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# Thermal extraction of bamboo with various solvents

By

Junghee Kim

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# ABSTRACT

This thesis is to describe the potential of improvement by liquefaction with various solvents in pyrolysis in terms of conversion of bamboo to gas and liquid and quality of the bio-oils and residues produced.

Fluidised sand bath and pressure gauge reactor were used for pyrolysis. The reactor was coupled with bamboo and a solvent and after 1 hour of pyrolysis and liquefaction at 410°C, the gas produced was collected in gas bag. To extract compounds uniformly from the chemically decomposed biomass mixture, soxhlet extraction was applied for between 17 and 20 hours. Then the residues were filtered. Solvents in the liquid were evaporated and distilled. Then, fractionation was performed and Gas Chromatography / Mass Spectrometry(GC-MS) was used to analyse the each fraction. Gas Chromatography(GC) and Elemental Analyser(EA) were used for analyses of the gas, bio-oil and residue.

The analytical results showed the liquefaction increased the overall conversion rate of bamboo to liquid and gas (13 -33% more than pyrolysis without using any solvents) and improved quality of the residues ( decreased O(%), increased H(%), H/O: 0.5 – 0.8, O/C: 0.5 -0.12, HHV:24 - 32 MJ/kg, ash content: 5 – 10%, ash free content: 12– 35 %) and bio-oils ( decreased O(%), increased H(%), H/C: 1 -2, O/C: 0 – 0.05, HHV: 38 - 48 MJ/kg). Solvents in the liquefaction carried out as carriers of H or donors preventing from a cross-linking effect. The highest conversion rate (around 90%) was shown in tetralin due to its high hydrogen donating nature.

The bio-oils are assumed as bitumen-like materials based on their dark brown colour, high viscosity and common functional groups with bitumen.

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# CHAPTER ONE
# INTRODUCTION

As concerns over environmental matters and the shortage of energy supply grow, the creation and use of renewable energy become more important. Biomass is one way with high potential. Because bio-fuels from biomass are reproducible, it has been considered as a promising energy source. However, the quality of bio-fuels is not as good as the petroleum derived fuels. There have been many efforts to improve the profitability and quality of bio-fuels. One effort to improve quality of bio-fuels is pyrolysis. The Pyrolysis is one of the thermo-chemical conversion processes of biomass. This is a good method of obtaining low molecular weight liquid, gas fuel and solid residue.  The majority of products are liquids usually called pyrolysis-oils or bio-oils.

However, the high operating temperature of pyrolysis (673-1273 K) can cause cross-linking reactions between hydrocarbons and aromatics which turn to tar difficult to further decompose. (Zhengang Liu and Fu-Shen Zhang, 2008) In addition, the pyrolysis-oils include more oxygen contents and water contents which reduce efficiency (Zhang et al.,2007).

According to Zhang Qi et al. (2004), one specialty of bio-oils is that they have water content of up to 15-30 weight % in original feedstock or the products. This can lower the heating value and flame temperature but can reduce the viscosity, increasing fluidity helpful to atomization and combustion of bio-oil.

Because of this disadvantage of pyrolysis, solvent extraction technology studied in coal for years was applied to pyrolysis of biomass.  Biomass is different from coal because it has a relatively high hydrogen-to-carbon ratio, but also has a very high oxygen content lowering its heating value significantly.  However, its oxygen content is around 50 wt% in comparison with 10 wt% for coal. Therefore, to convert direct liquefaction of biomass to upgraded-quality liquid fuels, two methods can possibly be used. First, the removal of oxygen by emitting carbon monoxide (as $CO_2$) from biomass used can allow the biomass to be converted to upgraded-quality liquid fuels. Second, the addition of hydrogen can allow the biomass to be converted to upgraded-quality liquid fuels.(Nicholas et al.,1985)

The solvent extraction technique called liquefaction is a focus of study in terms of converting biomass to useful energy source using solvent. Liquefaction has been in attention because it can overcome the main disadvantage of pyrolysis, the "cross-linking effect". The main advantages of the liquefaction (Zhengang Liu and Fu-Shen Zhang, 2008) are

1. Through usage of a solvent, the dilution of concentration of the products can prevent cross-linking reactions and reverse reactions.
2. Relatively low temperature (less energy consumption) compared with pyrolysis and gasification because the solvent plays an important role in the solvent liquefaction reaction.
3. In lowering the viscosity of heavy oil from biomass in liquefaction, solvolysis in the presence of organic solvents is proven to lower the viscosity of heavy oil effectively from biomass or coal.
4. In addition, through the solvent liquefaction, oxygen can be depleted which can improve properties of the final liquid product while the pyrolysis oil includes a large portion of oxygen.

Various solvents can play ɑ role of hydrogen donors as long as they include mobile carbon-hydrogen bonds. Hereby, good solvents can be defined as solvents that are able to dehydrogenate readily under pyrolysis conditions resulting in enhancement of its salvation capabilities. Tetralin is one of the highly effective hydrogen-donor solvents. (Nicholas, P. et al. 1985) Nicholas, P. et al. (1985) stated that hydrogen can play a role as the deoxygenating agent ($H_2O$ formation) or as a hydrogenolysis agent (causing a complicated scheme of biomass depolymerisation reactions.) Research was focused on the study of the use of molecular hydrogen as a reducing agent for biomass hydrogenolysis. Larsen(1988) studied the macromolecular network structure of bituminous coals by using the classical solvent-swelling techniques of polymer chemistry. Solvents were acting as hydrogen bond acceptors which strongly enhanced solubility (coal swelling). The coal swelling was correlated to the strength of the hydrogen bond between the solvent and p-fluorophenol. Pott and Broche (1934) proved that tetralin was the original hydrogen donor for the extraction of coal.

On the other hand, Triglyceride based agricultural fats and oils brought more interest as alternative feeds for the production of fuels from biomass. Sonntag (1979) stated that bio oils and fats are mainly water insoluble, hydrophobic substances in the animal and plant world. They are composed of one mole of glycerol and three moles of fatty acids which are usually called triglycerides. The composition of vegetable oils is almost completely composed of triglycerides and a small percentage of mono and diglycerides. Karaosmanoglu (1999) reported that advantages of utilizing vegetable oils include their liquid nature convenient for transport and processing, and their content (close to 90% of diesel fuel). Katikaneni et al. (1995) also stated that Vegetable oil fuels contain no water, are pH neutral, and are relatively stable. Shay (1993) mentioned the feasibility of the usage of triglycerides as a source of energy, demonstrating the usage of engines with vegetable oils.

However, Knothe et al. (1997) mentioned that the common use and commercialization of vegetable oil fuels was banned due to economical reasons and poor properties. Despite the disadvantage, Graboski and McCormick (1998) suggested a new possibility of upgrading the vegetable oils to useful alternative fuels due to the fact that pyrolysis of these materials could produce hydrocarbon rich liquid fuels which might contain a significant fraction of the hydrocarbon content of petroleum based distillates and petrochemicals. Knothe et al. (1997) reported that vegetable oils are suitable for diesel fuel due to the fact that their molecular structure and high energy content are significantly similar to the diesel fuel. Ali and Hanna (1994), Knothe et al. (1997) and Ma and Hanna (1999) reported that the heat content of raw fats and oils was about 80-90% of No. 2 diesel fuel.

Because solvent extraction has mostly been applied to coal until now, the benefit of the solvent extraction in biomass is not well known. In this research, Pyrolysis which has been done with biomass for a long time was applied with solvent extraction. For the usage of different solvents, the change of conversion rate has been checked.

In particular, bamboo and waste oil from cooking pork have been investigated as biomass and solvent respectively for renewable energy and recycling purposes. Bamboo is very popular and cheap in Asia, including Korea, as well as growing very fast, and the waste oil from cooking pork is all wasted despite the fact that Koreans eat a lot of pork and therefore generate a huge amount of waste oil. For these reasons there is a possibility for significant cost saving if it is recycled.

The overall goal of this research will be to assess the potential of improvement by liquefaction using bamboo biomass available in South Korea with various solvents in pyrolysis in terms of conversion of biomass to gas and liquid and quality of the bio-oils and residues produced and to characterise the bio-oils produced..
The following objectives will make the goal achievable.

1. To determine optimum operating solvents (generalised into; hydrogen donor solvent (tetralin) and non-hydrogen donor solvent (more strictly speaking,

less effectively hydrogen donating solvent; 1-methylnaphthalene, vegetable cooking oil and waste oil from cooking pork); hydrocarbon solvent (and bio-oil derived solvent) for the conversion of biomass to bio-oil products. Note: There are baseline runs of bamboo with no solvent and with water in the pyrolysis.

2. To determine n-alkane gases produced during the pyrolysis and liquefaction.
3. To determine elemental composition and ash contents of residues produced and to predict O/C, H/C and HHV of the residues during the process.
4. To determine elemental composition of bio-oils produced and to predict O/C, H/C, HHV of the bio-oils during the process.
5. To observe the bio-oils produced apparently.
6. To determine fractions of the bio-oils produced
7. To characterize the fractions of the bio-oils produced during the process qualitatively.
8. To explore the feasibility of using bamboo as a biomass and waste oil from cooking pork as a solvent in the process.

# CHAPTER TWO
# LITERATURE REVIEW

## 2.1 Biomass utilization

Gail Taylor et al.(2008) stated that renewable energy sources for sustainability are regarded as more important due to the growing importance of satisfying environmental concerns over fossil fuel usage. Bio-fuel products have been one of the most important methods to meet growing demands. Therefore, the bio fuels can help reduce common concerns among different countries referring to serious emissions such as $CO_2$, NOx, and SOx during conventional fuel combustion.

Zhang Qi. (2007) considered the fact that limited fossil fuels including petroleum derived fuels would be exhausted soon due to increasing energy consumption, populations and economic developments. They suggested biomass as a renewable energy source which can be widely explored for renovation of energy sources structure and sustainable development. The point that the biomass is clean was indicated in the sense that it has negligible content of sulphur, nitrogen and ash. When the biomass is used as energy source, less emissions of $SO_2$, $NO_x$ and soot were predicted than petroleum derived fuels. They also suggested that zero net emission of $CO_2$ could be possible if $CO_2$ released from biomass is recycled into the plants by photosynthesis alternatively.

Many efforts to find new bio-energy have been made by many countries;
Brammera et al.(2006) indicates European countries' efforts to invent or apply new bio-fuel to new energy. In this research, Bio-oil applications have been compared with previous fossil fuels. Based on a quantitative assessment of the economic competitiveness of standard applications in 14 European countries, with location-specific data being collected and being combined with technology-specific data, a competitiveness factor (Cf) was derived to analyse the total annual cost of the bio-fuels. The result showed that in all researched countries, at least one of the applications was useful and in the larger scale, the bio-oil application is more competitive.

According to Saxena et al. (2009), wood and other forms including crops, agricultural and forestry wastes are considered as biomass sources for bio-fuel, being able to be provided in the form of liquid, gaseous and solid fuels. The biomass fuels from these biomass sources can be changed to energy through thermal process.

Sunderasan Srinivasan (2009) indicated that there are negative points of view on bio-fuels produced due to the following reasons; In terms of the energy balance, the energy efficiency of bio products is not always good. In other words, production cost, maintenance cost in bio-refinery process, raw materials delivery cost (including transportation cost and capital cost) should be considered. In other words, some bio-fuels from crops or corns for feedstock could produce less valued energy.

Kumar et al.(2003) reported that the delivery cost of biomass is in the range of 54-57% of the total bio-ethanol cost, followed by operation and maintenance costs (27-31%) and capital costs (16-18%). The transportation cost is about 19% of the biomass delivery cost. So, rather than biomass costs, additional costs are a larger portion of the total price.

As one of the efforts to solve partiality of biomass resources, Bram, S. et al.(2009) suggest System Perturbation Analysis (SPA). SPA is able to identify the best usage of limited resources in Belgium looking into geographical system’s balance of resources and the resulting effects. So, SPA is able to identify the best usage of limited resources such as hectares, wood waste or imports within a given system. By sending and supplying biomass such as wood or paper through the most economical way, generation of bio-energy will be the most efficient.

### 2.1.1 Concept of Biomass

Saxena et al.(2009) stated that biomass is a known biological object that has originated from a living being, or living organisms.

### 2.1.2 Components of Biomass

Biomass including bamboo is composed of complex structures that are difficult to separate into basic components for downstream processing. According to Xiaoyu Zhang et al.(2007), bamboo is composed of components of lignin, cellulose and hemicelluloses. Component percentage of the biomass including bamboo is typically as follows (Cited from Nexant ChemSystems, 2008);

- 10-26 weight% Lignin: Lignin is a large hydrophobic (mostly aromatic) polymer composed primarily of amino acids, one of the most important being phenylalanine. The exact structure of lignin varies not only among plant species, but within species if members of populations are exposed to different environmental conditions (both biotic and abiotic).

- 40- 60 weight% Cellulose: Cellulose is a polymer of glucose molecules (6-carbon sugars) that have a beta 1-4 linkage. This bond is resistant to chemical attack due to the high degree of hydrogen bonding that can take place between the aligned strands. These bonds block the entry of chemicals or enzymes that could cleave the linkage between glucose molecules.

- 20-40 weight% Hemicellulose: Hemicellulose is a polymer made of 5-carbon sugars (usually xylose and arabinose), 6-carbon sugars (galactose, glucose and mannose) and uric acid. Hemicellulose is highly branched and unlike cellulose is easy to convert (via hydrolysis) into its constituent sugars.

Note: According to research on bamboo by Su-Hwa Jung et al., components of bamboo were composed of 25.3% Lignin, 41% Cellulose and 26.5% Hemicellulose.

Both cellulose and hemicellulose are hydrophilic and are at risk of being degraded when exposed to moisture. Therefore, lignin performs the important function of allowing the structural components of plants to remain watertight, except for that required to maintain their metabolism.

### 2.1.3 Lignin Molecular Structure

Lebo (2001) defined that Lignin is a complex chemical compound most commonly derived from wood and an integral part of the second cell walls of plants.

Boerjan et al.(2003) stated that it is one of the most abundant organic polymers on earth, superseded only by cellulose, constituting 30% of non-fossil organic carbon.

The lignin is made from complex organic polymers, the molecular structure is as below. Lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000 u. It is relatively hydrophobic and aromatic in nature. The degree of polymerization in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures which appear to repeat in a haphazard manner.(Cited from Lignin Institute, 2001)
Figure 2.1 shows chemical structure of lignin.

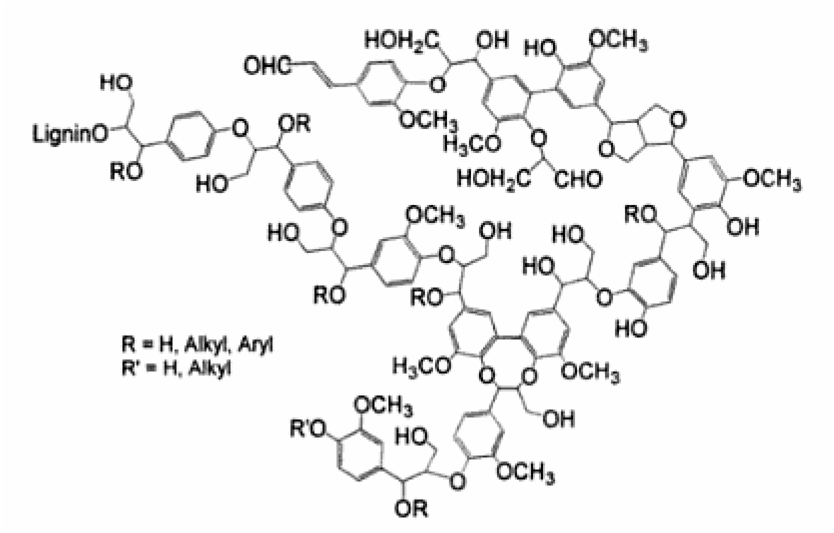


Figure 2.1: Chemical structure of lignin (Cited from Thomas Q. Hu, 2002)

Lignin is an aromatic polymer comprising hydroxy- and methoxy- substituted phenylpropanoid units linked by several ether and carbon-carbon bonds (Adler,1977).

Its native structure is not yet fully understood due to the lack of an isolation method that does not cause chemical alterations. Nevertheless, it is widely accepted that lignin is a polymer made of three different p-hydroxycinnamyl alcohols: p-coumaryl, coniferyl, and sinapyl alcohols linked through an enzyme-catalysed dehydrogenative polymerization process (Fengel and Wegener, 1983)

The aromatic portions of these phenylpropanoid precursors are known as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) moieties respectively. The syringyl to guaiacyl ratio (S/G) is used to distinguish between types of lignin. Angiosperms (e.g. beech, oak) contain lignin made from mixtures of guaiacyl and syringyl moieties, whereas gymnosperms (e.g. pine, spruce) contain lignin made only from guaiacyl alcohol. Most lignins have a small proportion (less than 10%) of p-hydroxyphenyl units (Kirk, 1981).

The first step in the polymerization of lignin monomers is the enzymatic dehydrogenation of p-hydroxycinnamyl alcohols forming phenoxy radicals that have the highest $\pi$-electron densities at the phenolic oxygen atom

This favours the formation of aryl ether linkages such as the $\beta$-o-4 by radical coupling reactions, which is sometimes followed by the nucleophilic addition of water or of primary, secondary, and phenolic hydroxyl groups (Fengel and Wegener, 1983). The most frequent interunit linkage is the β-o-4 between the C4 position of the aromatic ring in one monomer and the β- carbon of the side chain in another monomer..

According to Kirk et al.(1984), lignin is known to be the most thermally resistant of the three main components of biomass. The complexity of lignin polymers and the disadvantages of extracted lignins have made it difficult for low molecular weight compounds related to the structureal elements of lignin polymers to be used for research on the pyrolysis behavior of lignins.

### 2.1.4 Cellulose Molecular Structure

Definition: Cellulose is an organic compound having complex structure usually composing of plant tissues. This has the empirical constitution characteristic of the carbohydrates ($C_nH_{2m}O_m$).(Cross  2005)

Asri Gani and Ichiro Naruse (2007) found that active cellulose was quite unstable at high temperature, and easily decomposed into saccharides with lower DP, even char, volatiles and gaseous products. They proved that the cellulose is more unstable than lignin.

Sébastien Baumlin et al (2006) studied the rate of loss and production rates of lignin by forming a liquid compound that precedes the further formation of char, vapours and gases. High syngas and H2 contents (respectively 87 and 50 mol%) are analysed from produced gases.

Beramendi Orosco (2004) cited Mazany et al.(1980) said that cellulose appeared more sensitive to climate than lignin. And he also cited that Hedges et al.(1985) and Benner et al.(1987) demonstrated that under anaerobic conditions lignin is more resistant to degradation than the cellulose fraction, which makes it clear that any change in cellulose content because of decay can cause misinterpretation. Due to this fact, some studies have focused on lignin and lignin derivatives.

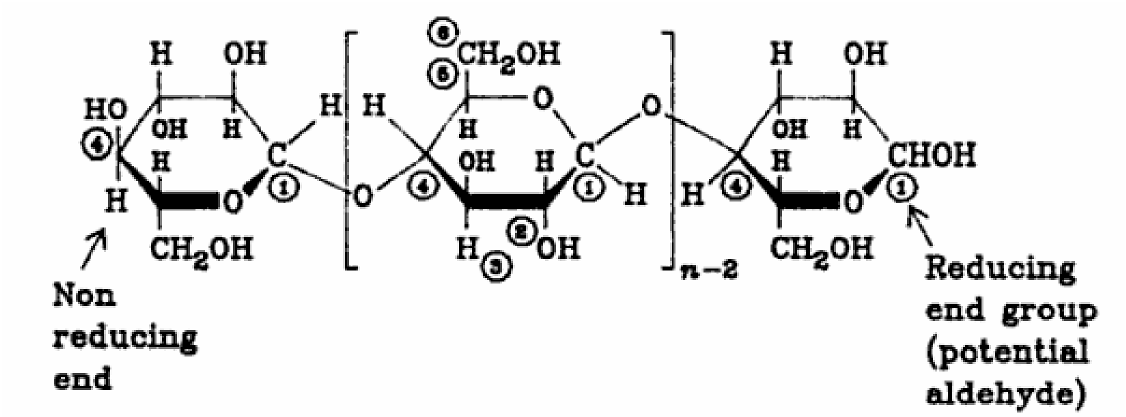


Figure 2.2: Chemical structure of Cellulose (Cited from Hans and Krässig, 1993)

### 2.1.5 Hemicellulose Molecular Structure

Definition – A hemicellulose can be any of several heteropolymers (matrix polysaccharides) present in almost all cell walls along with cellulose.

Their molecular weights are usually lower than that of cellulose and they have a weak undifferentiated structure compared to crystalline cellulose. But the chains form a 'ground' - they bind with pectin to cellulose to form a network of cross-linked fibres. Hemicelluloses include xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan. As percentage content of hemicellulose increases in animal feed the voluntary feed intake decreases.

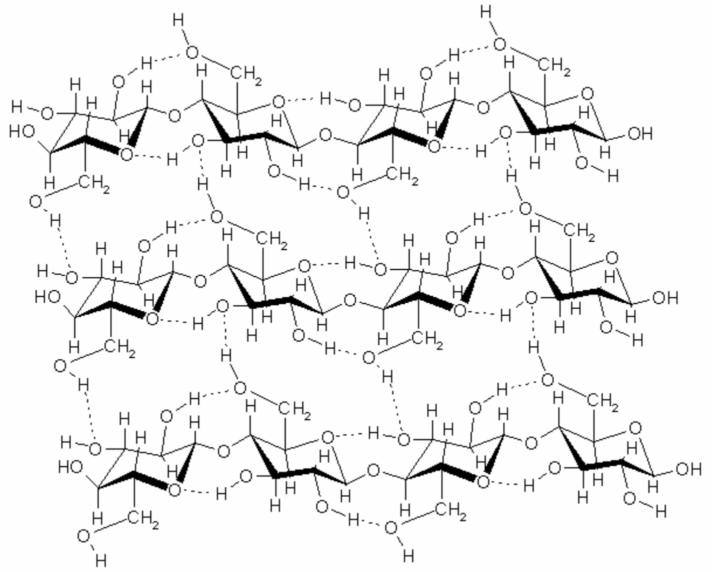


Figure 2.3: Chemical structure of Hemicellulose
(Cited from DoITPoMS, The University of Cambridge)

Haiping Yang et al.(2007) found that in TGA, pyrolysis of hemicellulose and cellulose occurred quickly with weight loss. However, lignin was relatively difficult to decompose and weight loss happened in a wide range of temperature. They also found that pyrolysis of cellulose was endothermic while that of lignin and hemicellulose was exothermic. However, gas products from pyrolysis of the three components were similar. Cellulose and hemicellulose among these main components are highly degradable in moisture. Therefore, liginin conducts the important role of allowing the biomass structural component to remain watertight.

## 2.2 Pyrolysis

Biomass decomposes into mostly vapours and aerosols some charcoal in pyrolysis. (Bridgewater et al. 2000)
A dark brown mobile liquid is formed after cooling and condensation.(Piyali Das et. al.) The liquid's heating value is around half that of previous petroleum fuel. Differently from the traditional pyrolysis processes for generating charcoal, the fast pyrolysis is an advanced process having controlled parameters to control generation of high yields of liquid. The main features of a fast pyrolysis process are as follows.

1. It requires very high heating and heat transfer rates at the reaction interface, which usually needs a finely ground biomass feed.
2. It requires a controlled pyrolysis reaction temperature of about 500ºC and vapour phase temperature of 400-450ºC,
3. It requires short vapour residence times of usually less than 2 seconds.
4. It requires fast cooling of the pyrolysis vapours to give the bio-oil product.

Bio-oil which is the main product is obtained in yields of up to 75% when fed with dry biomass and by-products (which are char and gas) are generated. All three of them can be used within the process. So, except for flue gas and ash, no waste streams would be generated. (Lu Qiang et al., 2009)

A fast pyrolysis process includes: drying the feed to typically less than 10% water in order to minimise the water in the product liquid oil [although up to 15% can be acceptable]; and grinding the feed [to around 2 mm in the case of fluid bed reactors] to give sufficiently small particles to ensure rapid reaction, pyrolysis reaction, separation of solids [char], and collection of the liquid product [bio-oil]. Any form of biomass can be considered for fast pyrolysis. Drying the feed to usually less than 10% is necessary for a fast pyrolysis because minimising the water in the product liquid oil is very important. In the beginning, grinding the feed to around 2 mm in case of fluid bed reactors to provide sufficiently small particles to make sure pyrolysis reaction, separation of solids(char), collection of the liquid product (bio-oil) and rapid reaction occur. However, in principal, up to 15% can be acceptable. All of the processes mentioned above are considered to help produce a fast pyrolysis. (Bridgwater,1999).

The pyrolysis is one of the thermo-chemical conversion processes for biomass conversion (Bridgwater A.V.,1999). One special thing about pyrolysis is the fact that it does not require any air and most of the products generated from this method are liquids called bio-oils (Demirbas, 2009).
Figure 1. explains the difference between pyrolysis and the other biomass thermal conversion processes.

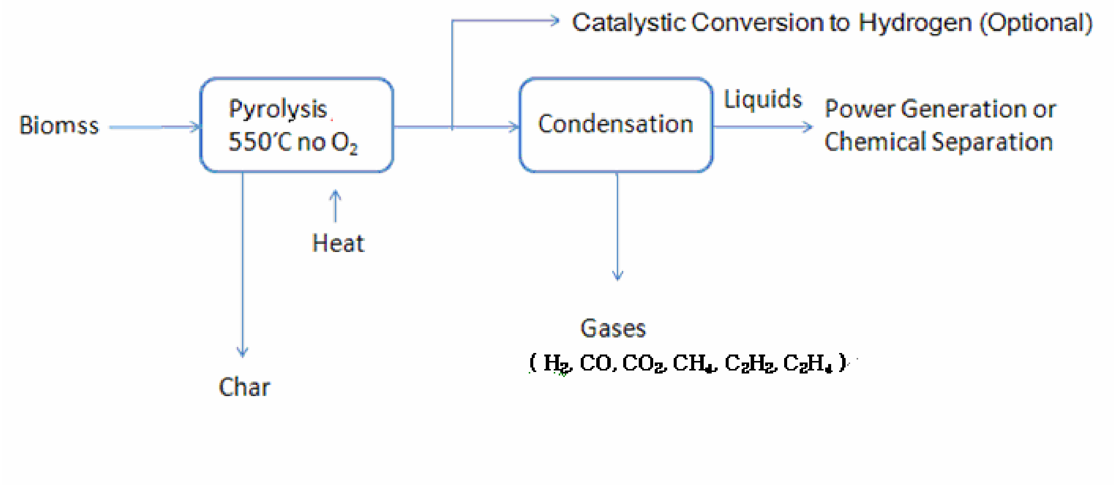


Figure 2.4: A schematic of pyrolysis (cited from Demirbas, 2009)

As seen above, the final products of the pyrolysis are mostly liquids, however, in the pyrolysis, partly gasification processes are also considered in the pyrolysis. Therefore, the final products from the pyrolysis, are a mixture of gases, liquids and solid residues. (Demirbas, 2009).

To increase the yield of liquid in pyrolysis, the following conditions were suggested by Bridgwater et al.(1999)

- high heating rate (>100 C/min)
- finely ground biomass feed (<1mm)
- carefully controlled temperature (around 500 'C)
- rapid cooling of the pyrolysis vapours when making the pyrolysis liquid products.

Sometimes, fast pyrolysis and slow pyrolysis are considered as separate concepts. Bridgwater et al.(2007) compared fast and slow pyrolysis liquids from mallee and found that fast pyrolysis can generate more liquid products than slow pyrolysis, while slow pyrolysis can generate more solid residues. Similarly, Pütün et al. studied slow and fast pyrolysis of tobacco residue and found that in slow pyrolysis, the amount of residue generated was more than in fast pyrolysis.

Fast pyrolysis has a short reaction time of few seconds or less. Therefore heat, mass transfer processes, phase transition phenomena and chemical reaction kinetics are all playing important roles. The goal of this process is to make the reacting conditions of biomass particles close to optimum process temperature and to reduce its exposure to the lower temperatures which might cause formation of charcoal. The pyrolysis process is an endothermic chemical process. This requires a substantial heat input which will raise the biomass to reaction temperature. (Bridgwater, 1999)

Bridgwater and Peacocke(1999) suggested reactors for the process of fast pyrolysis. Several reactors have been developed. The bubbling fluid bed, transport bed, circulating fluid bed, rotating cone, vacuum pyrolysis reactor, ablative reactor, and screw reactor can be used for the pyrolysis process. An important fact is that depending on the type of reactor, the final products from pyrolysis can be different.

Bubbling fluid beds are simply constructed and operated. They can control temperatures easily. Because of their high solids density, they can transfer heat to biomass particles very effectively. Scaling is very easy and they are a very well known technology. Because the efficiency, good and consistent performance with high liquid yields is maintained (usually, 70-75%wt. from wood on a dry feed basis). Heating is decided in various ways. The fluidising gas flow rate controls the residence time of solids and vapours.

Char functions as an effective vapour cracking catalyst in the condition of the fast pyrolysis reaction temperature. Therefore, fast and efficient char separation/elutriation is significantly important. To achieve high biomass, biomass particle sizes should be smaller than 2-3mm. Ejection and entrainment are used to separate char in one or more cyclones. Regarding scale-up limitations, heat transfer to bed at large scales should be considered

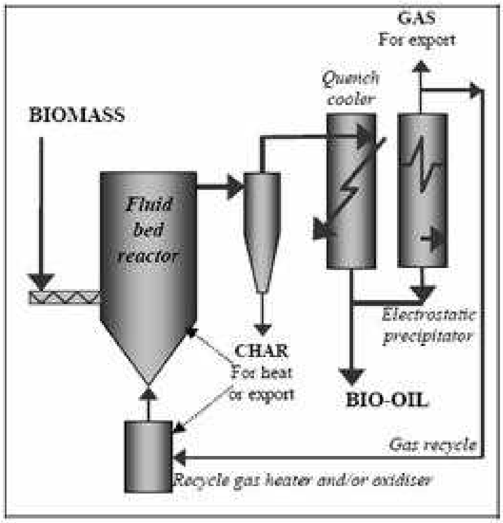


Figure 2.5: A schematic of bubbling fluid bed reactor(cited from Bridgwater,2003)

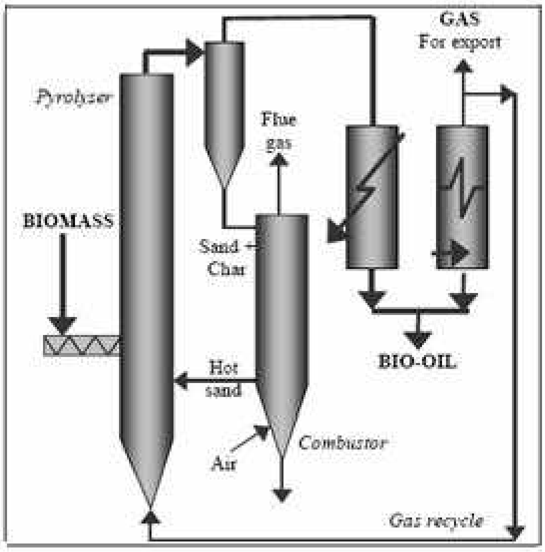


Figure 2.6: A schematic of circulating fluid bed reactor (cited from Bridgwater, 2003)

On the other hand, circulating fluid beds and transported beds can control temperature easily in the reactor. Residence time for the char is almost equal for vapours and gases. The circulating fluid beds are appropriate for use in very large throughputs. The technology is very well known but the hydrodynamics in this technology are more complex. Higher gas velocities cause char attrition. Cyclones can separate the char. Closely integrated char combustion in a second reactor needs more careful attention. At large scale, heat transfer should be proven.

In addition, ablative pyrolysis has high a pressure of particles on the hot reactor wall. This is caused by the centrifugal force or by a mechanical force. [Aston] high relative motion between particle and reactor wall is caused. The reactor wall temperature has to be less than 600°C.

The feed sizes are large. Inert gas is not necessary to make processing equipment smaller. This system is a more intensive reaction system because it is heat transfer to the reactor, not to the biomass, that limits reaction rates; the surface area involved in the process requires more money, and the mechanical process makes the reactor more complex.

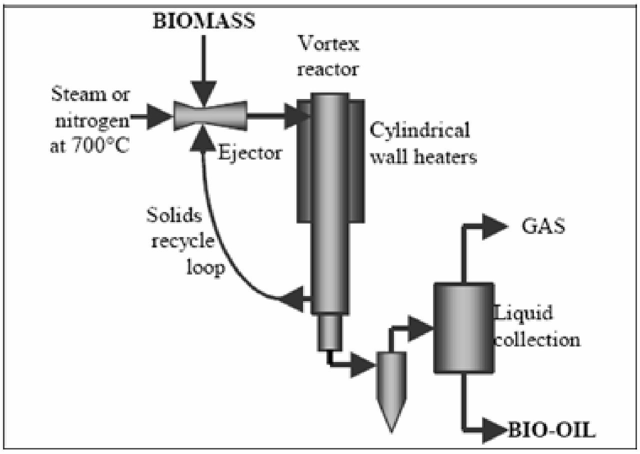


Figure 2.7: A schematic of NREL Vortex ablative reactor(cited from Bridgwater,2003)

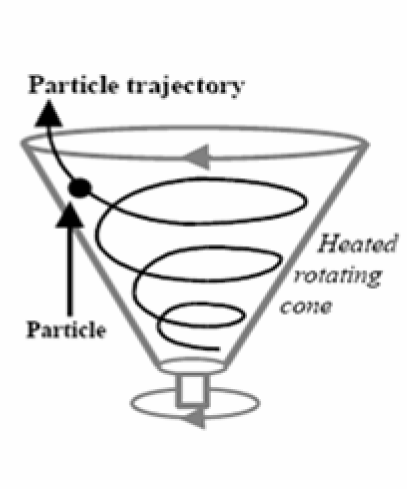


Figure 2.8: A schematic of rotating cone pyrolysis reactor(cited from Bridgwater, 2003)

The reactor named 'entrained flow' is a simple technology but has poor heat transfer. Its high gas flows requires large plants and results in difficult liquid collection. It has good scale-up ability but liquid yields are lower.

'Centrifugation of Rotating Cone' moves hot sand and biomass up a rotating heated cone. Traditionally, vapours are collected and processed. Char and sand drop into a fluid bed surrounding the cone. From the point, they are lifted to a spate fluid bed combustor. At that place, char is burned to heat the sand and then it is dropped back into the rotating cone. It burns char in a secondary bubbling fluid bed combustor and recirculates the hot sand to the pyrolyser. The required carrier gases in the pyrolysis reactor are much less than for fluid bed and transported bed systems. But it requires gas for char burn off and for sand transport. This reactor can expect liquid yields of 60-70% on dry feed even though it requires complex integrated operation of three subsystems of rotating cone pyrolyser, riser for sand recycling, and bubbling bed char combustor.

Bridgwater and Peacocke (1999) added vaccum pyrolysis as well as reactors mentioned above. They decribed vaccum pyrolysis as below.
Slow heating rates are performed. However, pyrolysis products are removed as fast as the other fast pyrolysis methods. Larger particles are necessary and larger equipment and higher costs are required involved with operation of a vacuum. Total liquid yields are between 60 and 65% which is lower than between 75 and 80 wt% in the two fast pyrolysis methods above.

#### – Heat supply

Bridgwater and Peacocke (1999) stated that the high heat transfer rate required to heat the particles sufficiently and quickly leads to a major design requirement to achieve the high heat fluxes to afford the high heating rates and endothermic pyrolysis reactions.
They cited that Reed et al. (1990) proposed heat fluxes of 50 $w/cm^2$ to achieve true fast pyrolysis conditions. However, he stated that it is not necessary to meet these conditions for a commercial process.
Bridgwater et al. (1999) mentioned that each mode of heat transfer has different methods of operating the reactors and can be complicated. Conductivity and convectivity can be mentioned as the two dominant modes of heat transfer in fast pyrolysis technologies.
Diebold et al. (1994a) stated that the IEA Bioenergy Agreement pyrolysis and liquefaction group proposed a furnace arrangement the same as an ethylene cracking furnace for ablative pyrolysis in a vortex reactor.
Vapour condensation such as sodium, induction heating of the reactor wall and the use of contact electrical heaters is another way of achieving the pyrolysis temperatures and heat transfer rates necessary.
Ensyn (1998) stated that in a circulating fluid bed, hot circulating sand would play an important role as the heat transfer method which requires an efficient sand reheating system.

The sand requires an external heat source typically coming from char in an integrated system in a conventional fluid bed.

Method of heating depending on the types of Fast pyrolysis reactors is listed in table 2.1.

| Reactor type | Method of heating |
|---|---|
| Ablative coil | Reactor wall heating |
| Ablative mill | Reactor wall (disc) heating |
| Ablative plate | Reactor wall heating |
| Ablative vortex | Reactor wall heating |
| Circulating fluid bed | In-bed gasification of char to heat sand |
| Cyclone or vortex | Reactor wall heating |
| Entrained flow | Char combustion products |
|  | Hot sand |
| Fluid bed | Heated recycle gas |
|  | Hot inert gas |
|  | Partial gasification |
|  | Fire tubes |
|  | Fire tubes |
| Horizontal bed | Hearth heating |
| Vaccum multiple hearth | Wall and sand heating |
| Rotating cone | Partial gasification of char |
| Stirred bed | Recirculated hot sand heated by char |
| Transported bed | combustion |
| Vacuum moving bed | Direct contact with hot surface |

Table 2.1: Fast pyrolysis reactors and heating methods(cited from Bridgwater,1999)

Table 2.2 explains suggested modes of heat transfer and specifications

| Reactor type | Suggested mode of heat transfer | Advantages/disadvantages/features |
|---|---|---|
| Ablative | 95% Conduction<br>4% Convection<br>1% Radiation | Accepts large size feedstocks<br>Very high mechanical char abrasion<br>from biomass Compact design<br>Heat supply problematical<br>Heat transfer gas not required<br>Particulate transport gas not always |

| | | |
|---|---|---|
| | | required |
| Circulating fluid bed | 80% Conduction<br>19% Convection<br>1% Radiation | High heat transfer rates<br>High char abrasion from biomass and char erosion<br>Leading to high char in product<br>Char/solid heat carrier separation required<br>Solids recycle required; Increased complexity of system<br>Maximum particle sizes up to 6m<br>Possible liquids cracking by hot solids<br>Possible catalytic activity from hot char<br>Greater reactor wear possible |
| Fluid bed | 90% Conduction<br>9% Convection<br>1% Radiation | High heat transfer rates<br>Heat supply to fluidising gas or to bed directly<br>Limited char abrasion<br>Very good solids mixing<br>Particle size limit <2 mm in smallest dimension<br>Simple reactor configuration |
| Entrained flow | 4% Conduction<br>95% Convection<br>1% Radiation | Low heat transfer rates<br>Particle size limit < 2 mm<br>Limited gas/solid mixing |

Table 2.2: Reactor types and heat transfer (cited from Bridgwater, 1999)

## 2.3 pyrolysis oil

The official name of the process to make pyrolysis oil is “Fast Pyrolysis”. Sometimes, it is called “Flash Pyrolysis”. Just name of bio-oil is correspondingly used as well. Zhang Qi et al. (2007) defined pyrolysis oil as biomass pyrolysis oil, and bio-oil and bio-crude as different terms. The fast pyrolysis process generates mainly the desired pyrolysis oil product and light gases.

Production of pyrolysis oil is carried out by the thermal treatment of biomass at high temperature in the absence of oxygen. The pyrolysis of biomass producing pyrolysis oil, syngas and so on, has been studied over recent years. (Bridgewater and Peacocke, 2000). Energy can be generated by these processes. Water, lignins, organic acids, other oxygenates and many other components are included in the pyrolysis oil.

Zhang et al.(2007) defined bio-oils as multi-component mixtures of different size molecules derived from depolymerisation and fragmentation of lignin, cellulose and hemicellulose. After all they found the elemental compositions of bio-oil and petroleum derived fuel are different. He investigated to find out the way of compensating for the defect of bio-oil so that it can be utilized considering the environment and costs, even though temporarily the cost of producing bio-oil is not as much as previous petroleum fuels.

### – Metals Content

One thing different about pyrolysis oils from conventional petroleum can be the high amount of metals included. They can poison the catalysts present. Therefore, they need to be removed. (cited from Nexant ChemSystems, 2008)

### – Water and oxygen content

Another difference of pyrolysis oils is that the pyrolysis oils include higher amounts of water and oxygen compared to conventional crude oils. According to Zhang et al.(2007), one specialty of bio-oils is that bio-oil has water content up to 15-30 weight % in original feedstock or the products. This can lower the heating value and flame temperature but it can also reduce the viscosity, increasing fluidity helpful to atomization and combustion of bio-oil. Shihadeh and Hochgreb (2002) compared the bio oils of NREL (National Renewable Energy Laboratory, US) to those of ENSYN (Ensyn Technologies, Inc., CA) and investigated that extra thermal cracking improved its chemical and vaporization characteristics, and they found that the better ignition ability of NREL oil was due to its lower water content and lower molecular weight.

- **Ash**

Zhang et al.(2007) stated that erosion, corrosion and kicking problems in the engines and valves can occur because ash is contained in bio-oils. If the ash content is higher than fragmentation of lignin, cellulose and hemicelluloses, deterioration will occur. Therefore, this ash content is one of the differences of elemental composition between bio-oil and petroleum derived fuel.

- **Viscosity**

The viscosities of bio-oils become different depending on what kind of biomass feedstocks are used and what sort of pyrolytic processes are applied.
Luo et al. (2004) studied bio-oils produced from Pterocarpus indicus and Fraxinus mandshurica. Kinetic viscosity between 70 and 350 mPa/s and between 10 and 70 mPa/s respectively were found. On the other hand, bio-oil produced from rice straw had a minimum kinetic viscosity which was between 5 and 10 mPa/s because of its high water content. Sipilae et al.(1998) studied the bio-oils from softwood, hardwood and straw in the fast pyrolysis process by using an atmospheric fluidsed bed. They found that the viscosities in the bio-oils with higher water content and less water insoluble components were decreased. They found that alcohols also affected the viscosity.

Bio-oils composed of considerable amounts of carboxylic acids such as acetic and formic acids cause low pH values between 2 and 3. The pH of the bio-oil of pine was 2.6 when that of hardwood was 2.8. The acidity of bio-oil can bring up some problems of corrosion which get severe when temperature increases. It is often suggested that this should be improved as one of the requirements for upgrading the process before using bio-oil in transport fuels.

- **Heating value**

Heating value is one of properties of bio-oils. Usually, a higher heating value is shown in the bio-oils of oil plants compared with those of straw, agricultural or wood residues. Beis et al.(2002) applied the pyrolysis process to a sample of safflower seed and found a heating value was 41.0MJ/kg and maximum yield was 44% in the obtained bio-oil. Ozcimen et al.(2004) generated bio-oil from rapeseed cake where they found a heating value was 36.4MJ/kg and a yield was 59.7%. However, in bio-oils using wood and agricultural residues as raw materials, a heating value was 20 MJ/kg and a yield was between 70% and 80%.

- **Biodegradability**

Another property of bio-oils is biodegradability. Piskorz and Radlein (1999) proved the respirometric biodegradation of bio-oils in both aquatic and soil environments. They inoculated the bio-oils with Returned Activated Sludge. BOD was measured for 5 days. The results showed that bio-oils were biodegradable. Feedstock and pyrolysis conditions can change pyrolysis oil compositions.

The moisture of biomass can be reduced as a pretreatment by drying the biomass. From the original biomass the moisture can be reduced from as high as 45 percent to less than ten percent. However, there is still water contained in the pyrolysis oil arising from the chemistry performed in the process and remaining after drying. The fact that there is a high concentration of oxygenated species is different from composition of fossil fuels.

### 2.4 Limitations of pyrolysis

Pyrolysis is a good method of obtaining low molecular weight liquid, gas fuel and solid residue. However, as I have already mentioned, the high operating temperature of the pyrolysis(673-1273 K) can cause cross-linking reactions between hydrocarbons and aromatics which turn to tar that is difficult to further decompose.(Zhengang Liu and Fu-Shen Zhang, 2008) In addition, in terms of the poor quality of pyrolysis oils compared to previous fossil fuels, there are problems to be overcome.(Lu Qiang et al.,2009) Unlike fossil fuels, pyrolysis oils include water, oxygenated species and acidic components which cause many problems. The lower energy density than fossil fuel (by 50%) and immiscibility with hydrocarbons that bio-oils have is because of their high oxygen content. Additionally, the strong acidity of bio-oils is a main cause of bio-oils' instability. The boiling point of bio-oils varies due to their complex compositions. (Lu Qiang et al.,2009) Furthermore, some studies have considered the toxicity of pyrolysis liquids and their derivatives. Diebold(1997) stated that degree of mutagenicity and teratogenicity from liquids is decided by source, chemical composition and dosage. Putnam et al.(1999) stated that some cytotoxic and mutagenic effects can be observed depending on the type of pyrolysis product. Lewis et al. (1988) suggested that aerosols of wood smoke are mutagenic. So, exposure to the aerosols is not desirable. To protect against the exposure of skin, use of protective gloves, clothing and safety glasses are suggested.

According to Diebold (1997), the compound of polycyclic aromatic hydrocarbons (PAHs) in bio-oils could cause the incidence of cancer. Tsai et al.(2007) stated that PAHs in bio-oils were dominated by the low molecular weight PAHs, such as naphthalene (1.10-2.45 mg/L) and acenaphthene (0.72-7.61 mg/L). They also proved that a lot of PAHs would be formed during the upgrading of bio-oils via catalytic cracking with zeolite catalysts. This has proven to be serious problem. Blin and Girard (2006) completed the Biotox project to completely assess the toxicity and biodegradability of representative bio-oils from different processes and temperatures. The bio-oils showed no eco-toxicological effects. But there were slight mutagenic effects which were less toxic than conventional fuels.

## 2.5 Importance of solvent extraction

As was said earlier Solvent extraction (this is often called liquefaction) has been studied attentively because it can overcome the main disadvantage of pyrolysis, the "cross-linking effect". The main advantages of the solvolysis (Zhengang et al. 2007) are

1. Through the usage of solvent, dilution of concentration of the products can prevent the cross-linking reactions and reverse reactions.
2. Relatively low temperatures (less energy consumption) compared with pyrolysis and gasification because the solvent plays an important role in the liquefaction reaction.
3. When lowering the viscosity of heavy oil from biomass in liquefaction, solvolysis in the presences of organic solvents is proven to lower the viscosity of heavy oil effectively from biomass or coal.
4. In addition, through the solvent liquefaction, oxygen can be depleted which can improve properties of the final liquid product while the pyrolysis oil include a large portion of oxygens.

Karagoz et al.(2004,2005) studied the effects of treatment conditions including temperature, catalyst and reaction time in low temperature (<553 K) liquefaction in water and methanol vapour. They studied thermal liquefaction of white birch wood and filter pulp in water and methanol vapour at 2 MPa pressure in a flow-through reactor. Dermirbas (2009) stated that either glycerol or alkaline glycerol in aqueous or non-aqueous media for the production of pulps was generated by delignification in the thermal liquefaction. Cemek et al.(2001) used supercritical fluid extraction to study the verbascum stalk liquefaction and fractionate the following liquid product into benzene and ethyl ether solubles. The fact that the dominant depolymerisation route is the solvolysis of ether linkages was proven by high conversions shown on depolymerisation of Kraft- and organosolv-derived liginin by KOH in supercritical methanol or ethanol in rapidly heated batch microreactors.

The qualities of products by biomass liquefaction are determined by various factors such as substrate type, heating conditions, reactor configuration, solvent type and catalyst.

Ionic reactions and free radical reactions are related to the solvent extraction process of biomass in pyrolysis. These include nucleophilic, electrophilic, elimination reactions and so on. In the nucleophilic, electrophilic and elimination reactions, polarity plays an important role in the reactions. If the polarity is higher, the higher conversion rate will be achieved. For example, the dipole moment of ethanol, water and acetone at their critical point are around 1.7, 1.8 and 2.9 D respectively. Additionally, In this case, acetone has the highest polarity which makes acetone the most reactive resulting in highest conversion rate. (Zhengang Liu and Fu-Shen Zhang, 2008)

Many studies about solvent extraction have previously been performed for coal. The phenomena found from the studies are quite similar to the phenomena in solvent extraction with biomass. (Nicholas et al., 1985) The introduction of developments in solvent extraction in coal was made to provide a better understanding of hydrogen donor effects and free radical effects.

## 2.6 Classification of solvents

Janet R.Pullen (1981) cited the concept of classification of solvents from Oele et al.(1951) and Wise (1971). He stated that solvent extraction processes for coal are largely as follows: Non-specific extraction, specific extraction, degrading solvents and reactive solvents. The explanation of solvents by Janet R. Pullwn(1981) is as follows.

- **Non-specific solvents**

Non-specific solvents dissolve less than a few percent of coal at temperatures up to 100ºC. He stated that low boiling point solvents such as ethanol, benzene, ether, chloroform, methanol and acetone could be included in the category.

- **Specfic solvents**

Solvents dissolving between 20 and 40% of the coal at the state of temperatures less than 200 ºC are called specific solvents. The nature of the extract is similar to the parent coal. Specific solvents extract chemically similar or identical insoluble residue.

- **Degrading solvents**

As the temperatures rise up to 400ºC, more than 90% of the coal can be extracted by degrading solvents. After extraction, the solvents almost totally recovered not changing. Phenanthrene, diphenyl and phenanthridine are included in degrading solvents.

- **Reactive solvents**

Reactive solvents as extractive chemical for disintegration. Chemical reaction causes reactive solvents dissolution, usually at high temperatures about 400ºC.

Thermal degradation into soluble fragments and hydrogen transfer reactions is involved in almost all work on reactive solvents. Hydrogenolysis is involved for solvents which are able to do transfer reactions. The solvents involving hydrogenolysis can donate hydrogen to coal or coal fragments, or act as hydrogen transfer agents.

Ross and Blessig (1977) stated that isopropyl alcohol and methyl alcohol could work as hydrogen donor solvents like tetralin. The presence of bases such as potassium isopropoxide or potassium hydroxide unlike tetralin can promote the transfer of hydrogen by the alcohols. At 335ºC a 50% yield of products in pyridine were produced in isopropyl alcohol treated coal. The run caused production of 48% pyridine (soluble product), which was similar to a run with tetralin.

## 2.7 Principle of Solvent

Furlong et al. (1977) and Davies et al. (1976) proved that hydrogenated solvents have been better solvents in coal conversion than original unhydrogenated material. Davies et al. (1977) proved that extraction efficiencies of hydrogenated anthracene oil are higher over the whole boiling point range than the original anthracene oil. They stated that it might be because of the presence of polycyclic hydroaromatic compounds known as good reactive solvents, and effective donors of hydrogen to coal fragments.

But it is important to notice that even the unhydrogenated anthracene oil has a higher solvent power than expected from the extraction efficiencies of its main components such as naphthalene, anthracene, phenanthrene and dibenzofuran. Stadelhofer et al. (1981) stated that 13C nmr spectroscopy showed that the relatively high solvent power of crude anthracene oil was because of the presence of a number of hydroaromatic compounds of low concentration but high efficiency actively taking part in hydrogen transfer. Therefore, it is assumed that the coal-derived solvents that have a large proportion of hydro-aromatics are efficient process solvents. Some aromatic solvent components can have a function as hydrogen shuttlers. In other words, hydrogen is transferred from one part of the coal fragment to another through the solvent. Larsen et al. stated that Phenolic components could improve the conversion rate because they act as hydrogen shuttlers. Clarke et al. emphasized that hydrogen donor is important to prevent the polymerization of coal in solution. For instance, Tetralin is an effective hydrogen donor. However it is an ineffective physical solvent even though it is often used to typify liquefaction solvents.

Witehurst et al. (1977) identified good liquefaction recycling solvents as having the following properties.

First, a good physical solvent
Second, ability as a hydrogen shuttler
Third, function as a container of hydrogen donor compounds
Lastly, relatively few hydrogen consumers

The effect of higher-boiling point non-donor components in the solvent such as pyrene and fluoranthene has been drawn to attention more recently.
Reduction happens in the hydrogen transferred from tetralin and $H_2$ and pyrene enhanced hydrogenation of coal.

$$\textit{Tetralin} + \textit{coal} \rightarrow \textit{naphthalene} + \textit{coal H} \quad \text{-------------------(1)}$$

$$\textit{Tetralin} + \textit{pyrene} \rightarrow \textit{naphthalene} + \textit{dihydropyrene} \quad \text{----(2)}$$

$$\textit{Pyrene} + H_2 \rightarrow \textit{dihydropyrene} \quad \text{---------------------------------(3)}$$

$$\textit{Dihydropyrene} + \textit{coal}\ * \rightarrow \textit{pyrene} + \textit{coal H} \quad \text{----------------(4)}$$

(Janet R.Pullen, 1981)

Furlong et al. (1976) stated that the index is different depending on degree of solvent hydrogenation. Details of the solvents quality index are all different, but when this parameter value is less than around 10, coal conversion decreases dramatically as shown in Fig.2.9.

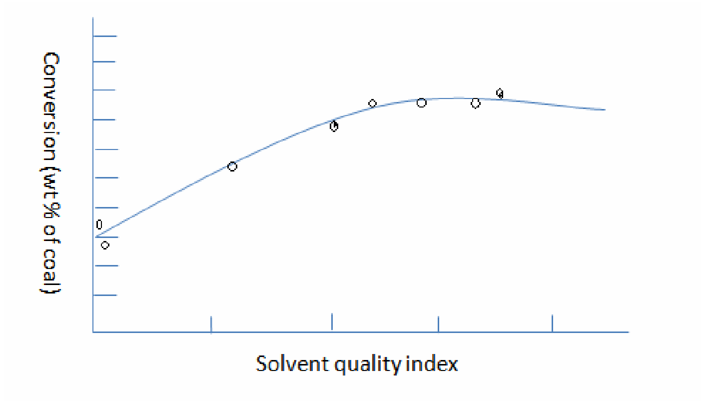


Figure 2.9: Influence of solvent quality index on conversion (Janet R.Pullen, 1981)

Bockrath et al. (1981) have evaluated the relative donor ability of liquefaction solvents by considering the main features of a free radical mechanism. Benxyl radicals are generated in the solvent as temperature rises, and by the hydrogen donor and free radical scavenger ability of the solvent the relative amounts of toluene and bibenzyl products can be measured.

Solvent quality is dependent on solvent composition. However performance depends on coal type and operating conditions: When one coal is good in a solvent, it is not guaranteed that the solvent is good for another coal. However, Curtis et al. (1979) defined a range of solvent parameters beneficial to coal conversion for various coals and process conditions. Optimum ranges for conversions greater than 80% for the parameters' hydrogen content, average proton chemical shift, proton distribution and infrared absorbance ratio were identified for a series of creosote oils and actual SRC recycle oils as table 2.4.

| Solvent parameter | Range | Optimum value |
|---|---|---|
| Hydrogen content (wt %) | 8.00-9.60 | 8.80 |
| Atomic C/H ratio | 0.78-0.97 | 0.87 |
| Degree of partial hydrogenation | Higher 0.65 | -- |
| infrared ratio (in $CCl_4$) | 0.25-0.42 | 0.30 |
| Aromatic hydrogen (wt %) | 2.75-4.3 | 3.55 |
| Alpha hydrogen (wt %) | 1.60-2.25 | 1.88 |
| Beta hydrogen (wt %) | 1.60-3.55 | 2.55 |
| Gamma hydrogen (wt %) | 0.60-1.25 | 0.90 |
| Average chemical shift (ppm) | 3.15-4.55 | 3.80 |

Table 2.4: A range of solvent parameters beneficial to coal conversion
(Janet R.Pullen, 1981)

The fact that benzophenone is a useful reagent for ranking of hydrogen donors was found by Raaen et al.(1978). The dehydrogenation of typical donor solvents, coals and phenols have been studied. The hydrogen donor abilities in terms of the variety of compounds in the conversion of $Ph_2CO$ to $Ph_2CH_2$ are stated in table 2.5.

| H-donor (in excess) | Conversion to $Ph_2CH_2$ (%) |
|---|---|
| Cholesterol | 39 |
| 1,2-dihydronaphthalene | 28 |
| Tetrahydrocarbazole | 28 |
| 1,2,3,4-tetrahydroquinoline | 21 |
| 9,10-dihydrophenanthrene | 20 |
| Tetralin | 17 |
| 9,10-dihydroanthracene | 13 |
| Decalin | 0 |

Table 2.5: Hydrogen-donor ability of various compounds for the conversion of $Ph_2CO$ to $Ph_2CH_2$ (Janet R.Pullen,1981)

## 2.8 Chemistry of coal/solvent interactions

Neavel (1976) found that around 90% of ash free coal in tetralin for less than 2 minutes at 400°C becomes soluble in pyridine.

Solvent extraction usually fractionated coal liquefaction products and their solubility in pyridine, benzene and hexane or pentane as preasphaltenes, asphaltenes and oils respectively characterize the coal liquefaction products. But, Farcasiu et al. (1976) emphasise that different soluble components of liquefaction products are not only because of molecular weight, hydrocarbon skeletal structure or chemical functionality but also because of interactions with other soluble species. A particular compound could be shown as an asphaltene or oil depending on the presence of other species in the liquefaction product.

Reduction of molecular weight is caused by dissolution. This sequence is made from partial degradation of coal to smaller fragments. Shah and Cronauer (1979) stated that this can be achieved by elimination of side-chained functional groups such as OH, C=O and SH, or breaking the hydrocarbon structure of the main molecules by C-C or C-O bond cleavages. Ring opening with or without elimination of the heteroatom is caused by other reactions occurring. Therefore, Whitehurst et al. (1977) stated that useful parameters for investigating the structures of liquefaction products are molecular weight, chemical functionality and hydrocarbon skeletal structures. Some indication of bond

cleavages and reaction mechanisms can be investigated by the changes of these parameters with time.
Tetralin, as the model solvent molecule, is used in the most pure solvent studies. This is the case even though the usefulness of the model is limited because only mechanisms of those particular compounds are included and there is the possibility of inaccuracies. However, it is still useful and can be used in direct structure studies of liquefaction products to obtain a fundamental understanding of liquefaction pathways.
Franz (1979) researched the thermal dissolution of Kaiparowitz sub-bituminous coal treated with tetralin at 500°C and 472°C for heating rates (150°C/s, 3°C/s and 1°C/s) and various periods of time.

A drop in the number-average molecular weight from about 1200 at 10 minutes to around 500 at 30 minutes or longer was shown by vapour pressure osmometry (vpo) of pyridine solutions of the THF soluble fraction of the 427°C reaction of coal and tetralin. Gel-permeation chromatography (gpc) results are consistent with vpo results with principal peaks happening at 1200MW which decreases to MW <= 500; a molecular weight below 500 dominates by 35 minutes. Conversion of higher molecular weight species to lower molecular weight products happens at 500°C rather than at 427°C. After 2 hours at 500°C, a substantial fraction of material of MW >1000 still exists. Farcasiu et al.(1976) and Whitehurst et al.(1977) proved that the SRC product included up to 40% of the high molecular weight material with MW>2000 that existed at a conversion time of less than 5 minutes by gpc results. It indicates that a relatively small number of weak bonds are broken to yield a large number of pyridine-soluble products by the rapid drop in number-average molecular weight in the first 10 minutes. Franz (1979) stated that very unstable oxygenated aliphatic structures could probably be the reason for the phenomena. It is indicated that there is a rupture of C-C bonds of intermediate stability by the gradual disappearance of the 1200 MW peak. Condensation reactions could probably cause the increase in molecular weight after 1 hour.

Whitehurst et al.(1977) stated that the average molecular weight of the liquefaction product was dependant on the coal it was derived from. In addition, the average molecular size of the product is reduced as hydrogen pressure or temperature rises.

These results express a general tendency in molecular weight distribution while converting. However, molecular weight determination techniques are not reliable because of the possibilities of distorted results due to the association of molecules in solution.

## 2.9 Free radicals

Curran et al. (1966, 1967) defined the general mechanism of coal liquefaction as a free radical process where coal is thermally decomposed into free radicals consequently causing a stabilizing process by abstraction of hydrogen: Neavel (1976) stated that free radicals were doing a very important role in liquefaction processes. In natural coal, a significant concentration of free radicals occurs. As it is heated, it cleaves and it stabilizes additional free radicals. In the presence of hydrogen, the liquefaction yield rate increases. However, in case there it is not sufficient hydrogen, repolymerisation of radicals and solidification of it will be caused. In addition, some problems such as reactor coking and low liquefaction yields will be caused.

Electron spin resonance (esr) spectroscopy allows more direct evidence for the existence of free radicals in coal and liquefaction products, and their fate during conversion, to be gained experimentally.

Important spectral parameters are the intensity of esr absorption proportional to the concentration of free radicals (such as g-value reflecting the chemical nature of the free radical), and the peak to peak line width proximity of the unpaired electron to nuclei with magnetic moments such as protons and nitrogen. 'In the case of the Nitrogen free radical, G-value of the free electron is 2.0023.

It was observed that tetralin was more efficient at consuming radicals than naphthalene in the hydrogen and nitrogen systems. Petrakis and Grandy (1978a,b) investigated tetralin/$H^2$ treated samples having a radical concentration of around $20\times10^{18}$/g compared to around $40\times10^{18}$ for the naphthalene/$H_2$ system. It is assumed that this difference happens due to the fact that tetralin is the more efficient hydrogen donor and quencher of free radicals. A significant difference occurred for samples treated with donor (tetralin/$H_2$) and non-donor (naphthalene/$N_2$) systems at about $420^{\circ}$C. When the temperature rises up to $430^{\circ}$C, the differences disappear.

Petrakis and Grandy (1980) studied how various solvents and gases in stabilizing free radicals become depending on different heating rates and residence times. The solvent effect was clearly shown. As an example, When Wyodak coal processed at $32^{\circ}$C $min^{-1}$ for

10 minutes resulted in a 5:1 ratio in radical concentration of naphthalene/$N_2$ treated coal relative to tetralin/$H_2$ treated, in the same coal at 13°C $min^{-1}$ for 2 hours, the ratio was 2:1. Hydrogen donor efficiency and quenching efficiency are the cause of the different radical concentrations. However, depending on heating rate and residence time, the degree of solvent effect varies. This made it possible to establish an order of effectiveness of solvents for quenching free radicals: In the case of aromatics, it was more effective that compounds lose hydrogen and form stable double bonded species, and hydroaromatics.

Retcofsky et al. (1979) stated that most esr measurements of coals showed pre-existing free radicals or free radicals remaining after some treatment such as liquefaction or pyrolysis. But, Petrakis and Grandy (1981 b, c) report a high pressure high temperature esr cavity which is uniquely designed for the first in situ observation of free radicals in coal. Coal conversion, coke formation and catalytic studies under conditions relevant to the process could be performed according to the facts above.

Petrakis and Grandy (1981b,c) studied the influence of process variables on free radicals and how the quantity and degree of conversion to the product are correlated with measured free radical parameters. Fig 2.10 and Fig 2.11 shows the variation of free radical concentration as a function of residence time at 400°C and 460°C for Powhatan No.5 coal in tetralin and in SRC-II heavy distillate oil. Free radical concentration in distillate oil was higher than in tetralin. This means tetralin played a role as better hydrogen donor and quencher.

Conversion yields in tetralin were 32 to 38% compared with 27 to 36% in SRC-II distillate; Also oil yields in tetralin were higher. From this result, we can see that different chemistry occurs in different solvents. Also, temperature was shown to be a very significant variable. (Janet R. Pullen, 1981)

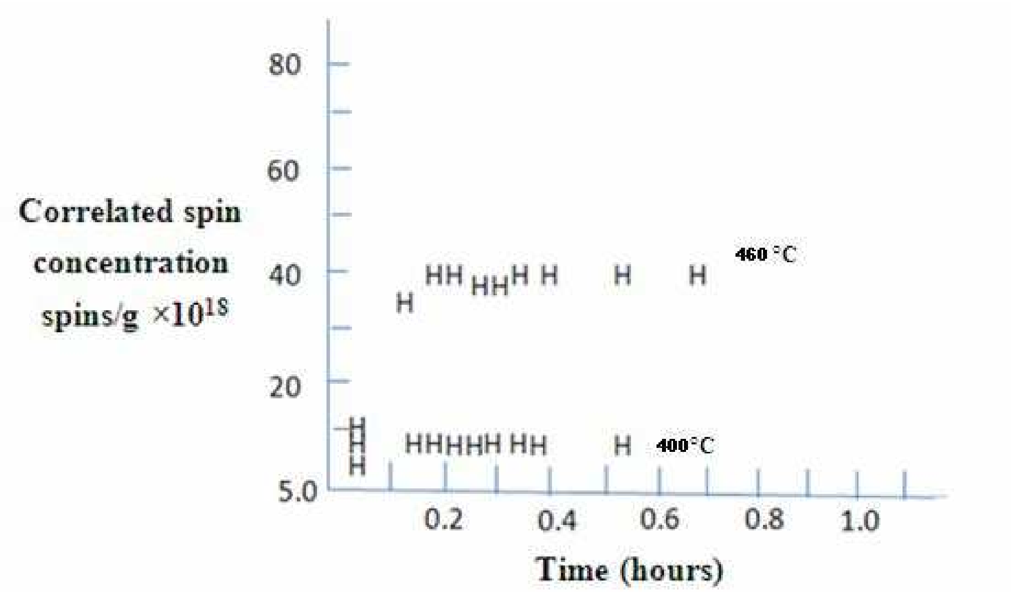


Figure 2.10: Spin concentration vs. elapsed time of Powhatan No5 coal and Tetralin (Janet R. Pullen, 1981)

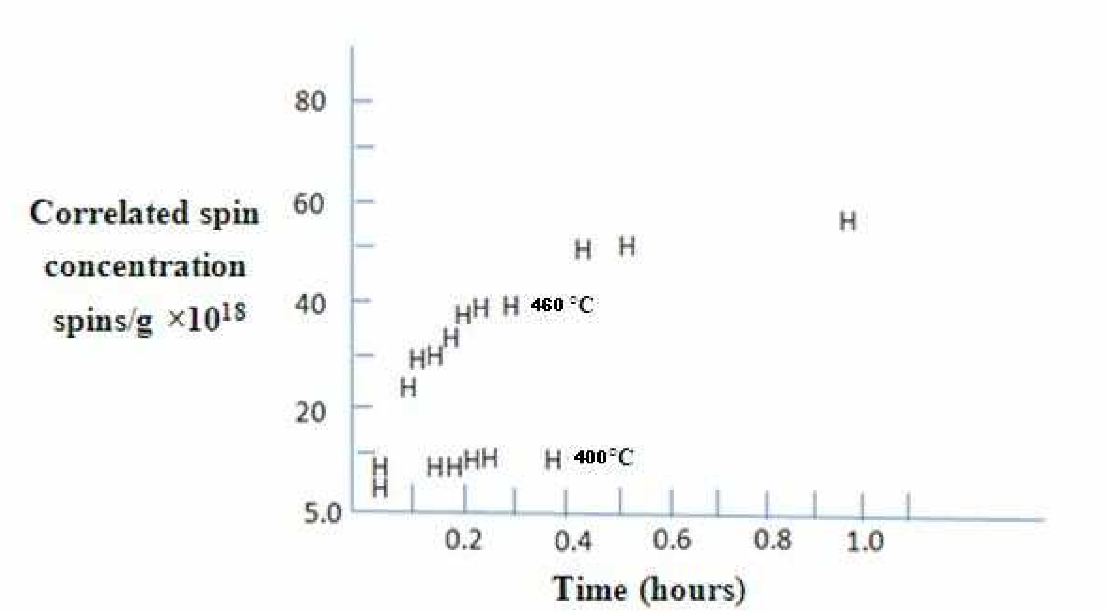


Figure 2.11: Spin concentration vs. elapsed time of Powhatan No5 coal and SRC-II (Janet R.Pullen,1981)

Grandy et al. (1979) studied the esr spectra of solvent refined coal where the radical concentration was about $2\times10^{18}$/g, when treated with solvent which is lower than concentration in coal treated only with heat (50 to 200 × $10^{18}$/g). This implies that some stabilization and hydrogen transfer happened.

Retcofsky et al. (1979) used esr spectrometry for observation of free radicals in liquefaction products in addition to endor (electron nuclear interpretation of esr spectra).

Radical concentration changed in the order: coal < preasphaltens >> asphaltenes > oils. Goldberg et al. (1980) found a similar result. Petrakis and Grandy (1981a) studied relative reactivities of macerals – fusinite, vitrinite and resinite – for liquefaction in naphthalene or tetralin between 425 and 480°C under 12.4 MPa of $H_2$ or $N_2$. Resinites had the lowest concentration of free radicals and were not sensitive to the solvent used. This implies high reactivity. The highest concentration of residual free radicals was shown in fusinites and low reactivity was also shown in fusinite. The phenomena were the same in liquefaction residues. Vitrinite showed it was intermediately reactive, with free radical concentrations depending on temperature and solvent.

## 2.10 Hydrogen transfer

Coal conversion is related to an increase in H/C ratio in the products compared to the original coal. The conversion is made by a function of the increase in hydrogen. Hydrogen-rich solvents have ability to donate hydrogen atoms to coal and coal products. Hydrogen transfer occurs as a function of thermally cracked coal: The following pathway is commonly known as route involving free radicals and hydrogen transfer: (5) (6)

$$\text{Coal-coal} \rightarrow 2\ \text{coal}\bullet \quad \text{------------------------} \ (5)$$

$$\text{Coal}\bullet \xrightarrow{\text{hydrogen rich}} \text{coal H} \quad \text{------------------------} (6)$$

(Janet R.Pullen, 1981)

Curran et al. (1966, 1967) reported that a practical maximum of hydrogen is transferable in a thermal process.

But, there were many theories about the mechanism of hydrogen transfer. There was a theory that hydrogen would be transferable from solvent to coal, and from the coal to another part of the coal via the solvent which aids by redistributing hydrogen. However, the whole amount cannot be related to the transfer of hydrogen in this theory.

Neavel (1976) reported that coal is converted quickly to pyridine-soluble material in naphthalene which is a non-hydrogen donor. Whitehurst et al. (1979) and Franz (1979) also stated that with eternal hydrogen donors thermal depolymerisation of coal was performed. They mentioned that autogenous hydrogen transfer occurred within coal. When phenol was there, internal hydrogen transfer occurred.

Chloroform-soluble was shown as hydrogen donor or transfer agents. Internal hydrogen transfer occurred by heating coal with phenol: According to Larsen et al. (1981a,b), the

H/C ratio of the pyridine-insolubles was decreased as time passed and on the other hand, the H/C ratio of the pyridine-solubles was increased as time passed. Franz (1979) reported that phenol can be a good hydrogen transfer agent. The pathway of application of phenol is as below.

$$\mathrm{Coal}^{\bullet} + C_6H_5OH \rightarrow \mathrm{CoalH} + C_6H_5O^{\bullet} \text{ -------------(7)}$$

$$C_6H_5O^{\bullet} + \mathrm{CoalH}' \rightarrow C_6H_5OH' + \mathrm{Coal}^{\bullet} \text{ ----------(8)}$$

(Janet R.Pullen, 1981)

Heredy et al. (1966) stated that Phenanthrene plays an important role as a hydrogen transfer agent.

In their theory, hydrogen is abstracted by free radicals from phenanthrene and then the hydrogen is abstracted from the phenanthrene free radical from another part of the coal. However, Whitehurst et al. (1976) stated that even though coal and phenanthrene under these conditions react, the solubility of coal wasn't affected. This implies that amount of hydrogen exchange that occurred wasn't enough for the solubilisation.

Collins et al. (1977) and Benjamin et al. (1978) proved that vitrinite of Illinois No.6 coal is a more effective hydrogen donor than tetralin. The reason for the effort to enhance internal hydrogen rearrangement in coal is to improve the efficiency of hydrogenation during processing.

Coal plays a role as the initial solvating medium, as residence time increases and the properties of the solvent are also very important. Neavel (1976) stated that when conversion process goes on, more donor hydrogen is abstracted from the solvent. This implies the importance of donor hydrogen from sources other than autohydrogenation.

Benjamin et al. (1978), Cronauer et al. (1978, 1979) and Shah and Cronauer (1979) used model compound study methods to investigate relative rates of thermal decomposition and hydrogen transfer reactions of compounds with functional groups in coal. Cronauer et al. (1979) paid an attention to hydrogen transfer in oxygen-containing compounds in a deuterium atmosphere or with deuterium-tagged donors. At this time, most of the necessary hydrogen is from the donor solvent or intramolecular rearrangement. However it is not from dissolved gas. Shah and Cronauer (1979) reported that acceptor radicals have a distinct preference when combining hydrogen into about molecular $H_2$. However, Vernon (1980) stated that molecular $H_2$ can take part directly in some donor reactions of coal model compounds. He stated that this phenomenon is activated by free radicals. He also stated that this effect stabilizes free radicals as well as initiating hydrocracking reactions which lower the molecular weight of the coal. Some other studies considered the effects of a mixture of solvents. For example, Derbyshire et al. (1981) reported that a substantially higher concentration of more active donors was caused from a mixture of tetralin and pyrene with molecular hydrogen.

### 2.11 Solvent extraction of biomass in pyrolysis

Nicholas et al. (1985) stated that biomass is different from coal because it has a relatively high hydrogen-to-carbon ratio, but also has a very high oxygen content lowering its heating value significantly. For example, pure cellulose has an H/C ratio of about 1.7 in comparison with that of 0.8 for a typical bituminous coal. However, its oxygen content is around 50 wt% in comparison with 10 wt% for coal. Therefore, to convert direct liquefaction of biomass to upgraded-quality liquid fuels, two methods can be used. First, the removal of oxygen by carbon monoxide (as $CO_2$) can allow the biomass to be converted to upgraded-quality liquid fuels. Second, the addition of hydrogen can allow the biomass to be converted to upgraded-quality liquid fuels. Appell et al. (1971, 1975) at U.S. Bureau of Mines during the early 1970's proposed the former route (carboxylolysis) to apply certain reaction schemes which were originally designed to liquefy pulverized biomass in a slurry medium with carbon monoxide with an alkali catalyst (5 wt % aqueous sodium carbonate). As a result, the conversion rate of biomass to upgraded quality liquid fuels was 90 wt% and oil yields generated were 40%.

According to Elliott (1981), a pilot plant using the principle of the Bureau of Mines' experimental studies was built at Albany, with funds from the US Department of Energy. 3 tons/day of wood chips were treated in this plant which started its operation in 1977. There were some problems. Plugging and corrosion of pipes and mechanical difficulties were shown to be problems. Finally, the plant was closed in 1979. Researchers at the Lawrence have sought some way of modifying some processes because of the problems. Berkeley Laboratory suggested a method of modifying the process of the Albany plant. It stated that prehydrolysis of the wood with dilute acid and the use of homogeneous hydrogenation catalysts, such as ferric chloride could result in the modification.

Nicholas et al.(1985) stated that production of liquid fuels by direct hydrogenation of biomass can help heighten the conversion rate from biomass to upgraded quality liquid fuels. Hydrogen can play a role as the deoxygenating agent ($H_2O$ formation) or as a hydrogenolysis agent (causing a complicated scheme of biomass depolymerisation reactions.) And hydrogen addition can also increase the H/C ratio of the final products. They pointed out that most of the early research on the hydrogenation of biomass was performed in terms of the determination of the chemical structure of lignin or production of certain oxygenated compounds apart from by obtaining liquid fuels from the biomass.

However, differently from this, Gupta et al.(1976) developed the research trend toward production of upgraded-quality hydrocarbon oils by the use of catalytic hydrogenation reactions. Gupta et al.(1976) at the Worcester Polytechnic Institute studied the nickel-promoted hydrogenation of cellulosic materials. They proved that cellulosic materials could convert into liquid hydrocarbon fuels by reaction with hydrogen at 425°C and 1000 psi in a slurry phase with paraffin oil and with 0.2 wt% nickel hydroxide catalyst.
Dissociation of hydrogen at the nickel metal sides produced hydrogen which reacted with partially pyrolyzed cellulose fragments and diffused through the liquid reaction medium. Oil yields were around 45%

On the other hand, Boocock et al.(1980) studied conversion of biomass to liquid fuels in terms of direct aqueous hydrogenation of poplar wood at temperatures of about 350°C and at pressures of 100atm with Raney nickel. Differently from the results of Gupta et al. (1976), they found that the oil was being derived from the lignin. And they found that the gases (mostly methane) deriving from the cellulose were shown (treatment of purified cellulose yielded only water-soluble organics and gases.). In their studies, they applied hydrogen as a reduction agent with fresh Raney nickel as catalyst. However, some of their experiments were performed with the mature catalyst without hydrogen. The results showed relatively high oil yields.

Chin et al.(1981) at the Pennsylvania State University attempted to convert algal material to liquid fuels at temperatures between 340 and 430°C and hydrogen pressures between 1 and 150 atm, with cobalt molybdate catalyst and an organic solvent. Results showed yields of up to 47 wt% of oil (in the C16 to C24 range). The oil yield increased as the temperature arose to 400°C. However, above that temperature, decomposition of the oil occurred which caused an increase in the yield of gaseous products. Higher hydrogen pressures and longer reaction times (up to 60 min) caused an increase in the oil yield. The research was focused on the study of use of molecular hydrogen as the reducing agent for biomass hydrogenolysis. Even if Wen and Lee (1979) didn't use hydrogen-donor solvents in their study and found certain advantages to these solvents, the general trend of research was usage of hydrogen-donor solvents. In fact, Oshima,

(1965) performed effective hydrogenation of wood lignin with cyclohexanol as the hydrogen-donor solvent

Nicholas et al.(1985) defined dissolution or solvent extraction of biomass as hydrogenation with a solvent. To enhance good solvent dissolution, the factors required are as follows: First, the biomass material should be heated up to the certain temperature of pyrolysis to cleave the labile bonds thermally; Second, readily available atomic hydrogen should exist to protect the reaction from repolymerisation of the thermally decomposed material. Therefore, the solvent should be able to donate hydrogen to the unstable biomass fragments. They conclude that various solvents can play a role of hydrogen donors as long as they include mobile carbon-hydrogen bonds. Good solvents can be defined as solvents able to dehydrogenate readily under liquefaction conditions resulting in enhancement of its solvation capabilities. Tetralin is one of the highly effective hydrogen-donor solvents. In addition, they suggested that to improve the bio-oil generated, oxygen in the bio-oil should be removed because heating value is inversely related to oxygen content. The most effective way of removing oxygen is using heat by which every two carbon atoms in a mole of biomass are converted into $CO_2$ removing two oxygen atoms as below. Production of carbon dioxide, however, means loss of carbon and lower oil yields. They warned that producing the carbon dioxide would mean loss of carbon and lower oil yields.

$$C_6H_{10}O_5 \xrightarrow{\text{heat}} C_4H_{10}O + 2CO_2 \quad \text{-----------------------------}(11)$$

(Nicholas,1985)

They also suggested another possibility of reaction of hydrogen which reacts with oxygen in biomass generating water.

$$C_6H_{10}O_5 + 4H_2 \xrightarrow{\text{heat}} C_6H_{10}O + 4H_2O \quad \text{---------------------}(12)$$

(Nicholas,1985)

## 2.12 Application of Triglycerides in solvent extract

Maher and Bressler (2007) stated that triglyceride based agricultural fats and oils can have an important role as alternative feeds for the production of fuels from biomass. Sonntag (1979) stated that oils and fats are mainly water insoluble, hydrophobic substances in the animal and plant world. They are composed of one mole of glycerol and three moles of fatty acids which usually are called triglycerides.

According to Maher and Bressler (2007), vegetable oils consist almost completely of triglycerides and a small percentage of mono and diglycerides. Graboski and McCormick

(1998) stated that pyrolysis of these materials could produce hydrocarbon rich liquid fuels which might be able to be up to a fraction of petroleum based distillates and petrochemicals. Karaosmanoglu (1999) reported that advantages of utilizing vegetable oils include their liquid nature, convenience for transport and processing and their high heat content (close to 90% of diesel fuel). Katikaneni et al. (1995c) also stated that vegetable oil fuels contain no water, are pH neutral, and are relatively stable. Shay (1993) mentioned the feasibility of the usage of triglycerides as a source of energy with a demonstration of the usage of engines with vegetable oils.

However, Knothe, G. et al. (1997) mentioned that common use and commercialization of vegetable oil fuels were banned due to economical reasons and poor properities. Petroleum derived fuels have been cheaper to produce compared to vegetable oils which have high value in the edible oil market. Recently, crude oil prices have increased and been recognised as a limited energy source, bio-diesel is getting more interest from global environmentalists as an alternative energy and more economical competitiveness is considered in recent times.

There are still many barriers to overcome for the vegetable oils to be a promising alternative fuels source. However, some efforts to improve the poor properties of vegetable oils and fats have been made. Ali and Hanna (1994), Knothe et al. (1997) and Ma and Hanna (1999) mentioned that typically, the following four methods have been included to improve the properties. First, diluting diesel fuel or solvents. Second, microemulsification. Third, transesterification, Fourth pyrolysis.

Pyrolysis or thermal cracking of triglyceride materials can be one method to produce renewable bio-based products suitable for use in fuel and chemical applications. This option is suitable to the areas where the hydroprocessing industry is well established due to the fact that the technology is very similar to that of conventional petroleum refineries. Stumborg et al. (1996) mentioned significant advantages of this type of technology better than transesterification. For example, there are advantages of compatibility with infrastrucuture, lower costs for processing, flexibility of feed stock, engines and fuel standards and so on.

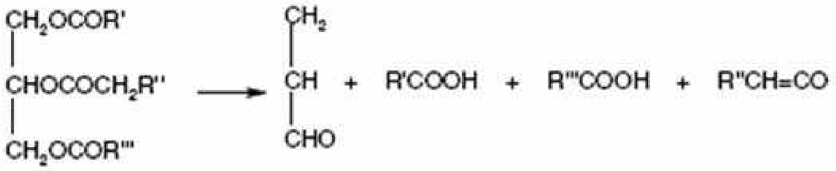
The most important point of usage of pyrolysis or thermal cracking of triglyceride materials is the fact that the final products of the process are similar to diesel fuel in composition.(Maher and Bressler, 2007) The pyrolysis of triglycerides can be performed with catalyst or without catalyst. Many model triglycerdies have been used to investigate reaction products and explain thermal decomposition pathways in pyrolytic conditions. For example, Kitamura (1971) used trilaurin, Higman et al.(1973) and Kitamura (1971) used tripalmitin for same usage and Higman et al. (1973) used tristearin as a model triglycerdies. This research was usually performed for food science purposes. Typical reaction products contained hydrocarbons, carboxylic acids, ketones, acrolein and esters.

Egloff and Morrell (1932) exemplified the process through early work including the cracking of cottonseed oil. Furthermore, Egloff and Nelson (1933) present examples of the process with Alaskan fur seal oil. These studies were conducted at increased temperatures of 445-485°C and under pressure of 0.93-1.3 MPa (which is 135 – 200 psi) and produced in the range of 57-60% gasoline hydrocarbons.

Chang and Wan (1947) reported that they produced motor fuels from Tung oil on a large scale for solution of potential fuel shortages during the war.

Fig.1 showed decomposition process of triglycerides as follows. [eq. (13) - (28) ]

- Decomposition of the glyceride



$$\begin{array}{l} CH_2OCOR' \\ | \\ CHOCOCH_2R'' \\ | \\ CH_2OCOR''' \end{array} \longrightarrow \begin{array}{l} CH_2 \\ | \\ CH \\ | \\ CHO \end{array} + R'COOH + R'''COOH + R''CH{=}CO \tag{13}$$

- Decomposition of fatty acids

$$RCOOH \longrightarrow CO_2 + RH \tag{14}$$

$$2RCOOH \longrightarrow CO_2 + H_2O + RCOR \tag{15}$$

- Decomposition of ketenes and acrolein

$$2R''CH{=}CO \longrightarrow 2CO + RHC{=}CHR \tag{16}$$

$$CH_2{=}CHCHO \longrightarrow CO + C_2H_4 \tag{17}$$

$$RCOCH_2R \longrightarrow R{-}R + CH_2CO \tag{18}$$

$$2RCOCH_2R \longrightarrow 2R_2 + CO + C_2H_4 \tag{19}$$

- Decomposition of paraffins

$$C_nH_{2n+2} \longrightarrow nC + (n+1)H_2 \tag{20}$$

- Dehydrogenation of paraffins

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2 \tag{21}$$

- Splitting Decomposition of paraffins

$$C_nH_{2n+2} \longrightarrow C_{n-m}H_{2n-2m+2} + C_mH_{2m} \tag{22}$$

- Alkylation of paraffins, the reverse of eq.(22).
- Isomerisation of paraffins

$$N - C_nH_{2n+2} \longrightarrow \text{iso} - C_2H_{2n+2} \tag{23}$$

- Aromatic cyclisation of paraffins

$$C_{(2n+6)}H_{(2n+14)} \longrightarrow C_nH_{2n+1} + 4H_2 \tag{24}$$

- Polymerisation of olefins

$$2C_nH_{2n} \longrightarrow C_{2n}H_{4n} \tag{25}$$

$$C_nH_{2n} + C_mH_{2m} \longrightarrow C_{(n+m)}H_{2(n+m)} \tag{26}$$

- Depolymerisation of olefins, reverse of eq.(25) and eq.(26).

- Decomposition of olefins to diolefins

- Decomposition of olefins to acetylenic hydrocarbons

- Aromatisation or cyclisation of olefins

- Hydrogentaion of olefins

$$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2} \text{ ------------------------------------ } (27)$$

- Isomerisation of olefins

$$n - C_nH_{2n} \rightarrow iso - C_nH_{2n} \text{ --------------------------- } (28)$$

Fig. 12 Decomposition of triglycerides (Chang and Wan, 1947)

Even though political and economic factors concerning the environment caused a significant interest in pyrolysis of vegetable oils for fuel production, there are still many requirements of instrumental and analytical techniques for better characterization of reaction products and understanding of reaction mechanisms related to the thermal decomposition of triglycerides. To carry out the research, cracking has been performed typically in batch reactors at temperatures of 300 -500°C and at atmospheric pressures. The final product bio-oils are typically collected and analysed as the organic phase.

Many feeds including a range of plant and vegetable oils have been used for study of pyrolysis products.

Chang and Wan (1947) used tung oil, Schwab et al. (1988) used sunflower oil, Schwab et al. (1988) used safflower oil, Idem et al.(1996) used canola oil, Lima et al.(2004) used soybean oil, Lima et al.(2004) used palm oil, Fortes and Baugh (1999,2004) used macauba fruit oil, Dandik and Aksoy(1998) used waste cooking oil, Lima et al.(2004) used castor oil, and Alencar et al.(1983) used various tropical vegetable oils.

The pyrolysis products of piqui, babbassu and palm oils were investigated by Alencar et al. (1983). Alencar et al. (1983) stated that after the cracking reactions carried out at 300-500°C at atmospheric pressure, the resulting chief products were alkanes and 1-alkenes. Schwab et al. (1988) showed simultaneously distilled and cracked soybean and high oleic safflower oil in the process of a destructive distillation. They collected 79% of the high oleic safflower oil and 70% of the soybean oil as distillates. The main products contained alkenes, alkanes, aromatics and carboxylic acids with carbon. The percentage of aromatics was between 1.9 and 2.3% and the percentage of carboxylic acids was between 9.6 and 16.1%. They tested the fuel properties of the pyrolyzates and found that pyrolysis generated products have lower viscosity and higher cetane values than the parent oil. This indicates that the properties of the oils were improved. Lima et al. (2004) investigated the pyrolysis of soybean, caster, and palm tree oils at temperatures between 350 and 400°C. They distilled the pyrolysis products into four fractions and analysed the heavy fraction (DT>200°C). They found that the pyrolysis products of the palm oil (including a higher percentage of saturated fatty acids) contained the largest heavy fraction. The main products generated included hydrocarbons and oxygenated organic compounds such as alkenes, alkadienes, carboxylic acids and alkanes. But they didn't find any aromatics. The result was different from previous results by Schwab et al. (1988). They used batch reactors to conduct the research. However, Idem et al.(1996) mentioned that the batch processes could not be converted to larger scale operations because clean-up and charging of the feed after each run are required and low throughput and frequent interruptions are involved. Thermal cracking of canola oil in a flow type reactor over a fixed bed of inert materials was investigated by Idem et al.(1996). The conversion rate by the experiment showed values between 54% and 100%. And the results were very dependent on operating variables. The final products were mainly composed of C4 and C5 hydrocarbons, C6 aliphatic and aromatic hydrocarbons, and C2–C4 olefins as well as a diesel-like fuel and hydrogen. The same group of researchers in earlier work reported results with very low oil conversions (14%) and little gas production despite the fact that the conditions and reactor were similar. 26% of the liquid products were composed of C6–C12, non-aromatic hydrocarbons. No aromatic compounds were found in the liquid fraction. Because the feeds are edible oils, the processes using many of the feeds were uneconomical.

Dandik and Aksoy (1998) investigated the conversion of used cooking oil to fuel and chemical feedstock through the use of a fractionating pyrolysis. They fed used cooking oil to a special fractionating pyrolysis reactor at temperatures between 400°C and 420°C for about 180 minutes. Various hydrocarbons in the C5–C17 such as paraffins, olefins and their isomers, aromatics, cycloparaffins, and cycloolefins were contained in the pyrolysis oil generated. Most research involving in the pyrolysis of vegetable oils has generally been conducted at temperatures between 300°C and 500°C with longer residence times. This cannot be said of fast or flash pyrolysis because true fast or flash pyrolysis generally requires the order of seconds for reaction time.

Fortes and Baugh (1999, 2004) investigated the pyrolysis of macauba fruit oil under conditions closer to fast pyrolysis. Compared with other studies on the pyrolysis of triglyceride based oils, the temperatures were as high as between 400 and 1000°C and the times were as short as between 10 and 30 seconds. They found the main products were aldehydes, carboxylic acids and alkenes, the secondary products were alkanes, cycloalkanes and unknowns.

Figure 2.13 depict the decomposition of triglycerides in pyrolysis.

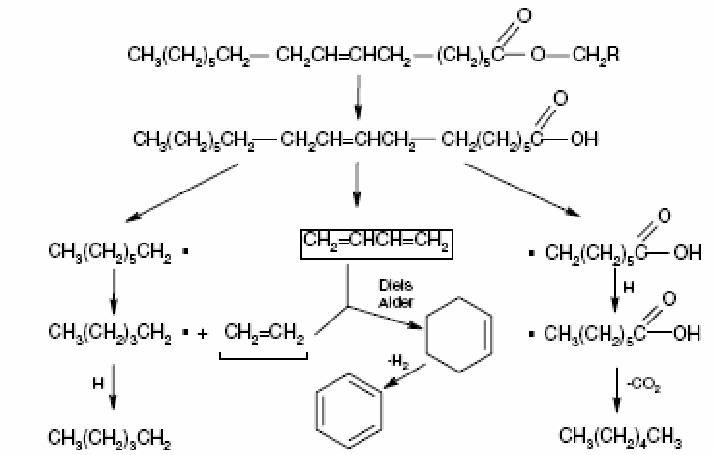


Figure 2.13: Decomposition of triglycerides by pyrolysis (Schwab et al. 1988)

## 2.13 Overview of crude oil (petroleum)

According to George W Mushrush and James G.Speight (1995), by different temperatures, crude petroleum can be separated into a variety of different generic fractions. Not only distillation, but also solubility and adsorption properties can separate the petroleum into fractions.

Petroleum is sometimes called crude oil covering an enormous amount of materials composing gaseous, liquid, and solid hydrocarbon-type chemical occurring in sedimentary deposits on earth. (Speight, 1991).

George W. Mushrush and James G. Speight (1995) mentioned that depending on viscosity petroleum can be divided into conventional crude oil, heavy oil, Extra-heavy crude oil and bitumen. They explained high viscosity of heavy oil is the different property from conventional petroleum. Thermal stimulation of the reservoir is required in the recovery of this type of petroleum. Differently from conventional crude oils, heavy oils have darker in colour and even black in some cases. Extra heavy oil is near- solid state and actually unable to flow free under ambient conditions. Bitumen (often called native asphalt) is a subclass of extra heavy oil and contains various reddish brown to black materials of semisolid, viscous to brittle character which can exist in nature.

Following table 2.6 explains type and characteristics of crude oils. And Figure 2.14 shows classification of crude oils. Furthermore, Figure 2.15 indicates typical compounds in bitumen.

| Type of crude oils | Characteristics |
|---|---|
| 1. conventional/"light" crude oil | Density <934 Kg/gm3 (>200°API) |
| 2. "Heavy" crude oil | Density:1000 kg/m3 > 934 kg/m3<br>100°API to < 20° API)<br>Maximum viscosity : 10,000 mPa (cp) |
| 3. "Extra-heavy" crude oil; may also include atmospheric residua | Density >1000 kg/m3<br>(<10°API)<br>Maximum viscosity: 10,000 mPa (cp) (b.P.>340°C; > 650'F) |
| 4. Bitumen may also include vacuum residua | Viscosity >10,000 mPa (cp)<br>Density >1000 kg/m3 <10°API<br>(b.p. > 510°C; > 950'F ) |

Table 2.6: Type and characteristics of crude oils (George W. Mushrush et. al.,1995)

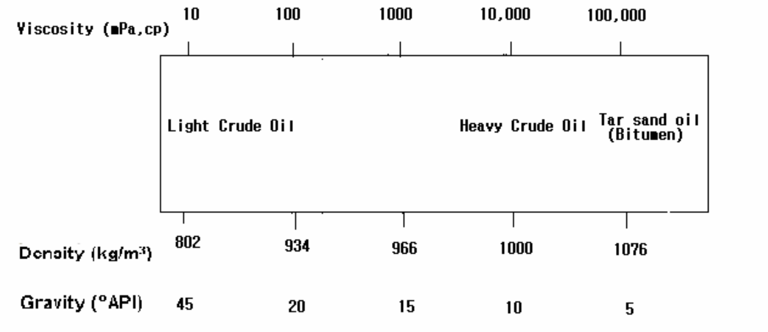


Figure 2.14: Crude oil classification by gravity, density and viscosity (George W. Mushrush et. al.,1995)

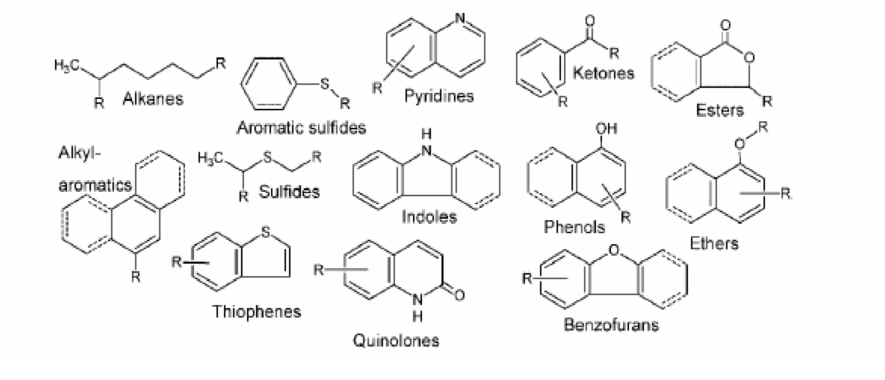


Figure 2.15: Typical organic functions in bitumen ( Masson, 2008)

According to Masson (2008), typical bitumen shows functional groups as shown in Figure 2.15.

# CHAPTER THREE
# MATERIALS AND METHODS

## 3.1 Introduction

This section introduces the sources of soil samples, their preparation technique and methodology. Procedure of experiments is as shown in Figure 3.29.

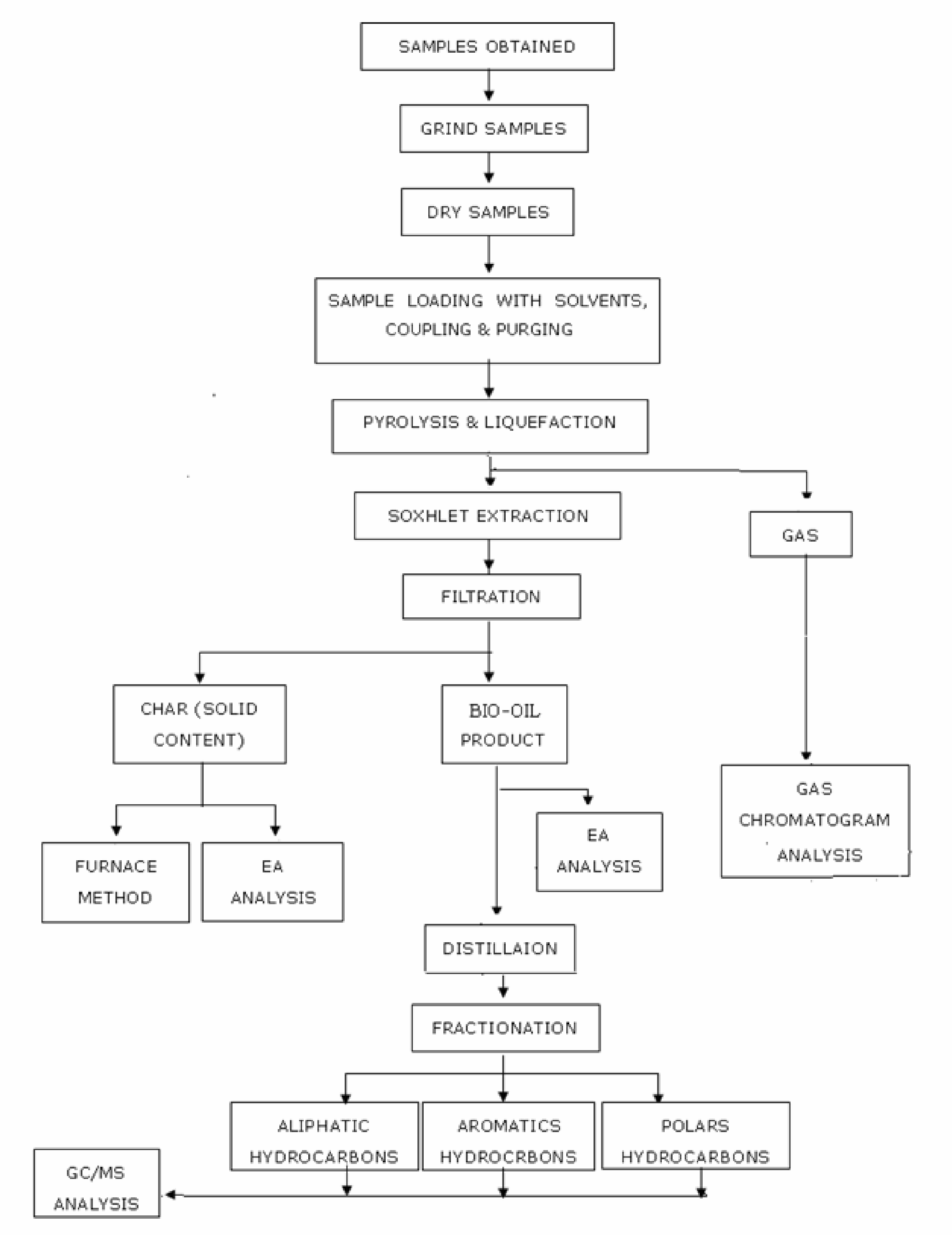


Figure 3.1: Schematic of experimental process

## 3.2 preparation

### 3.2.1 Bamboo sample

The raw bamboo sample used in this study was 3.4 kg bamboo collected from Non-san, South Korea. Only trunk part of the bamboo was collected. The sample was collected from the bamboo tree estimated to be about 6 years old. The tree was falled approximately 1 month before sampling.

The collected bamboo sample was ground with a Retsch SM 2000 mill to fine powder smaller than 20 meshes (-0.8mm) of B4 laboratory in the University of Nottingham. To remove moisture content of the bamboo sample, ground bamboo sample was dried in a vacuum oven for 24 hours at 100°C before use. The moisture content within the bamboo was determined using following oven method.

$$(\text{original weight of bamboo} - \text{dried weight of bamboo})/\text{original weight} \times 100\ \%$$

This moisture content is similar to the value of 7.3% from previous study by Su-Hwa Jung et al. (2008)

The bamboo samples were obtained after drying is maintained in a vinyl plastic bag to keep it from re-equalisation of moisture by vapours on the air.

Figure 3.2: Ground and dried bamboo maintained in the vinyl plastic bag

### 3.2.2 Solvent samples

#### 3.2.2.1 Hydrocarbon solvent

Tetralin (1,2,3,4-tetrahydronaphthalene; purity 95%) was selected as the high rate hydrogen-donor solvent because it has been shown as the higher rate of donating Hydrogen in comparison of many other solvents. On the other hand, 1-methylnaphthalene (purity 99%) was selected as the low rate hydrogen-donor solvent.

#### 3.2.2.2 Bio-oil derived solvent

Vegetable cooking oil was selected as the typical bio-oil derived solvent. Waste oil from cooking pork was selected as the bio-oil derived solvent to see if the waste oil can be used as a solvent for pyrolysis and liquefaction.

Waste oil from cooking pork was collected from a South Korean restaurant named "Bul-ta-neun Sam Gyup Sal" located in Korea Seoul. 3.4 kg was obtained. Vegetable cooking oil was purchased from a local supermarket named Sainsbury's in Nottingham, UK.( Stoney St. Beeston, Nottingham, Nottinghamshire, NG9 2LA, United Kingdom)

#### 3.2.2.3 Others

Toluene and DCM (Dichloromethane) for collecting products and washing devices were provided from the lab too. BBOT (2.5 Bis (5-tert-butyl-benzoxazol-2-yl) Thiophene) for standard analysis and Vanadium Pentoxide for sulphur analysis in EA (Elemental Analysis) were provided from the lab as well.

## 3.3 Thermal extraction experiments

### 3.3.1 Experimental Setup

The solvent extraction experiments were performed by using the pyrolysis equipment shown in Figure 2 and 3. The equipment is made of a Parr 4740 series stainless steel (22ml cylindrical) pressure vessel.

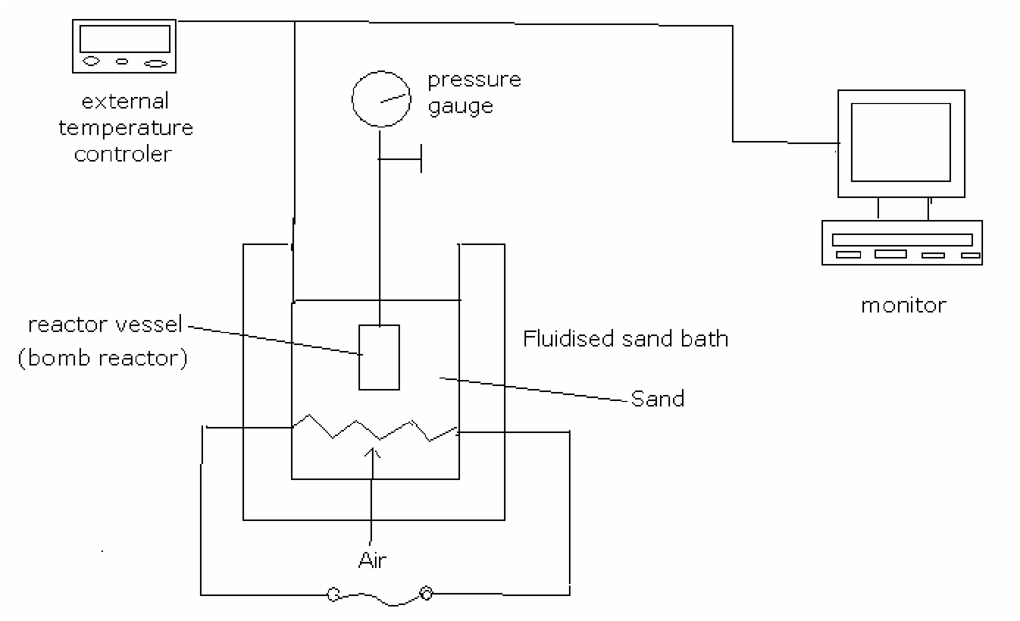


Figure 3.3: Schematic of thermal extraction (pyrolysis and liquefaction)

Figure 3.4: Fluidised sand bath and pressure gauge reactor set-up

Heat was supplied and controlled by a fluidized sand bath controlled by an external temperature gauge. An additional K-type thermocouple connected externally to a computer allowed temperature to be monitored every 10 seconds.

This is a batch type reactor for research purposes. Batch processes can be impractical in larger scale operations because they necessitate cleaning and charging of the feed after every run and often low throughput and frequent interruptions happen. (Idem et al., 1996)

Solvent extraction experiments were performed on bamboo powder (sawdust) at a stabilised temperature (410°C) for 1 hour with various solvents (tetralin(1,2,3,4-tetrahydronaphthalene), 1-methyl-naphthalene, vegetable oil and waste oil from cooking pork). Sample to solvent ratios of 1:2.5 were applied. Applied mass of bamboo was 5 g and mass of solvent was 12.5g.

As baseline experiments, 5 g masses of bamboo without solvents and with 5ml water were applied to the experiments respectively.

Note: in this study, reactor was injected into the sand bath after the temperature of sand bath reached 410°C and was stabilized. (It took around 40 minutes to reach at 410°C.) Therefore, heating rate is considered to be very short. (Almost ignorable)

### 3.3.2 Method of Reactor coupling, purge and sand bath operation

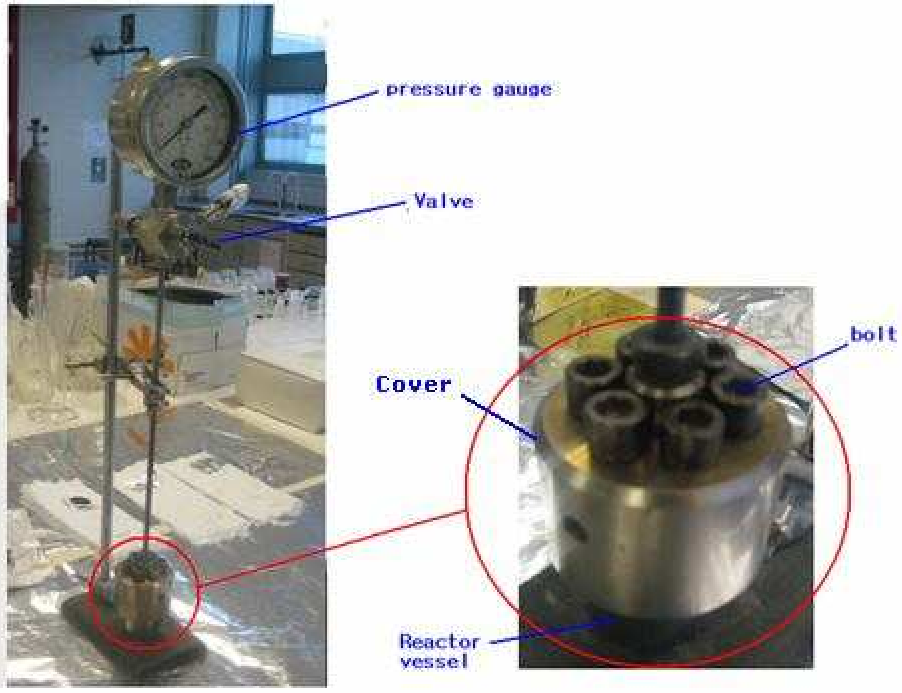


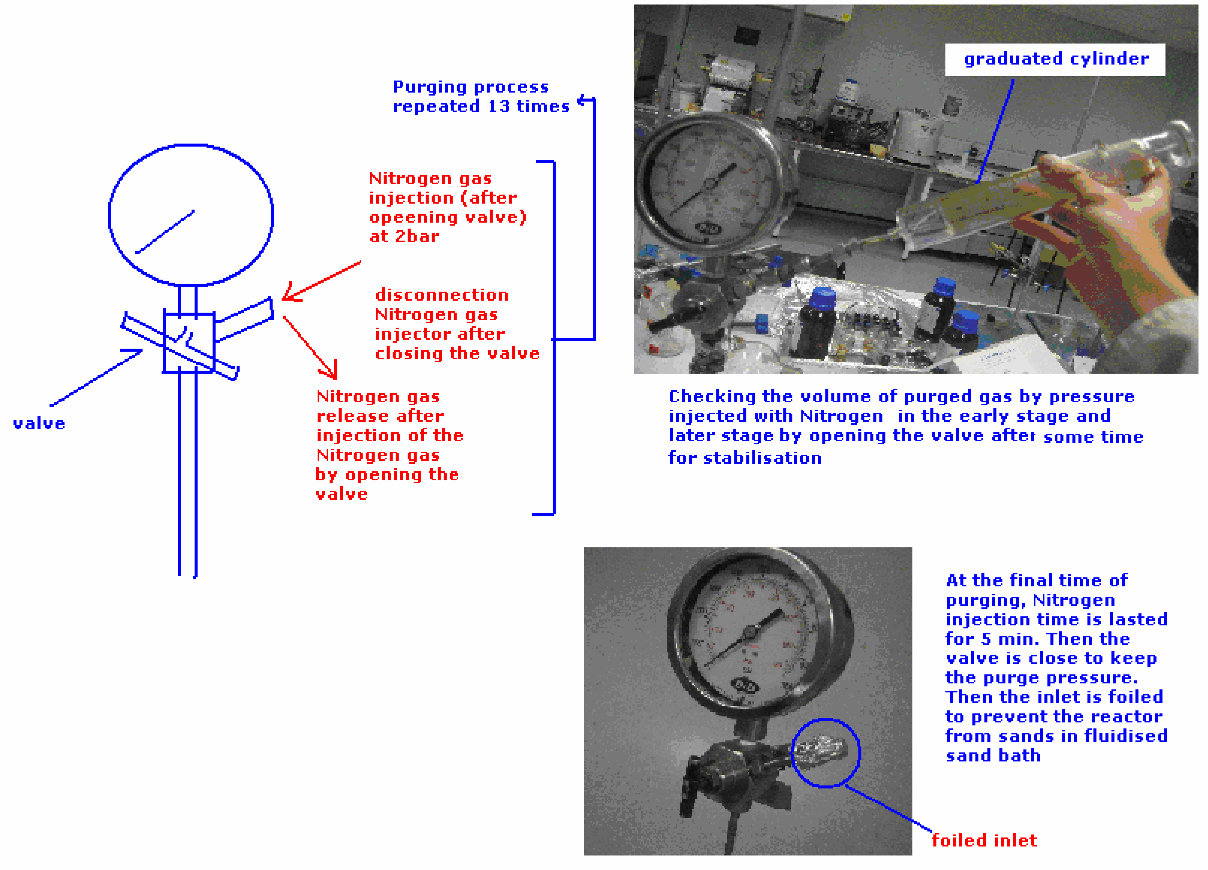
Figure 3.5: pressure gauge reactor (bomb reactor)

Figure 3.6: Breakdown of pressure gauge reactor (cover & reactor vessel)

To make sure during the process, all equipment was completely leak-tight and contamination free, before each new run, all equipment and devices were washed by using DCM. This is a kind of bomb reactor which is batch type reactor for research purpose. Six bolts were used to bolt the top to the vessel of pressure gauge reactor to create a leak free seal. Using torque wrench, the bolts were torque up to 15in-lb after torque to 10in-lb. Once the top was closed, the pressure gauge reactor was purged with inert gas (Nitrogen) and checked for leaks. For every experiment conducted, the experiment set up was purged for about 20 minutes with nitrogen gas to decrease the oxygen content of the system. Then, 2 bar pressure of nitrogen gas was applied into the system to keep the reactor to inert state with the pressure of 2 bar, the pressure gauge reactor was purged 13 times. After 13 times complete purge cycles the vessel was charged to the desired initial pressure 2 bar. The purged pressure of the reactor was checked twice at the early time and at the later time during the purge cycles. At the end of the purging, by waiting 5 minutes to pressurise the Nitrogen gas to the reactor and then close the valve of the pressure gauge reactor and wrap the tip of the reactor with foil to prevent the reactor from intrusion of sands in the sand baths.

Purged volume of each experiment was checked to see if the condition of experiments is consistent. Purging was done twice for each experiment (initial stage and final stage).

Pressure gauge reactor with bamboo without solvent purged the biggest amount of air inside. And pressure gauge reactor with bamboo with water solvent purged the second biggest amount of air. It is considered that the bamboo without solvent contained the biggest amount of air to be replaced by nitrogen. And the reactor with bamboo with water also contained 5 ml water only due to the fact that the water can be too volatile to set in the reactor with 5 g which was less than amount of the other solvent. Therefore, more amount of air needed to be replaced by nitrogen. Blank run of vegetable oil also would have required more nitrogen gas to purge since it doesn't contain Bamboo biomass. Overall, the purged pressure in the beginning stage and later stage of was pretty same. So, the consistency of the purging the previous air in the pressure gauge reactor with nitrogen inert gas was approximately assumed. Deviation was maximum around 5 ml which was quite a bit small.



Checking the volume of purged gas by pressure injected with Nitrogen in the early stage and later stage by opening the valve after some time for stabilisation

At the final time of purging, Nitrogen injection time is lasted for 5 min. Then the valve is close to keep the purge pressure. Then the inlet is foiled to prevent the reactor from sands in fluidised sand bath

Figure 3.7: schematic of purging process

The sand bath connected to an external temperature control and compressed air course was pre-heated to reach the required temperature (410°C) and left for around 45 minutes to equilibrate. In this study, concept of heating rate was not applied. After temperature was stabilized, the pressure gauge reactor was lowered onto the sand bath and left with a constant air flow through the sand bath to be run. A pressure was checked through gauge of the reactor. The temperature change was also checked on the monitor. Every 10 minutes, the average of temperature was checked and the average of temperature was calculated to see if the final temperature average becomes 410°C which is setting temperature.

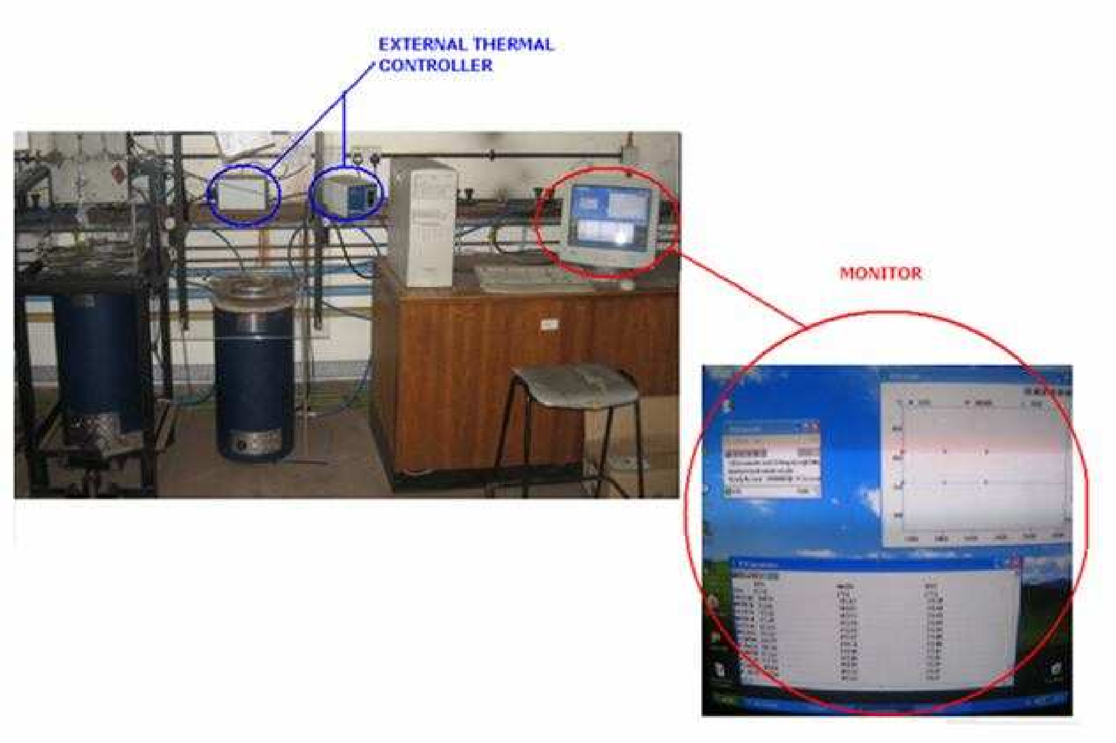
After one hour, the final pressure was recorded and the reactor was removed immediately from the sand bath. And then the reactor was cooled down to room temperature before product recovery.

Pressure changes in the pyrolysis and liquefaction process were checked to see if the condition of experiments is consistent. Pressure changes of pressure gauge before and after pyrolysis are as below.

Reaction of bamboo without any solvent was the smallest amount of pressure generated. It seems because there was no solvent in it which doesn't evaporate. Therefore, the pressure increase wouldn't big. Gas generated from bamboo was purely from bamboo itself based on the result of 18bar from time cooled down.  On the other hand, reaction of bamboo with water made the pressure of the reactor increase dramatically to 149 bar. It seems because the low boiling point water evaporated fast which would increase the pressure high. Even the amount of water put there wasn't large (only 5 ml). Based on the fact that the value of pressure in reaction of bamboo with tetralin or 1-methylnaphthalene is higher than reaction of bamboo without solvent, the pressure in the reaction of bamboo with solvents contains that of solvent vapours. The final pressure was found to be higher in reaction of bamboo with vegetable oil or waste oil from cooking pork. This would be because the vegetable oil or waste oil from cooking pork would be decomposed to bio-diesel generating quite a bit of gases. For pressure of the vegetable oil's generation, the blank vegetable run indicated that 70bar was caused by the vegetable oil not the pressure by generation of gas from bamboo. (Schwab et al.1988) Deviation value was shown as small. So, consistency of condition of pyrolysis and liquefaction was somewhat proved.

The temperature is very important parameter for operation during the pyrolysis process because it can directly affect thermal depolymerisation reactions. Way of controlling the vapour-liquid system inside the reactor was indirectly achieved through temperature control since the vapour-liquid system was in equilibrium after the operation became stable.

Figure 3.8: External Temperature Controller



<pico-log recorder, pico-log spread sheet, pico-log graph>

Figure 3.9: Fluidised sand bath monitoring system

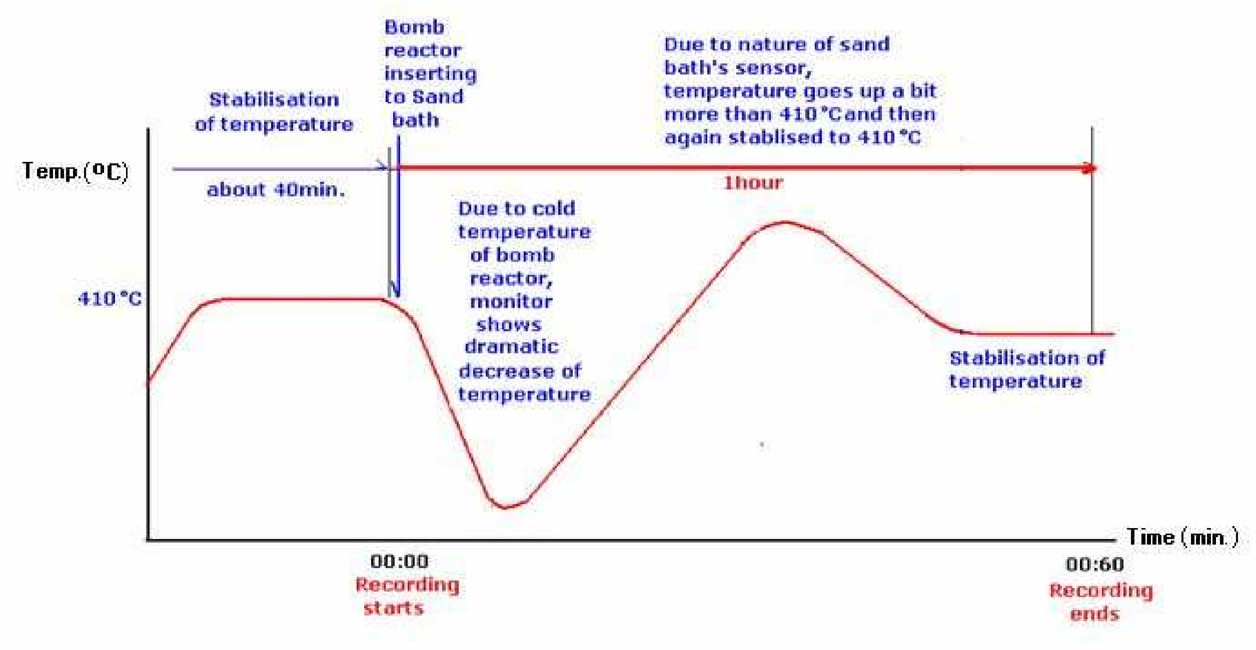


Figure 3.10: Pico-log graph

From starting point of recording to ending point of recording, the average temperature is around 410°C

## 3.4 Gas Analysis

### 3.4.1 Gas chromatography (GC)

To separate mixtures of chemicals to individual components, Gas Chromatography can be used. Each component can be analysed individually once it is separated one another. When the sample mixture is injected into a mobile phase, usually helium, the components in the mixture are separated. The sample mixture is carried through a stationary phase by the mobile phase. The mobile phase is a chemical selectively attracting components in a sample mixture usually contained in a column or tube. Interactions with the stationary phase occur by the mixture of compounds in the mobile phase. Interaction of each compound in the mixture occurs at a different rate. Elusion by the faster interacting compounds will occur first and that by the slower compounds will occur last. If the characteristics of the mobile or stationary phase are changed, different mixtures of chemicals can be separated completely. Adjustment of temperature or pressure in the system will be able to help further separation of compounds which might be able to elute too close together. When a compound is present, the detector can create an electronic signal. If the concentration is higher, the detector will send the higher electronic signal to a computer for processing.

### 3.4.1.2 Procedure, Instrumentation and Conditions

Gas generated while doing the pyrolysis process were collected from the pyrolysis pressure gauge reactor with a graduated cylinder (caution: open valve gradually not for liquid mixture to come out). And they were transferred into a gas bag (flushed three times with nitrogen before use) with graduated cylinder. Note: Graduated cylinder can hold only up to 100 ml at a time. So, several time collections are demanded by repeating closing an opening the valve of pressure gauge reactor.(only when collecting the gas, the valve should be opened.) After collecting gas sample with gas syringe from the gas bag, by injecting it to GC immediately, gas sample was analysed on a Carlo Erba HRGC 5300 gas chromatograph fitted with FID detectors operating at 200°C. Hydrocarbon gas was decided by FID using a Chrompak CPPorapakplotQ capillary column (27.5 m x 0.32 mm, 10µm film thickness) by injecting 200 µl at 100°C. As a carry gas, Helium was used and oven temperature was 70°C (hold 2 min) to 90°C (3 min) at 40°C min$^{-1}$, then to 140°C (3 min) at 40°C min-1 and finally to 180°C (49 min) at 40°C min$^{-1}$. On the base of an external gas standard with 10 µm $CH_4$ gas at 2 bar, which is analysed by GC before the sample gas was injected, individual gas yields were decided quantitatively.

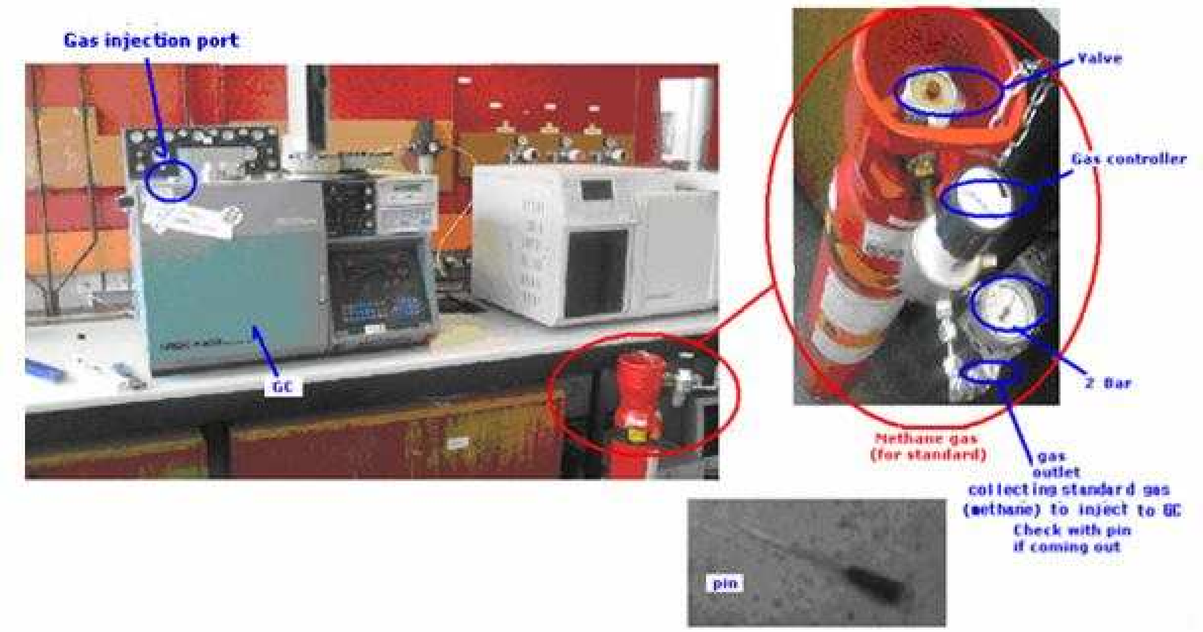


Figure 3.11: Gas Chromatography (GC) and Standard gas (Methane)

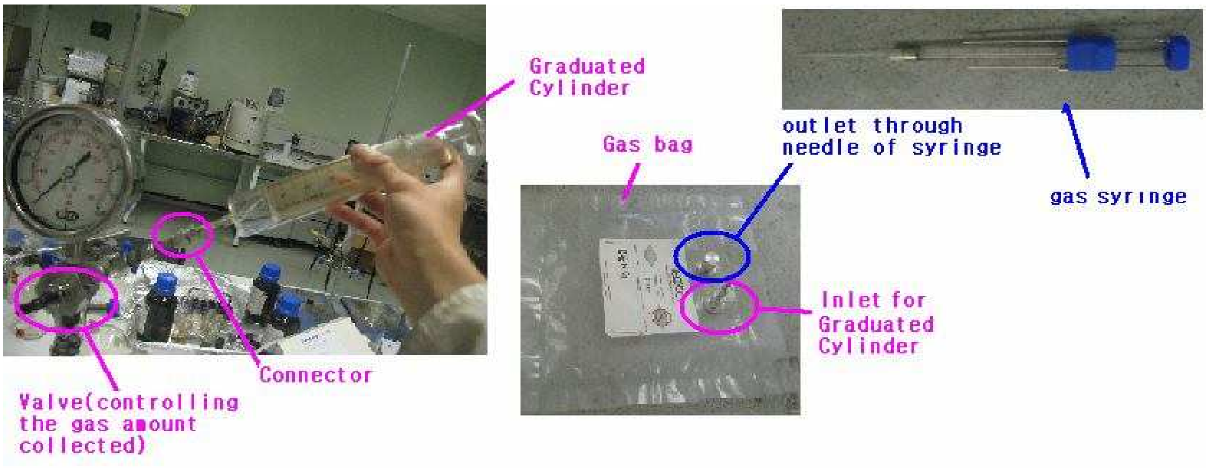


Figure 3.12: gas collection from pressure gauge reactor

### 3.4.3 Calculation of amount of hydrocarbon gas by GC.

1) % Volume of gas generated in sample analysed

= Peak Area of Gas / (Peak Area of Standard X Response factor) X % Volume Gas Present in standard

2) % volume of individual gas present in sample analysed in micrometers $(\mu m)$=% volume of individual gas present in sample analysed (1) above X volume of sample analysed.

3) Volume of gas generated = volume of whole gas generated during experiment /volume of sample analysed in mls X volume of individual gas present (ml) in sample analysed (ml)

4) Moles of individual gas generated = volume of individual gas generated/molar volume of gas at standard

5) Concentration of individual gas generated in $g/dm^3$= moles of the individual gas (from N) above X molar mass of gas

6) Mass of individual gas generated in mg = mass of gas in $g/cm^3$ X 1000

From Peak area of standard/ %volume of gas in standard = Peak area of gas/%volume of gas in sample

Calculating gas yield from methane standard = sample peak area × $C_3H_4$ standard peak / sample peak area in old standard.

Note: Response factors

$CH_4$ - 1.00
$C_2H_4$ - 1.7921
$C_2H_6$ - 1.8754
$C_3H_6$ - 2.6447

Note: $C_3H_8$, $C_4H_{10}$ and so on are omitted in this study because the GC used can not detect those and those are ignorable because peak areas of those are very small.

C1-C3 Gas yield from pyrolysis of bamboo biomass with tetralin solvent as an example

= $CH_4$ area in sample X $CH_4$ area in new standard / $CH_4$ area in old standard

For standard ($CH_4$), height of peak is higher than 300 mV

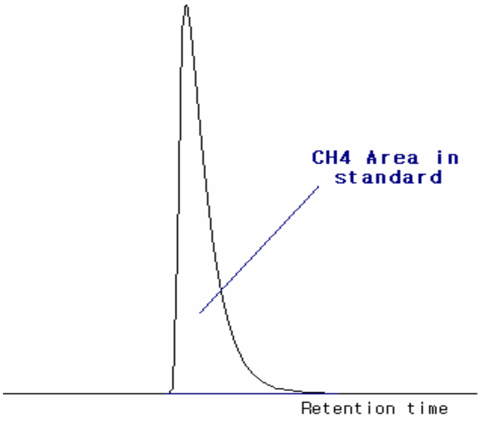


Figure 3.13: Peak of standard gas (Methane)

By integrating each area using mouse in the monitor, the areas of peaks of $CH_4$, $C_2H_4$, $C_2H_6$ and $C_3H_6$ are obtained automatically.

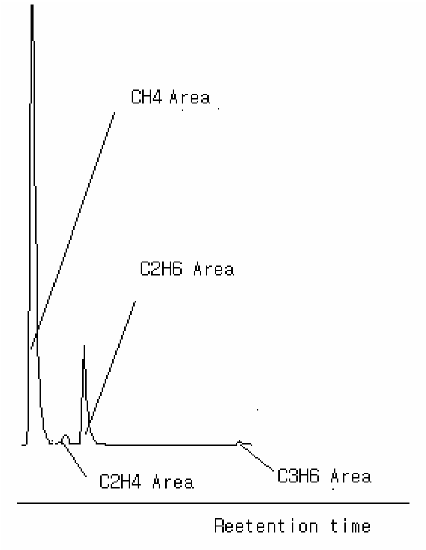


Figure 3.14: Peak of sample Gas

## 3.5 Recovery of generated liquid products

### 3.5.1 Soxhlet extraction

To recover the liquid generated from the experiments, the reactor contents were washed with toluene and transferred to a round bottom flask. With a soxhlet apparatus, the toluene washing was refluxed for between 17 hrs and 20 hrs. At this time, 150 ml toluene is used to wash.

Note: Soxhlet apparatus is usually applied to experiments where precise extraction of very precise quantities of materials is required. The reflux is performed at the boiling temperature of the solvent applied. In case for toluene (Boiling point (111 °C)), a lot of energy would be consumed which is not economical.

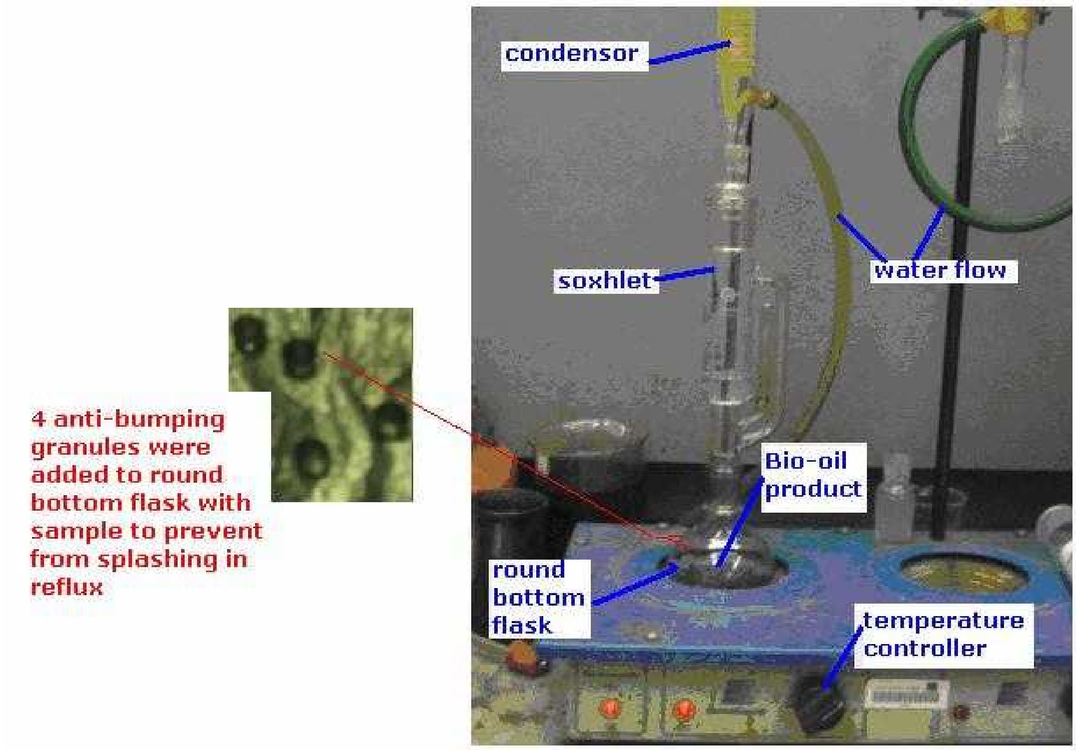


Figure 3.15: Soxhlet Extraction

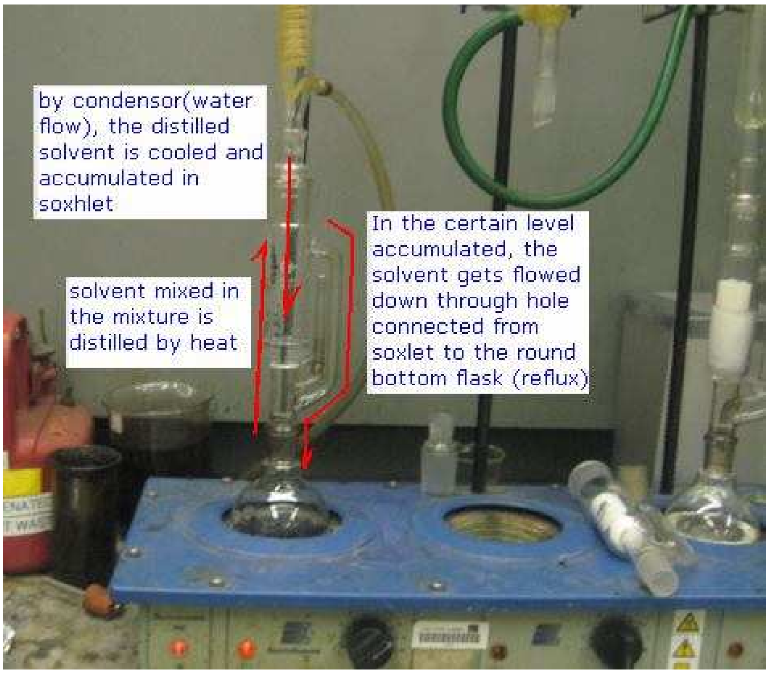


Figure 3.16: Reflux

### 3.5.2 Filtration

After refluxing ended, the whole material in soxhlet was left for 10 minutes to cool the equipment down. Then, soluble materials in the material were filtered from the non-soluble materials. The non-soluble materials left on the round bottom flask were washed with fresh solvent, any soluble materials left were filtered again from the non-soluble materials. The residue was separated from the liquid and solvent (toluene soluble) by filtering with a 0.5 glass fibre filter paper. After that, the toluene used to wash is evaporated on the air.

Differently from the other experiments, materials generated from experiment of bamboo with water solvent was dried in vacuum oven at 45°C for 3-4 hrs to remove the water before refluxing.

After the separation of insoluble materials and soluble, the insoluble (solid char or residue) was left on air to be dried before being weighed. The soluble (liquid product) was left in a vial to be dried.

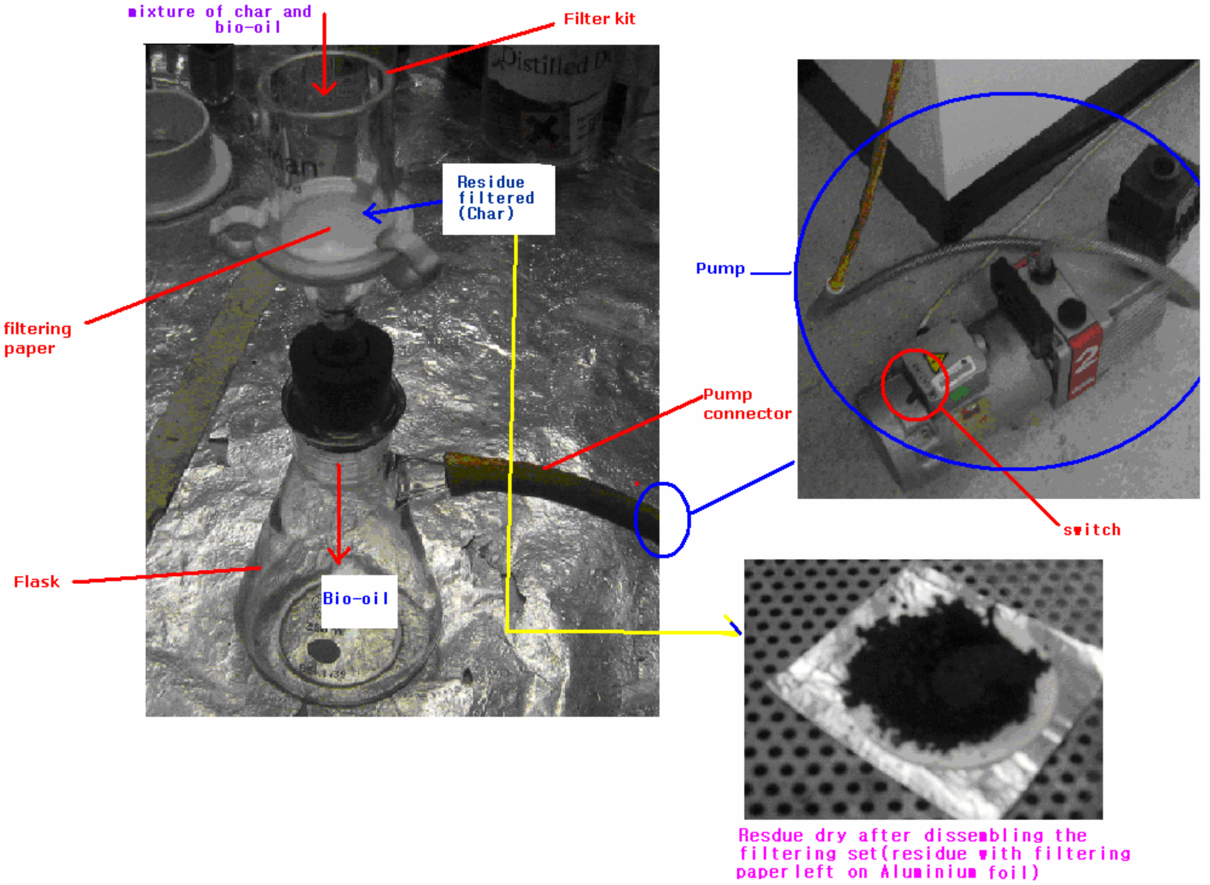


Figure 3.17: Filtration

### 3.5.3 Evaporation

To evaporate the solvents used in the liquefaction, rapid evaporation by a rotary evaporator and evaporating in the vacuum oven for around one day would be necessary. However, in this study, evaporating on the air atmosphere has been performed to simplify procedure of these experiments. (Note: This method performed in this study cannot completely remove solvent used in the liquefaction to 100%. Solvent dominated results were obtained in this study.)

### 3.5.4 Distillation

Dried materials (DCM solubles) from the liquid were collected in the small steel container using DCM and final product was recovered by distilling the solvent at about 60°C on the magnetic heater stirrer (hot plate). At this time, the magnetic heater stirrer was used only for heating not stirring. One thing to caution was the bio-oil should not be thermally altered when it is not thermally stable by controlling temperature. And another reason for applying low temperature is if it is too high, the liquid can be splashed, which could cause loss of the sample. (Note: Most of the hydrocarbon is assumed to be DCM solubles.)

After a while, after cooling down, the bio-oil moved out of the magnetic heater stirrer to cool down for about 15 minutes to 20 minutes and poked with pasture pipette to check if distilled enough or not by hardness of the bio-oil(if hard enough after cooled, the distillation is done). If not, the bio-oil sample container was put back to the magnetic heater stirrer to be distilled more. The reason why this procedure is necessary is because if the bio-oils are distilled too much, it became like rock which is very hard to be recovered for analysis.

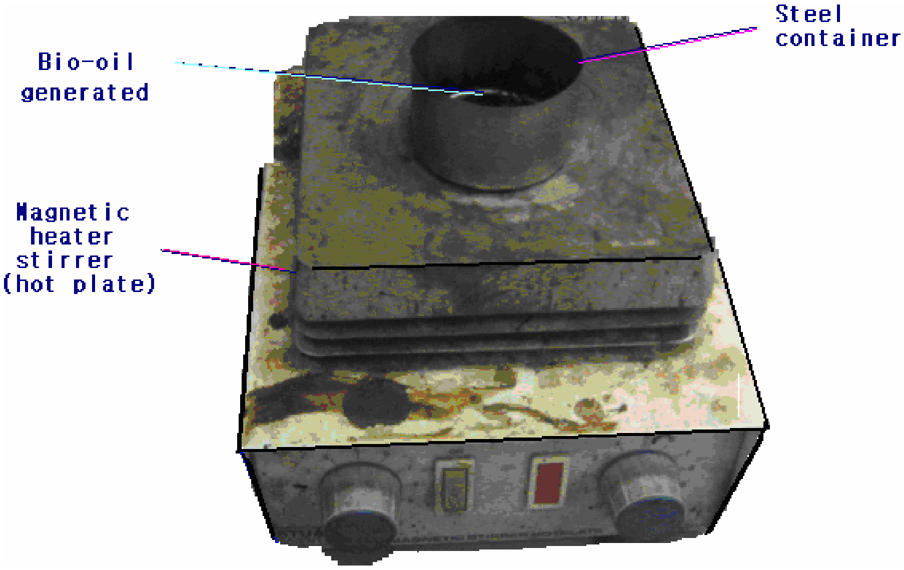


Figure 3.18: Distillation

After distillation, the heavy bio-oils were investigated by the elemental analyser and were fractionated to be analysed by Gas Chromatography/Mass Spectrometry (GC-MS).

### 3.5.4 Fractionation

To find characteristics of the bio-oils, fractionation was performed. By deleting an empty vial weight from weight of the vial with fraction obtained, the fraction weight was found. In this study, the fractionation was applied to investigate distribution and compounds of each fraction in different view after fractionation of the heavy liquid products obtained from the experiments in detail by GC-MS. (note: the vials used in this study were weighed around 7.0 g to 7.2 g.)

### 3.5.4.1 Preparation of sample

Two glass vials were prepared for each sample. In one vial, by deleting original vial weight from total weight including sample (distilled bio-oil) scooped in the vial, the weight of the sample was recorded. At this time, the range of weight applied to the sample was from 40mg to 60mg. In the other glass vial, silica was weighed by deleting the original vial weight from total weight including silica added in the vial. The range of silica was applied to weight around 78mg.

A few drops of DCM dissolved bio-oils added to silica in a glass vial and left under fume cupboard for the DCM to dry off with a pasture pipette for around 15 minutes to dry faster by ventilating air in the fume cupboard. After distillated completely, the dried part is mixed uniformly by shaking and another drops of DCM dissolved bio-oils added to the silica in the glass vial again. And the vial was left under fume cupboard for another 15 minutes. Until all transferred bio-oil in one side glass vial transferred to the other glass vial with silica, the process was continuously repeated. This uniformed sample is to make the bio-oil sample held in the column without passing through before fractionation is done.

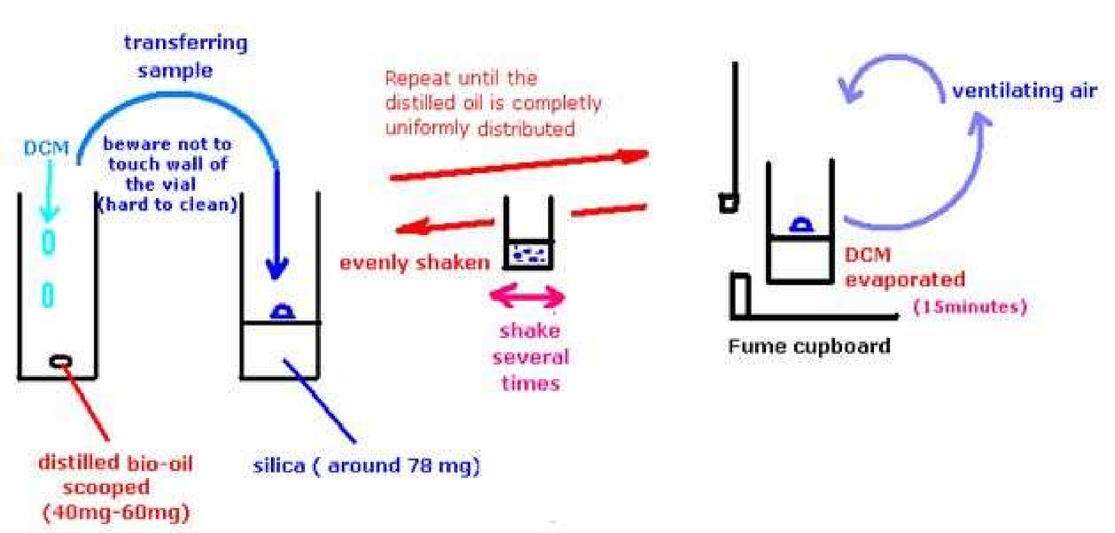


Figure 3.19: Sample preparation for fractionation

### 3.5.4.2 Fractionation procedure

The prepared columns are first rinsed with DCM opening the top and rinsed with Hexane afterwards to clean. The separation of the organics extracted was performed by a silica-alumina column (Figure 4.5). Proportion of silica and alumina in the column was 5 to 1 respectively. 78 milligrams of silica were mixed with 40 to 60 milligrams of bio-oil sample.

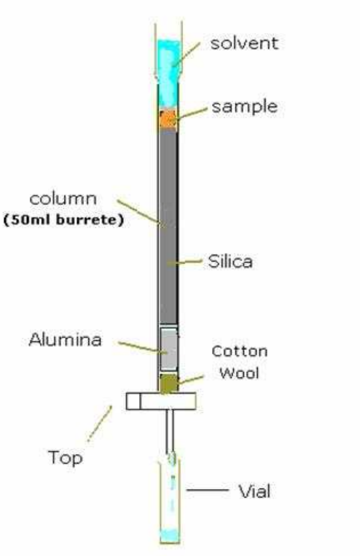


Figure 3.20: Fractionation set-up

In the start, by pouring hexane of 15 ml, aliphatics were separated in the first glass vial which was set in the bottom of the 50 ml burret to collect. At this time, pouring small amount on the top of the burret because it could only hold limited amount of solvents. Aliphatic liquid was collected drop by drop up to 15 ml. The colour of the collected aliphatic liquid is colourless. Once the aliphatics were separated, the extraction of the aromatics with the hexane-DCM solution was performed. In this case, the colour of aromatic liquid is yellow which was collected in another glass vial under the bottom of the 50 ml burret by switching previous aliphatic collecting vial. After collecting 15 ml of aromatic liquid, polar compounds separation was conducted. At this time, the extraction of the polars with the methanol-DCM solution was performed. In this case the colour of polar liquid is dark brown which was collected in different glass vial under the bottom of the 50 ml burret by switching previous aromatic collecting vial.

After the solvents evaporated, the vials were weighed again to make sure the mass of the aromatics and aliphatics extracted from the samples.

By deleting the value of weight of collected aliphatics, aromatics from that of initial sample weight, polar compound weight was found. At last, aliphatic fractions, aromatic fractions and polar fractions were prepared for the GC-MS analyses. To prepare the samples for GC-MS, some DCM was added to the extracts in the vials. At this time, each vial was washed with DCM three times and transferred to each GC-MS vial. Pipettes used were changed in every different sample not to mix one another. Caution was paid not to lose any solution concentration. The prepared samples were used for GC-MS analyses.

## 3.6 Analysis of bio-oil

### 3.6.1 Gas Chromatography / Mass Spectrometry (GC/MS)

#### 3.6.2.1 Instrumentation and Conditions of GC/MS

Two devices are actually composed in GC/MS combining to make a single method of analysing mixtures of chemicals. The components of a mixture are separated and are characterised individually. Both qualitative and quantitative evaluations of a solution including many chemicals are possible by combining the two devices.

When the individual compounds elute from the GC column, they enter the electron ionization (mass spec) detector. In this chamber, bombardment of the compounds with a stream of electrons causes to break the compounds apart into a large variety of fragments from the original molecules. The fragments are charged ions which are a certain mass. The mass of the fragment divided by the charge (M/Z) usually represents the molecular weight of the fragment. In most fragments, a charge is +1. By quantisation of atoms or molecules, the detection is performed. MS determines chemical and structural information about molecules. A group of four electromagnets named a quadrapole focuses each of the fragments into the detector through a slit. A computer programs the quadrapoles to direct only certain M/Z fragments through the slit letting the rest bounced away. The quadrapoles cycle through different M/Z's one at a time is performed until a range of M/Z's are covered by the computer. The cycle referred to as a scan happens several times per second.

In this work, only MS was used to analyse composition of final bio-oils from the experiments. The bio-oils were fractionated and analysed. Only organic solution (aliphatic and aromatic compounds) from fractions of the final liquid products was injected into the MS equipped in GC-MS to identify each individual component. For this thesis, TIC was applied to analyses of aromatic compounds and polar compounds. For aliphatic compounds, SIC (m/z=71) was applied, because aliphatic compounds would be broken down to detectable chain compounds (n-alkane) in GC-MS. Even though SIC(m/z=71) is set, GC-MS can detect most of the n-alkane compounds. Setting the SIC can reduce noises significantly to make analyses much easier.

Note: TIC = total ion chromatogram – all of the ions monitored, if done in full SCAN = mz 51 + 52 + 53 …….. up to m/z 450

SIC = single ion chromogram – i.e. m/z 71, can be derived from either a full SCAN run or a SIM (or SIR) run

SIM = single ion monitoring (or single ion response) when a limited collection of ions are monitored to improve sensitivity as against a full SCAN run e.g for aliphatic fractions m/z 69 (for alkenes) m/z 71 (for alkanes) m/z 191 (for hpanes), m/z 217 (for steranes). The TIC in this case reflects 69+71+191+217.

(mentioned by William Meredith )

The data in this work are to identify the compounds in the bio-oils. They are approximately analysed and not confirmed. More specialised analyses are required to identify exact compounds to prove the value of the bio-oils.( rheological test, ICP-AS and so on).

The model of the GC/MS that I used was Varian CP-3800 gas chromatograph equipped with a Fisons 1200 quadrupole mass spectrometer. Introduction from a GC to MS allows better accurate identification of the peaks of the chromatograph. A non polar J & W DB5-MS(50mX0.32mm) was used as the chromatographic column employing a cross-linked phenylmethylsiloxane stationary phase, and using helium as the carrier gas.

Figure 3.21: Gas Chromatography/Mass Spectrometry (GC/MS)

### 3.6.2.2 Preparation of sample

After rinsing fractionated and dried samples with DCM by using pipette three times. Each time, transfer the sample to small vial. At this time, caution to put all samples to the vial without wasting and not to reach to the cover because it can leak in sample injection. In case it is too full, using Nitrogen gas emitter, dry up to level which is moderate.

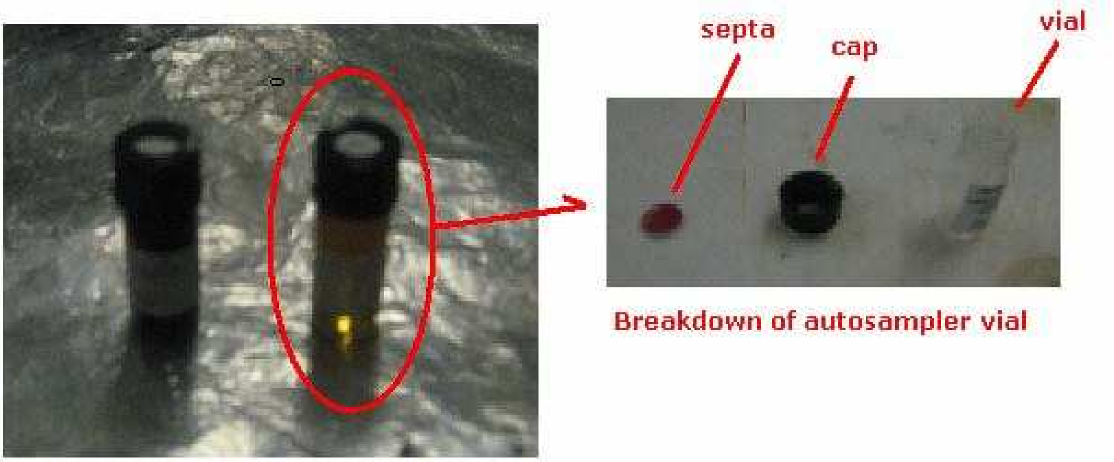


Figure 3.22: Autosampler vials

### 3.6.2.3 Experimental procedure of GC/MS

At a first stage of the operation in the GC/MS, the initial temperature is 50°C and 1µm of sample was injected into the GC/MS holding the programme for 3 minutes. In the GC/MS, the inlet carrier gas (helium) was carried out at 1.5ml/min, followed by temperature between 50°C to 300°C at 8°C/min and it was held at 300°C for 20 minutes at the end. In the mass spectrograph analysis, used specifications are one second scan time, 70eV of ion energy, a scan range of 20-500 daltons and inter-scan time of 0.5 second.

The entire spectra were required to identify the compounds extracted. By generated Total Ion Chromatogram (TIC) from ions detected by the mass spectrometer, the GC-MS performed the chromatographic analysis. This study focused on analysis of n-alkane (m/z 71) for aliphatics because this method can reduce significant amount of noises. The mass spectra of individual components were found when the GC-MS combined both scans about a chromatographic peak and deleted the background spectra from the close baseline signals. The combined spectra were matched with those available in the

National Bureau of Standards (NBS) library provided with the equipment. Through this, the individual extracted compounds were approximately interpreted.
To analyse elemental composition of residue and bio-oils from the experiments, Elemental analyser was applied.

### 3.6.2 Elemental analyser (EA)

#### 3.6.2.1 Instrumentation and Conditions of EA

Elemental Analyser analyses C, H, N, S and O. The main focus in this research was to see how much C and H would be in the residue generated from pyrolysis. Depending on how much portion of C and H exists in the residue, possibility as a fuel with the residue was investigated. In our lab, a column for detecting O wasn't available.

Note: Here, C is Carbon, H is Hydrogen, N is Nitrogen, S is Sulphur and O is Oxygen.
According to Chao Wang et al., the oxygen content was calculated from the C, H, and N by difference as follows:

$$\text{Wt.}(\%) = 100-[\text{C wt.}\% + \text{H wt.}\% + \text{N wt.}\% + \text{ash wt }\%]$$

They stated that the oxygen in ash components of biomass wouldn't be used during the pyrolysis. So, the oxygen in ash is excluded in the oxygen content calculation. However, for oil, ash is assumed to be 0. However, if formula from Scholze et al. (2001) is used, the oxygen in the ash is also counted. In case of bio-oil, formula from Scholze et al. (2001) can be adopted because the amount of ash is very small in case of the liquid.
In short, in this study, for residue analysis, only oxygen from organics was considered. So, the oxygen from ash was ignored. And for bio-oil analysis, ash content is almost 0. So, the ash content was ignored in the bio-oils.

In general, micro-analytical sample preparation methodology and combustion chemistries are standard between different instrument designs. To analyse a sample a weighted (1-2 mg) quantity is introduced into a high temperature furnace and the sample is combusted in oxygen. Typically the sample is weighed into a tin container, which gives the advantage of strong exothermic combustion ensuring complete sample oxidation at approximately 1800 °C. The resulting combustion products pass through specialized oxidation reagents, to produce from the elemental carbon, hydrogen, and nitrogen, carbon dioxide ($CO_2$), water($H_2O$), nitrogen ($N_2$) and N oxides respectively.

These gases are then passed over copper to remove excess oxygen and reduce the oxides of nitrogen to elemental nitrogen.

Elemental analyser detects the combustion products and measure those. In a static system, the mixture of combustion products ($CO_2$, $H_2O$ and $N_2$) is pulsed into a mixing chamber to ensure a homogeneous mixture at constant temperature and pressure. This known volume of combustion mixture now passes through a series of traps where $H_2O$ and $CO_2$ are completely absorbed, with high precision trap. The difference between the output of each set of detectors before and after absorption can be seen to be proportional to the trapped component and hence the quantity of carbon and hydrogen in the original sample can be determined. The remaining component of the combustion products i.e. nitrogen, is measured with reference to pure helium carrier gas, the difference in thermal conductivity being proportional to nitrogen content. Detection is in the steady state and thus highly accurate and precise. (Exeter Analytical (UK) Ltd.)

### 3.6.2.2 Preparation of sample

BBOT (2.5 Bis(5-tert-butyl-benzoxazol-2-yl) Thiophene) for standard analysis and Vanadium Pentoxide are prepared. Vanadium Pentoxide was to analyse Sulphur.

Bypass, Blank, standard and unknown materials are run. Analysis of unknown standard at the end can give assurance of consistency.

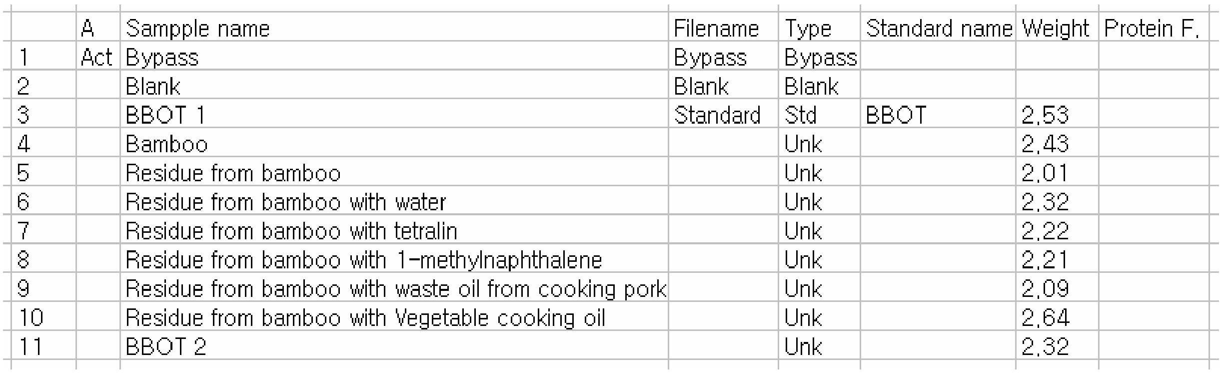
| Type | Purpose | Preparation | Sample table |
|---|---|---|---|
| Bypass | Conditions the instrument ready for analysis | Capsule containing standard material | No weight required |
| Blank | Provides baseline signal to be substracted from sample signal | Capsule without any contents | No weight required |
| Standard | Provides calibration data for sample calculations | Capsule containing standard material | Weight required |
| Unknown | Sample for elemental determination | Capsule containing sample | Weight required |

Table 3.1: Preparation and definition of bypass, blank, standard and sample

Two runs have been operated for solid such as residue and bamboo biomass) and viscous liquid such as liquid product. Analysis of the liquid was possible because it was very viscous to be set in capsule. For liquid, double capsulation was applied to protect the leaking different from solid analysis which was applied to single capsulation. BBOT of 2-3 mg was added and Vanadium Pentoxide of 5-10mg was added.

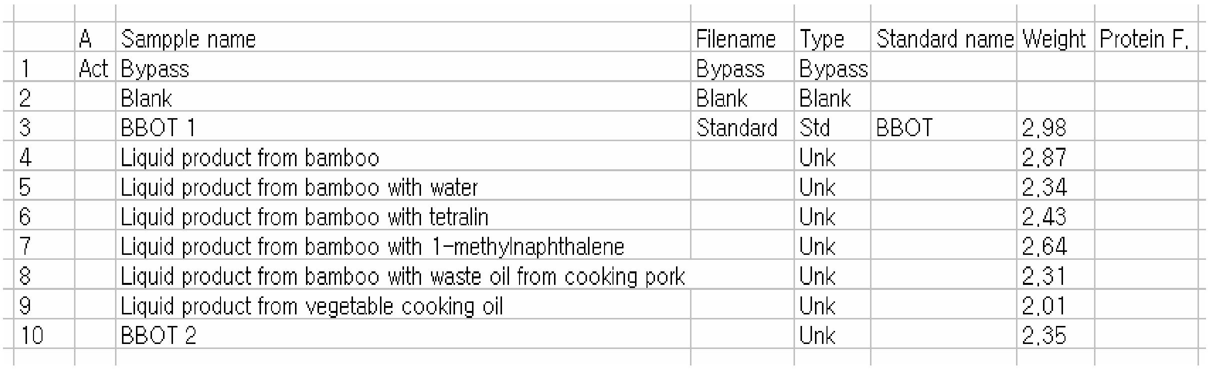
EA table set-up in the EA should be done to set the action root of EA before starting run. For convenience of making the data uniform that could get different depending on liquid phase and solid phase, set-up for Solid and set-up for liquid by inputting the data of the sample, BBOT(standard material used) and Vanadium Pentoxide weighed have been made separately as below.

Image of set-up tables in the EA (on monitor screen) was as follows.



| | A | Sampple name | Filename | Type | Standard name | Weight | Protein F. |
|---|---|---|---|---|---|---|---|
| 1 | Act | Bypass | Bypass | Bypass | | | |
| 2 | | Blank | Blank | Blank | | | |
| 3 | | BBOT 1 | Standard | Std | BBOT | 2,53 | |
| 4 | | Bamboo | | Unk | | 2,43 | |
| 5 | | Residue from bamboo | | Unk | | 2,01 | |
| 6 | | Residue from bamboo with water | | Unk | | 2,32 | |
| 7 | | Residue from bamboo with tetralin | | Unk | | 2,22 | |
| 8 | | Residue from bamboo with 1-methylnaphthalene | | Unk | | 2,21 | |
| 9 | | Residue from bamboo with waste oil from cooking pork | | Unk | | 2,09 | |
| 10 | | Residue from bamboo with Vegetable cooking oil | | Unk | | 2,64 | |
| 11 | | BBOT 2 | | Unk | | 2,32 | |

Figure 3.23: Setup table for residue sample in EA



| | A | Sampple name | Filename | Type | Standard name | Weight | Protein F. |
|---|---|---|---|---|---|---|---|
| 1 | Act | Bypass | Bypass | Bypass | | | |
| 2 | | Blank | Blank | Blank | | | |
| 3 | | BBOT 1 | Standard | Std | BBOT | 2,98 | |
| 4 | | Liquid product from bamboo | | Unk | | 2,87 | |
| 5 | | Liquid product from bamboo with water | | Unk | | 2,34 | |
| 6 | | Liquid product from bamboo with tetralin | | Unk | | 2,43 | |
| 7 | | Liquid product from bamboo with 1-methylnaphthalene | | Unk | | 2,64 | |
| 8 | | Liquid product from bamboo with waste oil from cooking pork | | Unk | | 2,31 | |
| 9 | | Liquid product from vegetable cooking oil | | Unk | | 2,01 | |
| 10 | | BBOT 2 | | Unk | | 2,35 | |

Figure 3.24: Setup table for liquid sample in EA

Figure 3.25: Sample preparation for EA

### 3.6.2.3 Experimental procedure of EA

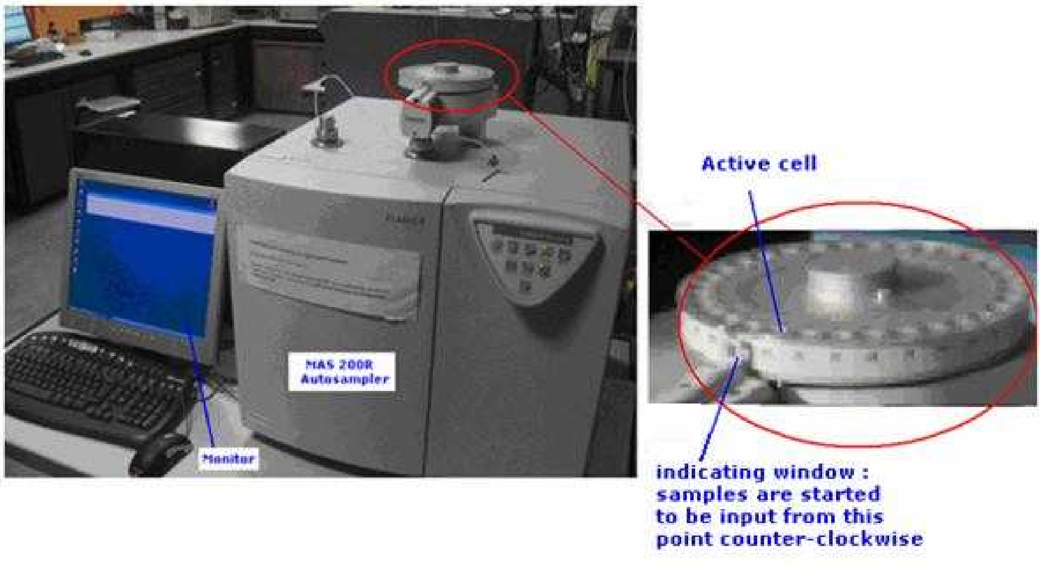


Figure 3.26: Elemental Analyser (EA)

After selecting a tin capsule of the correct size, BBOT (Standard) and samples of 2-3 mg with Vanadium Pentoxide of 5-10mg were capsulated. The weights of the BBOT and samples were recorded. For residues, single capsulation and for bio-oils, double capsulations were applied. The BBOT and samples were transferred to MAS 200R autosampler cell anti-clockwise.

After all parameters such as helium gas, hydrogen gas, furnace temperature and so on are met, the EA were run to analyse the BBOT and samples. After finishing the run, chromatogram of the results was checked if the integration is proper. If not, it is necessary to integrate properly by dragging the cursor. It showed as below.

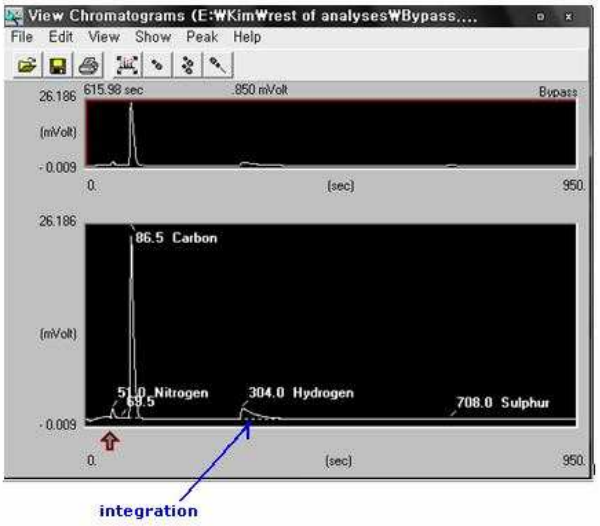


Figure 3.27: EA Chromatogram

Results of compositions of residues and bio-oils were obtained after confirming integration was right. When new method was uploaded, reset calibration factors and recalculation were performed.

### 3.6.3 Furnace method

Furnace method is applied to find out ash content. The ash content can be used to calculate dry ash free reside (%) and oxygen content (%) in residue

Note: Ash free residue was found by equation below.
Ash free residue (%) = ((Residue (mg) – Ash (mg))/(Initial bamboo sample (mg) – Ash (mg))) × 100 (%)

According to Chao Wang et al., the oxygen content was calculated from the C, H, and N by difference as follows:

$$\text{Wt.}(\%) = 100-[\text{C wt.\%} + \text{H wt.\%} + \text{N wt.\%} + \text{ash wt \%}]$$

They stated that the oxygen in ash components of biomass wouldn't be used during the pyrolysis. So, the oxygen in ash is excluded in the oxygen content calculation. However, for oil, ash is assumed to be 0. However, if formula from Scholze et al. (2001) is used, the oxygen in the ash is also counted. In case of bio-oil, formula from Scholze et al. (2001) can be adopted because the amount of ash is very small in case of the liquid.
In short, in this study, for residue analysis, only oxygen from organics was considered. So, the oxygen from ash was ignored. And for bio-oil analysis, ash content is almost 0. So, the ash content was ignored in the bio-oils.

In case of pyrolysis and liquefaction of bamboo with bio-derived oil solvent, trace metals from the bio-derived oil used as a solvent are assumed to remain into residue produced. However, the amount of the trace metals is assumed to be very small. So, in this study, the amount of trace metals was ignored.

About 0.02g of each residue sample and crucibles to put the samples were weighed using balance and put in the furnace. The furnace was set at 800°C and 1 hour was spent for temperature to reach the 800°C and the samples were left in ceramic crucibles to stay for 1 hour. After this time, the samples were removed from the furnace and weighed again. The loss in mass was recorded by deleting later weight of the samples from prior weight of the samples and based on this data, the percentage of ash content of residue samples were determined. This method was used for all the residue samples generated from pyrolysis.
Ash content and volatile content are found as following equations.

Ash content = mass of residue sample left after furnace heating / mass of residue sample before furnace heating.

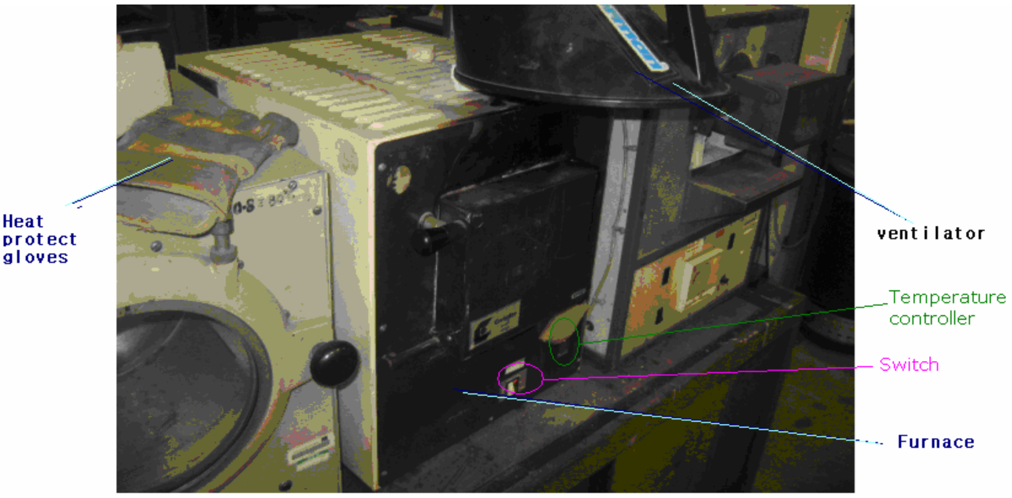


Figure 3.28: Furnace

This is made of ceramic and highly heat-endurable . Flat typed crucible is preferred because it can make the sample contact more in funace environment

Figure 3.29: Crucible used in furnace

# CHAPTER FOUR
# RESULTS AND DISCUSSION

## 4.1 Verification of experimental findings

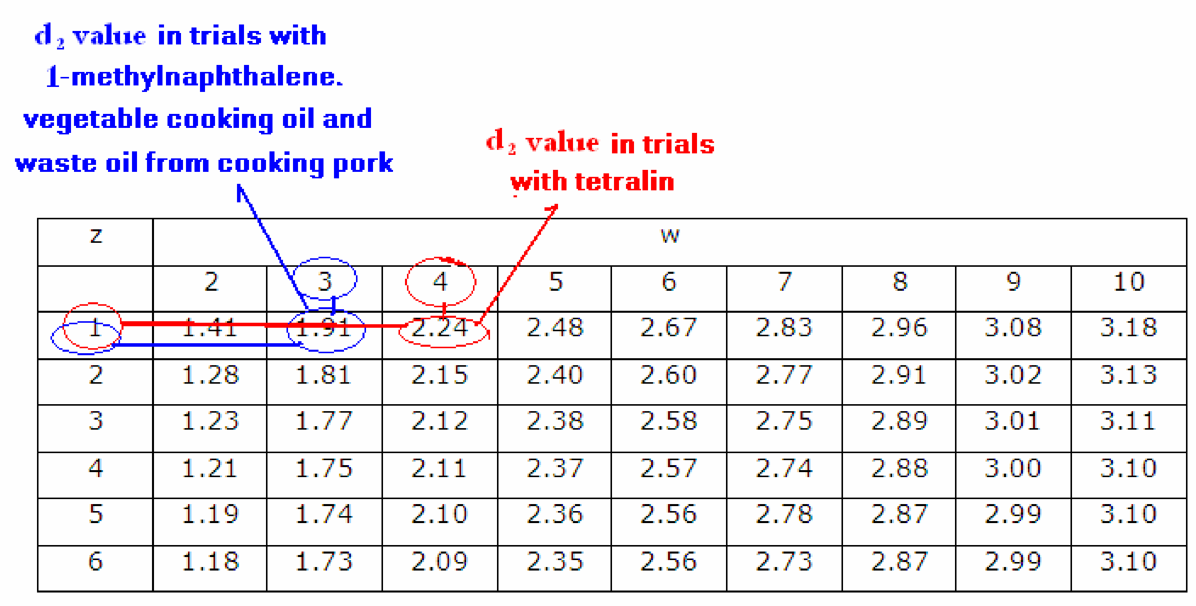
Repetition of the experiments to find conversion rate of bamboo to gas and liquid has been performed to obtain more accurate data. Experiment for Conversion rate of bamboo with tetralin was repeated four times. That of the bamboo with 1-naphthalene, vegetable cooking oil and waste oil from cooking pork was repeated three times each. That of bamboo without solvent and with water and vegetable cooking oil blank run(without bamboo) wasn't repeated because they were performed to investigate influence of some particular conditions.

$$\text{Repeatability} = \frac{5.15\bar{\bar{R}}}{d_2}$$

(Cited from Hayward. )

Where $\bar{\bar{R}}$ is the average of the ranges for all appraisers and parts, and

$d_2$ is found in table 1.23 with Z = the number of parts times the number of appraisers, and W= the number of trials.



$d_2$ value in trials with 1-methylnaphthalene, vegetable cooking oil and waste oil from cooking pork

$d_2$ value in trials with tetralin

| Z | W | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 1 | 1.41 | 1.91 | 2.24 | 2.48 | 2.67 | 2.83 | 2.96 | 3.08 | 3.18 |
| 2 | 1.28 | 1.81 | 2.15 | 2.40 | 2.60 | 2.77 | 2.91 | 3.02 | 3.13 |
| 3 | 1.23 | 1.77 | 2.12 | 2.38 | 2.58 | 2.75 | 2.89 | 3.01 | 3.11 |
| 4 | 1.21 | 1.75 | 2.11 | 2.37 | 2.57 | 2.74 | 2.88 | 3.00 | 3.10 |
| 5 | 1.19 | 1.74 | 2.10 | 2.36 | 2.56 | 2.78 | 2.87 | 2.99 | 3.10 |
| 6 | 1.18 | 1.73 | 2.09 | 2.35 | 2.56 | 2.73 | 2.87 | 2.99 | 3.10 |

Table 4.1: Values of $d_2$

Note: Here, the appraiser is only me (Junghee Kim) who did this research and the number of trials is 4 for experiments using tetralin solvent and 3 for experiments using

1-methylnaphthalene solvent, vegetable cooking oil solvent and waste oil from cooking pork solvent. The repeatability is the variability of the measurements gained by one person during measurement of same item repeatedly. This is known as the inherent precision of the measurement equipment as well. (Cited from Hayward. )

The repeatability has been found and recorded in each experiment.

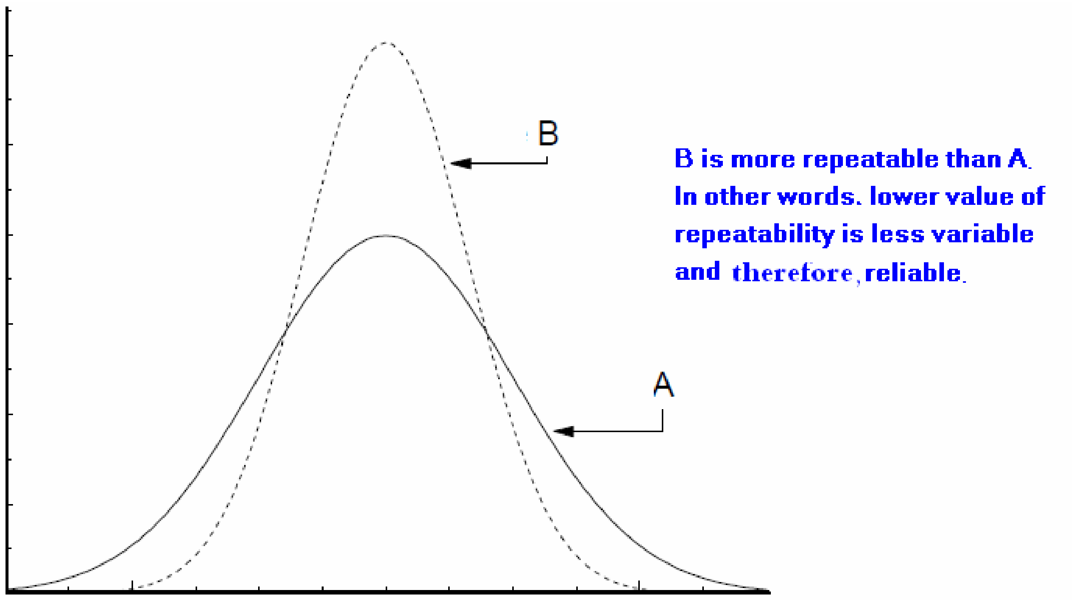


Figure 4.1: probability density functions for the thickness of 2 cases

(Cited from Hayward. )

Standard deviation was also recorded to measure variability of the data found in this study. Note:

$$\sigma = \sqrt{\frac{(x_1-\mu)^2+(x_2-\mu)^2+\cdots+(x_N-\mu)^2}{N}}$$

Here, $\sigma$ = standard deviation,

data set $x_1, x_2, \ldots, x_N$ with each value having the same probability.

$\mu$ = mean value.

(cited from Paul A. Tobias and David C. Trindade)

## 4.2 Overall conversion rate of pyrolysis and liquefaction

### 4.2.1. Overall Conversion

The total conversion rate from bamboo is shown in Figure 5. The highest conversion rate was shown in bamboo with tetralin. The maximum conversion rate value of around 90% was achieved with bamboo with tetralin. This result indicated that the Hydrogen-donor effect in the solvent extraction process influenced the strongest to the conversion of bamboo to gas and liquid product.

Conversion rates of bamboo with 1-methylnaphthalene, vegetable cooking oil and waste oil from cooking pork respectively were shown similar together. And those were higher than pyrolysis of bamboo without any solvent. It might be involved in the process of liquefaction such as ionic reactions, free radical reactions, nucleophilic reactions, electrophilic reactions or elimination reactions. However, these reactions would be less effective than Hydrogen-donor and receiver reactions based on the result shown.
Furthermore, there are hydrogen donating effects on 1-methylnaphthanale, vegetable cooking oil and waste oil from cooking pork even though they are much less effective hydrogen donor than tetralin.

On the other hand, conversion rate of Bamboo with water was shown somewhat low. According to Zhengang Liu et al., the different conversion rate in liquefaction process may due to the polarity constant values of the solvent. Despite the fact that the water solvent is highly polar, the reason why the conversion rate was somewhat low seems to be because of the low boiling point of water. Because at 100’C water was already evaporated, the water doesn’t seem to work as proper solvent for liquefaction. Even in the experiment of bamboo with water solvent, cross-linking effect has been shown in the bamboo biomass similar to the bamboo without any solvent in the pyrolysis. This fact makes it more convincing that the water doesn’t work much as a solvent.

The overall conversions from bamboo were shown in Figure 4. The highest conversions were achieved for bamboo with tetralin. Maximum conversion of about 90% was obtained in tetralin.

**Notes:** Overall conversion rate of bio-material(%) = (bamboo biomass weight(g) – char(residue) weight generated (g))/bamboo biomass weight(g) ×100

| Biomass | Solvent | Biomass weight (g) | Solvent weight (g) | Char (residue) weight (g) | Overall conversion rate (%) to gas and liquid | Mean (%) | Standard deviation (%) | Repeatability (%) |
|---|---|---|---|---|---|---|---|---|
| Bamboo | Tetralin | 5 | 12.5 | 0.71<br>0.74<br>0.71<br>0.47 | 85.82<br>85.22<br>85.76<br>90.57 | 86.84 | 2.17 | 12.30 |
| | 1-methyl naphthalene | 5 | 12.5 | 1.60<br>1.69<br>1.54 | 68.00<br>66.17<br>69.12 | 67.76 | 1.22 | 7.95 |
| | Waste oil from cooking pork | 5 | 12.5 | 1.51<br>1.61<br>1.59 | 69.72<br>67.79<br>68.35 | 68.62 | 0.81 | 5.20 |
| | Vegetable cooking oil | 5 | 12.5 | 1.50<br>1.49<br>1.51 | 70.04<br>70.20<br>69.80 | 70.01 | 0.16 | 1.08 |
| | Water | 5 | 12.5 | 1.80 | 64.00 | 64.00 | Not determined | Not determined |
| | None | 5 | 0 | 2.13 | 57.32 | 57.32 | Not determined | Not determined |

Table 4.6: Comparison of overall conversion rate from bamboo to gas, liquid and residue obtained by different solvents used

Fig. 4.3 shows that conversion rate in bamboo by liquefaction with tetralin solvent was the highest significantly. For the other cases in liquefaction with the other solvents were similar conversion rate. Conversion rate in the liquefaction by water solvent was a bit lower than that by the other solvents. And the conversion rate by only pyrolysis without any solvent was the lowest. The H-donor from the tetralin solvent might react with bamboo generating $H_2O$ and bio-oil effectively. The basic principle of the water generation by hydrogen suggested by Nicholas(1985) is as following eq.(46).

$$C_6H_{10}O_5 + 4H_2 \xrightarrow{heat} C_6H_{10}O + 4H_2O \text{ --------------------(46)}$$

In addition, the residue generated in tetralin was shown to be the least amount which clarified that the highest conversion was conducted in tetralin by Hydrogen donating effect. Additionally, more effective way of possibility for energy source can be assumed by these phenomena from tetralin liquefaction.

## 4.2 Gas generated from pyrolysis and liquefaction

### 4.2.1 Total gas yields

The gas amount (mg) generated from bamboo with various solvents are shown Table 4. Generally, low gas yield was detected in hydrocarbon gas. At this time, gas volume unit ml was calculated to find conversion rate of gas yield as mg.

| Solvent used | Pressure cooled down after pyrolysis (bar) | Gas yield (ml) | Mean value of gas yield (ml) | Standard deviation of gas yield (ml) | Repeatability (ml) |
|---|---|---|---|---|---|
| Tetralin | 25<br>28<br>26<br>30 | 760<br>788<br>770<br>847 | 791.25 | 33.71 | 200.02 |
| 1-methylnaphthalene | 28<br>25<br>31 | 728<br>692<br>756 | 725.33 | 26.20 | 172.57 |
| Waste oil from cooking pork | 45<br>37<br>42 | 1197<br>1027<br>1131 | 1116.33 | 70.01 | 458.38 |
| Vegetable cooking oil | 38<br>43<br>47 | 1220<br>1349<br>1351 | 1306.67 | 61.29 | 353.22 |

Table 4.3: Comparison of total gas yields (ml) obtained by different solvents used

As seen above, the highest gas yield was shown in reaction of bamboo with vegetable cooking oil and waste oil from cooking pork. However, it seemed that the vegetable cooking oil and waste oil from cooking pork themselves were reacted generating their own gases. (Schwab et al.1988) Therefore, mean values of gas yield, 1116.33 ml and 1306.67 ml for bamboo with the bio-derived solvent to gas were not convincible.

Gas yields can be predicted from pressure cooled down after pyrolysis as seen on the pressure gauge. Higher pressure cooled down implies that the gas yield would be higher amount as shown in table 4.3.

### 4.2.2 N-alkane gas yield (mg)

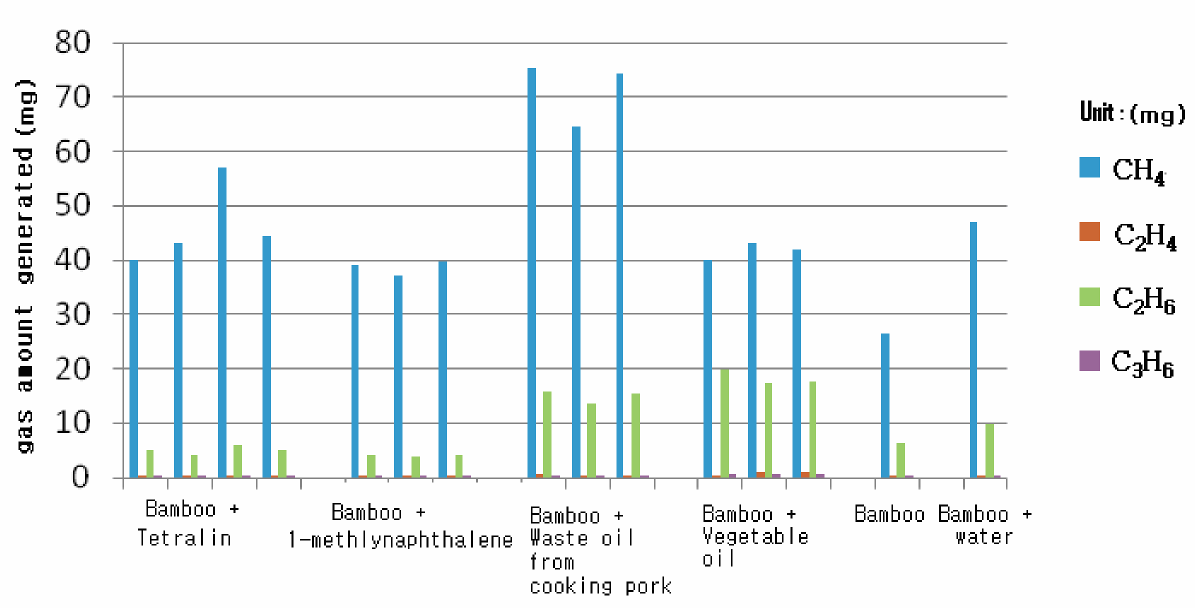


Figure 4.2: Comparison of n-alkane gas yields (mg) obtained by different solvents used

Figure 4.2 showed amount of each C-alkane gas in every each run. Overall, $CH_4$ gas was the largest amount among the Hydro-carbon gases and $C_2H_6$ gas was the second largest amount generated. $C_2H_4$ and $C_3H_6$ were detected as a small amount. The C1 – C3 are major amount of hydrocarbon gas. In this study, only the C1-C3 which are assumed to be the most of the n-alkane gases based on the peak area trend were investigated. In fact, peaks after $C_3H_6$ were almost shown near 0.

Liquefaction of bamboo with the waste oil from cooking pork generated the largest amount of $CH_4$ gases. This seems because decomposition reaction of derivatives of Triglycerides which could be decomposed to $CH_4$ gases (Chang and Wan, 1947)

- Hydrogenation of olefins

$$C_nH_{2n} + H_2 \Rightarrow C_nH_{2n+2} \quad \text{------------------------}(29)$$

- Splitting Decomposition of paraffins

$$C_nH_{2n+2} \Rightarrow C_{n+m}H_{2n+2}+C_mH_{2m} \text{----------------}(30)$$

On the other hand, liquefaction of bamboo with the vegetable cooking oil generated relatively less $CH_4$. However relatively more $C_2H_4$ and $C_2H_6$. This indicates following reactions possibly occurred. (Chang and Wan, 1947)

- Polymerisation of olefins

$$2C_nH_{2n} \Rightarrow C_{2n}H_{4n} \text{ ---------------------------------}(31)$$

$$C_nH_{2n} + C_mH_{2m} \Rightarrow C_{n+m}H_{2n+2} \text{ -----------------}(32)$$

And Depolymerisation of olefins can be one of the reasons which is

$$C_{2n}H_{4n} \Rightarrow 2C_nH_{2n} \text{ ----------------------------------}(33)$$

$$C_nH_{2n} + C_mH_{2m} \Rightarrow C_{n+m}H_{2n+2} \text{ ------------------}(34)$$

- Decomposition of olefins to diolefins
- Hydrogentaion of olefins

$$C_nH_{2n} + H_2 \Rightarrow C_nH_{2n+2} \text{ ------------------------------}(35)$$

(Chang and Wan, 1947)

On the other hand, as an indicator in baseline run of water solvent which is polar, pretty large amount of gases generated from the liquefaction with the water solvent indicates that the different conversion rate of bamboo to gas in liquefaction process may be dependent on the polarity of the solvent (Zhengang Liu, et al.)

| Biomass | Solvent | Total n-alkane gas weight produced (mg) | Mean value(mg) | Standard deviation(mg) | Repeatability (mg) |
|---|---|---|---|---|---|
| Bamboo | Tetralin | 45.17<br>47.46<br>63.30<br>49.69 | 51.41 | 7.05 | 41.68 |
| | 1-methylnaphthalene | 43.16<br>41.16<br>43.95 | 42.76 | 1.17 | 7.52 |
| | Waste oil from cooking pork | 91.91<br>78.83<br>90.58 | 87.11 | 5.88 | 35.27 |
| | Vegetable cooking oil | 60.64<br>62.12<br>60.86 | 61.21 | 0.65 | 3.99 |
| None | Vegetable cooking oil | 37.58 | 37.58 | Not determined | Not determined |

Table 4.4: Total n-alkane gas yield (mg) obtained by different solvents used (total weight of $CH_4$, C2H4, C2H6 and C3H6)

### 4.2.4 Net gas yield from bamboo in liquefaction by bio-oil derived solvent

|  | Biomss | Solvent | Total Gas Produced (ml) | n-alkane Gas produced (mg) |
|---|---|---|---|---|
| 1 | Bamboo | Vegetable cooking oil | 1220 | 60.64 |
|  |  |  | 1349 | 62.16 |
|  |  |  | 1351 | 60.86 |
| 2 | None | Vegetable cooking oil | 697 | 37.58 |
| 1 - 2 (deleting) = Actual gas produced from bamboo |  |  | 523 | 23.06 |
|  |  |  | 652 | 24.53 |
|  |  |  | 654 | 23.27 |
| Mean |  |  | 609.67 | 23.62 |
| Standard Deviation |  |  | 61.29 | 0.65 |
| Repeatability |  |  | 353.22 | 3.96 |

Table 4.5: Net gas yields (ml, mg) from bamboo in liquefaction by vegetable cooking oil

The amount of gases generated from bamboo with bio-oil derived solvent was investigated. As a typical bio-oil derived solvent, vegetable cooking oil was chosen. To find out the actual amount (net amount) of gas generated from bamboo with vegetable cooking oil, vegetable cooking oil blank run has been performed. As a result, the actual amount of conversion from bamboo is not as much as the other solvents used. The amount generated from vegetable itself occupied a lot of portion which is assumed as gases generated from pyrolysis of vegetable oil. (Schwab et al.1988).

The findings on the net amount of each gas generation of bamboo were shown in the graph below.

As a result of findings on net weight generated from bamboo in pyrolysis and liquefaction in the gas generated from bamboo with vegetable cooking oil, In fact, the gas amount generated only from bamboo when it applied to the vegetable cooking oil solvent (vegetable cooking oil’s own pyrolysis gas generation ignored) was smaller than that from bamboo with petroleum derived solvent as a result. This means the bio-derived solvent is less effective than petroleum-derived solvent for conversion to gas.

### 4.2.3 Other gas yield ($H_2$, CO and $CO_2$)

Gases produced other than n-alkane gases are expected as $H_2$, CO and $CO_2$ (Demirbas, 2009). By deleting the number of moles of the n-alkane gases from the number of moles of the total gases, the number of moles of $H_2$, CO and $CO_2$ was approximately determined.

| Biomass | Solvent used | The number of moles of total gas yield | The number of moles of n-alkane gas yield | The number of moles of sum of CO, $CO_2$ and $H_2$ | Proportion (%) of sum of CO, $CO_2$ and $H_2$ | Mean (%) | Standard deviation (%) | Repeatability |
|---|---|---|---|---|---|---|---|---|
| Bamboo | Tetralin | 31.67<br>32.83<br>32.08<br>35.29 | 1.88<br>1.98<br>2.64<br>2.07 | 29.79<br>30.85<br>27.44<br>33.22 | 94.06<br>93.97<br>85.54<br>94.13 | 91.93 | 2.13 | 19.75 |
| | 1-methylnaphthalene | 30.33<br>28.83<br>31.50 | 1.80<br>1.72<br>1.83 | 28.53<br>27.11<br>29.67 | 94.07<br>94.03<br>94.19 | 94.10 | 0.12 | 0.43 |
| | Waste oil from cooking pork | 49.88<br>47.79<br>47.13 | 3.83<br>3.28<br>3.77 | 46.05<br>44.51<br>43.36 | 92.32<br>93.14<br>90.00 | 91.82 | 2.30 | 8.47 |
| | Vegetable cooking oil | 50.83<br>56.21<br>56.29 | 2.53<br>2.59<br>2.54 | 48.30<br>53.62<br>53.75 | 95.02<br>95.39<br>95.49 | 95.3 | 0.35 | 1.26 |

Table 4.6: The number of moles and proportion (%) of sum of CO, $CO_2$ and $H_2$

As seen in table 4.6, the amount of CO, $CO_2$ and $H_2$ is assumed to be much more than the amount of n-alkane gases in the produced gases.

Furthermore, based on the fact that the number of moles of sum of CO, $CO_2$ and $H_2$ in vegetable cooking oil and waste oil from cooking pork is much higher than in tetralin and 1-methylnaphthalene, the amount of CO,$CO_2$ and $H_2$ gas yield in the vegetable cooking oil and the waste oil from cooking pork is more.

One of the reasons why the amount of $CO_2$ gas yield in vegetable cooking oil and waste oil from cooking pork is more can be considered as follows. According to Moore, Patrick et al. oxygen in the bio-oil should be decomposed because heating value is reversely related to oxygen content. The most effective way of decomposing oxygen is to use heat by which every two carbon atoms in a mole of biomass are converted into $CO_2$ removing two oxygen atoms as below. Production of carbon dioxide, however, means loss of carbon and lower oil yields. They warned that producing the carbon dioxide would mean loss of carbon and lower oil yields. (Nicholas et al., 1985)

$$C_6H_{10}O_5 \xrightarrow{\text{heat}} C_4H_{10}O + 2CO_2 \text{ ----------------------(36)}$$

Hereby, quite bit of portion of vegetable oil and waste oil from cooking pork is composed of $C_6H_{10}O_5$. Therefore, when it is heated more, $CO_2$ would be generated from vegetable oils according to equation of Moore, Patric et al.

According to GeorgeW. Mushrush et.al.(1995), gaseous products (Syn-gas) can be produced reacting with Carbon as eq.(37).

$$\mathbf{C + H_2O = CO + H_2} \text{ ------------------------(37)}$$

Therefore, the gas generated is assumed to be $H_2$, $CO_2$ and CO as well as C1-C3 gases. The amount of $CO_2$, CO and $H_2$ gases was much more than n-alkane gases in this study.

Liquefaction by hydrocarbon solvents produced a bit more gases than in pyrolysis without solvent. This seems because petroleum derived solvent could cause its dimmers.

Again, the amount of the $CO_2$, CO and $H_2$ gases from bamboo with bio-derived solvents could not be convincing because the solvent could be pyrolysed themselves.
The generation of $CO_2$, CO and $H_2$ gases is assumed because of decomposition of triglycerides of the bio-derived solvent. Triglycerides can be many derivatives which could be decomposed to $CO_2$, CO and $H_2$ gases (Chang and Wan, 1947)

- Decomposition of fatty acids

$$RCOOH \longrightarrow CO_2 + RH \text{ ------------------------(38)}$$

$$2RCOOH \longrightarrow CO_2 + H_2O + RCOR \text{----------(39)}$$

- Decomposition of ketenes and acrolein

$$2R''CH{=}CO \longrightarrow 2CO + RHC{=}CHR \qquad (40)$$

$$CH_2{=}CHCHO \longrightarrow CO + C_2H_4 \qquad (41)$$

$$2RCOCH_2R \longrightarrow 2R_2 + CO + C_2H_4 \qquad (42)$$

- Decomposition of paraffins

$$C_nH_{2n+2} \longrightarrow nC + (n+1)H_2 \qquad (43)$$

- Dehydrogenation of paraffins

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2 \qquad (44)$$

- Aromatic cyclisation of paraffins

$$C_{(2n+6)}H_{(2n+14)} \longrightarrow C_nH_{2n+1} + 4H_2 \qquad (45)$$

(Chang and Wan, 1947)

## 4.4 Analysis of Residue generated from pyrolysis and liquefaction

### 4.4.1 Analysis of ash content from the residue by furnace

For this study, original bamboo sample and residue samples generated from pyrolysis and liquefaction were combusted in furnace for 1hr in stabilised temperature of 800°C.

| | Ash (mg) | Residue(mg) (average) | Ash content rate (%) | Residue (%) | Ash free residue(%) |
|---|---|---|---|---|---|
| Bamboo | 98 | | 1.96 | | |
| Residue from bamboo | 76.7 | 2134.2 | 3.59 | 42.68 | 41.79 |
| Residue from bamboo with water | 77.2 | 1799.9 | 4.29 | 36.00 | 34.99 |
| Residue from bamboo with 1-methylnaphthalene | 80.1 | 1600 | 5.01 | 32.24 | 30.89 |
| Residue from bamboo with tetralin | 69.7 | 709 | 9.83 | 13.16 | 12.97 |
| Residue from bamboo with waste oil from cooking pork | 89.1 | 1514.1 | 5.88 | 31.38 | 29.02 |
| Residue from bamboo with vegetable cooking oil | 91.5 | 1497.8 | 6.11 | 29.99 | 28.65 |

Table 4.7: Analysis of ash contents from residues obtained by different solvents used using furnace

As seen above in the table, residue from bamboo with tetralin has the biggest value of ash content. The reason seems because the Hydrogen donor reaction by tetralin converted the bamboo to the final liquid product the most. In other words, ash content which is not changeable remained in the residue which shows relatively higher rate of composition compared the other cases of liquefactions. On the other hand, residue generated by pyrolysis without any solvent contained the lowest rate of ash content. This seems because the conversion from bamboo biomass to bio-oil and gas was the lowest leaving volatile compounds in the residue which decreased ash content relatively. This implies that the ash content rate is relevant to the conversion rate from biomass to bio-oil. These values are shown in the graph below. Here, one interesting fact is that contrary to the fact that residue from bamboo by vegetable cooking oil solvent and waste oil from cooking pork solvent showed pretty high value of residue, in dry ash free residue, values of the ash free residue weight were pretty low. This implies the amount of volatile substance is not much for those residues that could mean these residues could not be good source for energy due to the limit to energy conversion. On the other hand, Residue generated from liquefaction by 1-methylnaphthalne showed pretty large amount of weight but it showed high value of weight of dry ash free residue. This means there are more volatile substances in the residue implying it can be better energy source.

In terms of results of bamboo biomass ash content(%), the value of 1.96% (ash content (wt%)) was similar to the value of 1.7% (ash content (wt %))found by Su-Hwa Jung et al.(2008). However, in terms of results of ash content (%) of residue from bamboo after pyrolysis without using any solvents was a bit different. The value of ash content in this study was 3.59% while the value of ash content in a pyrolysis experiment by Su-Hwa Jung et al.(2008) was 34.6%. This seems different because the condition of the research was different.(heating rate, configuration (batch system, continuous system, different reactor used), quenching applied by solvent, feedstock size, temperature and so on.)

Note: Ash free residue was found by equation below.

Ash free residue (%) = ((Residue (mg) – Ash (mg))/(Initial bamboo sample (mg) – Ash (mg))) × 100 (%)

The ash content rate was different between each sample. These data are much higher value than conventional petroleum ash content (<0.04%). (Cited from Minor et al.1952)

According to Chao Wang et al., the oxygen content was calculated from the C, H, and N by difference as follows:

$$\text{Wt.}(\%) = 100-[\text{C wt.}\% + \text{H wt.}\% + \text{N wt.}\% + \text{ash wt }\%]$$

Note: they stated that the oxygen in ash components of biomass wouldn’t be used during the pyrolysis. So, the oxygen in ash is excluded in the oxygen content calculation. However, for oil, ash is assumed to be 0. However, if formula from Scholze et al.(2001) is used, the oxygen in the ash is also counted. In case of bio-oil, formula from Scholze et al.(2001) can be adopted because the amount of ash is very small in case of the liquid. The heating values were obtained from calculation by Dulong’s formula (Scholze et al., 2001)

$$\text{HHV (MJ/kg)} = [338.2\times\%\text{C} + 1442.8 \times (\%\text{H} - \%\text{O}/8)] \times 0.001$$

By these equations, values of oxygen contents and HHV were found with the other values of elemental contents by elemental analysis. This will be explained next following context.

### 4.4.2 Elemental analysis of residue

#### 4.4.2.1 Composition

The result of comparison between residues obtained from this experiments and the objective data is shown in Table 4.8. Table 4.8 shows results of elemental analysis of bamboo before pyrolysis and of residue after pyrolysis.

| Composition of residue | N (%) | C (%) | H (%) | O (%) | H/C (no unit) | O/C (no unit) | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|
| Bamboo | 0.27 | 47.17 | 6.86 | 43.74 | 1.5 | 0.35 | 17.15 |
| Residue from bamboo | 0.46 | 48.81 | 2.91 | 44.23 | 0.72 | 0.34 | 12.73 |
| Residue from bamboo with water | 0.47 | 68 | 5.61 | 21.63 | 0.62 | 0.12 | 24.16 |
| Residue from bamboo with tetralin | 0.55 | 67.36 | 4.01 | 18.25 | 0.71 | 0.10 | 25.28 |
| Residue from bamboo with 1-methylnaphthalene | 0.49 | 75.19 | 3.7 | 15.61 | 0.59 | 0.08 | 27.95 |
| Residue from bamboo with waste oil from cooking pork | 0.36 | 74.76 | 4.3 | 14.7 | 0.69 | 0.07 | 28.84 |
| Residue from vegetable cooking oil | 0.43 | 77.11 | 5.12 | 11.23 | 0.80 | 0.05 | 31.44 |

Table 4.8: Comparison of composition of bamboo and residues obtained by different solvents used using EA

Note: N= Nitrogen, H= Hydrogen, C= Carbon, O = Oxygen, H/C = Hydrogen mass (weight)/ Carbon mass (weight), O/H = Oxygen mass (weight) / Carbon mass (weight). HHV = Higher Heating Value. 0 % of sulphur composition was shown in all cases.

There has been some improvement on increasing carbon and decreasing oxygen. However, it doesn’t reach petroleum properties. It can not be alternative energy source to petroleum. There was no sulphur detected that implies the process including pyrolysis without solvents as well as liquefaction process are environmentally clean method and can contribute to the clean environment. For Nitrogen, residues from bamboo with vegetable cooking oil and waste oil from cooking pork showed the least amount of the

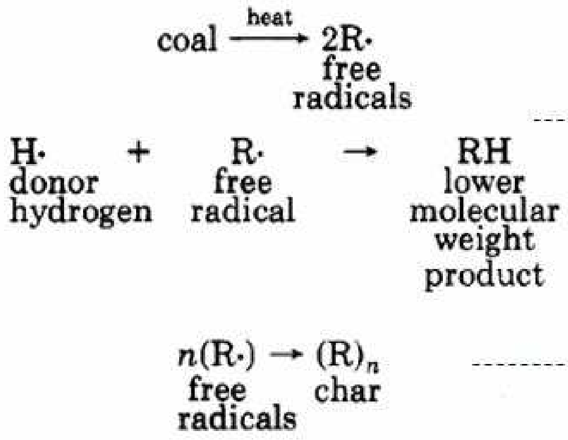
Nitrogen which tells bio-oil derived solvent reacted the most environmentally friendly.

High oxygen content in the residues indicates that the material generated is acid in comparison to petroleum itself. When solvent extraction process (liquefaction) was applied, the oxygen content value was significantly decreased compared with oxygen content value in only pyrolysis without any solvent.

#### 4.4.2.2 H/C & O/C

Petroleum has very small amount of O/C and relatively higher amount of H/C.(George W. Mushrush,1995) It seems to be shown as these numbers because high amount of hydrocarbon composed of the petroleum and very small amount of O element in the petroleum. Bamboo biomass also has relatively high amount of H/C but, O/C of the Bamboo biomass was very high.( Su-Hwa Jung et al., 2008) It is considered that the biomass contains a lot of Oxygen contents and less portion of hydrocarbon. Without solvent extraction, just only pyrolysis reduced the amount of O/C to certain level in the residue but the value of the amount was still high.

The reason why by pyrolysis, the H/C was decreased dramatically is expected because the Hydrogen in bamboo biomass was used to generate lower molecular weight product partly. (Nicholas et al.,1985)



$$\text{coal} \xrightarrow{\text{heat}} \underset{\text{free radicals}}{2\text{R}\cdot}$$

$$\underset{\text{donor hydrogen}}{\text{H}\cdot} + \underset{\text{free radical}}{\text{R}\cdot} \rightarrow \underset{\text{lower molecular weight product}}{\text{RH}} \quad \text{--------------------(47)}$$

$$\underset{\text{free radicals}}{n(\text{R}\cdot)} \rightarrow \underset{\text{char}}{(\text{R})_n} \quad \text{------------------------(48)}$$

(Cited from Nicholas et al.,1985)

In case of liquefaction with hydrogen donor solvent like tetralin, the hydrogen used from bamboo was less because tetralin itself supplied the hydrogen. However, it seems to be used from the bamboo biomass based on the fact that the H/C values from pyrolysis and liquefaction are low. The chemical reaction involved in hydrogen donor from bamboo biomass is as follows.

For liquefaction by bio-derived oil, the H/C values showed pretty high. It seems because the bio-derived oil itself could generate its own Hydrogen and Carbon involved chemical compounds which affect the H/C values of the residues. The chemical reactions expected increasing H/C values of the bio-oils from liquefaction by bio-oil derived solvent can be expected as follows. (Chang and Wan, 1947)

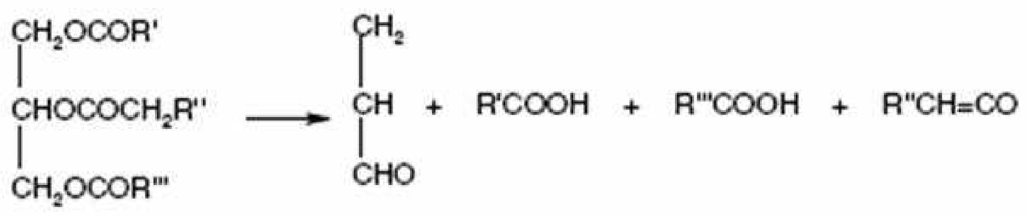
- Decomposition of ketenes and acrolein

$$2R''CH{=}CO \longrightarrow 2CO + RHC{=}CHR \quad \text{--------------}(49)$$

$$RCOCH_2R \longrightarrow R{-}R + CH_2CO \quad \text{-----------------}(50)$$

$$2RCOCH_2R \longrightarrow 2R_2 + CO + C_2H_4 \quad \text{-------------}(51)$$

- Decomposition of the glyceride



$$\begin{array}{l} CH_2OCOR' \\ | \\ CHOCOCH_2R'' \\ | \\ CH_2OCOR''' \end{array} \longrightarrow \begin{array}{l} CH_2 \\ | \\ CH \\ | \\ CHO \end{array} + R'COOH + R'''COOH + R''CH{=}CO \quad \text{---}(52)$$

(Chang and Wan, 1947)

The derivatives such as RHC=CHR, $CH_2CO$, $C_2H_4$, R'COOH, R'''COOH and R''CH=CO from the bio-oil derived solvent might increase the C/H values of the residues.

Meanwhile, the other residues applied to solvent extraction in the pyrolysis process were significantly shown as low O/C values. HHV was significantly higher in the solvent extraction process even if it was still lower than petroleum.

Even though these phenomena occur in residue other than liquid products, this fact is somewhat consistent in the residue O/C value and HHV value in terms of statement of

Differently from this assumption, biomass hydrogenolysis by Nicholas et al. (1985) can be considered in Pyrolysis without solvent uses hydrogen in biomass. So, H/C of the final material generated from pyrolysis of the biomass can become low because it consumes the hydrogen in composition of the biomass.

### 4.4.2.3 HHV (Higher Heating Value)

Heating value of residue from liquefaction was rather higher than that without solvent extraction. This shows that residues generated by liquefaction can be more effective energy source than residues generated by just pyrolysis without solvent.

## 4.2 External property observation of bio-oil

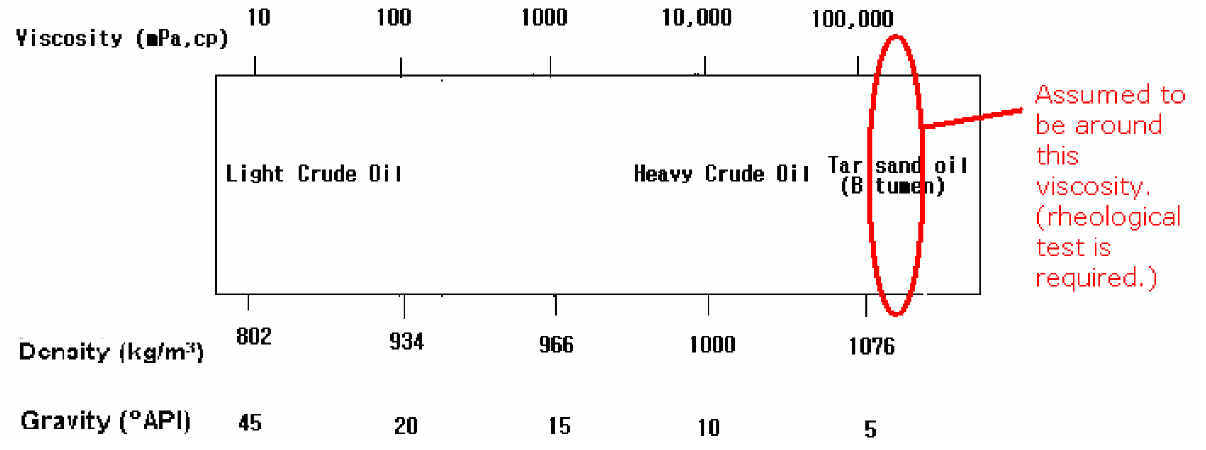
The property of the bio-oils after evaporation and distillation was observed by naked eyes and the hardness was checked by poking with pipet. The colour of the bio-oils was brown-dark colour and they were very viscous state. Their state was similar to the bitumen apparently.

Bio-oil evaporating solvent on air. (usually bowl was used to make the liquid surfacce contact air more to make evaporation easier. After this, by collecting the bio-oils to steel container, the bio-oils were distilled to remove more solvents.

After distillation of solvent used in bio-oil, the bio-oil was cooled down to check the hardness. It was highly viscous and dark brown colour.

Figure 4.3: Apparent state of bio-oil after evaporation & distillation of solvents

Note: viscometer test, shear test and viscosity test will be required to investigate precisely.



Assumed to be around this viscosity. (rheological test is required.)

Figure 4.4: Crude oil classification by gravity and viscosity

Therefore, this bio-oil seems to be bitumen-like material apparently**.**

### 4.3 Elemental analysis of bio-oil by EA.

#### 4.3.2.1 Composition

The result of EA analysis of bio-oils is shown in table 4.9.

| | N (%) | C (%) | H (%) | O (%) | H/C (no unit) | O/C (no unit) | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|
| Bamboo | 0.27 | 47.17 | 6.86 | 43.74 | 1.5 | 0.35 | 17.15 |
| Bio-oil from bamboo | 0.52 | 74.41 | 0.16 | 24.91 | 0.03 | 0.13 | 20.90 |
| Bio-oil from bamboo with tetralin | 0.60 | 82.93 | 7.96 | 8.51 | 1.15 | 0.04 | 38.00 |
| Bio-oil from bamboo with 1-methylnaphthalene | 0.67 | 80.17 | 10.54 | 8.62 | 1.58 | 0.04 | 40.77 |
| Bio-oil from bamboo with waste oil from cooking pork | 0.2 | 79.98 | 9.69 | 10.13 | 1.45 | 0.05 | 39.20 |
| Bio-oil from vegetable cooking oil | 0.1 | 84.09 | 10.89 | 4.92 | 1.55 | 0.02 | 43.26 |

Table 4.9: Comparison of composition of bamboo and bio-oils obtained by different solvents used using EA

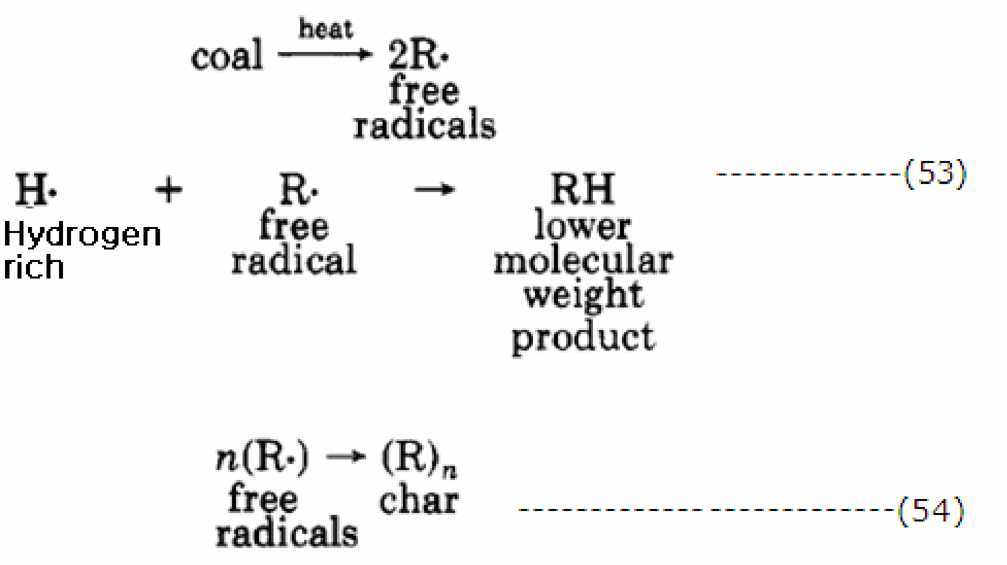
Note: N= Nitrogen, H= Hydrogen, C= Carbon, O = Oxygen, H/C = Hydrogen mass (weight)/ Carbon mass (weight), O/H = Oxygen mass (weight) / Carbon mass (weight). HHV = Higher Heating Value. Sulphur composition was less than 0.02 in all cases.

By solvent extraction (liquefaction), the Oxygen content rate was significantly decreased. This means acidity of the bio-oils was incredibly improved by the liquefaction.

Composition of C and H was higher proportion in the liquefaction which is assumed that hydrocarbon generated in bio-oil by liquefaction was more than just pyrolysis without solvents. This implies liquefaction is more efficient to generate energy source more similar to petroleum. This can be referred to the carbonization implying thermal decomposition generating more carbons (Holowaty et al., 1981)

By the liquefaction, value of H/C was increased compared with pyrolysis without solvents. On the other hand, value of O/C was decreased.

The reason why it happened is assumed that the bamboo might emit radicals just like coal and the Hydrogen was used to generate low molecular weight bio-oils which can explain why cross-linking effect doesn't occur in liquefaction. Differently, even though the bamboo in pyrolysis without any solvent emitted the radicals, there was no hydrogen to be reacted which seemed to cause the cross-linking effect. The following equation can clarify these findings. In this example, bamboo biomass is assumed same as coal in terms of emitting free radicals.



(Cited from Nicholas et al.)

Bio-oils generated after pyrolysis with or without solvents, didn't show any sulphur composition. This implies these bio-oils are very environmentally clean.

For Nitrogen atom, bio-oils from bamboo with vegetable cooking oil and waste oil from cooking pork showed the least amount of the Nitrogen which tells bio-oil derived solvent reacted the most environmentally friendly.

In terms of composition of carbon and hydrocarbon and value of H/C as well as HHV, bio-oils generated by solvent extraction (liquefaction) are very similar to Bitumen. However, oxygen content was still a bit higher than bitumen in bio-oils generated by the liquefaction. However, the bio-oils don't contain any sulphur which is environmentally superior to bitumen.

As can be seen in the graph above, the amount of carbon and hydrogen was improved by liquefaction than just simple pyrolysis. In addition, the amount of oxygen was reduced by liquefaction. This implies defects of bio-oils can possibly be solved by the use of liquefaction.

#### 4.3.2.2 H/C & O/C

It seems that hydrogenation effect has occurred in pyrolysis from bamboo without solvent based on the fact that comparing H/C of bamboo, C/H of bio-oil from bamboo without solvent was very low. H/C was significantly improved by liquefaction as seen in the graph above. O/C was reduced by liquefaction. In this result, the bamboo biomass emitted free radicals just like coal when it was heated in all cases. However, in the pyrolysis of bamboo without any solvent, the free radicals didn’t react with hydrogen because there was no hydrogen donor solvent. However, the other cases having solvents which could donate hydrogen (whether or not the amount is large) the free radicals could react with the hydrogen to lower molecular weight product. The amount of the hydrogen doesn’t seem to be important according to this finding that the lower molecular weight of bio-oil was proved as long as it exists. Following equation explain the phenomena.

Following is exemplified with coal. Bamboo biomass is assumed to emit free radicals just like this case.

$$\text{coal} \xrightarrow{\text{heat}} \underset{\substack{\text{free}\\\text{radicals}}}{2R\cdot}$$

$$\underset{\substack{\text{Hydrogen}\\\text{rich}}}{H\cdot} + \underset{\substack{\text{free}\\\text{radical}}}{R\cdot} \rightarrow \underset{\substack{\text{lower}\\\text{molecular}\\\text{weight}\\\text{product}}}{RH} \qquad \text{-------------------}(55)$$

$$\underset{\substack{\text{free}\\\text{radicals}}}{n(R\cdot)} \rightarrow \underset{\text{char}}{(R)_n} \qquad \text{--------------------------}(56)$$

(Cited from Nicholas et al.)

In different point of view, the solvent used in liquefaction played a role as a hydrogen transferring method (in other words, a carrier) which might bring the high Hydrogen value raising H/C value because the hydrogen in biomass would be transferred to bio-oil by the solvent intermediate method.

These phenomena are correspondent to the theory of Chunbao Xu et al. on the purpose of liquefaction which is another term of solvent extraction. They stated that the main purpose of liquefaction is to produce oil products of increased H/C ratios and decreased C/O ratios so that a higher caloric value relative to those existing in the feedstocks.

The reason why bio-oil produced from pyrolysis and liquefaction by tetralin is because as seen in equation (58), H2 produced from tetralin more likely reacts with C6H10O5 to C6H10O than disposing reaction to C4H10O as shown (57). Therefore, H/C value of the reaction involved with tetralin is less than those of the reactions with the other solvents at the end, because in (58), more C6H10Os remains that makes value of H/C smaller.

$$C_6H_{10}O_5 \xrightarrow{\text{heat}} C_4H_{10}O + 2CO_2 \quad \text{--------------------} \; (57)$$

$$C_6H_{10}O_5 + 4H_2 \xrightarrow{\text{heat}} C_6H_{10}O + 4H_2O \quad \text{--------------------} \; (58)$$

(cited from Nicholas(1985) )

### 4.3.2.3 HHV (Higher Heating Value)

Higher Heating values(HHV) are shown as above. This tells liquefaction can generate better energy source (higher HHV) than that of just pyrolysis only without any solvents. This indicates that the bio-oils generated from liquefaction can be better energy course than that from only pyrolysis without using any solvent.

### 4.4 Fractionation of bio-oil

| Solvent used in liquefaction | Name of fraction | Sample weight (g) |
|---|---|---|
| 1-methylnaphathalene | Aliphatics | 0.004 |
| | Aromatics | 0.0087 |
| | Polar(+asphaltene) | 0.051-(0.004+0.0087) = 0.0383 |
| Tetralin | Aliphatics | 0.001 |
| | Aromatics | 0.0033 |
| | Polar(+asphaltene) | 0.062-(0.001+0.0033) = 0.0577 |
| Vegetable cooking oil | Aliphatics | 0.0028 |
| | Aromatics | 0.0031 |
| | Polar(+asphaltene) | 0.058-(0.0028+0.0031) = 0.0521 |
| Waste oil from cooking pork | Aliphatics | 0.0019 |
| | Aromatics | 0.0032 |
| | Polar(+asphaltene) | 0.061-(0.0019+0.0032) = 0.0559 |
| No solvent | Aliphatics | 0.0006 |
| | Aromatics | 0.002 |
| | Polar(+asphaltene) | 0.049-(0.0006+0.002) = 0.0464 |
| Water | Aliphatics | 0.002 |
| | Aromatics | 0.004 |
| | Polar(+asphaltene) | 0.052-(0.002+0.004) = 0.046 |

Table 4.10: Fractions of bio-oils obtained by different solvents used

This result showed that the liquid material generated doesn’t contain much aliphatic and aromatic compounds. Most of the compounds were polar compounds. This shows that the liquid generated is highly polar. This point is very different from crude petroleum which is highly non-polar. According to record from research centre in the University of Nottingham, in the polars, a high amount of asphaltenes up to 40% was included which implies this liquid might be bitumen-like material.

Fig. 4.5 shows the percentage of the fractions.

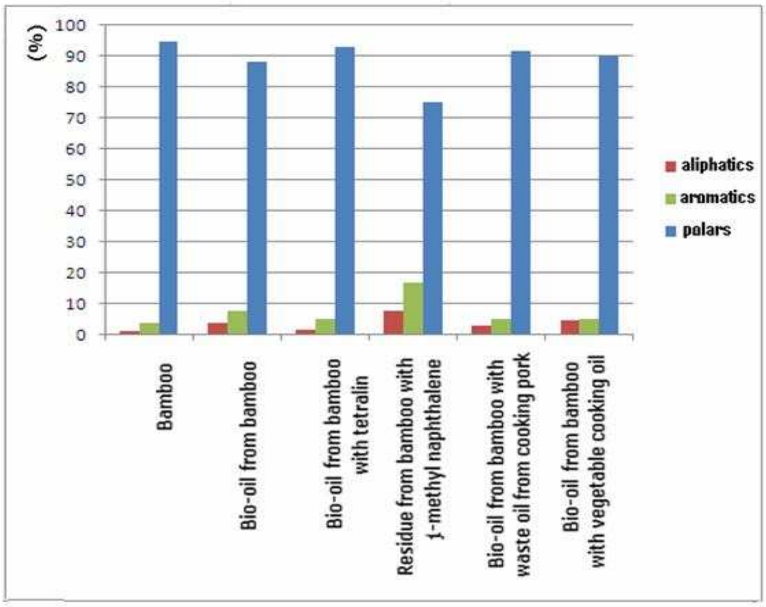


Figure 4.5: Fractions (%) (Bio-oils) obtained by different solvents used

## 4.5 GC-MS analysis of bio-oil

### 4.5.1 GC-MS distribution analysis

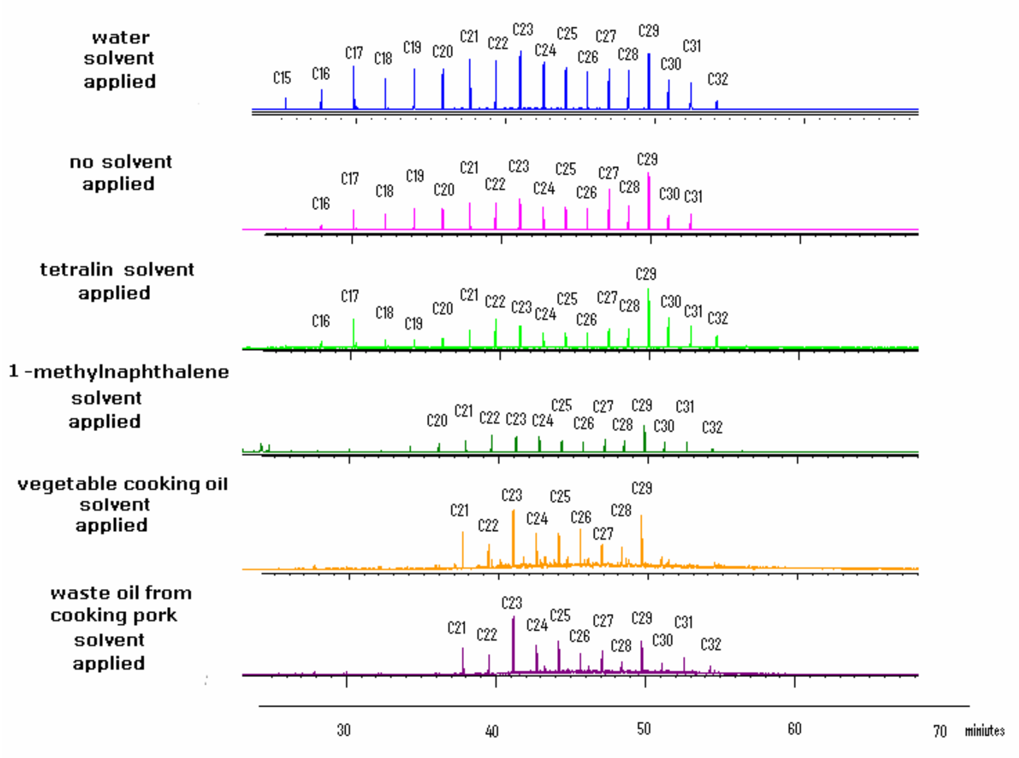


Figure 4.6: GC-MS distribution analysis of aliphatics of bio-oils obtained by different solvents used

Overall, the peaks shown in the each analysis, were evenly well distributed. For aliphatic compounds in bio-oil from bamboo with water , C15–C22 were detected. For aliphatic compounds in bio-oil from bamboo, C16-C30 were detected. For aliphatic compounds in bio-oil from bamboo with tetralin, 1-methylnaphthalene, vegetable cooking oil and waste oil from cooking pork, C16-C32, C20-C32, C21-C29 and C21-C32 were detected respectively. The aliphatic compounds are the most typical compounds of petroleum. So, This bio-oils are reasonable to be mentioned as similar material to the petroleum.

The peaks are well distributed in all samples representing characteristics of crude oil.

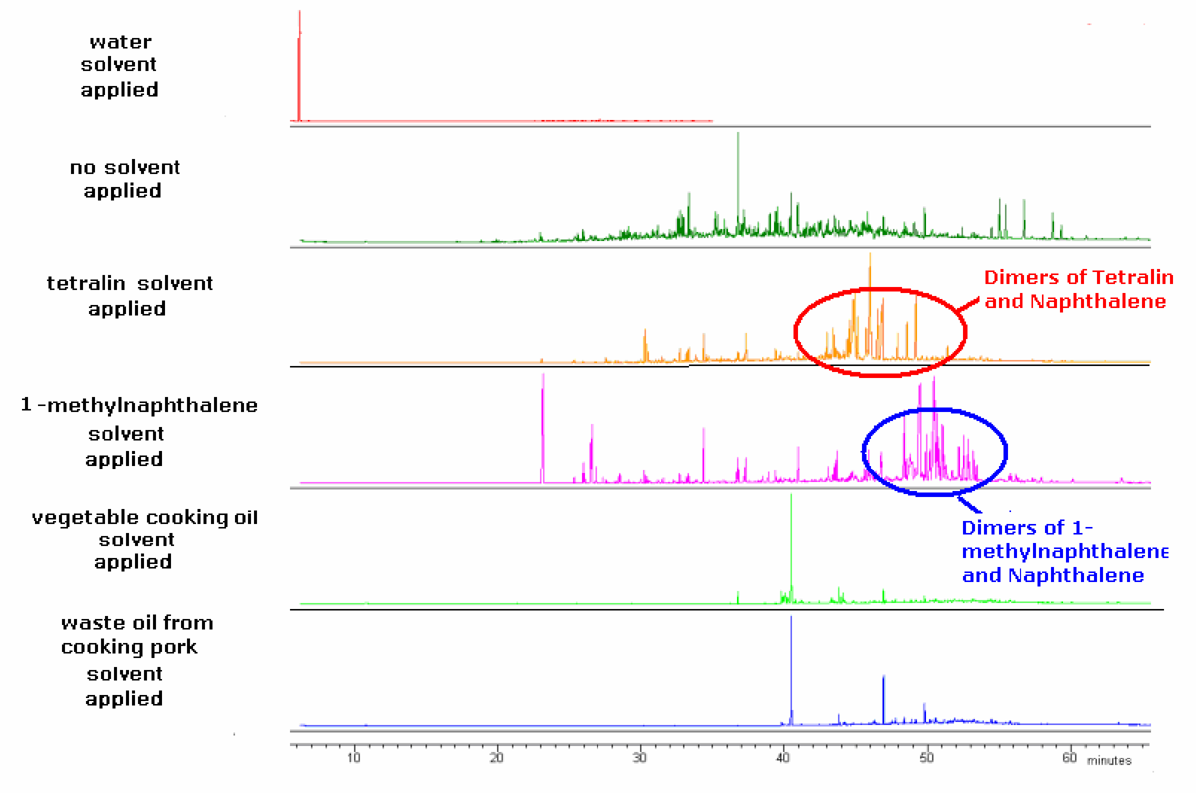


Figure 4.7: GC-MS distribution analysis of aromatics of bio-oils obtained by different solvents used

In GC-MS analysis of aromatic compounds, Irregularly sudden high peaks is assumed to be solvents that was used in fractionation process such as hexane, methanol and so on. Except for the irregular peaks, overall, the peaks are well distributed in all samples representing characteristics of crude oil.

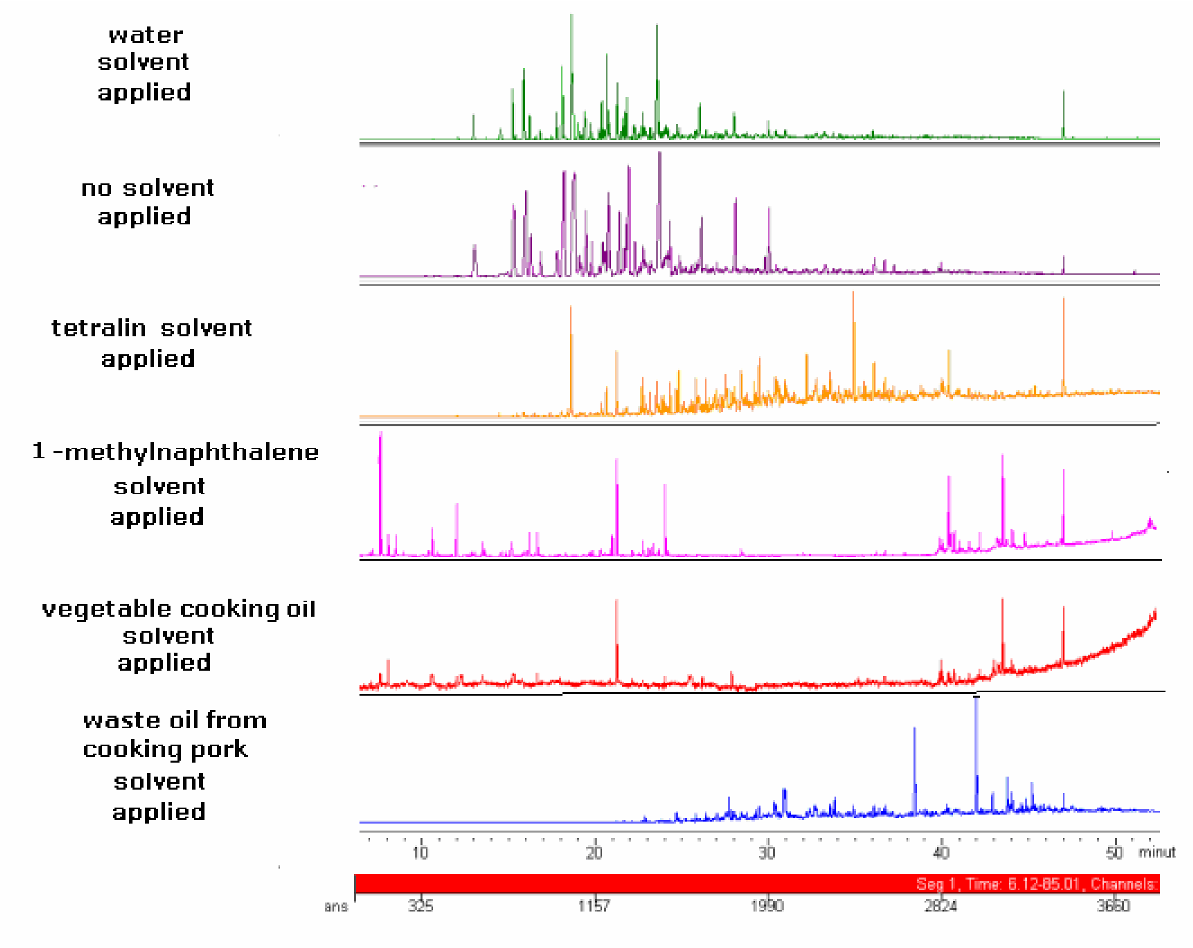


Figure 4.8: GC-MS distribution analysis of polars of Bio-oils obtained by different solvents used

For polar analyses, all peak areas were very small. There was not significant major peak area. However, to see if there is some compounds to show this bio-oil has similar to the previous petroleum, this polar compounds were investigated. In the sample of bio-oil from bamboo with 1-methylnaphthallen and bio-oil from bamboo with vegetable cooking oil, the curve was gone up high and stabilized the high level not shown much peaks. This seems to be machinery reason such as high pressure or temperature increase in GC-MS.

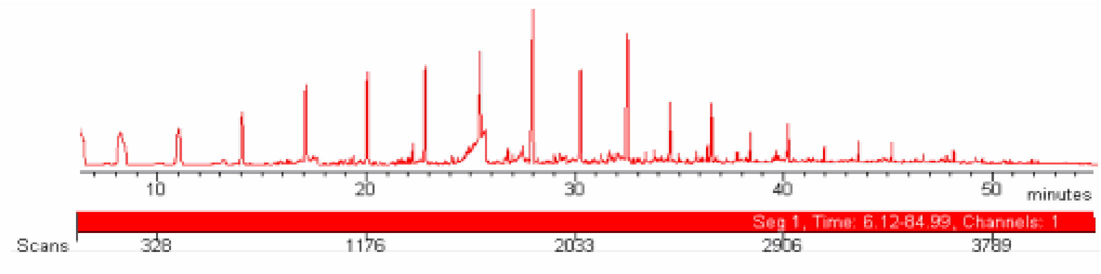


Figure 4.9: GC-MS distribution analysis of bio-oil obtained by vegetable cooking oil

To see what compounds are generated from vegetable cooking oil (bio-derived solvent), bio-oil from vegetable cooking oil (blank run) by pyrolysis and liquefaction was investigated in the full scan version of GC-MS. It was well distributed and seems to have some aliphatic compounds just like bio-oils generated from bamboo by pyrolysis and liquefaction.

### 4.5.2 Compound analysis by GC-MS

Fractionation performed in this study is not absolute separation. Groups of compounds along a continuum of polarity in an operation defined way were divided. Depending on solvent choice, column length, silica grade etc in fractionation process, the values can be a bit different.
For example, sometimes, not very polar aromatic compounds like naphthalene can be detected in the supposedly non-polar aliphatic fraction.(William Meredith )
Second thing to think about is that the bio-oils analysed are highly solvent dominated because distillation performed in this study can not perfectly reduce the solvent used in the liquefaction. (note: it can reduce a certain amount of the solvent)
In addition, GC-MS is not 100% accurate device. This device only tells possibilities of occurrences of the chemicals which can be more or less. So, to confirm the data obtained, further analyses such as rheological test are required.
Based on the supposition above, the main compounds found from analyses were performed as below.

#### 4.5.2.1 GC-MS analysis of aliphatic compounds obtained by different solvents used

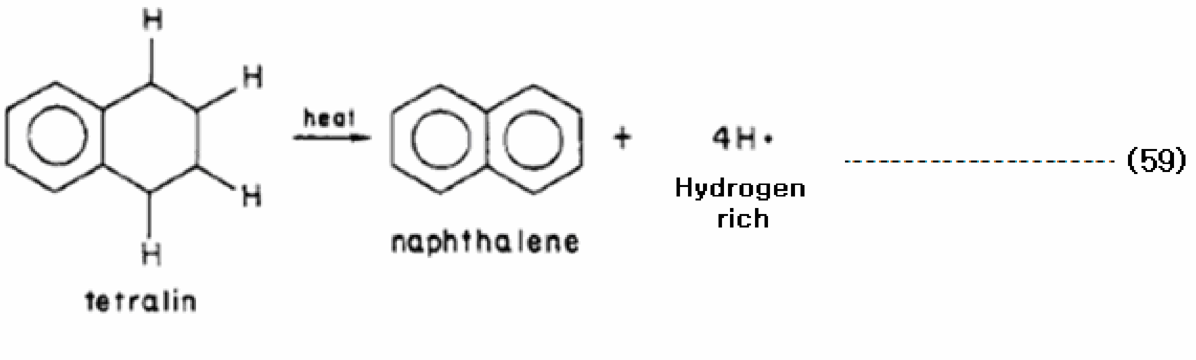
In aliphatic fraction from bamboo with water , the major compound was Tricyclo[20.8.0.0 (7,16) triacontane,1(22),7(16)-dieppoxy, 1-Hexaconaene and E-8-Methyl-9-tetradecen-1-ol acetate (respectively, 7.8%, 5.95% and 5.49%) for water liquefaction. Some ester compounds' formation could be suggested by sulfurous acid, butyl tridecyl ester possibly produced via esterification reaction. Esters in butyl tridecyl ester imply this material can be bitumen.

Among aliphatic compounds from bamboo, the major compound in the aliphatic fraction of pyrolysis without solvent was Hentriacontane (6.65%) in retention time 41.812 min. Benzene, (3-octylundecyl-) implies this material can be bitumen. Benzene, (3-

octylundecyl), Tetracontane, 3,5,24-trimethyl- and Tetracontane, 3,4,24-trimethyl- implies this material can be bitumen. In aliphatic compounds from bamboo with Tetralin The major compound in aliphatic fraction of tetralin liquefaction was Hentriacontane (17%, 9.66%).

And some compounds, e.g., Naphthalene, 1-(2-propenyl)- generated in the solvent tetralin liquefaction process were detected.

This might be because when Tetralin donates Hydrogens, it remains to Naphthalene as follows.



(Cited from Nicholas et al.,1985)

1-(2-propenyl)-, 3,5,24-trimethyl-,3,5,24-trimethyl- and butyl heptadecyl ester which were found in this fraction implies this material can be bitumen.

As an Aliphatic compound from bamboo with 1-methylnaphthalene, The major compound in aliphatic fraction of tetralin liquefaction was Naphthalene and Tritetracontane (11.1% and 3.3% respectively). And some compounds, e.g., Naphthalene, -methyl-, Naphthalene, 1,3-dimethyl-generated in the solvent 1-methylnaphthalene liquefaction process were detected. -methyl- and 1,3-dimethyl- found in this case implies this material can be bitumen.

For Aliphatic Compounds from bamboo with vegetable oil, the major compound in aliphatic fraction of vegetable cooking oil liquefaction was 1-Heptatriacotanol (0.903% and 0.929%).

In Aliphatic compounds from bamboo with waste oil from cooking pork

The major compound in aliphatic fraction of waste oil from cooking pork liquefaction was Tritetracontane (11.2%).

### 4.5.2.2 GC-MS analysis of aromatic compounds obtained by different solvent used

Aromatic compounds from bamboo obtained by water solvent in GC-MS analysis are shown in table 4.11.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 27.5 | Butanoic acid, 3-hexenyl ester,(2)- | 2.18E+00 | $C_{10}H_{18}O_2$ | 170 |
| 28.9 | 4-Hydroxy-3methyl-2-butanon | 2.28E+00 | $C_5H_{10}O_2$ | 102 |
| 29.7 | Propanoic acid, 2-methyl, anhydride | 2.58E+00 | $C_8H_{14}O_3$ | 158 |
| 30.45 | Propanoic acid, 2-methyl, anhydride | 2.71E+00 | $C_8H_{14}O_3$ | 158 |
| 31.2 | Propanoic acid, 2-methyl, anhydride | 1.86E+00 | $C_8H_{14}O_3$ | 158 |
| 31.95 | Propanoic acid, 2-methyl, anhydride | 1.80E+00 | $C_8H_{14}O_3$ | 158 |
| 32.92 | 2-Dimethyl(ethyl) silyloxyundecane | 1.38E+00 | $C_{15}H_{34}OSi$ | 258 |
| 33.59 | Cydopropyl methyl carbinal | 1.50E+00 | $C_5H_{10}O$ | 86 |

Table 4.11: Aromatic compounds obtained by water solvent in GC-MS analysis

Aromatic compounds obtained without using any solvent in GC-MS analysis are shown in table 4.12.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 29 | naphthalene, 1,4,5-tri methyl- | 1.28E+00 | $C_{13}H_{14}$ | 170 |
| 32.7 | 5,8,11,14-Eicosatetraynoic acid | 1.29E+00 | $C_{20}H_{24}O_2$ | 296 |
| 33.3 | Benzene, 1,1'-methylenebis[4-methyl-] | 3.61E+00 | $C_{15}H_{16}$ | 196 |
| 36.7 | Hexadecanoic acid, methyl ester | 1.86E+00 | $C_{17}H_{34}O_2$ | 270 |
| 41.5 | Fluoranthene | 1.55E+00 | $C_{16}H_{10}$ | 202 |
| 49.7 | Tetra cosanoic acid, methyl ester | 2.21E+01 | $C_{31}H_{62}O_2$ | 466 |
| 54.98 | Nonacosane | 1.53E+00 | $C_{29}H_{60}$ | 408 |
| 55.3 | Octacosanoic acid, methyl ester | 3.80E+00 | $C_{29}H_{58}O_2$ | 438 |
| 57.7 | Nonacosane | 3.25E+01 | $C_{29}H_{60}$ | 408 |
| 58.6 | Octacosane | 2.22E+01 | $C_{28}H_{58}$ | 394 |
| 59.2 | Triacontanoic acid, methyl ester | 2.33E+00 | $C_{31}H_{62}O_2$ | 466 |

Table 4.12: Aromatic compounds obtained without using any solvent in GC-MS analysis

Aromatic compounds obtained by tetralin solvent in GC-MS analysis are shown in table 4.13.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 30.2 | 1.1'-Biphenyl, 2-methyl- | 13.96119 | $C_{13}H_{12}$ | 168 |
| 30.4 | 1,1'-Biphenyl, 4-methyl- | 14.05102 | $C_{13}H_{12}$ | 168 |
| 32.6 | 2,2'-Dimethylbiphenyl- | 14.98544 | $C_{14}H_{14}$ | 182 |
| 46.8 | 1,2'-Binaphthalene,1',2',3',4'-tetrahydro- | 21.7829 | $C_{20}H_{18}$ | 258 |

Table 4.13: Aromatic compounds obtained by tetralin solvent by GC-MS analysis

Aromatic compounds obtained by 1-methylnaphthalene solvent in GC-MS analysis are shown in table 4.14

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 23 | Naphthalene, 1-methyl- | 8.28E+01 | $C_{11}H_{10}$ | 142 |
| 25.9 | Naphthalene, 1,8-dimethyl- | 1.32E+00 | $C_{12}H_{12}$ | 156 |
| 28.4 | Naphthalene, 1,3-dimethyl- | 3.67E-01 | $C_{12}H_{12}$ | 156 |
| 29.2 | Naphthalene, 1-(1-methylethyl)- | 1.21E-01 | $C_{13}H_{14}$ | 170 |
| 30.2 | 1-Isopropenylnaphthalene | 8.26E-01 | $C_{14}H_{16}$ | 184 |
| 49.2 | Naphthalene | 1.03E+00 | $C_{21}H_{16}$ | 268 |

Table 4.14: Aromatic compounds obtained by 1-methylnaphthalene solvent by GC-MS analysis

Aromatic Compounds obtained by vegetable cooking oil solvent in GC-MS analysis are shown in table 4.15.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 36.7 | Pentaecanoic, 14-methyl-,methyl ester | 3.56E+00 | $C_{17}H_{34}O_2$ | 270 |
| 39.7 | Methyl trans-4-(2-nonylcyclo pentyl) butanoate | 3.10E+00 | $C_{19}H_{36}O_2$ | 296 |
| 40.3 | Hexacosanoic acid, methyl ester | 3.68E+01 | $C_{27}H_{54}O_2$ | 410 |
| 43.8 | Triacontanoic acid, methyl ester | 6.31E+00 | $C_{31}H_{62}O_2$ | 466 |
| 46.8 | Triacontanoic acid, methyl | 5.75E+00 | $C_{31}H_{62}O_2$ | 466 |
| 49.7 | Cyclopropanebutanoic acid,2-[[2-[[2-pentylcyclo propyl]methyl](yclopropyl)methyl]cyclopropyl]methyl]-,methyl ester | 1.79E+00 | $C_{25}H_{42}O_2$ | 374 |

Table 4.15: Aromatic compounds obtained by vegetable cooking oil solvent by GC-MS

Aromatic compounds obtained by waste oil from cooking pork solvent in GC-MS analysis are shown in table 4.16.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 40.2 | Hexade canoic acid, 15-methyl-, methyl ester | 2.37E+01 | $C_{18}H_{36}O_2$ | 284 |
| 43.8 | Eicosanoic acid, methyl ester | 2.43E+00 | $C_{21}H_{42}O_2$ | 326 |
| 46.8 | Triacontanoic, methyl ester | 1.08E+01 | $C_{31}H_{62}O_2$ | 466 |
| 49.8 | Triacontanoic, methyl ester | 5.61E+00 | $C_{31}H_{62}O_2$ | 466 |
| 51.8 | Rhodopin | 1.56E+00 | $C_{40}H_{58}O$ | 544 |
| 54.4 | Rhodopin | 1.06E+00 | $C_{40}H_{58}O$ | 544 |

Table 4.16: Aromatic compounds obtained by waste oil from cooking pork solvent by GC-MS

### 4.5.2.3 GC-MS analysis of polar compounds obtained by different solvents used

Polar compounds obtained by water solvent in GC-MS analysis are shown table 4.17.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 12.9 | Phenol | 0.179344 | $C_6H_{60}$ | 94 |
| 14.6 | 2-Cydopenten-1-one,2,3-dimethyl- | 0.201008 | $C_7H_{10}O$ | 110 |
| 15.3 | Phenol, 2-methyl- | 0.210667 | $C_7H_8O$ | 108 |
| 15.8 | Phenol, 4-methyl- | 0.224041 | $C_7H_8O$ | 108 |
| 16.2 | Mequinol | 0.232428 | $C_7H_8O_2$ | 124 |
| 16.8 | Phenol, 2,3-dimethyl- | 0.245458 | $C_7H_8O_2$ | 122 |
| 17.7 | Phenol, 2-ethyl- | 0.251979 | $C_8H_{10}O$ | 122 |
| 18.2 | Phenol, 2,4-dimethyl- | 0.258708 | $C_8H_{10}O$ | 122 |
| 18.7 | Phenol, 3-ethyl- | 0.264235 | $C_8H_{10}O$ | 122 |
| 19 | Phenol, 2,3-dimethyl- | 0.268255 | $C_8H_{10}O$ | 122 |
| 19.4 | Phenol, 3,4-dimethyl- | 0.272801 | $C_8H_{10}O$ | 122 |
| 19.7 | Phenol, 2,4,6-trimethyl- | 0.287806 | $C_8H_{10}O$ | 136 |
| 20.8 | Phenol, 2 ethyl-4-methyl- | 0.294135 | $C_9H_{12}O$ | 136 |
| 21.2 | Phenol,2 ethyl-4-methyl- | 0.299813 | $C_9H_{12}O$ | 136 |
| 21.7 | Phenol,2,3,5-trimethyl- | 0.321271 | $C_9H_{12}O$ | 136 |
| 22.2 | Phenol,2-ethyl-4,5-dimethyl- | 0.327074 | $C_{10}H_{14}O$ | 150 |
| 22.7 | Phenol,4-(1-methyl(propyl)- | 0.334908 | $C_{10}H_{14}O$ | 150 |
| 23.2 | 2-methyl-6-propylphenol | 0.343157 | $C_{10}H_{14}O$ | 150 |
| 23.6 | Phenol, 2,6-dimethoxy- | 0.327074 | $C_8H_{10}O_3$ | 154 |
| 24.2 | 2-Ethyl-5-n-propylphenol | 0.354611 | $C_{11}H_{16}O$ | 164 |
| 24.8 | Acetic acid [6,8,9- trimethyl-4-(3,4-methylenedio[3.3.1]non-6-en-1-yl) | 0.365886 | $C_{21}H_{26}O_5$ | 358 |
| 25.7 | 1,5-Dihydroxy-1,2,3,4-tetra hydronaphthalene | 0.381692 | $C_{10}H_{12}O_2$ | 164 |
| 26.4 | Acetic acid,[6,8,9-trimethyl-4-(3,4-methylene dioxyphenyl)3-oxabicyclo[3,3,1] non-6-en-1yl] methyl ester | 0.385437 | $C_{21}H_{26}O_5$ | 358 |
| 27.6 | Bezoldehyde, 2,3,4,5-tetramethyl- | 0.397001 | $C_{11}H_{14}O$ | 162 |
| 27.9 | 2-Propanone, 1-(4-hydroxy-3-methoxy phenyl) | 0.420297 | $C_{10}H_{12}O_3$ | 180 |
| 28.7 | Benzene, 3-ethyl-1,2,4,5-tetramethyl- | 0.427786 | $C_{12}H_{18}$ | 162 |
| 30.4 | 1-Hydroxy-1,2,3,4-, tetrahydronaphthalene-,8-carboxaldehyde | 0.452241 | $C_{11}H_{12}O_2$ | 176 |
| 30.9 | 1-Naphthalenol, 2-methyl- | 0.480152 | $C_{11}H_{10}O$ | 158 |
| 32.7 | 1-Naphthalenol, 1,2,3,4-, tetrahydro-2,5,8-trimethyl- | 0.452241 | $C_{13}H_{18}O$ | 190 |
| 34.7 | 1-naphthol, 5,7-dimethyl- | 0.452241 | $C_{12}H_{12}O$ | 172 |
| 36.1 | (d-Threo-2,3- diphenyl)-2-butanol | 0.499772 | $C_{16}H_{18}O$ | 226 |
| 39.2 | Naphtho[2,1-b] buran, 1,2-dimethyl- | 0.54107 | $C_{14}H_{12}O$ | 196 |
| 47.1 | 1,2-Benzenedicarboxylic acid, diisooctyl ester | 0.649768 | $C_{24}H_{38}O_4$ | 390 |

Table 4.17: Aromatic compounds obtained by water solvent in GC-MS analysis

Polar compounds obtained without using any solvent in GC-MS analysis are shown table 4.18.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 6 | Phenol | 1.16E-09 | $C_6H_6O$ | 94 |
| 10.5 | Phenol,2-methyl- | 1.34E-09 | $C_7H_8O$ | 108 |
| 12 | Phenol,4-methyl- | 1.58E-09 | $C_7H_8O$ | 108 |
| 13 | Phenol,2-methoxy- | 1.73E-09 | $C_7H_8O_2$ | 124 |
| 14.8 | Phenol,2,3-dimethyl- | 1.98E-09 | $C_8H_{10}O$ | 122 |
| 15 | Phenol,2-ethyl- | 2.08E-09 | $C_8H_{10}O$ | 122 |
| 16.5 | Phenol,2,5-dimethyl- | 2.46E-09 | $C_8H_{10}O$ | 122 |
| 17.2 | Phenol,4-ethyl- | 2.61E-09 | $C_8H_{10}O$ | 122 |
| 18.7 | Phenol,2-methoxy-4 methyl- | 3.02E-09 | $C_8H_{10}O_2$ | 138 |
| 21.5 | Phenol, 4-ethyl-3-methyl- | 4.46E-09 | $C_9H_{12}O$ | 136 |
| 23 | Phenol, 2-ethyl-4-methyl- | 5.60E-09 | $C_9H_{12}O$ | 136 |
| 23.4 | Dimethoxyamphetamine | 5.76E-09 | $C_{11}H_{17}NO_2$ | 195 |
| 27 | Phenol, 2,6-dimethoxy- | 9.20E-09 | $C_8H_{10}O_3$ | 154 |
| 28.2 | 3-(3-Hydroxy-4 methoxy phenyl)-1-alanine | 1.08E-08 | $C_{10}H_{13}NO_4$ | 211 |

Table 4.18: Polar compounds obtained without using any solvent in GC-MS analysis

Polar compounds obtained by tetralin solvent in GC-MS analysis are shown in table 4.18.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 18.5 | Phenol, 3-ethyl- | 0.141537 | $C_8H_{10}O$ | 122 |
| 20.7 | Phenol, 4-ethyl-3-methyl- | 0.158831 | $C_9H_{12}O$ | 136 |
| 21.3 | Phenol, 3-propyl- | 0.163266 | $C_9H_{12}O$ | 136 |
| 22.7 | 2,5-Diethylphenol | 0.174542 | $C_{10}H_{14}O$ | 150 |
| 23.6 | 1H-Iniden-5-ol,2,3,-dihydro- | 0.181744 | $C_9H_{10}O$ | 134 |
| 24.7 | 1(2H)-Naphthalenone, 3,4-dihydro | 0.189699 | $C_{10}H_{10}O$ | 146 |
| 24.9 | Phenol,p-(2-methylallyl)- | 0.190806 | $C_{10}H_{12}O$ | 148 |
| 26.4 | Oxacyclotetradeca-4,11-diyne | 0.203496 | $C_{13}H_{18}O$ | 190 |
| 27.6 | 4,5-Dimethyl-3H-isobenzo, furan-1-one | 0.21232 | $C_{10}H_{10}O_2$ | 162 |
| 28.4 | Megastigma-4,6(E),8(E)-triene | 0.218508 | $C_{13}H_2O$ | 176 |
| 29.4 | 2-Naphthyl methyl, Ketone | 0.226048 | $C_{12}H_{10}O$ | 170 |
| 32.7 | 1-Naphthalenol, 1,2,3,4-tetrahydro-,2,5,8-trimethyl- | 0.251183 | $C_{13}H_{18}O$ | 190 |
| 34.9 | 1,4-methanonaphthalene-9-ol,1,2,3-4-tetrahydro-,stereoisomer | 0.268262 | $C_{11}H_{12}O$ | 160 |
| 36.2 | 1-Naphalene ethanol acetate | 0.279392 | $C_{14}H_{14}O$ | 214 |
| 36.7 | 5,8,11-Heptadecatriynoic acid, methyl –ester | 0.282097 | $C_{18}H_{24}O_2$ | 272 |
| 47 | 1,2-Benzenedicarboxylic acid, mono(2-ethylhexl)ester | 0.361428 | $C_{16}H_{22}O_4$ | 278 |

Table 4.18: Polar compounds obtained by tetralin solvent in GC-MS analysis

Polar compounds obtained by 1-methylnaphthalene solvent in GC-MS are shown in table 4.19.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 27.8 | 2-Naphthalene carboxol dehyde | 2.95E-01 | $C_{11}H_8O$ | 156 |
| 30.3 | 1-Hydroxy-1,2,3,4-tetrahydronaphthalene-8-carboxaldehyde | 6.97E-01 | $C_{11}H_{12}O_2$ | 176 |
| 41 | 9-Acetylphenanthrene | 4.62E-01 | $C_{16}H_{12}O_2$ | 220 |
| 41.8 | 1-(10-Methylanthracen-9-yl) ethanone | 6.11E+00 | $C_{17}H_{14}O$ | 234 |
| 42 | Morphinan-4,5-diol-(-one,1-bromo- | 1.83E-01 | $C_{16}H_{18}Br$ | 351 |

Table 4.19: Polar compounds obtained by 1-methylnaphthalene solvent in GC-MS analysis

Polar compounds obtained by vegetable cooking oil solvent are shown in table 4.20.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 21.25 | 2-Dodecenol,(E)- | 3.57E+01 | $C_{12}H_{22}O$ | 182 |
| 43.5 | 2-Hexadecanol | 3.50E+01 | $C_{16}H_{34}O$ | 242 |

Table 4.20: Polar compounds obtained by vegetable cooking oil solvent in GC-MS analysis

Polar compounds obtained by waste oil from cooking pork solvent in GC-MS analysis are shown in table 4.21.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 21.1 | 2-Decenal, (z)- | 2.69E+00 | $C_{10}H_{18}O$ | 154 |
| 24 | 2-Doclecenal, (E)- | 6.95E+00 | $C_{12}H_{22}O$ | 182 |
| 40.2 | 9-Hexadecenoic acid | 7.61E+00 | $C_{16}H_{30}O_2$ | 254 |
| 43.5 | Oleic acid | 9.40E+00 | $C_{18}H_{34}O_2$ | 282 |
| 47 | 1,2-Benzenedicarboxylic acid diisooctyl ester | 7.22E+00 | $C_{24}H_{38}O_4$ | 390 |

Table 4.21: Polar compounds obtained by waste oil from cooking pork solvent in GC-MS analysis

#### 4.5.2.4 Compounds obtained by Vegetable cooking oil

Compounds obtained by Vegetable cooking oil solvent itself (blank run without bamboo) are shown in table 4.22.

| Retention time | Compound | Area(%) | Formula | Mw |
|---|---|---|---|---|
| 7.366 | pentanoic acid, 2-ethylhexyl ester | 4.18E-02 | $C_{13}H_{26}O_2$ | 214 |
| 11.005 | Nonane, 2,5-dimethyl- | 4.21E+00 | $C_{11}H_{24}$ | 156 |
| 14.421 | Tetracontane, 3,5,24-trimethyl- | 7.13E-02 | $C_{43}H_{88}$ | 604 |
| 17.113 | Tetracontane, 3,5,24-trimethyl- | 4.16E+00 | $C_{43}H_{88}$ | 604 |
| 20.037 | Pentadecane, | 3.48E+00 | $C_{15}H_{32}$ | 212 |
| 23.062 | Oleic Acid | 1.10E-01 | $C_{18}H_{34}O_2$ | 282 |
| 28.116 | Tritetracontane | 1.75E-01 | $C_{43}H_{88}$ | 604 |
| 30.26 | Tritetracontane | 3.13E+00 | $C_{43}H_{88}$ | 604 |
| 32.503 | Oleic Acid | 5.82E+00 | $C_{18}H_{34}O_2$ | 282 |
| 40.21 | Tetrapentacontane 1,54-dibromo- | 1.44E+00 | $C_{54}H_{108}Br_2$ | 914 |
| 42.043 | Cholestan-3-ol, 2-methylene-, (3a', 5a')- | 1.37E-01 | $C_{28}H_{480}$ | 400 |
| 43.753 | Cholestan-3-ol, 2-methylene-, (3a', 5a')- | 1.83E-01 | $C_{28}H_{480}$ | 400 |
| 48.222 | 1-Heptatriacotanol | 1.56E-01 | $C_{37}H_{76}O$ | 536 |

Table 4.22: Compounds obtained vegetable cooking oil solvent itself without bamboo in GC-MS analysis

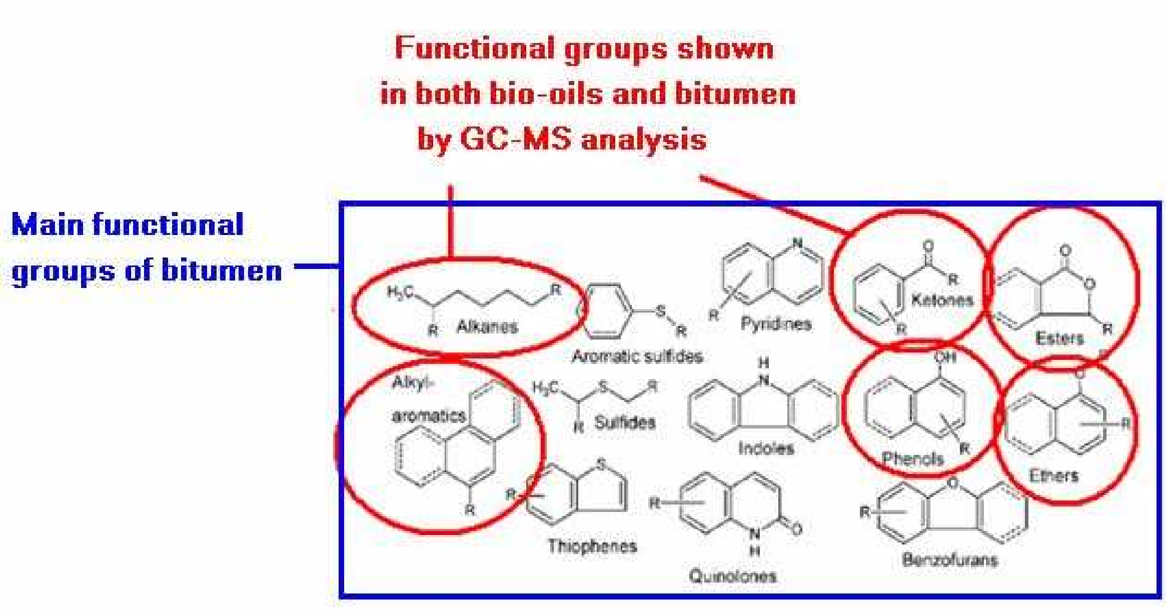


Figure 4.10: Functional groups shown in both bio-oils and bitumen by GC-MS analysis (Masson,2008)

In summary, the product distribution was affected by the solvent type used. Peaks shown in each fraction were well distributed implying this bio-oil is crude-oil. As seen in fig.4.10, functional groups of Alkanes, Ketones, Esters, Alkyl- aromatics, Phenols and Esters were found in the bio-oil which implies this bio-oil is possibly bitumen-like material. In addition, for all fractions, it was worthwhile to notice less compounds with nitrogen and sulfur atom were detected which implies this bio-oil is environmentally clean.

## 4.6 Overall mass & Energy (Calorific energy) balance

### 4.6.1 Mass & Energy (Calorific energy) balance in pyrolysis of bamboo without solvent

#### 4.6.1.1 Mass balance

Mass of Bio-oil product was found by deleting gas mass from total input mass (bamboo 5g). Here, the gas weight was found by assuming the gas collected is mainly $CO_2$ and Methane because these gases are major gases. Because the proportion of n-alkane and the other gases is known from the GC, by assuming n-alkane as methane and the other gases as $CO_2$, gas mass can be found from total gas volume, density of methane and $CO_2$ and the proportion of the n-alkane as follows.

$$\text{Gas mass(mg)} = CO_2\ \text{density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of } CO_2$$

$$+\ \text{Methane density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of Methane}$$

$$\longrightarrow$$

$$\text{Gas mass(mg)} = 1.9\ \text{(mg/ml)} \times 697\text{(ml)} \times 91.93/100$$

$$+\ 1.82\text{(mg/ml)} \times 697\ \text{(ml)} \times 8.07/100$$

$$= 1319.80\ \text{(mg)}$$

Therefore, it is about 1.32 (g)

$$\text{Bio-oil product (g)} = \text{Total input mass (g)} - \text{Char mass (g)} - \text{Gas mass (g)}$$

$$= 5\ \text{(g)} - 2.13\ \text{(g)} - 1.32\ \text{(g)}$$

$$= 1.55\ \text{(g)}$$

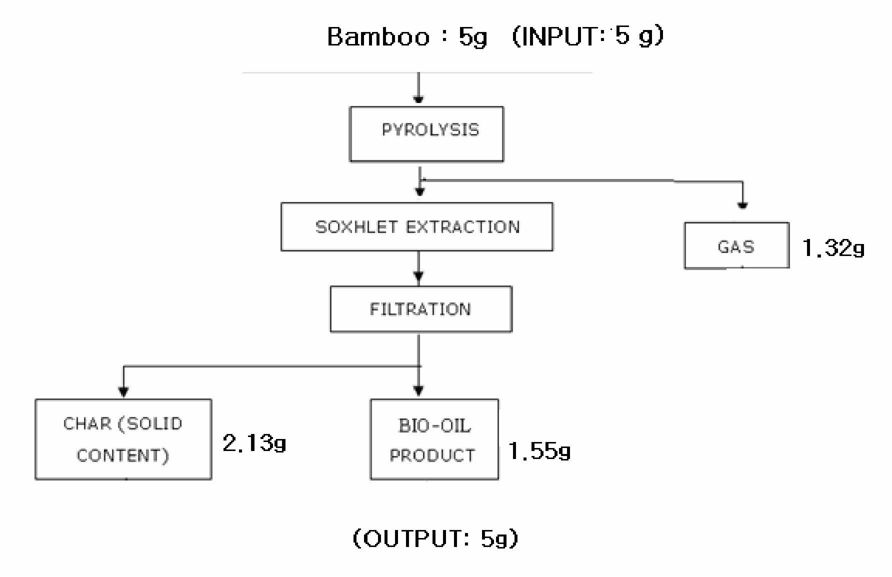


Figure 4.11: Mass balance in pyrolysis of bamboo without solvent

### 4.6.1.2 Energy (Calorific value) balance

By law of energy conservation, sum of calorific values (HHV) of char, bio-oil product and gas must be same as that of biomass (bamboo) and energy supply by pyrolysis.
Here the calorific value of the gas was found by assuming the gas collected is mainly $CO_2$ and Methane because these gases are major gases. Because the proportion of n-alkane and the other gases is known from the GC, by assuming n-alkane as methane and the other gases as $CO_2$, that of the gas can be found from total gas volume, density of methane and $CO_2$ and the proportion of the n-alkane.

INPUT ENERGY = bamboo 17.15 MJ/kg X 1kg/1000g X 5g X 1000 KJ/1MJ = 86 KJ
(because the bamboo applied was 5g)
Calorific value (HHV) = (338.2 X %C + 1442.8 X (%H - %O/8)) X 0.001

%C of $CO_2$ = 12(molecular weight of C) / (12 (molecular weight of C) + 16 (molecular weight of O) X 2) X 100 (%) = 27.27%
%O of $CO_2$ = 16(molecular weight of O) X 2 / (12 (molecular weight of C) + 16 (molecular weight of O) X 2) X 100 (%) = 72.73%

Calorific value (HHV) of $CO_2$ = (338.2 X 27.2 + 1442.8 + (-73.73/8)) X 0.001 = 10.63 MJ/kg

%C of $CH_4$ = 12(molecular weight of C) / (12 (molecular weight of C) + 1 (molecular weight of H) X 4) X 100 (%) = 75 %
%H of $CH_4$ = 1 (molecular weight of O) X 4 / (12 (molecular weight of C) + 1 (molecular weight of H) X 4) X 100 (%) = 25%

Calorific value (HHV) of $CH_4$ = (338.2 X 75 + 1442.8 + (4)) X 0.001 = 26.81 MJ/kg

The calorific value (HHV) of the gas = 10.63 MJ/kg X 97.2/100 + 26.81 MJ/kg X 2.8/100 = 11.08 MJ/kg

Therefore, energy of the gas = 1.32gX1kg/1000g X 1000 KJ/1MJ X 11.08 MJ/kg = 15 KJ

Ash free residue (g) = residue (g) – ash (g) = 2.13 g – 0.08 g = 2.05 g = char (g)

Therefore, energy of the char (ash free residue) = 2.05 g X 1000g X 1000KJ/1MJ X 12.73 MJ/kg = 26 KJ

Energy of Bio-oil product = 1.55 g X 1000g X 1000KJ/1MJ X 20.90 MJ/kg = 32 KJ

Therefore, HHV of char + HHV of bio-oil + HHV of gas = 26 KJ + 32 KJ + 15 KJ = 73 KJ = OUTPUT

ENERGY LOSS = INPUT – OUTPUT = 86 (KJ) – 73 (KJ) = 13 (KJ)
(probably, in evaporation, distillation)

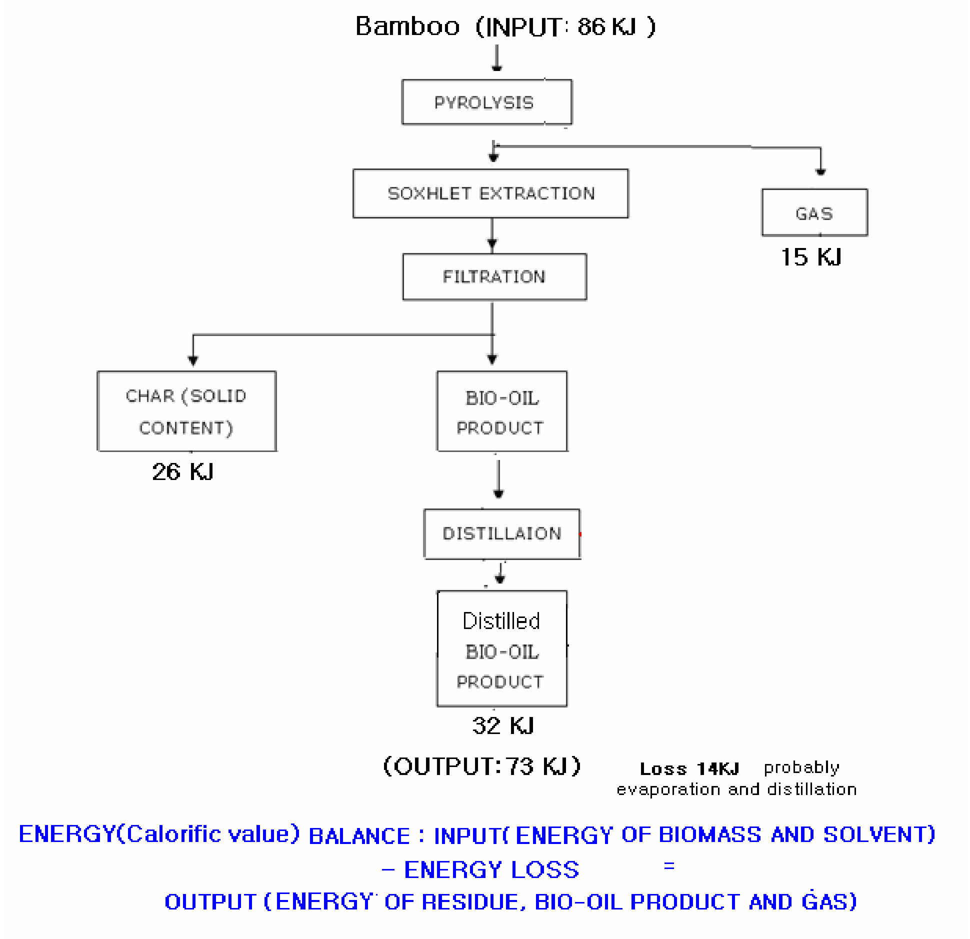


Figure 4.12.Energy balance in pyrolysis without solvent

As Figure 4.12, for mass balance, bamboo powder (5g) is used as input. Because the values of residue were weighed, the values of mixture of each bio-oil product and gas are decided by deleting the values of residue from sum of bamboo powder and solvent according to the law of mass conservation.

### 4.6.2 Mass & Energy (Calorific energy) balance in pyrolysis and liquefaction of bamboo by tetralin

#### 4.6.2.1 Mass balance

$$\text{Gas mass(mg)} = \text{CO}_2\ \text{density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of CO}_2 + \text{Methane density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of Methane} \longrightarrow$$

Gas mass (mg) = 1.90 (mg/ml) X 791.25 (ml) X 91.93/100 + 1.82 (mg/ml) X 791.25 (ml) X 8.07/100 = 1498.27mg

Therefore, it is about 1.50 (g)

Bio-oil product (g) = Total input mass (g) – Char mass (g) – Gas mass (g)

= 17.5 (g) – 0.66 (g) - 1.50 (g) = 15.33 (g)

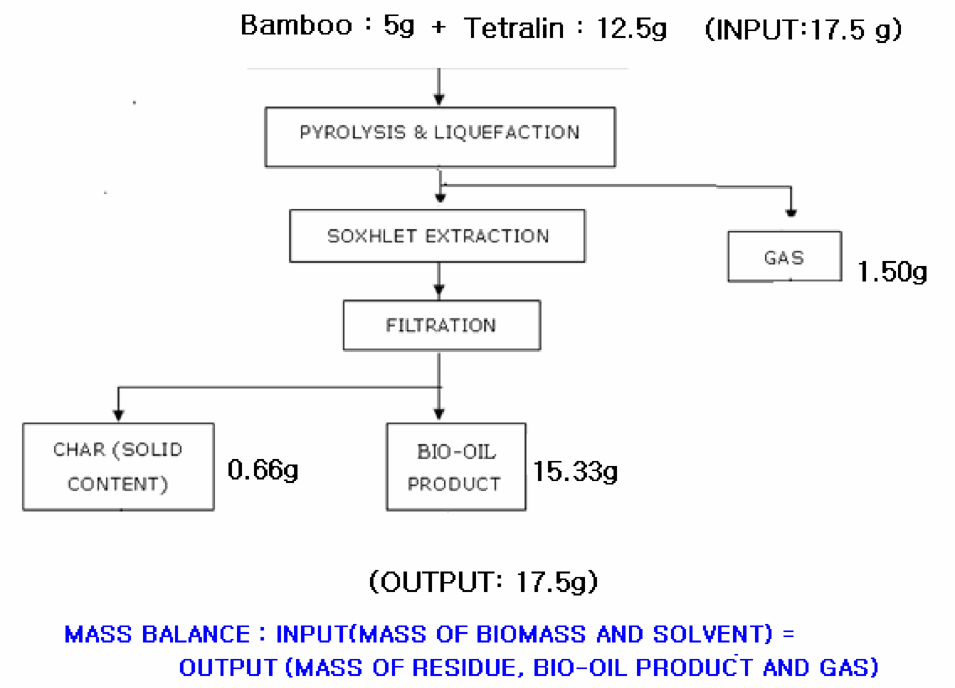


Figure 4.13: Mass balance in pyrolysis and liquefaction of bamboo by tetralin

As Figure 4.13, for mass balance, bamboo powder (5g) and solvent (12.5g) are used as input. Because the values of residue were weighed, the values of mixture of each bio-oil product and gas are decided by deleting the values of residue from sum of bamboo powder and solvent according to the law of mass conservation.

### 4.6.2.2 Energy (calorific value) balance

Calorific value (HHV) = (338.2 X %C + 1442.8 X (%H - %O/8)) X 0.001

Tetralin (1,2,3,4 – tetrahydronaphthalene) = $C_{10}H_{12}$
C (%) = 12 X 10 / (12 X 10 + 12) X 100 = 90.91%
H (%) = 100 (%) – 90.91 (%) = 9.09 (%)

HHV of Tetralin = (338.2 X 90.91 + 1442.8 X (9.09 – 0)) X 0.001 = 43.86 MJ/kg
Therefore, energy of the tetralin = 43.86 MJ/kg X 1kg/1000g X1000KJ/1MJ X12.5g = 548 KJ
Energy of bamboo = 17.15 MJ/kg X 1kg/1000g X1000KJ/1MJ X 5g = 86 KJ

Therefore, INPUT ENERGY = 548 KJ + 86 KJ = 634 KJ

%C of $CO_2$ = 27.27%
%O of $CO_2$ = 72.73%

Calorific value (HHV) of $CO_2$ = 10.63 MJ/kg

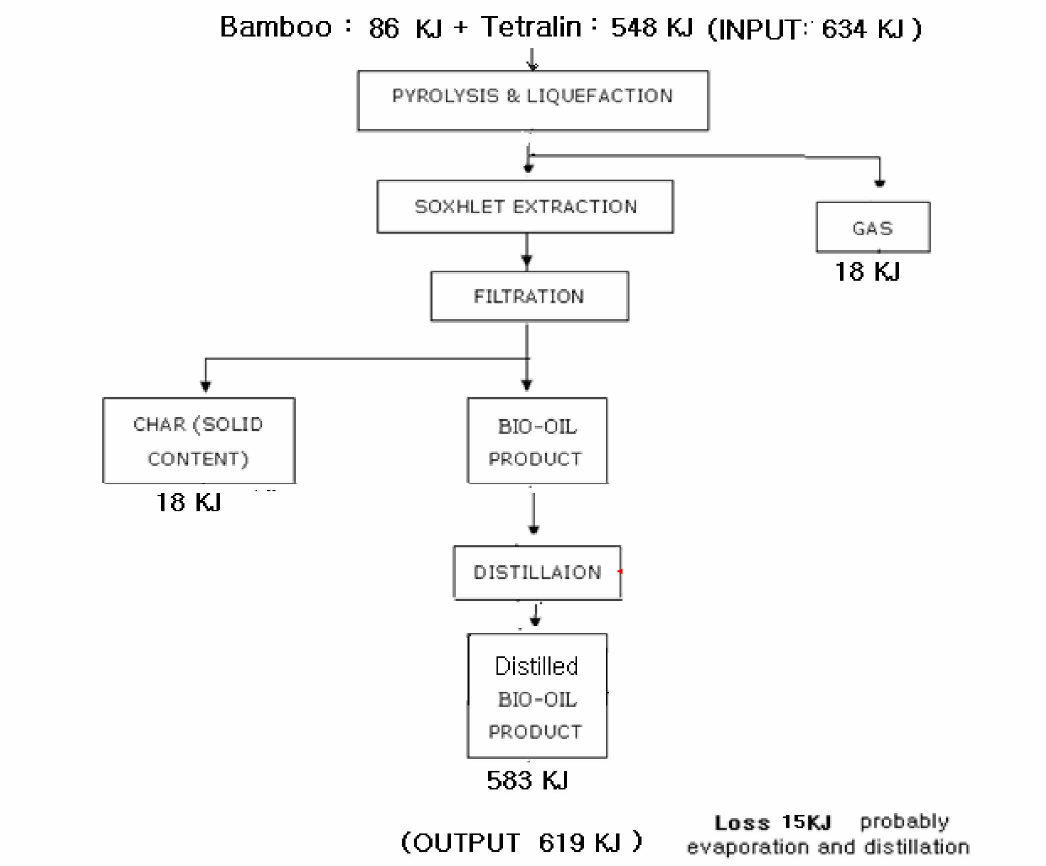
%C of $CH_4$ = 75 %
%H of $CH_4$ = 25%

Calorific value (HHV) of $CH_4$ = 26.81 MJ/kg

The calorific value (HHV) of the gas = 10.63 MJ/kg X 91.93/100 + 26.81 MJ/kg X 8.07/100 = 11.94 MJ/kg
Therefore, energy of gas = 11.94 MJ/kg X 1kg/1000g X1000KJ/1MJ X 1.5g = 18 KJ

Energy of bio-oil product = 38.00 MJ/kg X 1kg/1000g X1000KJ/1MJ X 15.33g = 583 KJ

Ash free residue (char) = residue(mg) – ash(mg)= 709.00 mg – 69.70 mg = 639.30mg
= 0.64 g
Energy of char = 28.28 MJ/kg X 1kg/1000g X1000KJ/1MJ X 0.64 g =18 KJ
Therefore, OUTPUT = energy of char + energy of bio-oil + energy of gas = 18 KJ + 583 KJ + 18 KJ = 619 KJ
ENERGY LOSS = ENERGY INPUT – ENERGY OUTPUT = 634 KJ - 619 KJ = 15 KJ



ENERGY(Calorific value) BALANCE : INPUT( ENERGY OF BIOMASS AND SOLVENT)
+ ENERGY SUPPLY − ENERGY LOSS
= OUTPUT ( ENERGY OF RESIDUE, BIO-OIL PRODUCT AND GAS)

Figure 4.14: Energy balance in pyrolysis and liquefaction of bamboo by tetralin

### 4.6.3 Mass & Energy (Calorific energy) balance in pyrolysis and liquefaction of bamboo by 1-methylnaphthalene

#### 4.6.3.1 Mass balance

$$\text{Gas mass(mg)} = CO_2 \text{ density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of } CO_2$$
$$+ \text{ Methane density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of Methane}$$

$\longrightarrow$

Gas mass (mg) = 1.90 (mg/ml) X 725.33 (ml) X 94.10/100 + 1.82 (mg/ml) X 791.25 (ml) X 5.90/100 = 1374.70mg

Therefore, it is about 1.37 (g)

Bio-oil product (g) = Total input mass (g) – Char mass (g) – Gas mass (g)

= 17.5 (g) – 1.6 (g) - 1.37 (g) = 14.53 (g)

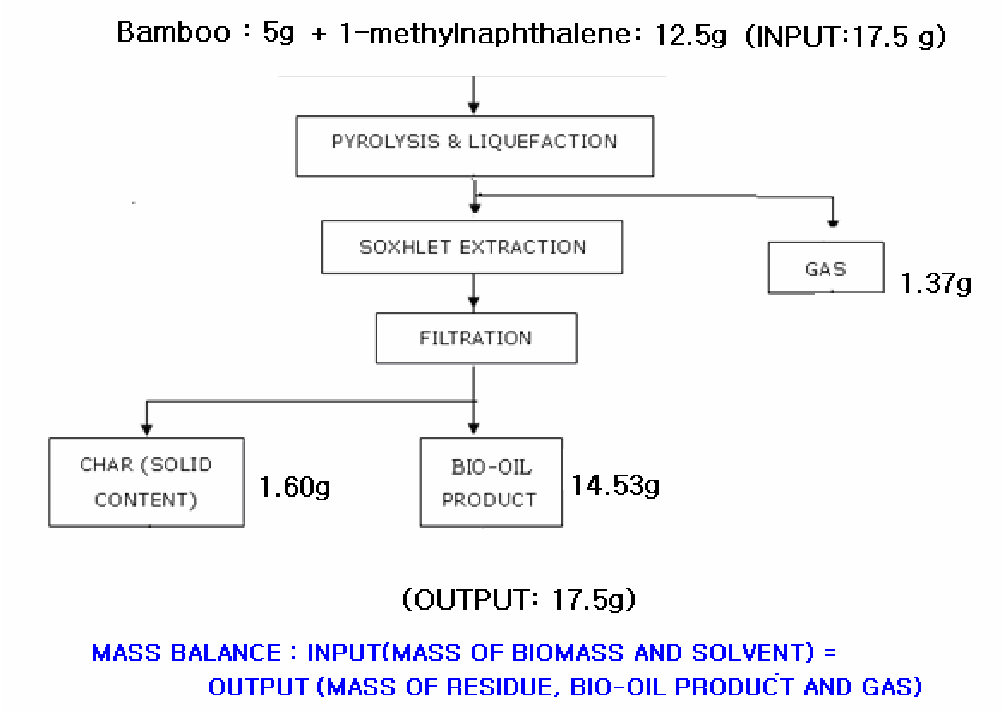


Figure 4.15: Mass balance in pyrolysis and liquefaction of bamboo by 1-methylnaphthalene

#### 4.6.3.2 Energy(Calorific value) balance

Calorific value (HHV) = (338.2 X %C + 1442.8 X (%H - %O/8)) X 0.001

1-methylnapthalene = $C_{11}H_{10}$
C (%) = (12 X 11)/ (12 X 11 +10) X 100(%) = 92.96 (%)
H (%) = 100 (%) – 92.96 (%) = 7.04 (%)

HHV of 1-methylnaphthalene = (338.2 X 92.96 + 1442.8 X (7.04 – 0)) X 0.001 = 41.60 MJ/kg
Therefore, energy of 1-methylnaphthalene = 41.60 MJ/kg X 1kg/1000g X1000KJ/1MJ X 12.5g = 520 KJ
Energy of bamboo = 17.15 MJ/kg X 1kg/1000g X1000KJ/1MJ X 5g = 86 KJ

INPUT ENERGY= 520 KJ + 86 KJ = 606 KJ

%C of $CO_2$ = 27.27%
%O of $CO_2$ = 72.73%
Calorific value (HHV) of $CO_2$ = 10.63 MJ/kg

%C of $CH_4$ = 75 %
%H of $CH_4$ = 25%

Calorific value (HHV) of $CH_4$ = 26.81 MJ/kg

The calorific value (HHV) of the gas = 10.63 MJ/kg X 94.10/100 + 26.81 MJ/kg X 5.9 /100 = 11.58 MJ/kg

Therefore, energy of the gas = 11.58 MJ/kg X 1kg/1000g X1000KJ/1MJ X 1.37g = 16 KJ
Energy of bio-oil = 40.77 MJ/kg X 1kg/1000g X1000KJ/1MJ X14.53g = 592 KJ

Ash free residue (char) = residue(mg) – ash(mg)= 1600 mg – 80.1 mg = 1519.9mg
= 1.52g
Energy of char = 27.95 MJ/kg X 1kg/1000g X1000KJ/1MJ X 1.52 g = 42 KJ

Therefore, OUTPUT ENERGY = HHV of char + HHV of bio-oil + HHV of gas = 42 KJ + 592 KJ + 16 KJ = 650 KJ

ENERGY OBTAINED = OUTPUT ENERGY – INPUT ENERGY = 650 KJ - 606 KJ = 44 KJ

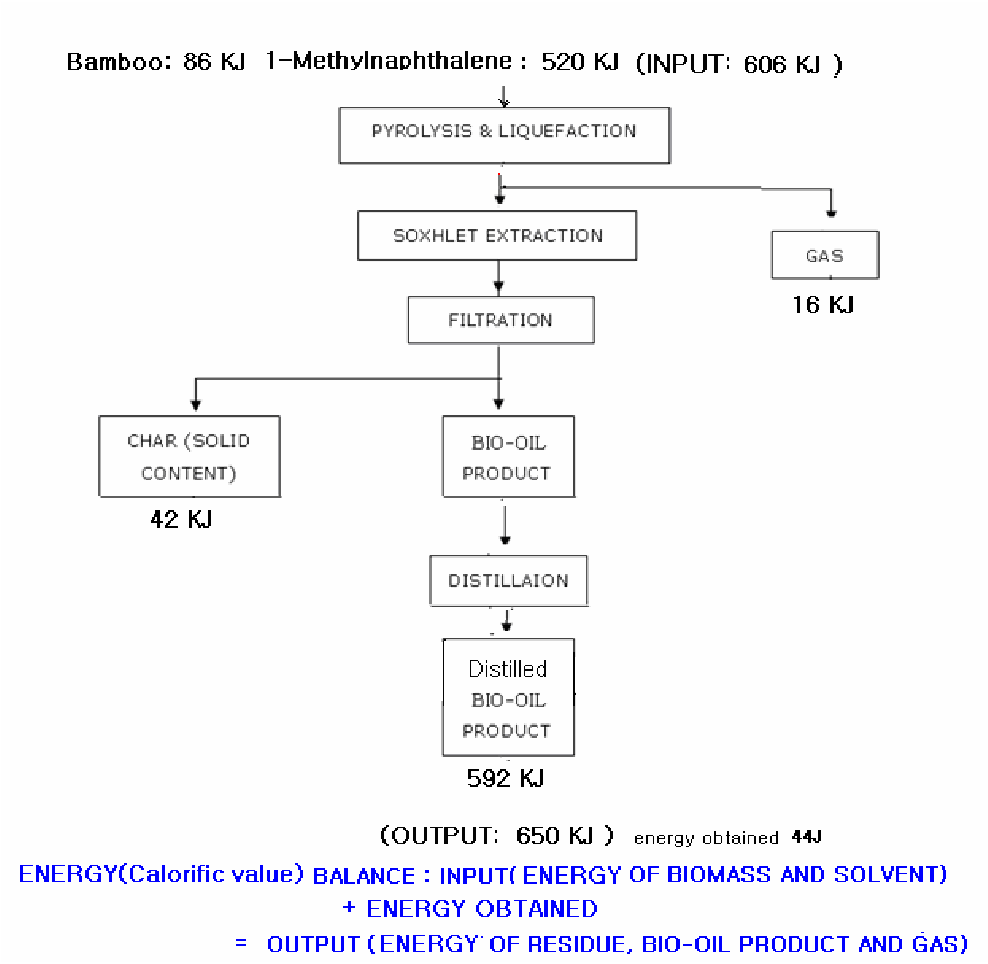


Figure 4.16: Energy balance in pyrolysis and liquefaction of bamboo by 1- methylnaphthalene

### 4.6.4 Mass & Energy (Calorific energy) balance in pyrolysis and liquefaction of bamboo by waste oil from cooking pork

#### 4.6.4.1 Mass balance

$$\text{Gas mass(mg)} = \text{CO}_2\ \text{density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of CO}_2$$

$$+ \ \text{Methane density(mg/ml)} \times \text{Total gas volume(ml)} \times \text{Proportion of Methane}$$

$$\longrightarrow$$

Gas mass (mg) = 1.90 (mg/ml) X 1116.33 (ml) X 91.82/100 + 1.82 (mg/ml) X 1116.33 (ml) X 8.18/100 = 2113.72mg

Therefore, it is about 2.11 (g)

Bio-oil product (g) = Total input mass (g) – Char mass (g) – Gas mass (g)

= 17.5 (g) – 1.51 (g) – 2.11 (g) = 13.88 (g)

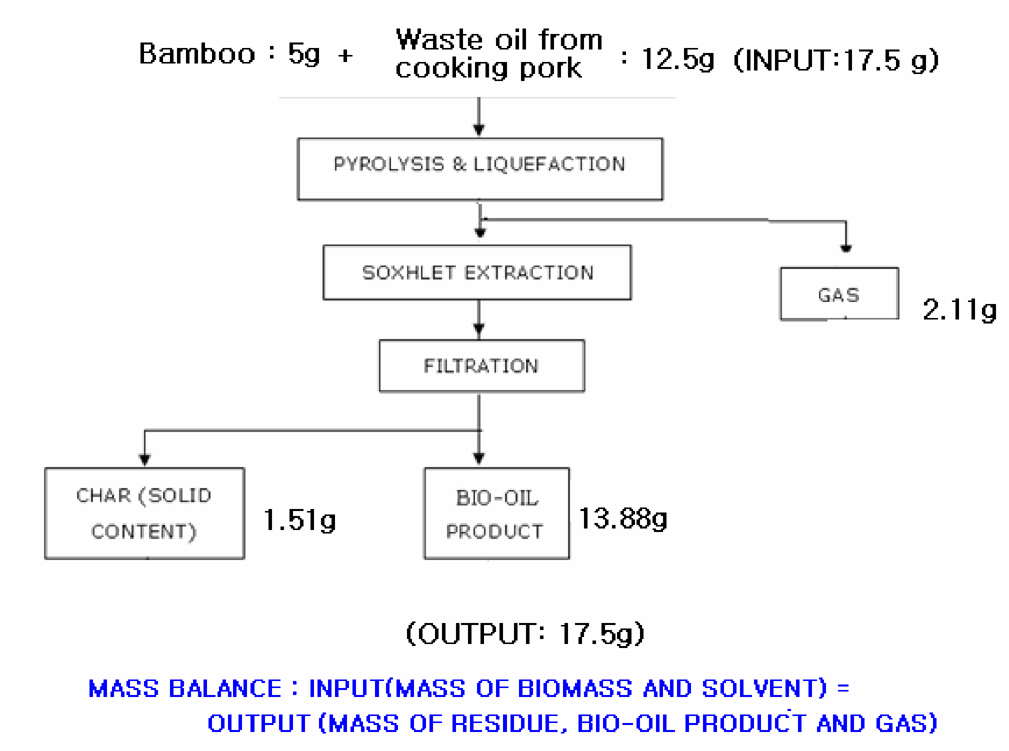


Figure 4.17: Mass balance in pyrolysis and liquefaction of bamboo by waste oil from cooking pork

#### 4.6.4.2 Energy (Calorific value) balance

Calorific value (HHV) = (338.2 X %C + 1442.8 X (%H - %O/8)) X 0.001

Assume that majority of waste oil from cooking pork is composed of Triglyceride.

Triglyceride = $C_{55}H_{98}O_6$

C (%) = (12 X 55)/ (12 X 55 + 98 + 16 X 6 ) X 100(%) = 77.00 (%)

H (%) = 98 / (12 X 55 + 98 + 16 X 6 ) X 100(%) = 11.45 (%)

O (%) = (16 X 6) / (12 X 55 + 98 + 16 X 6 ) X 100(%) = 11.55 (%)

HHV of Triglyceride = (338.2 X 77.00 + 1442.8 X (11.45 – 11.55/8)) X 0.001 = 40.48 MJ/kg

Therefore, energy of Triglyceride = 40.48 MJ/kg X 1kg/1000g X1000KJ/1MJ X 12.5g = 506 KJ

Energy of bamboo = 17.15 MJ/kg X 1kg/1000g X1000KJ/1MJ X 5g = 86 KJ

INPUT ENERGY = 506 KJ + 86 KJ = 592 KJ

%C of $CO_2$ = 27.27%

%O of $CO_2$ = 72.73%

Calorific value (HHV) of $CO_2$ = 10.63 MJ/kg

%C of $CH_4$ = 75 %

%H of $CH_4$ = 25%

Calorific value (HHV) of $CH_4$ = 26.81 MJ/kg

The calorific value (HHV) of the gas = 10.63 MJ/kg X 91.82/100 + 26.81 MJ/kg X 8.18 /100 = 11.95 MJ/kg

Therefore, energy of gas = 11.95 MJ/kg X 1kg/1000g X1000KJ/1MJ X 2.11g = 25 KJ

Energy of bio-oil = 40.48 MJ/kg X 1kg/1000g X1000KJ/1MJ X 13.88g = 562 KJ

Ash free residue (char) = residue(mg) – ash(mg)= 1514.1 mg – 89.1 mg = 1425 mg
= 1.43g

Energy of char = 28.84 MJ/kg X 1kg/1000g X1000KJ/1MJ X 1.43 g = 41 KJ

Therefore, OUTPUT ENERGY = HHV of char + HHV of bio-oil + HHV of gas = 41 KJ + 562 KJ + 25 KJ = 628 KJ

ENERGY OBTAINED = OUTPUT ENERGY – INPUT ENERGY = 628 KJ – 592KJ = 36 KJ

It seems due to fat in the solvent used (waste oil from cooking pork). Especially, polyunsaturated fat.

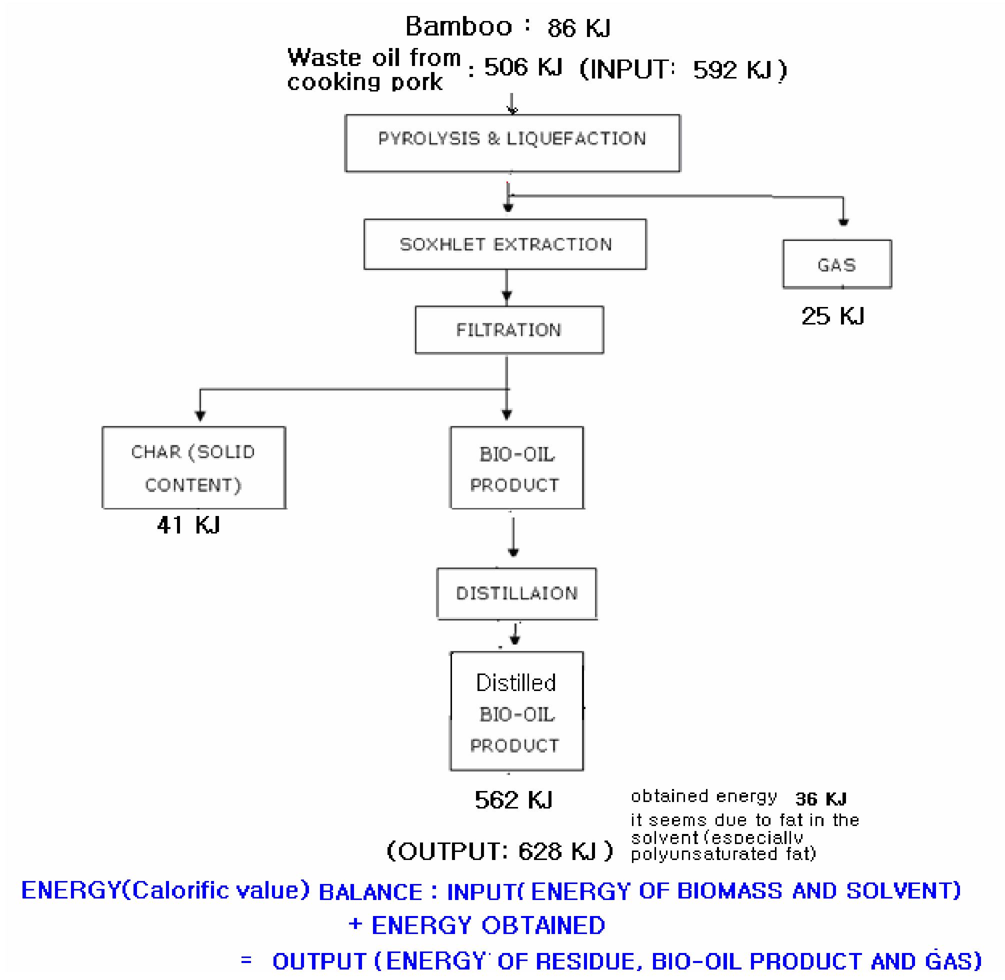


Figure 4.18: Energy balance in pyrolysis and liquefaction of bamboo by Waste oil from cooking pork

### 4.6.5 Mass & Energy (Calorific energy) balance in pyrolysis and liquefaction of bamboo by waste oil from vegetable cooking oil

#### 4.6.5.1 Mass balance

Gas mass(mg) = $CO_2$ density(mg/ml) x Total gas volume(ml) x Proportion of $CO_2$

+ Methane density(mg/ml) x Total gas volume(ml) x Proportion of Methane

$\longrightarrow$

Gas mass (mg) = 1.90 (mg/ml) X 1306.67 (ml) X 95.30/100 + 1.82 (mg/ml) X 1306.67 (ml) X 4.7/100 = 2477.76mg

Therefore, it is about 2.47 (g)

Bio-oil product (g) = Total input mass (g) – Char mass (g) – Gas mass (g)

= 17.5 (g) – 1.50 (g) – 2.47 (g) = 13.53 (g)

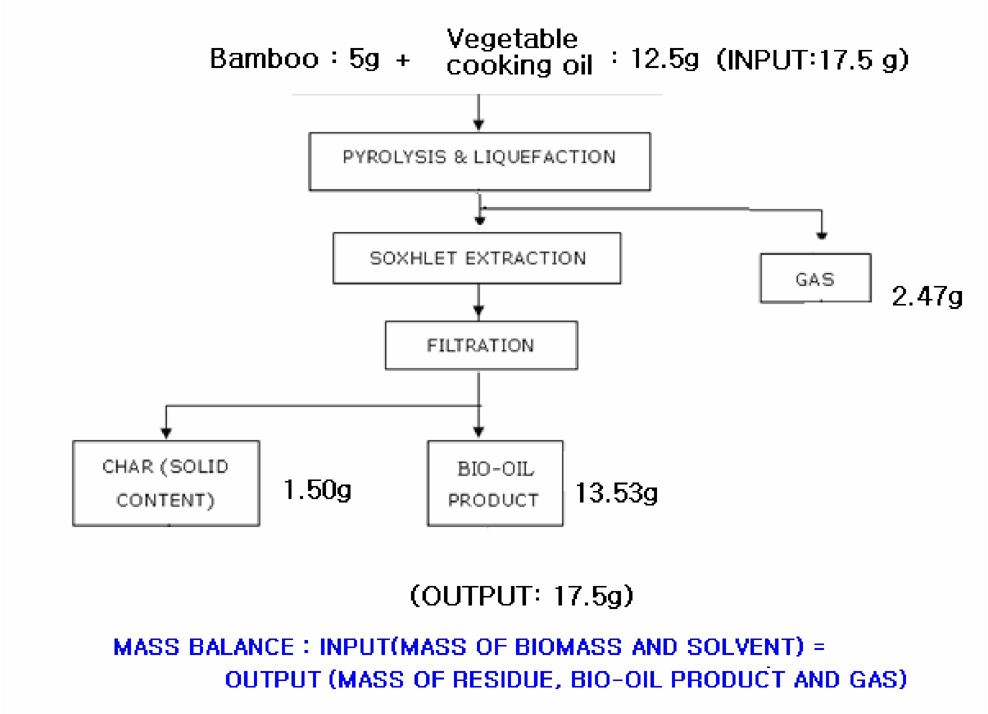


Figure 4.19: Mass balance in pyrolysis and liquefaction of bamboo by vegetable cooking oil

### 4.6.5.2 Energy(Calorific value) balance

Calorific value (HHV) = (338.2 X %C + 1442.8 X (%H - %O/8)) X 0.001

Assume that majority of vegetable cooking oil is composed of Triglyceride.

Triglyceride = $C_{55}H_{98}O_6$

HHV of Triglyceride = (338.2 X 77.00 + 1442.8 X (11.45 – 11.55/8)) X 0.001 = 40.48 MJ/kg

Therefore, energy of Triglyceride = 40.48 MJ/kg X 1kg/1000g X1000KJ/1MJ X 12.5g = 506 KJ

Energy of bamboo = 17.15 MJ/kg X 1kg/1000g X1000KJ/1MJ X 5g = 86 KJ

INPUT ENERGY= 506 KJ + 86 KJ = 592 KJ

%C of $CO_2$ = 27.27%

%O of $CO_2$ = 72.73%

Calorific value (HHV) of $CO_2$ = 10.63 MJ/kg

%C of $CH_4$ = 75 %
%H of $CH_4$ = 25%

Calorific value (HHV) of $CH_4$ = 26.81 MJ/kg

The calorific value (HHV) of the gas = 10.63 MJ/kg X 95.30/100 + 26.81 MJ/kg X 4.70 /100 = 11.39 MJ/kg
Therefore, energy of the gas = 11.39 MJ/kg X 1kg/1000g X1000KJ/1MJ X 2.47g = 28 KJ

Energy of bio-oil product = 43.26 MJ/kg X 1kg/1000g X1000KJ/1MJ X 13.53g = 585 KJ

Ash free residue (char) = residue(mg) – ash(mg)= 1497.8 mg – 91.5 mg = 1406.3 mg
= 1.41g
Energy of char = 28.84 MJ/kg X 1kg/1000g X1000KJ/1MJ X 1.41 g = 41 KJ

Therefore, OUTPUT ENERGY = HHV of char + HHV of bio-oil + HHV of gas = 41 KJ + 585 KJ + 28 KJ = 654 KJ

ENERGY OBTAINED = OUTPUT – INPUT = 654 KJ – 592 KJ = 62 KJ
It seems due to fat in the solvent used (waste oil from cooking pork). Especially, polyunsaturated fat.

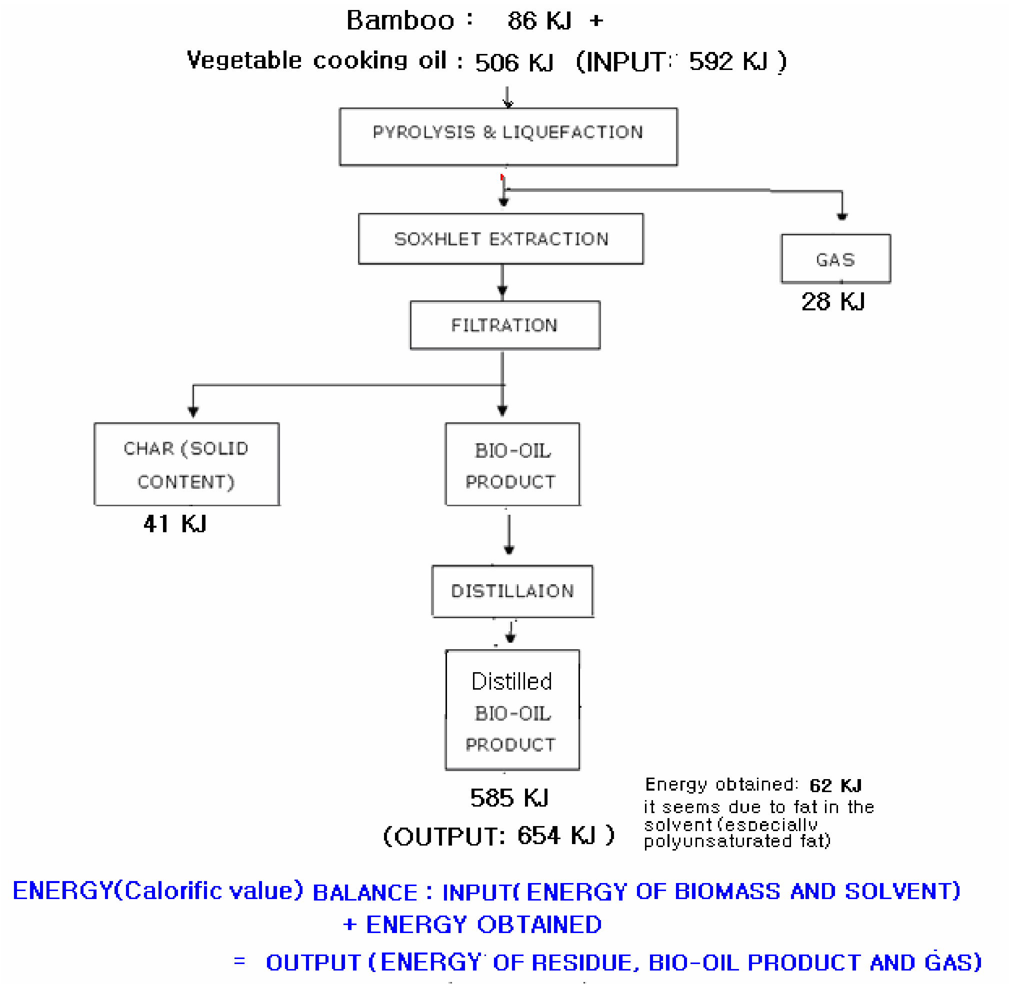


Figure 4.20: Energy balance in pyrolysis and liquefaction of bamboo by vegetable cooking oil

In brief, as shown in figures of mass & energy balance above, pyrolysis and liquefaction by tetralin converted the bamboo the most effectively to bio-oil products and gas leaving the least chars. On the other hand, pyrolysis without solvent converted the bamboo the least effectively to bio-oil products and gas leaving the most chars. Pyrolysis and liquefaction by the other solvents were shown better in conversion from bamboo to bio-oil product and gas than pyrolysis without solvent although the conversion efficiency was less than in tetralin.

# CHAPTER FIVE
# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

The different conversion rate to gas and liquid by thermal extraction (pyrolysis and liquefaction) with different solvents was investigated. It has been confirmed that liquefaction increased the overall conversion rate significantly and improved properties of the bio-oils and residues generated from pyrolysis and liquefaction. Tetralin solvent which is effective Hydrogen-donor solvent contributed to the highest rate of conversion of bamboo. It was shown total conversion rate up to around 90%.

Liquefaction seemed to allow free radicals generated from bamboo to use the hydrogen (regardless of the generated amount of hydrogen as long as it occurs) from solvents making low molecular weight bio-oils. As another assumption, the nature of solvent as a carrier transferring H, the H in biomass might be transferred to bio-oil more effectively which made the bio-oils have higher H/C value and lower O/C value. Therefore, H/C of residues obtained by pyrolysis and liquefaction seemed to be reduced due to the transferring H of bamboo into the bio-oils. This explains in liquefaction, cross-linking effect shown in pyrolysis was disappeared implying the free radicals generated were mostly used to obtain H from solvents or to carry H from bamboo not wasting causing char (residue) and a cross-linking effect. However, in case of water solvent, this theory didn’t work much because of its low boiling point supposedly causing evaporation of the water and a cross-linking effect. The free radicals from bamboo would not have any hydrogen to react to be lower molecular weight (Nicholas et al.,1985). This explains the reason of the large amount of residues produced by pyrolysis by not using any solvent and by water solvent.

The amount of generated liquid was found by deleting produced residue weight from initial bamboo weight (5g). Tetralin produced the largest amount of liquid which caused relatively higher ash content rate (%) in proportion because the ash content is fixed unconvertible in residue different from volatile matter. The liquid involved in tetralin is assumed to have highest amount of water contents and bio-oils. This is consistent with the fact that in terms of ash free residue(%) of tetralin (12.97%) which is relatively lower than the others, more volatile matters of the bamboo reacted with the tetralin would be transferred to the bio-oils.

Total amount of generated gas was measured and n-alkane gas was measured by GC. $CH_4$ gas was the largest amount among the Hydro-carbon gases and $C_2H_6$ gas was the second largest amount generated. $C_2H_4$ and $C_3H_6$ were detected as a small amount. By deleting the number of moles of the n-alkane gas obtained by different solvents from the number of moles of the total gas obtained by the different solvents, approximate proportion of CO, $CO_2$ and $H_2$ were found to be much more than that of n-alkane gas. To find net volume of generated gas from bamboo in case of bio-derived solvent such as vegetable cooking oil, vegetable cooking oil blank run was performed to check generated gas volume of vegetable cooking oil. As a result, hyrocarbon solvent such as tetralin or 1-methylnaphthalene converted the bamboo to the gas more effectively because the bio-oil derived solvent such as vegetable cooking oil or waste oil from cooking pork was spent up itself in generating gases by self-pyrolysis rather than being used as a solvent for liquefaction.

For residues produced from liquefaction, high HHV showed a possibility that it can generate more Carbon-abundant energy source than residues from liquefaction by the other solvents. HHV of the residues after liquefaction was increased much more than pyrolysis without using any solvent. Even though it wasn't as high as petroleum (bitumen), it implied that the residue can be an energy source due to the high value of HHV.

In case of bio-oils, those generated from the liquefaction also contained less oxygen content than bio-oil from just pyrolysis without using any solvent. Based on cross-linking effect which wasn't shown in liquefaction except for that by water (assumed that it was evaporated not reacting) and much higher H/C values of bio-oils from pyrolysis and liquefaction by various solvents, radicals from bamboo were assumed to be used to react with Hydrogen which might be from bamboo or hydrogen donor solvent. One of solvent's role is expected as a carrier of hydrogen which might makes easier to carry hydrogen from bamboo to low molecular final product.

H/C and HHV of bio-oils were similarly as high as those of bitumen which makes more convinced of the fact that this bio-oil might be bitumen. The dark brown colour and the high viscosity of the bio-oils brought more doubts on whether the bio-oil can be bitumen. To clarify this doubtful mystery, GC-MS was used and typical bitumen's functional groups such as phenol, alkanes, ketones, esters and alkyl- from these bio-oils were found. This fact implies that the material produced could be bitumen-like material.

The distribution of compounds from fractions of bio-oils was affected by the solvent type used and showed that the bio-oils would be crude oils in the GC-MS analysis

A common fact between residues and bio-oils produced was the fact that there was no sulphur elements found. This means the technology has enough possibilities to be used to seek new green fuel as long as there is a better solution for improving the defects such as high ash content rate, high water content rate and high oxygen content rate compared with conventional petroleum.

The possibilities of using bamboo and reusing waste oil from cooking pork converting to an energy source were proven possible in this study. However, it is too early to use them commercially because accurately scrutinized tests have not been performed yet.

## 5.2 Recommendation

More work is recommended to better investigate the property of samples such as gas, bio-oils and residues. GC having Column to detect CO, $CO_2$ and $H_2$ is highly recommended to increase accuracy of data and to see if the gases generated by liquefaction can be used commercially. For one example, by knowing $CO_2$ gas generated, the energy source loss such as carbon from bio-oil can be assumed by following equation (58).

$$C_6H_{10}O_5 \xrightarrow{\text{heat}} C_4H_{10}O + 2CO_2 \text{ ---------------------------- } (58)$$

(Nicholas, 1985)

For n-alkane gas detection with GC, ability to detect gases of more than C3 such as C4, C5 so on for more accurate results. For pyrolysis, it would be worth to investigate on change by feed rate, feed size, flow rate, heating rate, catalyst, quenching rate and so on. Applying continuous configuration not just batch configuration in the pyrolysis would be good to compare the difference. Fractionation of asphaltene in polar would give general concept to us on whether or not this bio-oil generated is bitumen in that it includes quite a portion of asphaltene.

To check the exact value of PH (acidity) of the bio-oils, measurement of bio-oil's PH by ph meter is recommended because the low acidity of bio-oil is the one of the defects of the bio-oils as a fuel, the investigation to see how much the liquefaction improve the acidity of bio-oil is important. To investigate the metal substances generated from bamboo biomass by pyrolysis and liquefaction, ICP-AES analysis also can be suggested. High metal elements in bio-oil are one of the defects of bio-oil as well. The improvement by liquefaction can be investigated by the analysis. Analyses by rheological measurement using a Bohljn CVO dynamic shear rheometer (DSR) fitted with either an enclosed fluid (water and antifreeze solution) chamber temperature control system or a thermoelectric Peltier system are recommended. By comparing bitumen and bio-oils using the measurement method, the property of bio-oils can be identified if they are bitumen or not.

For solid analysis, TBP-GLC, MR and FTIR are recommended further. For gas analysis, FTIR and MS, for bio-oils, NMR and FTIR are recommended to be used. TGA could also be used to investigate more precise characteristics of the volatile compounds contained in solid residue not only obtaining value of ash content because it can show the weight change depending on the time flow. Furthermore, the value of ash content from TGA can be compared to value of ash content found from furnace.

Finding new solvents which can donate hydrogen as more effectively as tetralin would be interesting. Furthermore, mixtures such as mixture of tetralin and pyrene can be tested if it can work better as a hydrogen donor solvent similarly as it did in coal in a study of Derbyshire et al. (1981)

More experimental devices can be used to increase accuracy of the data from gas, residues and bio-oils generated from liquefaction. To consider trace metals in the bio-oil derived solvent in residues, activated carbon adsorption method can be considered because the weight value of trace metal is very small, adsorption to the activated carbon which already has known value. And the activated carbon is combusted in the furnace. The difference between the known ash content value of the activated carbon and the actual ash content value will be the trace metal weight value.

There are some points to beware of in sand bath, EA and furnace method. For fluidized sand bath, because it is very sensitive device, temperature by weather can affect the results. For example, in very hot summer weather, the setting temperature in the external temperature controller of pyrolysis system was lower than usual to reach 410°C and to be stabilised. Checking the room temperature would increase the accuracy of the results. In EA, if integration in the curves of each element after running the EA, the data reported would be very different values from right values. So, checking the integration of each peak if it is proper in the curve is very essential. In the furnace method, the crucible shape can affect the results. Flat shaped crucible is preferred because it contacts the furnace environment the most. Ellipse (cone) typed crucible is better to be avoided since the biomass deep inside the crucible doesn’t contact the furnace environment. In this case, higher value of ash content can be brought because enough combustion of the biomass doesn’t happen.

One thing which could’ve been done was that the bio-oil yield (%) could be calculated by weighing distilled bio-oil. In addition, more correct data of water generation by pyrolysis and liquefaction can be estimated in this case.

Weight of bamboo applied – weight of residue generated - weight of distilled bio-oil = approximate amount of generated water. ---------------------------------------------(59)

Lastly, influence by catalyst in the pyrolysis and liquefaction would be good thing to do to see if the conversion rate of bamboo to energy source can be improved better than hydrogen-donating reaction itself.

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