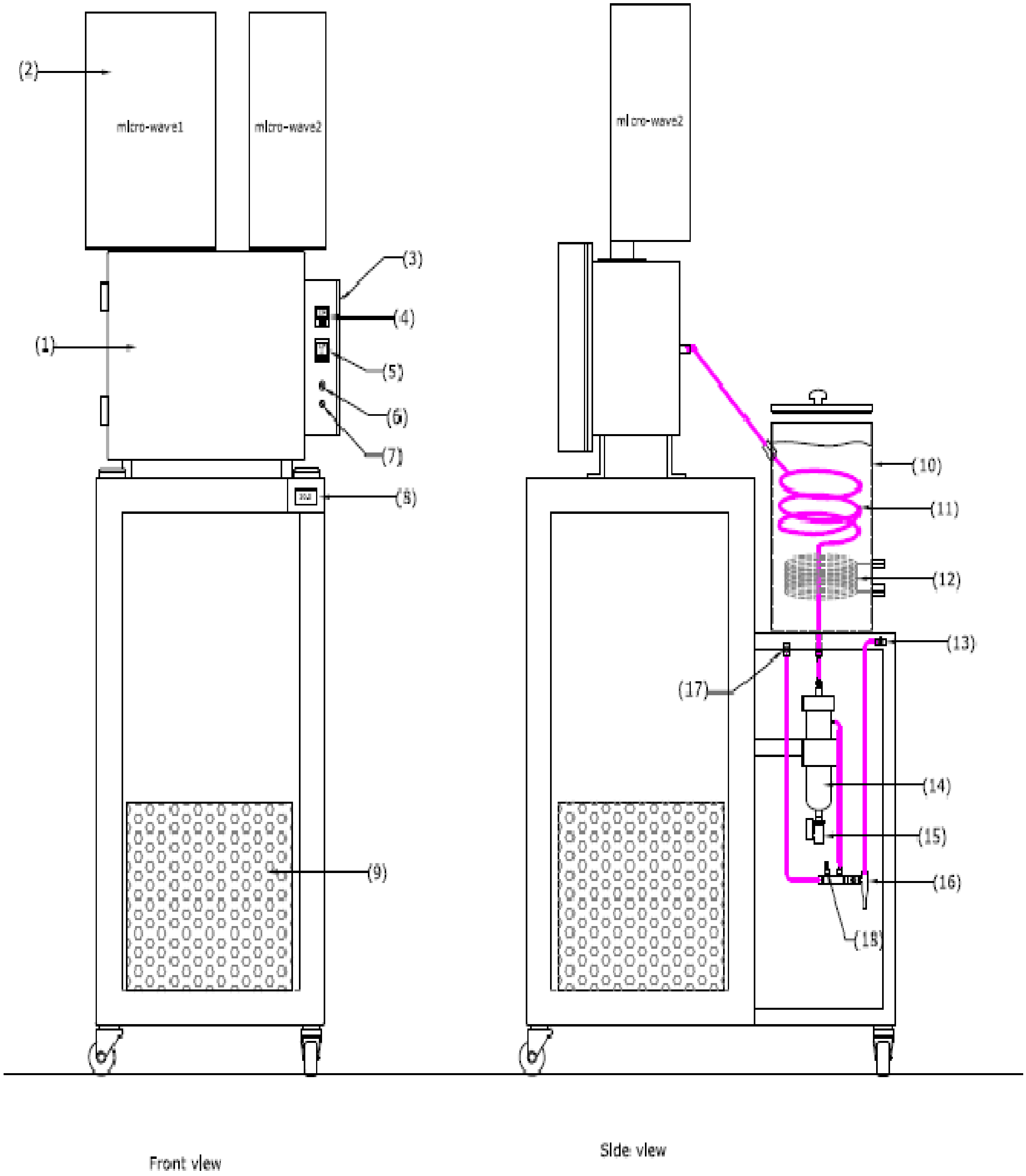

Figure 4.6: Microwave Pyrolysis Oven machine layout

Legend ID number	**Name**	**Function**
1	Oven chamber	Stainless steel casing with ceramic fiber insulation chamber, air tight seal door.
2	Micro-wave generator	2kw, 240Vac Micro-wave generator.
3	Electrical control enclosure.	Power: 240Vac / 1 phase / 50hz.
4	Digital timer (pulse type)	To program the on/off pulse sequence of the micro-wave generator. Pulse duty cycle 50%.
5	Temperature indicator	Indicates the temperature in the bio-mass.
6	Micro-wave generator power switch	Micro-wave generator on/off control power switch.
7	Chiller power switch	Chiller power on/off switch control.
8	Chill water temperature indicator.	To indicate and control the chill water temperature.
9	Chiller	R134a, ½ HP refrigeration chiller. 240Vac / 50Hz.
10	Condenser vessel	10 liter water cool condenser tank with insulation. To condensed the pyrolysis vapor.
11	Condensing coil	Heat exchanger coil for condensed the pyrolysis vapor.
12	Refrigerant cooling coil	Copper cooling coil, internal flow with refrigerant from chiller unit.
13	Water inlet port	Water supply line for vacuum injector generator.
14	Bio-mass collection vessel	Stainless steel vessel for pyrolysis liquid collection.
15	Drain valve	Drain valve for drain out the pyrolysis liquid.
16	Liquid vacuum injector	To create a vacuum suction for extract the vapor from the combustion chamber.
17	Nitrogen purging inlet valve	To connect to nitrogen gas for purging prior to pyrolysis process.
18	Gas sampling port	To connect the gas sample during the Pyrolysis process.

Table 4.1: Microwave Pyrolysis detailed equipment table

1. Connect the power socket to a 240 V AC power supply
2. Start the chiller motor. (Experiment can only be carried out once the cooling temperature drop 16^{o}C or below to enable the condensation of Pyrolysis liquid.)
3. Placed the weighed sample in the glass vessel and place in the oven chamber. Make sure the thermocouple is properly placed in the glass vessel and both hands of the vessel are properly clipped to the outlet tube.
4. Properly close and lock the combustion oven.
5. Purge the whole system with N_2.for 15 – 20 minutes (**Refer to the N_2 purging steps**)
6. Introduced water flow through the water inlet port and open the vacuum injector valve to allow the vacuum suction.
7. Check the cooling water temperature, if it is already at the target temperature, set the pulse timer accordingly based on the power input required.
8. Turn on the microwave motor switch and the experiment will begin.
9. During the experiment the liquid Pyrolysis (liquid product) can be collected from time to time accordingly through the drain valve of the biomass collection vessel.
10. The Pyrolysis vapor sample can also be collected during the experiment, through the gas sampling port by using a gas bag or a syringe.
11. Once the experiment is complete, the microwave motor should be turned off first.
12. The balance liquid pyrolysis can be collected.
13. The oven chamber should not be open until the temperature inside the oven is below 100^{o}C (to avoid sudden cooling, exposure of high temperature char to oxygen and fracture of the glass vessel).
14. Once the oven is at ambient temperature the char (solid product) can be collected within the glass vessel.
15. Turn off the chiller and also the water supply.
16. Turn off the main power supply to the system.

Nitrogen Purging Steps

1. Close the liquid vacuum injector valve (to stop the suction from within the oven chamber).
2. Connect the Nitrogen supply to the Nitrogen purging inlet valve and open the valve.
3. The oven chamber should be closed at all time to avoid the chamber to be contaminated by air and Oxygen.
4. Slowly open the Nitrogen regulator and set the inlet pressure to be about 1.2 atm.
5. Purge the whole system for about 15 to 20 minutes, to make sure there are no more air and Oxygen within the system.
6. Turn off the Nitrogen supply and close the Nitrogen purging inlet valve.

4.2 CHNS Elemental Analyzer.

CHNS elemental analyzers provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulfur in organic matrices and other types of materials. They are capable of handling a wide variety of sample types, including solids, liquids, volatile and viscous samples, in the fields of pharmaceuticals, polymers, chemicals, environment, food and energy (Thompson, 2008).

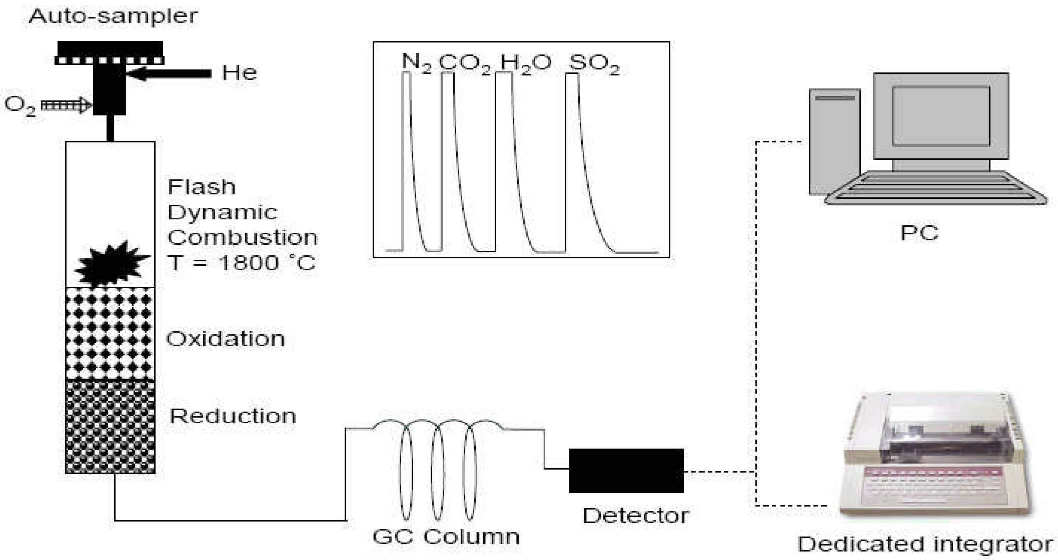

Figure 4.7: Typical process of a CHNS Elemental Analyzer.

The analyzers are often constructed in modular form such that they can be set up in a number of different configurations to determine, for example, CHN, CHNS, CNS or N depending on the application. This adaptability allows not only flexibility of operation but also the use of a wide range of sample weights from a fraction of a milligram to several grams (macro-systems.) In its simplest form, simultaneous CHNS analysis requires high temperature combustion in an oxygen-rich environment and is based on the classical Pregl-Dumas method. This combustion can be carried out under both static conditions i.e. introduction of a set volume of oxygen or dynamic conditions i.e. a constant flow of oxygen for a set period of time. Often, catalysts are also added to the combustion tube in order to aid conversion (Thompson, 2008).

4.3 Bomb Calorimeter

A bomb calorimeter is a type of constant-volume calorimeter used in measuring the heat of combustion of a particular reaction. Bomb calorimeters have to withstand the large pressure within the calorimeter as the reaction is being measured. Electrical energy is used to ignite the fuel; as the fuel is burning, it will heat up the surrounding air, which expands and escapes through a tube that leads the air out of the calorimeter. When the air is escaping through the copper tube it will also heat up the water outside the tube. The temperature of the water allows for calculating calorie content of the fuel.

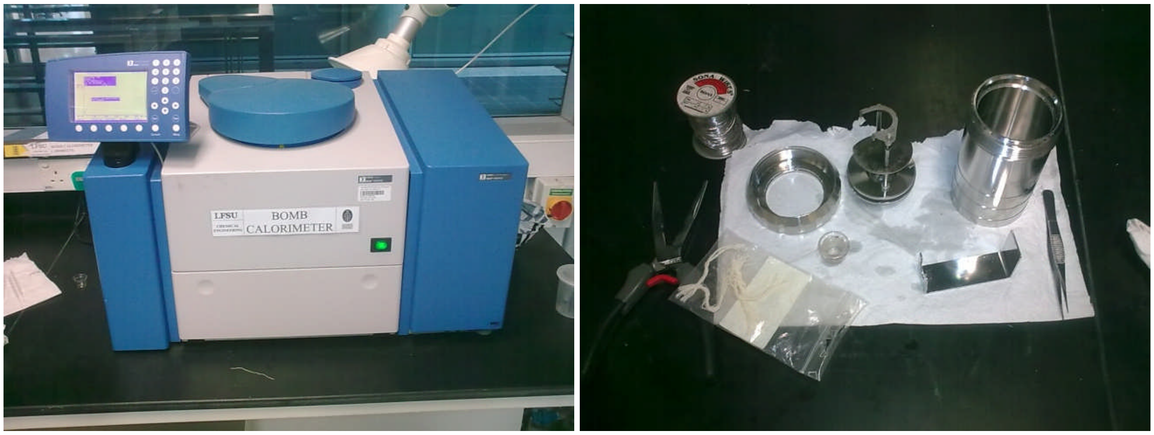

Figure 4.8: Bomb Calorimeter.

4.4 Muffle Furnace

Muffle furnace is a front-loading box-type oven or kiln for high-temperature applications such as fusing glass, creating enamel coatings, ceramics and soldering and brazing articles. They are also used in many research facilities, for example by chemists in order to determine what proportion of a sample is non-combustible and non-volatile (i.e., ash). Some digital controllers allow RS232 interface and permit the operator to program up to 126 segments, such as ramping, soaking, sintering, and more. Also, advances in materials for heating elements, such as molybdenum disilicide, can now produce working temperatures up to 1800 degrees Celsius, which facilitate more sophisticated metallurgical applications. The furnace is usually heated to desired temperatures by conduction, convection, or blackbody radiation from electrical resistance heating elements. Therefore there is (usually) no combustion involved in the temperature control of the system, which allows for much greater control of temperature uniformity and assures isolation of the material being heated from the byproducts of fuel combustion.

Figure 4.9: Muffle Furnce.

CHAPTER 5

RESULTS AND DISCUSSION

In Chapter 5, the product produced from the pyrolysis decomposition functions as the project's result. The product can be divided into three types, which are char, pyrolysis liquid and pyrolysis vapour. Analysis that was carried out for char was to get the CHNS content, calorific value, ash content and lastly moisture content. Next for pyrolysis liquid which also known as bio oil (project's main focus) the analysis that was carried out was CHNS content, calorific value and water content. The results obtain will also be compared with establish work and research on the similar field. In this chapter, discussion is included along with the graphs plotted to show the comparison and the effectiveness between Microwave decomposition and conventional heating method.

Two sets of experiments were carried out, which are the pre-experiment (run 1 and run 2) and main experiment (run 3, run, run 4, run 5, and run 6). The pre-experiment was carried out in order to validate and come up with a proper standard operating procedure. During this period lots of the parts of the reactor has been improved. These include the mechanical part of it, where certain equipment needs to be changed such as the thermocouple. During the pre-experiment the thermocouple which was originally installed was burnt out due to the excessive power of the microwave and the sharp angel that exist within the surface of the thermocouple. We learned that sparks will be produced if microwave comes in contact with a sharp angle, which will increase the temperature greatly and lead to the melting of the thermocouple. A new thermocouple was installed, which is slightly thicker from the previous and it was made sure not to have any sharp angle within its surface.

Besides the mechanical part of it, the operating procedures also were improved during the pre experiment. Some of the improvements that were carried out are, firstly on the mass input of the samples itself. For run 1 the input sample was 46 g while for run 2 the mass was doubled. For both the run we observed that mass input of 100 g was selected for the main experiments as the best product yield is obtain from run 2. This is because higher amount of samples will result in higher amount of char. Char acts as a microwave absorber when in contact with microwave. Higher amount of microwave absorber will absorb more microwaves which will lead to a better overall heating.

Char (%)	Liquid (%)	Gas (Estimated) (%)
48.65	**44.70**	**6.65**

Table 5.1: Product distribution and product yield of run #1

Char (%)	Liquid (%)	Gas (Estimated) (%)
38.46	**35.47**	**26.07**

Table 5.2: Product distribution and product yield of run #2

Secondly during the pre-experiments, few details were observed and need to be taken into consideration in order to get a better quality of product distribution as well as product quality. During the experiment the whole system will be in partial pressure due to the suction from the water aspirator. As liquid samples are collected this partial vacuum condition will first allow air to come in to the system to equalize the pressure. The air will contaminate the liquid product as water vapor in the air will condense and contaminate the bio-oil produced. In order to avoid this from taking place a graduate cylinder was attached and properly taped to the bio-oil sample port. When the valve is open the bio-oil will flow into the cylinder due to gravitational force and no air will enter the system as the system is still in a closed condition.

The highest temperature selection is 300^{o}C and 350^{o}C. this is because based on the 2 runs carried out, it is observed that 300^{o}C and 350^{o}C is the optimum temperature. The system cannot go more than 400^{o}C as the glass vessel for the placement of biomass samples may not withstand temperature greater that 400^{o}C.

The other method that was improved is for the collection of the balance char. During the experiment run 1, once the experiment was completed the oven chamber was left to cool up to 200^{o}C. Once the system is at 200^{o}C the oven chamber was open. The moment the chamber was open the balance char started to go into flames where the whole char turn into glowing red. This phenomenon that takes place will burn the char and convert the char into ashes, which will contaminate and spoil the char produced. This mainly occurs as the char is still at high temperature and any contact with Oxygen will definitely cause the char to burn.

To avoid this from taking place in the main experiment, the oven chamber will only be open when it reaches below 100^{o}C. This is proven during run 2 where the chamber was open when it's below 100^{o}C and the char did not catch fire. This point was also included in the Standard Operating Procedure for the reactor, in order to have a better quality of products.

Main Experiment

There were four runs of experiment that was carried out for the main experiment. All four runs that were performed have the objective of producing bio-oil at different conditions. The four runs that were carried out are as follow:-

Run#3	**2kW power input and maintain till 350^{o}C for total 70 minutes**
Run#4	**2 kW power input and maintain till 300^{o}C for total 70 minutes**
Run#5	**1 kW power input and maintain till 350^{o}C for total 70 minutes**
Run#6	**1 kW power input and maintain till 300^{o}C for total 70 minutes**

Table 5.3: Runs Specification

Liquid samples collected from all the runs can be classified into two categories. These two categories can be distinguished by the color of the liquid product produced. Based on the picture taken below there are two types of liquid produce which are brown in color and black in color.

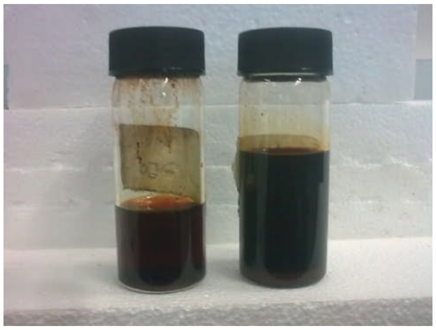

Figure 5.1: Run 3 Liquid Product

Figure 5.2: Run 4 Liquid Product

Figure 5.3: Run 5 Liquid Product

Figure 5.4: Run 6 Liquid Product

Based on the color of the liquid itself we can say that the liquid samples which are black in color are mainly bio-oil while the brown liquid are mainly mixture of water and light end of the bio-oil. This can be explained by observing the temperature profile where the water produced are mainly from the drying process that takes place before the Pyrolysis decomposition takes place. The water is mainly evaporated between the temperatures 100 – 130℃. On the other hand for the black liquid that was produced is mainly the product of the microwave Pyrolysis decomposition. Bio-oil samples which are the black liquid at the lower layer of the bio-oil sample collected are the one which is tested for all the analysis carried out.

	Run#3	**Run#4**	**Run#5**	**Run#6**
Initial Weight of Sample (g)	**100**	**100**	**100**	**100**
Char Collected (g)	**40.6**	**47.85**	**44.72**	**48.05**
Bio-Oil Collected (g)	**36.5**	**36.17**	**43.4**	**39.12**
Gas Estimated (g)	**22.9**	**15.98**	**11.88**	**12.83**

Table 5.4: Product Yield

5.1 Temperature Profile

All the experiments were set to complete within 70 minutes and the temperature of the experiment was recorded every two minutes for seventy minutes. Once the data of the temperature was collected, a temperature profile of the particular experiment was plotted.

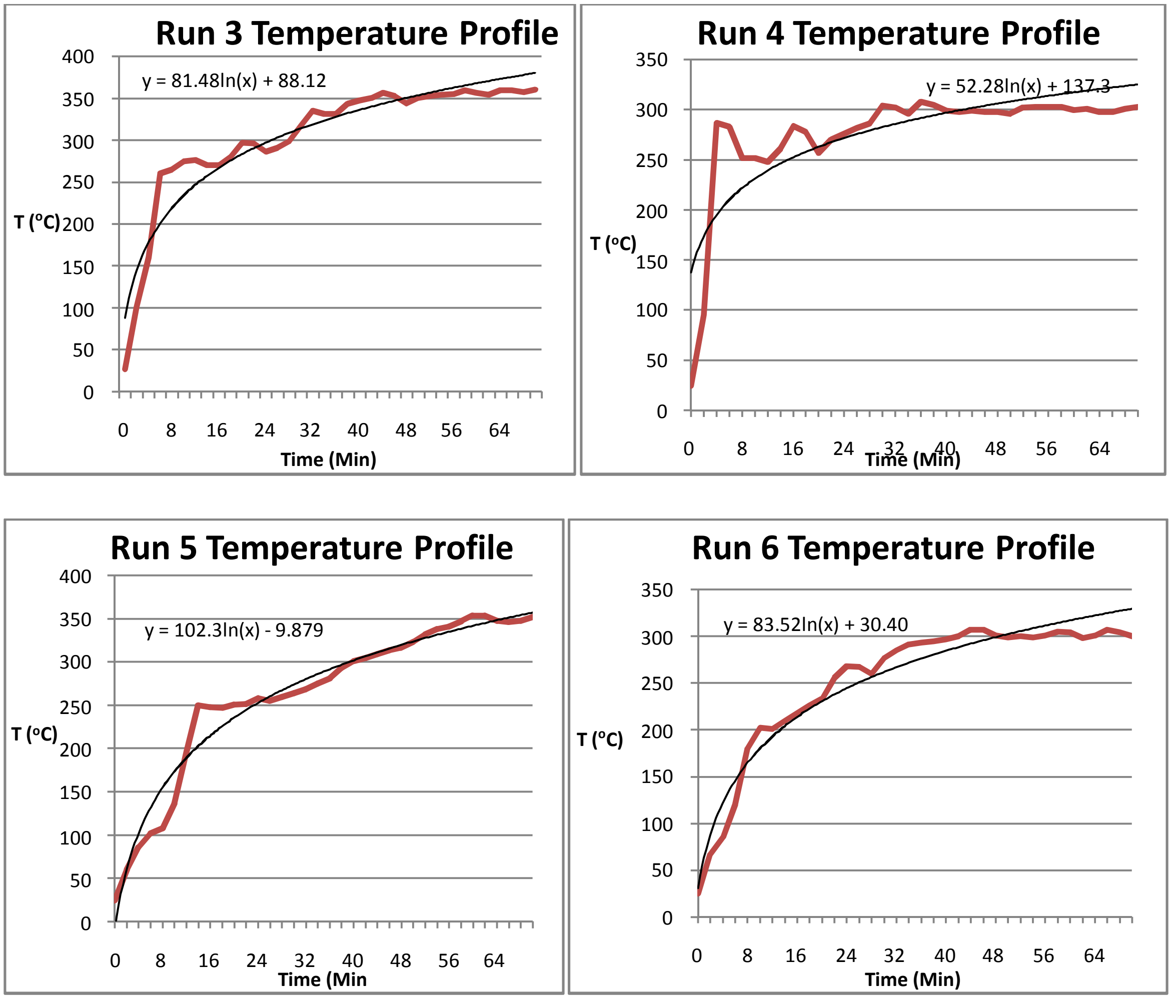

Figure 5.5: Runs Temperature Profile

All the temperature profile plotted has similar characteristic where all of the runs have a very steep slope for the first ten to fifteen minutes. For the next forty minutes the system have the lowest temperature increment, where the temperature will increase slightly, maintain and drop slightly through the forty minutes. Lastly the temperature is maintained to the desired set temperature. For the first stage, the biomass heating is very rapid because microwave carries very high amount of power. Since the drying of the biomass was also carried out before the main experiment less amount of moisture will be within the biomass sample. In accordance to this, not much energy are be absorb for the first 10 minutes to remove water from the samples, which results in the rapid temperature hike.

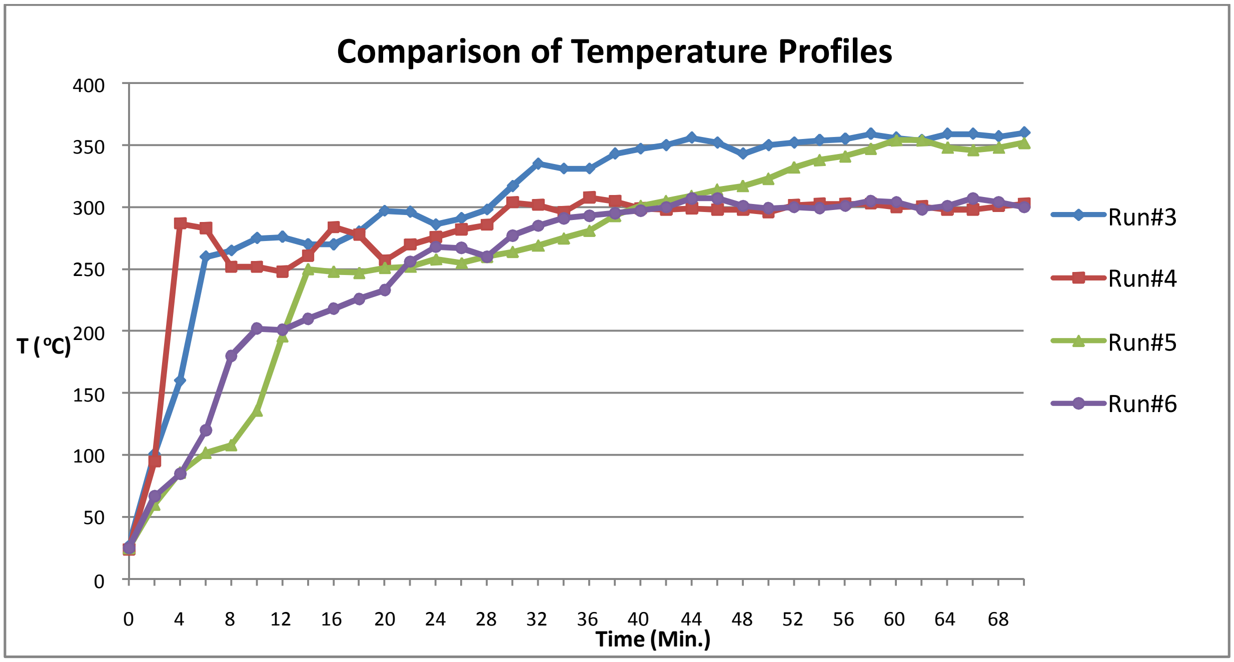

Figure 5.6: Comparison of temperature profiles

The next stage it has a lower temperature increment as the Pyrolysis process takes place in the stage. Lots of energy from microwave is being absorbed in order for the decomposition to take place making the temperature increment low. It is observed that the Pyrolysis process mainly takes place between the temperatures of 250 – 300℃. As shown in the figure above, the temperature hold up is longest within the range of 250 – 300^{o}C, where lots of activities is taking place during this period. This shows that the optimum temperature for microwave induced Pyrolysis that was carried out is between 250 – 300^{o}C, which is very much lower compare to the Pyrolysis temperature using conventional heating which is in the rage of 400^{0}C

From the product produced, it is observed that the liquid product is mainly produce within the temperature range of 200 – 300^{o}C. After 300^{o}C the production of liquid decreases but the production of Pyrolysis vapor still occurs till the end of the experiment.

5.2 Calorific Value

Calorific value for bio-oil is very much less compared to hydrocarbon fuel. This is mainly due to the high water content in bio-oil and also the lower carbon content in the bio-oil compared to Petroleum based oil. The calorific value for all the runs are stated in the table below:-

	CV#1 (j/g)	CV#2 (j/g)	Average CV (j/g)
RUN 3	22330	22481	22406
RUN 4	24245	24070	24158
RUN 5	27801	25586	26694
RUN 6	22968	23596	23282

Table 5.5: Bio-Oil Calorific value

	CV#1 (j/g)	CV#2 (j/g)	Average CV (j/g)
RUN 3	27492	27336	27414
RUN 4	27222	27318	27270
RUN 5	26726	26538	26632
RUN 6	26554	26182	26368

Table 5.6: Char Calorific value

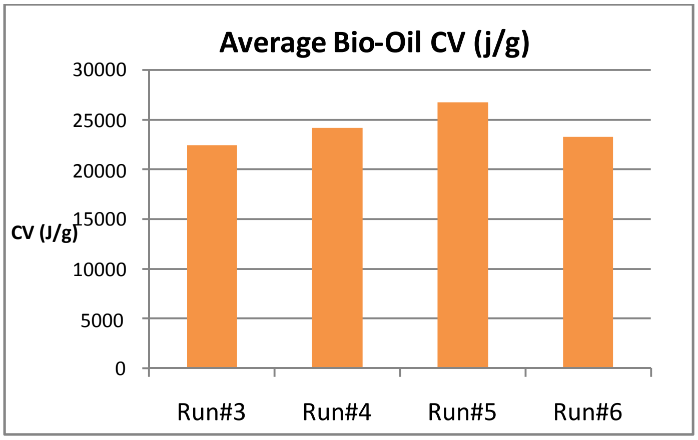

Figure 5.7: Average Bio-oil CV

From the figure above we can see that run 5 has the highest calorific value compared to the runs. This shows that the operating condition for run 5 (1 kW and maintain at 350 °C) produced bio-oil with the highest calorific value.

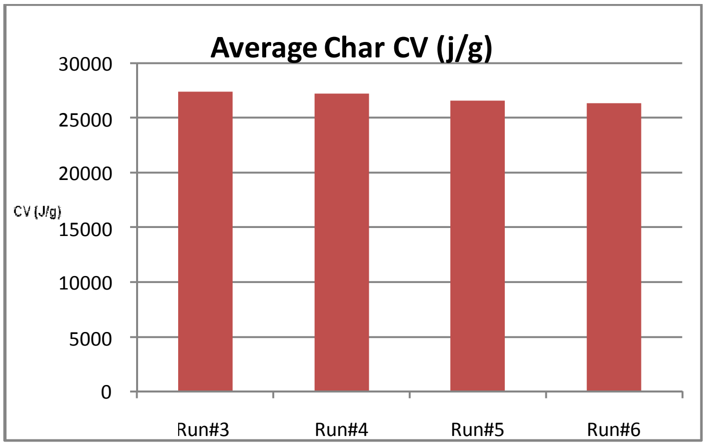

Figure 5.8: Average Char CV

The Calorific values for the char produced are almost the same for all run. This shows that the quality of char produced from all the runs are almost equal with run 3 the highest about 27400 j/g. Figure below shows the comparison of run 3, run 4, run 5 and run 6 with other types of bio-oil. Bio-oil from rapeseed has the highest value of calorific value which is 38400 j/g. As stated in the literature, the existence of water will highly affect the calorific value of the bio-oil. The calorific value can also be affected by the number of carbon in the bio-oil. The calorific values of the bio-oil produced are compared with the bio-oil from other source.

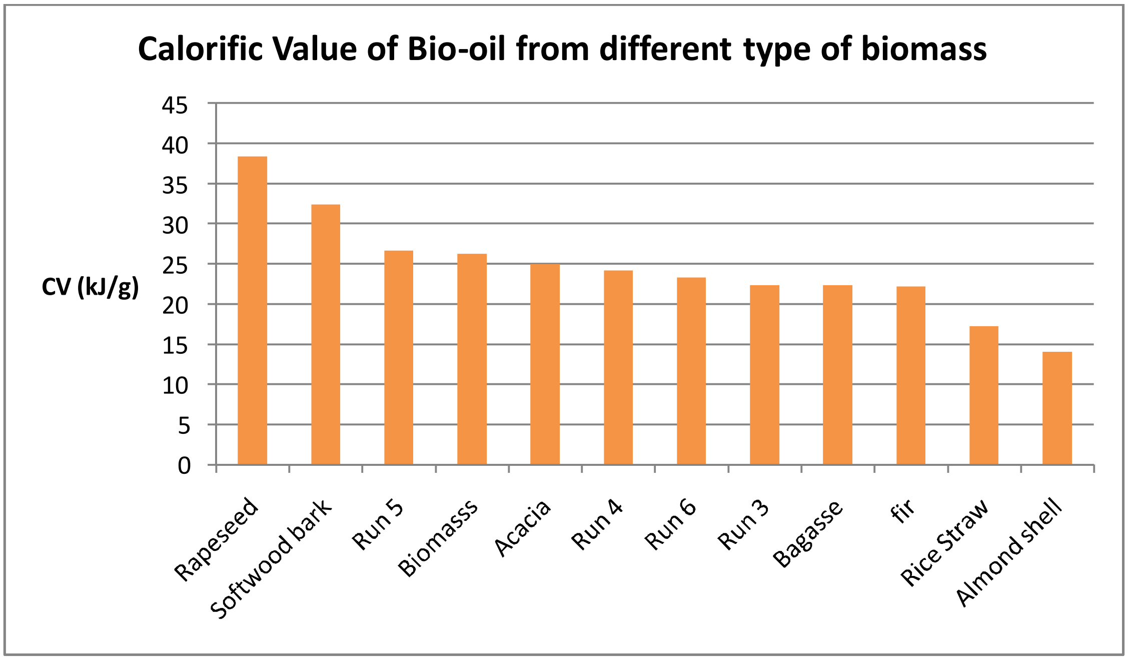

Figure 5.9: Calorific Value from different type of Biomass

The comparison of the bio-oil produced with the establish bio-oil shows that the bio-oil produce is up to the quality of an establish bio-oil from other source n method. We can also see that run 5 has one of the highest calorific value compare to all type of bio-oil shown above.

5.3 Elemental Analysis (C, H, N)

The elemental analysis for Carbon, Hydrogen and Nitrogen was carried out to determine the main content of the bio-oil and char produced. Figure below shows the elemental content of the product produced.

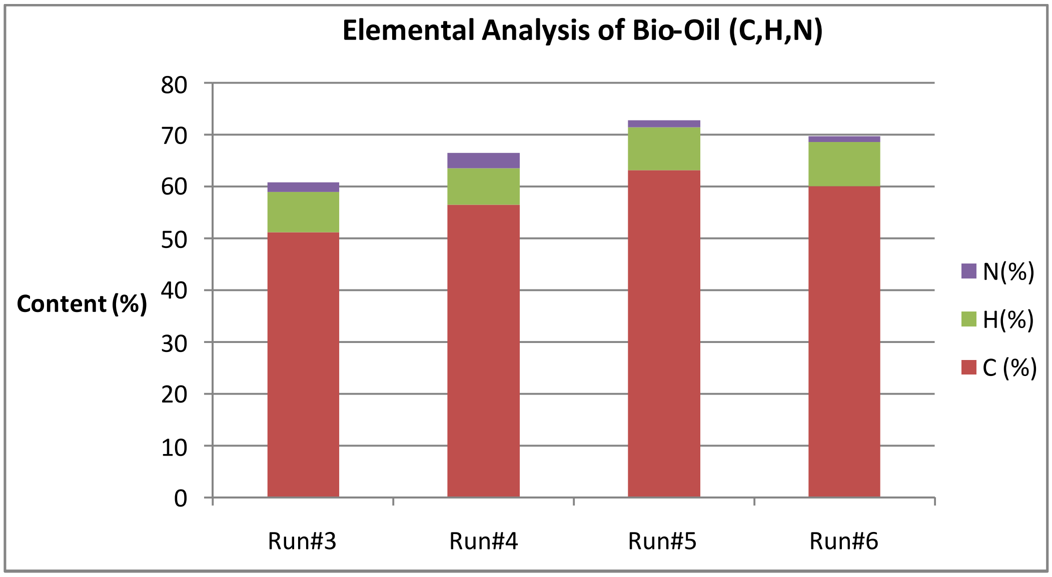

Figure 5.10: Elemental analysis of bio-oil produced

The carbon content for all the run are high which shows that the bio-oil produced is very fine. This shows that microwave manage to decompose the biomass sample into bio-oil accordingly and effectively because of the heating approach of the microwave itself. Microwave heating is from the core of the sample and move outwards to the surface. This phenomenon will allow the entire volatile component in the sample to escape without being altered by the high amount of heat on the surface.

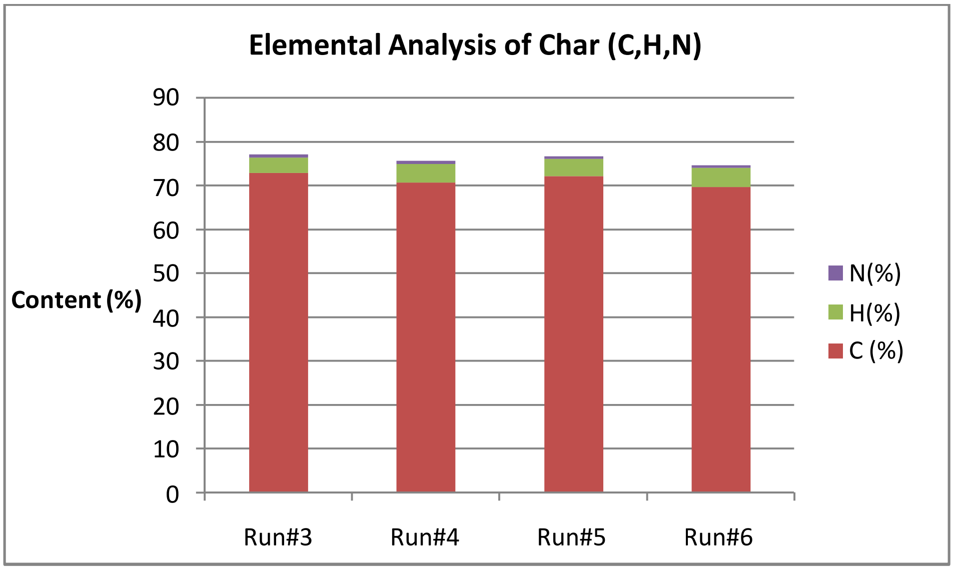

Figure 5.11: Elemental analysis of char produced

	C (WT%)	H (WT%)	N (WT%)
RUN 3	51.14	7.77	1.77
RUN 4	56.43	7.07	2.96
RUN 5	63.06	8.33	1.29
RUN 6	59.98	8.60	0.99

Table 5.7: Elemental analysis of Bio-oil

	C (WT %)	H(WT %)	N(WT %)
RUN 3	72.87	3.46	0.77
RUN 4	70.65	4.21	0.71
RUN 5	72.04	3.93	0.60
RUN 6	69.56	4.43	0.59

Table 5.8: Elemental analysis of Char

The difference between the elemental content of the bio-oil and char is mainly the amount of Hydrogen content. Bio-oil has a higher amount of hydrogen because the bio-oil produced is made of hydrocarbon compound, making it necessary for amount of Hydrogen to be high. While on the other hand for char mainly compose of carbon. This shows that the results obtained are justified.

Figure below shows the comparison between Carbon, Hydrogen, Nitrogen and Oxygen in various type of bio-oil. The sulfur content is very low and is neglected. The amount of Oxygen is obtained by subtracting 100 with the total amount of Carbon, Hydrogen and Nitrogen. When the carbon content is high indirectly it shows that the amount of oxygen is low. The trend can be observed below where when the carbon content is getting lower the oxygen content will increase. The amount of Oxygen in the bio-oil is mainly produced by water and other oxygenated compound.

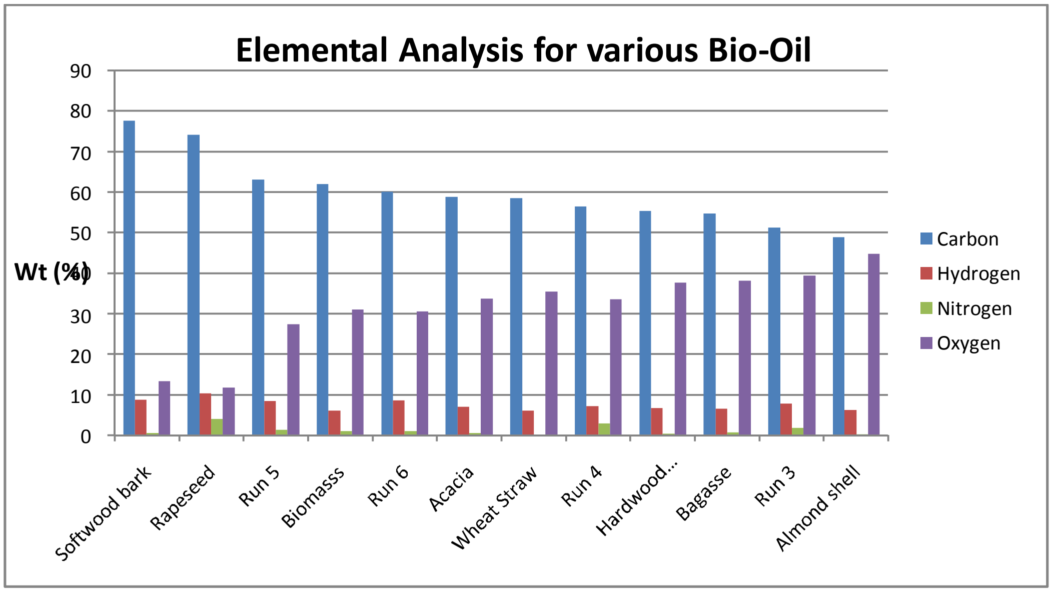

Figure 5.12: Elemental analysis of various bio-oil

5.4 Ash Content Analysis.

The main purpose of finding out the ash content is mainly to know how much is the balance ash that will remain within a certain system after the combustion takes place. Based on the literature obtained the ash content for Bio-oil supposed to be very low between 0.03 wt% - 0 wt%.

	Char (wt%)	Bio-Oil (wt%)
RUN 3	1.93	0.268
RUN 4	2.21	0.32
RUN 5	1.88	0.392
RUN 6	1.96	0.351

Table 5.9: Ash Content of Char and Bio-oil

Based on the results obtained the bio-oil ash content is slightly higher than the commercial Bio-oil, this is because the bio-oil obtain from the experiment are not filtered and treated and it may contain some impurities from the char causing the amount of ash within the samples to be slightly elevated.

5.5 Comparison between Experiment Runs

Four runs of experiment were carried out. All of the runs have at least one difference in operation condition, where it is either power input or the end temperature. Comparisons of all the four runs are tabulated in the figures below.

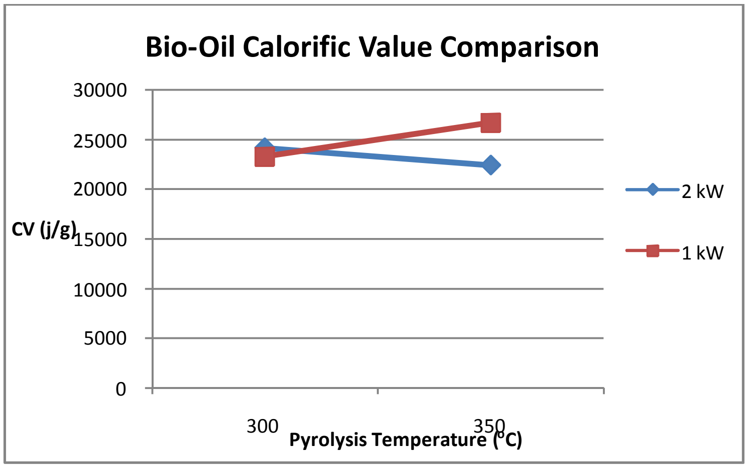

Figure 5.13: Bio-oil Calorific Value Comparison

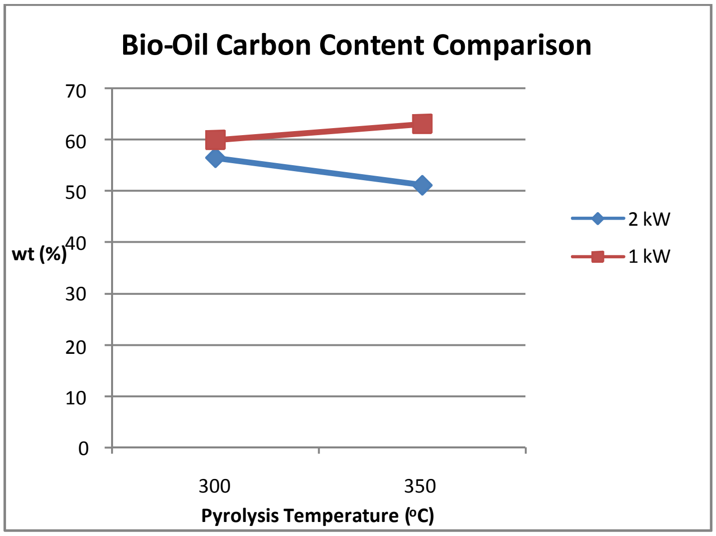

Figure 5.14: Bio-oil Carbon Content Comparison

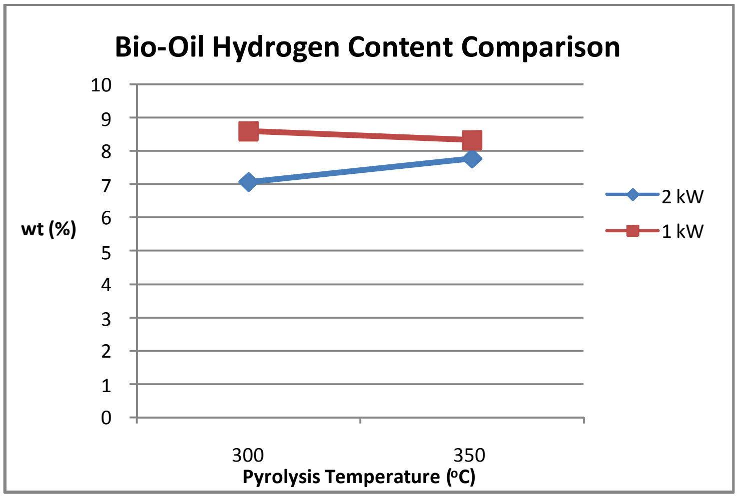

Figure 5.15: Bio-oil Hydrogen Content Comparison

From all the runs, we can conclude that run 5 (1 kW and 350^{o}C), has the best Bio-oil properties compared to the other runs (Highest Calorific value and highest carbon content for bio-oil). This can be explained by looking at the amount of power input. Lower power input will enable slow and better heating as the heating will be graduate and overall. Too high power input will results in overheating of the sample which will slightly alter the desired product. Higher pyrolysis temperature will enable the entire component to be decomposed entirely and effectively.

The highest content of carbon is from the liquid collected at 350℃ which is almost the same as the carbon content of the char. This shows that at 350^{o}C the decomposition is at its optimum temperature and most of the samples decomposed into liquid Pyrolysis during this period as what can be seen in the temperature profile. The physical appearance of the bio-oil collected at 350℃ which is really black in color shows that during this period the production of bio-oil is at its optimum.Based on the experiment carried out the optimum operating condition to produced the best bio-oil is using 1 kW of power input and maintains the temperature at 350^{o}C.

CONCLUSION

This research has investigated the decomposition behavior and properties of the bio-oil from kernel shell using microwave induced Pyrolysis. Throughout the research period all the information was gathered from all reliable resources such as article, journals and online resources. The main focus of this project is to study the decomposition behavior, obtained the best operating condition and basic product analysis (calorific value and elemental analysis). Therefore the knowledge and experience in Chemical Engineering study has fully utilized to conduct the experiment and research. The research is conducted using various types of equipment and apparatus according to the characteristic of bio-oil that need to be studied. Data obtained from the experimental work have been analyzed and compared with properties of several types of bio-oil. Thus, this project has fully completed and meets the objectives.

The carbon content in the bio-oil produced from the microwave induced Pyrolysis decomposition at low Pyrolysis temperature which is 350^oC, is between 50 – 65 wt %. Hence, the bio-oil has a potential to be a renewable source of energy since the high content of carbon in bio-oil encourage toward high calorific value. However the water content and oxygen reduces the bio-oil effectiveness as fuel and also imparted to several unwanted characteristic. High water content makes the bio-oil less viscous and easy to handle. Since there are various advantages and disadvantages in property of bio-oil, further studies need to be done according to the purpose of bio-oil for marketing purposes. Moreover utilization of bio-oil from Kernel Shell could reduce the environmental pollution and waste of palm oil resources.

Lastly Fast pyrolysis using microwave as a thermal heat source have improved the product distribution and yield. It also brought down the Pyrolysis temperature to 350^oC and with the power input of 1 kW. This is shown in previous studies that microwaves has a better heating mechanism compared to the conventional way of heating.

RECOMMENDATIONS

For recommendations, the main product produced through the microwave induced Pyrolysis which is Bio-oil and Char can be further enhanced and upgraded into fuel source and also activated carbon for commercial use and distribution. The experiment carried out should also use other sample of biomass such as Empty Fruit Bunch (EFB), Fiber, Trunk and also Frond. As these other components of the palm oil are yet to be explored using microwave decomposition.

Different sizes of biomass should also be tested to get the best and optimum size for the decomposition to take place. Different sizes will lead to a different pattern of production and the best size should be chosen for further studies of this technology. Microwave absorber (SiC) should also be included within the system in order to increase the microwave absorption rate hence increase the heating and also decomposition rated of the biomass.

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