Liquefaction of dry leaves

by

Shariffah Alawiyah Binti Syed Hussin

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CERTIFICATION OF APPROVAL

Liquefaction of Dry Leaves via Solvolysis

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Chemical Engineering Programme
Universiti Teknologi PETRONAS
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CERTIFICATION OF ORIGINALITY

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

SHARIFFAH ALAWIYAH BINTI SYED HUSSIN

ABSTRACT

Degradation and decomposition were studied in an acid catalyzed solvolysis treatment of biomass using ethylene carbonate and ethylene glycol as novel liquefying reagents in order to establish a rapid liquefaction technique converting lignocellulosic waste into useful chemical. The solvolysis reaction was followed by a typical reaction system of dry leaves liquefaction that uses sulfuric acid catalyst at elevated temperature (80-200 °C) and reaction time (60-200 mins). The degraded cellulose in the solvolyzed product is discussed. The rate of the EC-liquefaction of cellulose was approximately 2 times faster than glycol. The effect of reaction temperature also plays a big role in liquefaction process. Optimum temperature will give the highest percentage yield. EC promotes faster conversions of the reaction. GC-MS revealed that EC and EG liquefaction products from cellulose include carboxylic acid such as butyric acid, succinic acid and lactic acid. The degradation and decomposition of cellulose is proven in FTIR where the hemicellulose peak is decreasing while carboxylic acid peak is increasing. The density and viscosity were measured and the results are the same with current bio oil in the literature review.

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Shariffah Alawiyah Binti Syed Hussin

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Renewable energy is growing important in responding to concerns over the environment pollution and the shortage of energy supplies. Biomass is viewed as one of the most important potential and the only carbon-containing renewable energy resources. The term biomass can generally be defined as all the biologically produced matter mainly in form of abundant agricultural and forestry wastes.

Biomass ultization has received great attention due to environmental considerations and increasing energy demands worldwide. Due to the high moisture content and low caloric value, biomass is not suitable to be used as energy directly, thus many investigations have been carried out to convert it into transportable liquid fuel with high energy density.

Among the available biomass conversion methods, thermo chemical conversion is the most commonly used to upgrade biomass, which can then be further divided into gasification, pyrolysis and direct liquefaction. In the case of liquefaction, biomass is decomposed into small molecules in water with or without a solvent or a catalyst. These small molecules are unstable and reactive and can repolymerize into oily compounds with a wide range of molecular weight of alkalies, formate of alkaline metals, propanol and butanol or by direct liquefaction. Liquefaction has many advantanges such as:

1. The presence of solvent dilute with concentration of the products preventing the cross linked reactions and reverse reations

2. Relative low temperature (less energy consumption) in comparison with pyrolysis and gasification.

Dry leaves is among the most abundant and widely distributed biomass resources, however, due to its complex multi-component structure it is difficult to use it directly as chemical feedstock. Normally it is first separated into its main components: cellulose, lignin, and hemicelluloses, which are then further processed. Transformation of dry leaves via liquefaction – a process that combines solubilization and depolymerization of dry leaves in a liquid reagent under elevated temperatures. The most thoroughly researched liquefaction reagents are phenols that lead to feedstock for phenolic resins and glycols that give products rich in hyhydroxyl groups.

1.2 Problem Statement

With the increasing contribution of fossil fuels to global warming and climate change the Kyoto Protocol that had been introduced in 1997 came into enforcement in 2004. The signing of the Kyoto Protocol by the developed nations forces them to adhere to the low greenhouse gas emission levels, and hopefully curb its effect on global climate. Following this development governments are pursuing more environmental friendly means to produce energy, and in the process lift the heavy dependence on fossil fuel.

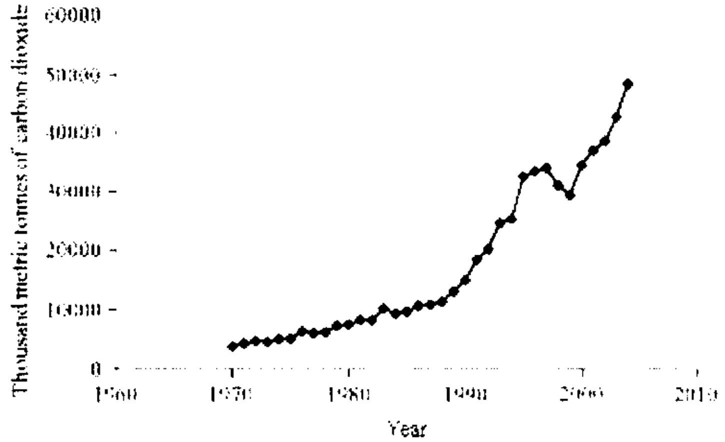


Figure 1.1 : CO_2 emission in Malaysia from 1974 to 2004

Converting these waste into energy reduces pollution of the environment, otherwise the biomass waste would be left to rot in a clearing or most of the time subjected to open-burning by farmers to dispose of it. In neighboring Sumatera, Indonesia, large areas of open burning to clear out bushes for development has caused haze hazards in Malaysia, which reached its peak in 2005 with the air pollution index (API) reaching 500. Visibility was very poor while people were having difficulty breathing and some were admitted to hospitals to receive treatment for shortness of breath.

Unlike other renewable energy sources that require costly technology, biomass can generate electricity with the same type of equipment and power plants that now burn fossil fuels (Yan et al, 1997). However low thermal efficiencies have hindered its development and the main challenge now is to develop low cost high efficiency systems.

1.3 Malaysia's Biomass Energy Outlook

Presently there are not much government policies regarding the development and use of biomass resources for power generation and combined heat and power (CHP). The most notable progress came with the Fifth Fuel Policy conceived under the Eight Malaysian Plan in 1998. It enlists renewable energy as the fifth fuel and under this policy it was targeted that renewable energy would supply 5% of the national electricity demand by the year 2005 (Mohamed and Lee, 2006). In 2006 the government has announced the usage of bio-fuels which is a blend of 5% palm oil and 95% diesel fuel in certain vehicles belonging to the ministry (MIDA, 2006).

Despite this development and the potential of biomass energy there are several barriers that limit its commercialization and application in the industry. Financially, as biomass energy projects are capital-intensive, it is difficult to obtain loans from banks as there are no records of experience to rely upon. Bank loan officers also do not have the experience to evaluate the loan for the projects which are backed by performance guarantees. This might be the reason why Energy Service Companies (ESCOs), which are supposedly companies which develop energy projects, have not been successful. Independent Power Producers (IPPs) have set up numerous power plants in the country but no information is available regarding their activities in biomass utilization. The IPPs mainly rely on natural gas fired power plant technologies (M. Zamzam Jaafaret al, 2003).

Overall biomass energy utilization is still in its infant stage in Malaysia although there are abundant potential resources in the country as shown in Table 1. It is still undergoing development towards the goal of technology commercialization. Cooperation and commitment from parties involved are needed in other to realize the implementation of biomass energy as a supplementary energy source on national scale.

Table 1.1: Recent renewable energy potential in Malaysia

Renewable Energy	**Resource Annual Energy Value (RM Million)**
Forest residues	11984
Palm oil biomass	6379
Solar thermal	3023
Mill residues	836
Hydro	506
Solar PV	378
Municipal waste	190
Rice husk	77
Landfill gas	4

Source: Ministry of Energy, Communications, and Multimedia, 2006

1.4 Objectives and Scope of Study

There are few objectives that have been identified and are related to the commencement of this project. All of these objectives need to be accomplished as the benchmark of project completion. The objectives are:

1. To study the mechanism liquefaction process
2. To study the effect of the processes with respect to reaction operating temperature and reaction time

3. To study the effect of solvent used in the process that yield high conversion of biomass to bio-oil.

CHAPTER 2

LITERATURE REVIEW

2.1 An Overview of Biomass

Biomass energy has presented itself as a very promising alternative to fossil fuels. Biomass is a name given to any organic matter available on a renewable basis. There are a wide variety of biomass energy resources, including forest and mill residues, agricultural crops and wastes, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, fast-growing trees and plants, and municipal and industrial wastes.

In third world countries especially, the agricultural and wood industry would provide a constant supply of fuel for small to medium scale electrification, which include rural areas. Biomass has low sulfur content, thus thermal conversion of biomass emits low SOx unlike combustion of diesel and coal (M.T. Lim, Z. Alimuddin (2008) and Uma R et al.(2004)).

The energy of biomass from plant originally comes from solar energy. Plants use solar energy during photosynthesis, and store it as organic material as they grow.(Figure 2.2) In other words, as trees and plants grow, the process of photosynthesis uses energy from the sun to convert carbon dioxide into carbohydrates (sugars, starches and cellulose). Carbohydrates are the organic compounds that make up biomass. As the plants died, they reverse the process and releases the energy stored in carbohydrates and discharges carbon dioxide back into the atmosphere.

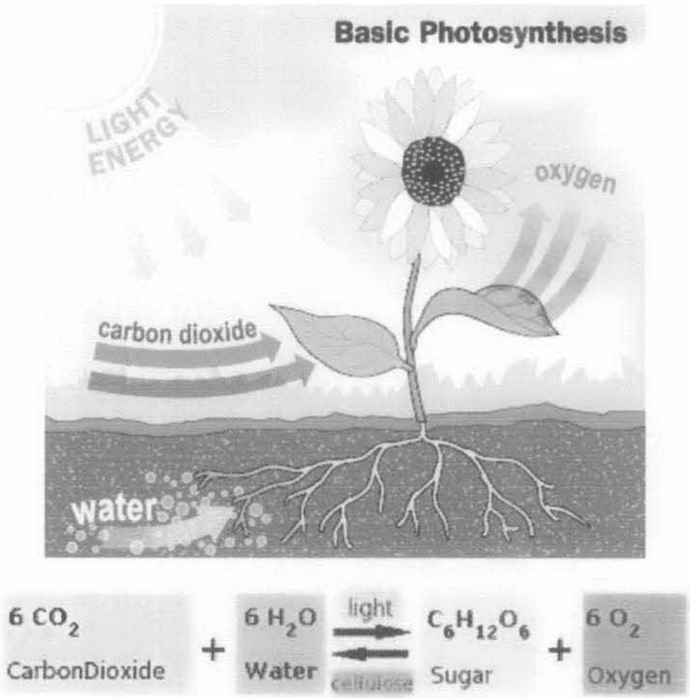


Figure 2.1: Process and Equation for photosynthesis

From the older time to the present, the most common way to capture the energy from biomass was to burn it to make heat, steam, and electricity. But advances in recent years have shown that there are more efficient and cleaner ways to use biomass.

The chemical composition of biomass varies among species, but plants consist of about 25% lignin and 75% carbohydrates or sugars. The carbohydrate fraction consists of many sugar molecules linked together in long chains or polymers. Two larger carbohydrate categories that have significant value are cellulose and hemicelluloses. The lignin fraction consists of non-sugar type molecules. Nature uses the long cellulose polymers to build the fibers that give a plant its strength. The lignin fraction acts like a "glue" that holds the cellulose fibers together. Babu (2008) has stated that biomass is mainly composed of three constituents which are hemicelluloses, cellulose, and lignin. There are minor amounts of extractives also present.

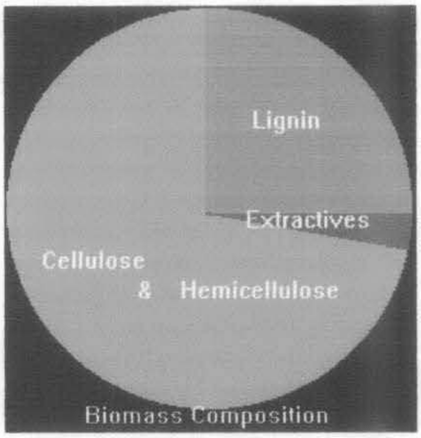


Figure 2.2: Compositions of Biomass

Q. Lu et al. (2009) reported that each component of biomass pyrolyzes at different rates and by different mechanisms and pathways. It is believed that as the reaction progresses, the carbon becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases. Cellulose and hemicelluloses decomposes over a very narrow temperature range as compared to lignin. The rate and extent of degradation of each of these components depends on the process parameters of reactor type, temperature, and particle size heating rates and pressure. Thermal degradation properties of hemicelluloses, cellulose, and lignin can be summarized as follows: **Thermal degradation of hemicelluloses > of cellulose > of lignin.**

2.2 An overview of Bio-Oil

Bio-oils are dark brown, free flowing liquids with an acrid or smoky odor. They are complex mixtures of compounds that are derived from the depolymerization of cellulose, hemicelluloses and lignin. Chemically, they comprise quite a lot of water, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, and multifunctional compounds.

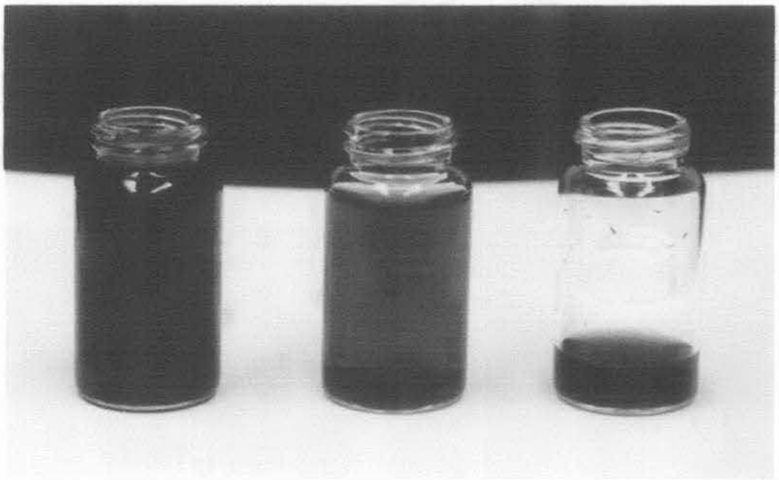


Figure 2.3: The Bio-Oil Extracted from different biomass sources

2.2.1 Characteristics of Bio-oil

Molecular Weight

Based on the report by Q. Lu et al. (2009) and A. V. Bridgwater et al. (2004), the average molecular weight varies in the range of 370–1000 g/mol. Until now, over 300 organic compounds have been dentified in different bio-oils. Most of the compounds are in low concentrations. Fractionation is widely used to separate bio-oils into groups of compounds to facilitate analysis and quantification of compounds (Oasmaa et al. (2003) and Pérez MG et al. (2007)). However, complete chemical characterization of bio-oils is almost impossible mainly due to the presence of pyrolytic lignins as by the research done by Meier D (1999).

Homogeneity

In general, most bio-oils are homogeneous in appearance. However, some forestry and agricultural materials contain substantial amounts of extractives whose pyrolysis products are different in solubility, polarity and density from normal bio-oils. It was reported that bio-oils produced from extractive-rich feedstocks would separate into two phases: a top phase rich in extractives and a bottom phase resembling the normal bio-oils (Oasmaa et al. (2003) and Pérez MG et al. (2007). The proportions of the top phase depend on the feedstocks, and can reach up to 20 wt% of the whole bio-oils. The major compounds in the top phase are extractives (25-50 wt%), pyrolytic lignins (20-40 wt%) and water soluble compounds (20-40 wt%) (Harinen S (2004)). It is to be noted that many raw biomass materials contain a few extractives. The bio-oils produced from them will not undergo this kind of phase separation, because the small amounts of extractives can be dispersed in the bio-oil matrix (Q. Lu et al. (2009)).

Oxygen Content

Bio-oils retain most of the original oxygen in the feedstocks. Their oxygen contents vary in the range of 35-60 wt% (wet basis), which is determined mainly by the water contents. Oxygen is present in almost all organic compounds in bio-oils. It is known to be the primary reason for the vast differences between bio-oils and petroleum fuels. These oxygenated compounds make bio - oils polar, and thus non-miscible with non-polar petroleum fuels. This will be a defect for the utilization of bio-oils. Moreover, the high oxygen content is responsible for the low heating value, corrosiveness and instability of bio-oils (Q. Lu et al. (2009) and A. V. Bridgwater et al. (2004)).

Water Content

Water is the most abundant single component in bio-oils. It results from original moisture in feedstocks and dehydration reactions during fast pyrolysis process. The water contents of bio-oils usually vary in the range of 15–30 wt%, depending on the initial moisture in feedstocks and pyrolysis conditions. Some water in bio-oils is in the form of aldehyde hydrates, while much of it is probably hydrogen bonded to polar organic compounds. The content is recommended to be determined by Karl-Fischer titration (Oasmaa et al. (2005) and A. V. Bridgwater et al. (2004)).

Water is hard to be removed from bio-oils. The presence of water has both negative and positive effects on the storage and utilization of bio-oils. On the one hand, it lowers heating values, and may cause phase separation of bio-oils. Moreover, it increases ignition delay, and reduces combustion rates and adiabatic flame temperatures during the combustion process. In addition, it will lead to premature evaporation and subsequent injection difficulties during the preheating process. On the other hand, it helps to reduce viscosity and facilitate atomization. Furthermore, it is beneficial for reducing pollutant emissions during combustion (Pérez MG et al. (2006) and A.V. Bridgwater et al. (2004)).

Viscosity and Aging

The viscosity of bio-oils can vary over a wide range (35-1000 cP at 40 °C) depending on the feedstock and process conditions, and especially on the efficiency of collection of low boiling components. It decreases at higher temperatures much faster than for petroleum-derived oils, so that even very viscous bio-oils can be easily pumped after a moderate preheating. A significant reduction in viscosity can also be achieved by addition of polar solvents such as methanol or acetone. An undesired effect, especially observed when the oils are stored or handled at higher temperature, is the viscosity increase with time. This is believed to result from chemical reactions between various compounds present in the oil, leading to the formation of larger molecules. There is also evidence of reaction with oxygen from air.

Heating Value

Heating value refers as the amount of heat produced from the complete combustion of a specific amount of fuels.The lower heating value (LHV) of bio-oils is typically 14-18 MJ/kg, which is much lower than that of petroleum fuels (41-43 MJ/kg). It is attributable to the high oxygen content. However, the density of bio-oils is about 1.2 g/ml compared with that of petroleum fuels, which is 0.8–1.0 g/ml. Therefore, the volumetric energy density of bio-oils can reach 50–60% of that of petroleum fuels. The bio-oils are usually directly measured for their high heating values (HHVs). The LHV can then be calculated by the following equation proposed by Oasmaa et al. (1997):

$$\text{LHV} = \text{HHV} - 218.3 \times \text{H\%}\ (\text{wt\%}) \qquad (\text{KJ/kg})$$

Solid Content

Bio-oils contain more or less solids, mainly char particles and other materials such as fluidized-bed materials used in the pyrolysis process. The solid content can reach as high as 3 wt%, and the particle size usually varies in the range of 1–200 μm with most particles being below 10 μm. Solid content is measured as the amount of solvent insoluble materials. Ethanol is powerful for extractive-free bio-oils. Whereas a neutral solvent is required to dissolve bio-oils with extractives, and a mixture of methanol and dichloromethane is recommended by Oasmaa et al. (2005). The particle size distribution of solids can be determined by optical instruments (Oasmaa et al. (1997), Elliot (1994), and Agblevor FA, Besler S (1996)).

Solid particles will bring many negative effects to the storage and combustion of bio-oils (Oasmaa et al. (1999)). First, the char particles tend to agglomerate slowly and settle at the bottom of the vessels. Even if filtration is performed to remove large particles, the left submicron particles will aggregate to form large ones during storage. Second, the solids increase the apparent viscosity of bio-oils, leading to difficulties in pumping and atomization. Third, the solids will cause erosion and blockage to the fuel injection systems. Fourth, the char particles will act as catalysts to accelerate the ageing reactions of bio-oils, resulting in the increase in viscosity and even in phase separation with solids adsorbed with pyrolytic lignins to form gummy tars. Fifth, the char particles will contribute to form slow-burning carbonaceous cenospheres and consequently unburned particles in the flue gas.

Ash Content

During the pyrolysis process, most inorganic compounds (ashes) in biomass sequester in char particles. Hence, the ash contents of the char particles are 3–8 times higher than those of the feedstocks. For some raw biomass materials with high ash contents such as rice husks (around 15 wt% ash), the ash contents of char particles can reach as high as 50 wt%. A study conducted by Agblevor and Besler (1996), revealed that alkali metals would not leach from the char particles to bio-oils under storage conditions.

Ash content is determined as the amount of residues when heating bio-oils to 775 °C with oxygen supply. Direct heating of bio-oils will result in foaming and splashing due to their high water contents. Thus, the first controlled evaporation of water at 105 °C is needed before rapid heating to 775 °C (Oasmaa et al. (1997)).

Metals in ashes are believed to cause significant high-temperature corrosion and deposition to thermal devices during the combustion of bio-oils (Morris KW (2001)). Alkali metals of potassium and sodium can form low melting compounds that will stick to the hot components such as turbine blades and then corrode these components. As can be seen, the presence of solids and ashes is highly undesirable. Therefore, it is necessary to reduce the solid content. It is difficult to solve this problem by filtration of bio-oils.

Acidity and Corrosion Property

Bio-oils usually contain about 7-12 wt% acids, and have a pH of 2-4 and an acid number of 50-100 mg KOH/g. It has been reported by Aubin and Roy (1990), that bio-oils are very corrosive to aluminum, mild steel and nickelbased materials. The corrosion rates would be enhanced at elevated temperatures or with the increase in water contents of bio-oils.

2.3 Direct Liquefaction

In the direct liquefaction, the biomass is converted into a liquid fuel without a synthetic gas being produced in-between. This promises a considerable improvement in thermal efficiency compared with the synthesis gas process. This development is comparable with the direct liquefaction of coal (developed by IG Farben in the thirties), which also has greater thermal efficiency (up to 63%) than gasification of coal followed by FT synthesis (about 44 % with coal, but about 70% with natural gas). Both processes, the direct liquefaction and the Fischer-Tropsch technology, are currently going through a renaissance in China because the low raw material and wage costs allow economic coal liquefaction. The processes for direct liquefaction of biomass, however, are only at the start of their development and are currently only in the planning phase or laboratory stages at the most.

A corresponding process for the direct conversion of organic substances (DoS) is being developed on a laboratory scale, for example, by Prof. Thomas Willner at the Hamburg University of Applied Sciences. However, continuous operation, which could guarantee a technically useful scale, and a self-sufficient hydrogen supply needs to be provided or developed. Further variants of direct liquefaction are, for example, depolimerisation, also known as catalytic breaking of hydrocarbon chains – e.g. biomass, plastics or old oils. The catalytic breaking is already used successfully with old oils and plastics. As the product quality is not yet in line with the requirements of modern diesel car engines, there is a considerable need for development in this area, in particular with the use of biomass.

2.3.1 Mechanism of liquefaction

Hydrolysis is a chemical process in which a certain molecule is split into two parts by the addition of a molecule of water. One fragment of the parent molecule gains a hydrogen ion (H^+) from the additional water molecule. The other group collects the remaining hydroxyl group (OH^-).

The most common hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water. Water autoionizes into negative hydroxyl ions and positive hydrogen ions. The salt breaks down into positive and negative ions. For example, sodium acetate dissociates in water into sodium and acetate ions. Sodium ions react very little with hydroxyl ions whereas acetate ions combine with hydrogen ions to produce neutral acetic acid, and the net result is a relative excess of hydroxyl ions, causing a basic solution.

However, under normal conditions, only a few reactions between water and organic compounds occur. In general, strong acids or bases must be added in order to achieve hydrolysis where water has no effect. The acid or base is considered a catalyst. They are meant to speed up the reaction, but are recovered at the end of it.

Acid–base-catalyzed hydrolyses are very common; one example is the hydrolysis of amides or esters. Their hydrolysis occurs when the nucleophile (a nucleus-seeking agent, e.g., water or hydroxyl ion) attacks the carbon of the carbonyl group of the ester or amide. In an aqueous base, hydroxyl ions are better nucleophiles than dipoles such as water. In acid, the carbonyl group becomes protonated, and this leads to a much easier nucleophilic attack. The products for both hydrolyses are compounds with carboxylic acid groups.

Reduction of newly formed carbonyl group to the corresponding alcohol with formate ion and water

$$HCOO^- + CH_2CO \rightarrow CH_2CH(O^-) + CO_2$$

$$CH_2CH(O^-) + H_2O \rightarrow CH_2CH(OH) + OH^-$$

The hydroxyl ion reacts with additional carbon monoxide to regenerate the formate ion $OH^- + CO \rightarrow HCOO^-$. According to this mechanism, deoxygenation occurs through decarboxylation from ester formed by the hydroxyl group and formate ion derived from the carbonate. Alkali salts, such as sodium carbonate and potassium carbonate, can act as catalysts for hydrolysis of macromolecules, such as cellulose and hemicellulose, into smaller fragments.

In the liquefaction process, the amount of solid residue increased in proportion to the lignin content. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure.The degradation of biomass into smaller products, mainly proceeds by depolymerization and deoxygenation. During these reactions, however, some condensation and repolymerization of intermediate products also do proceed. To prevent these undesirable reactions of intermediates, various methods have been attempted. The use of hydrogen is believed to be one of the highly effective methods. When hydrogen is not used, another stabilizer is needed.

The heavy oil obtained from the liquefaction process was a viscous tarry lump, which sometimes caused troubles in handling. For this purpose, some organic solvents were added to the reaction system. Among the organic solvents tested, propanol, butanol, acetone, methyl ethyl ketone and ethyl acetate were found to be effective on the formation of heavy oil having low viscosity. All these solvents, except ethyl acetate, may be reproduced from wood during liquefaction. This suggests that the solvent can be recovered for reuse. The behavior of an added organic solvent is an important factor in its recovery. The effects of 2-propanol, one of the most effective solvents.

2.4 Review From Journal

Rapid liquefaction of lignocellulosic waste by using ethylene carbonate

By T Yamada and H. Ono (1999)

Cyclic carbonates were selected as novel liquefying reagents in order to establish a rapid liquefaction technique converting lignocellulosic waste into useful chemicals. Lignocellulosic materials such as wood and cellulose were liquefied using ethylene carbonate (EC) or propylene carbonate (PC) in the presence of acid catalyst at elevated temperature (120–150°C). Very rapid and complete liquefaction occurred in the EC-liquefaction of cellulose and white birch (hardwood). The rate of the EC-liquefaction of cellulose was approximately 10 times faster than that of current polyhydric alcohol liquefaction. Satisfactory liquefaction is dependent on the type of lignin, i.e. hardwood lignin or softwood lignin. This problem was solved by blending ethyleneglycol (EG) with EC.

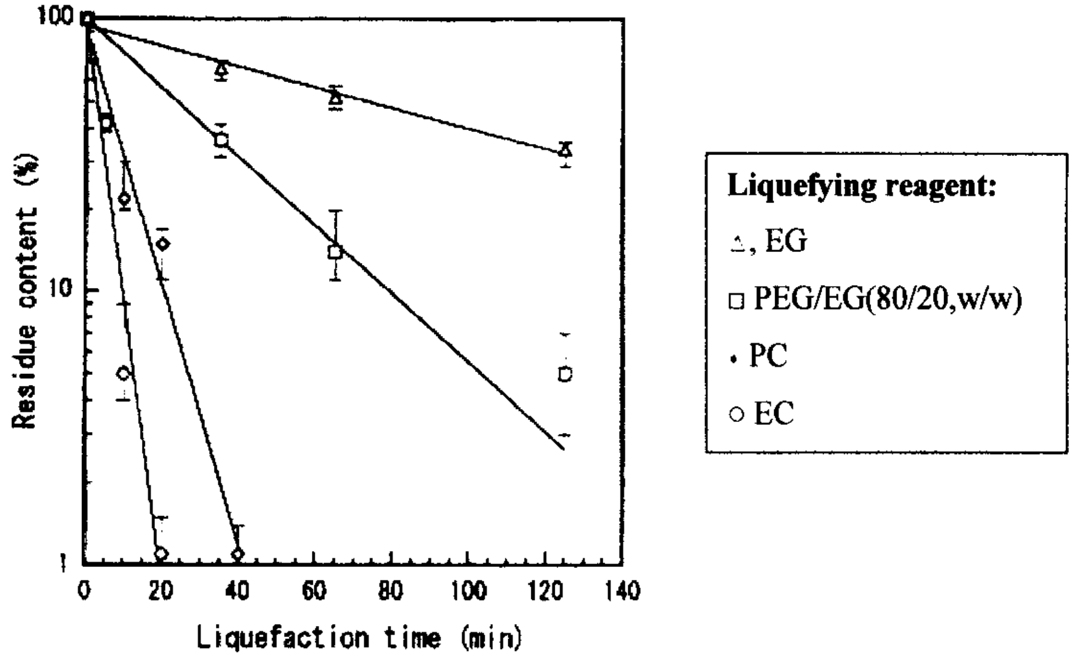


Figure 2.4: Residue content as a function of liquefaction time during each cellulose liquefaction. Each data point represents the average of six experiments.

The average residue content as a function of liquefaction time is shown in Figure 6. Six experiments were carried out for each plot in order to examine variation. The residue contents are plotted in logarithmic scale. It is implied from this figure that the liquefaction of cellulose follows the pseudo-first-order reaction during the early stage. In the case of ethylene glycol (EG), the liquefaction is sufficiently slow that 30% residue still remains at 120 min. Even in the case of using PEG400/EG (8/2, w/w) blend which provides the most rapid liquefaction among alcohols investigated so far (Yamada and Ono, 1998), more than 100 min were required for satisfactory liquefaction. On the other hand, cellulose was liquefied very rapidly and almost completely within 10–20 min when ethylene carbonate (EC) was used. Similarly, when propylene carbonate (PC) was used, cellulose was liquefied rapidly and thoroughly within 30–40 min.

The liquefaction rate constants of cellulose liquefactions with various liquefying reagents are shown in Table 3. These rate constant values were calculated from the slopes of lines at the early stage of the liquefaction as shown in Figure 6. EC gives a

27.9 times faster liquefaction rate than EG, and almost 10 times faster rate than PEG400/EG (8/2, w/w) blend. PC provided 12.9 times faster liquefaction rate than EG. These findings indicate that both EC and PC are quite effective liquefying reagents for cellulose liquefaction.

Table 2.1: Liquefaction rate constants of cellulose liquefactions with various liquefying reagents

	Liquefying reagent			
	EG	PEG400/EG(80/20, w/w)	EC	PC
Rate constant	0.00858 ± 0.0011	0.0240 ± 0.005	0.239 ± 0.043	0.111 (min^{-1}) ± 0.025
Relative rate	1 ± 0.13	2.8 ± 0.58	27.9 ± 5.01	12.9 ± 2.91

EC and PC have been used as effective solvents in the field of electrical engineering due to high permittivity value. Those of EC and PC are 89.8 (40°C) and 64.9 (25°C), respectively (Riddick et al., 1986). It has been known that, for an acid catalyzed reaction in non-aqueous solvent, the acid potential depends on the permittivity of the solvent. In general, the higher the permittivity of solvent is, the higher the potential of acidity is (Yoshino, 1989). Taking this concept into account, the liquefaction of cellulose by EC or PC in the presence of acid catalyst, acid catalyzed degradation of cellulose would be satisfactory because of their high permittivity and could lead to complete liquefaction in a short time.

Considerable amounts of volatile compounds were generated when PC was used for the liquefaction. It is known that PC converts to propyleneglycol (PG) when heated under acidic conditions (Peppel, 1958) and generates some volatile compounds such as dioxolanes during prolonged heating (Chernysheva and Polyanskii, 1971). These volatiles are toxic, which would make PC for liquefaction troublesome. Therefore, no further investigation of PC liquefaction was undertaken.

CHAPTER 3

METHODOLOGY

3.1 Experimental Work

As being discussed, the experimental work will be done on liquefaction process. Even though there is no research on liquefaction on dry leaves, the experimental acquired from literature review of liquefaction of wood can be used since both composition have cellulose.From the literature review, Malaysia land is covered 60% with forest, thus tree dry leaves were used as raw material.

3.1.1 Collection and Preparation of Raw Materials

Dry leaves were collected around UTP and used it as lignocellulosic waste. The samples were firstly dried in the oven at 100°C for 24 hr. It needs to be ensured that the temperature used must be lowered than the ignition point of the raw material to avoid it for being burn. They were then ground into 500 micron mesh size. Smaller particles will favor the conversion process because of larger surface area. After the drying process, the samples were kept in a desiccator at room temperature before use.

Several testing will be done on the raw materials to determine a few parameters on them:

Moisture Content Analysis

Moisture content inside raw materials was analyzed by measuring weight different before and after drying process. The data is taken for a few hours until the weight drop is insignificant. Moisture content calculation will be done by using following equation:

$$\boxed{\%\ \text{Moisture Content} = \frac{\text{Initial weight} - \text{Final weight}}{\text{Initial weight}} \times 100\%}$$

Ash Content Analysis

The raw materials placed inside porcelain respectively, weighted and inserted into a furnace. The raw materials leave inside the furnace to be burnt up to the desired temperature, which is 500°C for 7 hours. The weight for each container weighted for after burning process.

Carbon Hydrogen Nitrogen Sulfur (CHNS) Content Analysis

3.2 Experiment Procedure

The methodology was based from literature. (T. Yamada H. Ono, 2007)

3.2.1 Solvolysis Liquefaction Process

The liquefaction was carried out in a 200ml flask equipped with stirrer, cooler and thermometer. The flask was charged with 5 g of lignocelluloses powder was immersed at oil bath preheated at 150°C. The mixture of 10g of liquefying reagent (ethylene carbonate and ethylene glycol) and 0.15g (3 wt% for the liquefying reagent) of 97% sulfuric acid preheated at 140-150°C was then added to the flask. The liquefaction was conducted at 150°C. The time when the hot mixture was added to lignocelluloses is defined as the starting point of liquefaction. After the preset time (2hrs), the flask was immersed in cold water for 10-15 minutes to quench the reaction. The aim of this project is to study the effect of reaction temperature and reaction time with the percentage of liquefaction.

3.2.2 Measurement of Residue Content

The reaction mixture was diluted by about 80% with 1,4-dioxane. The dioxane-diluted mixture was separated into residue and filtrate it with filter paper. The residue was dried in an oven for 100 °C for 24 hr. The residue content was defined as the percent dry weight of insoluble substance to the total lignocellulosic charged. It has been usually used as an index of the extent of liquefaction.

3.2.3 Separation Process

Since the rotary evaporator in lab cannot be used, distillation method was used instead. The liquefied substance was obtained by the removal of dioxane and water from the filtration at temperature of 110 °C.

3.3 Characterization of Products

3.3.1 Liquid Products

3.3.1.1 Density Determination

Density is a measurement that could also shows the characteristic of the product yield from the experiments. The solutions' densities were measured by using a measuring cylinder and weighing balance.

3.3.1.2 Viscosity Determination

Viscosity is a measurement also shows the characteristic of the product yield from the experiments. The viscosity was measured by using viscosity meter at temperature 25 °C and 40 °C.

3.3.1.3 Gas Chromatography-Mass Spectrometry

Biomass derived oil was analyzed gas chromatograph equipped with mass selective detector. It was used to for identification of compounds in the oil. Both injector and detector were kept at 553 K and the carrier gas He velocity was 1ml.min. HP-5 column (5% phenyl methyl siloxane, 30m X 250μm X 0.25 μm) were used. In order to give good product separation, the oven program was 1 min isothermal at 313 K, followed by a heating rate of 6K/min to fina 553 K and hold 5 min at the final temperature. The injected volume was 1 μm with split ratio of 30/1.

3.3 .2 Residue Content

3.3.2.1 Fourier Transform Infra-Red (FTIR) Spectra

Infrared spectra of the catalyst samples were obtained using Perkin–Elmer Spectrum One spectrometer. FTIR spectra are useful for the identification of functional groups (such as CH_3–, NO_3-, –OH, C–O, etc.) present in the residue before and after the calcinations process. Approximately 1 mg of each sample powder was grind with 200mg of IR-grade KBr. Then, the samples were transferred into a diecast and pressed into pellet using a hand-press. The disc was later placed in a sample holder to be scanned by instrument.

Figure 3.1 summarizes the liquefaction method.

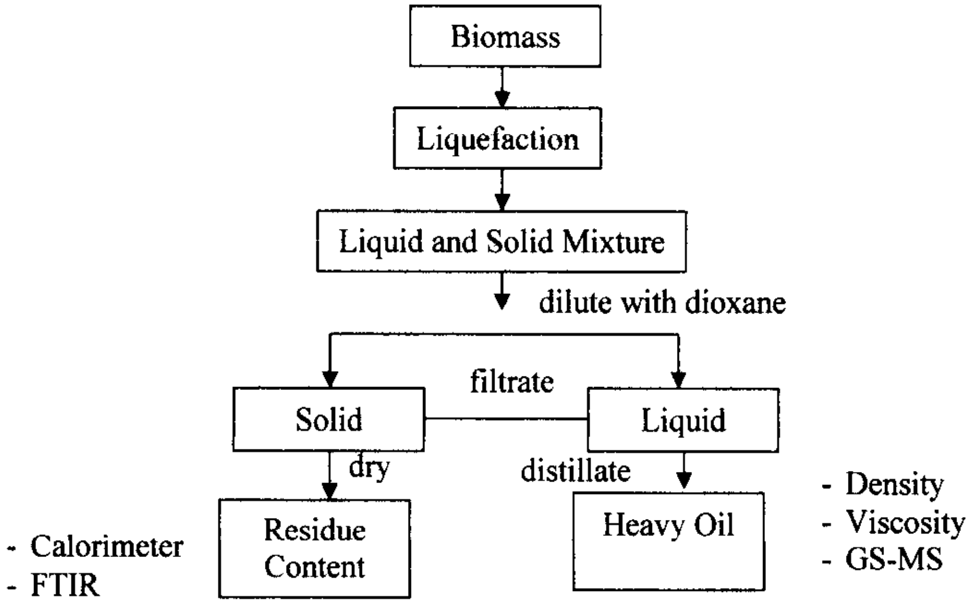


Figure 3.1 : A brief scheme of the product separation and analysis approach

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Analysis of Raw Materials

4.1.1 Moisture Content

Table 4.1 : Moisture Content Analysis

Sample	**Biomass**		**Moisture Content Percentage (%)**
	Initial Mass	**Final Mass**	
1	5	4.848	3.040
2	5	4.857	2.860
3	5	4.843	3.140
Average	**5**	**4.849**	**3.013**

Moisture Content Calculation:

Dry leaves : $\frac{5 - 4.848}{5} \times 100\% = \mathbf{3.04\ \%}$ **of moisture content**

The result shows that a dry leaf contains 3.013% of water. The presence of water will effect the reaction. The aim of this project is to find the effect of ethylene glycol and ethylene carbonate in the base hydrolysis reaction of degradation of cellulose. Hence, drying of the raw material is very essential before starting the project.

4.1.2 Ash Content Analysis

Table 4.2: Ash Content Analysis

Sample	Raw Material (g)		Ash (g)
	Before	After	
1	5	4.57	0.43
2	5	4.68	0.32
3	5	4.62	0.38
Average	**5**	**4.62**	**0.377**

The ash contain in dry leaves is 0.377.

4.1.2 CHNS Analysis

Table 4.3: Elemental compositions of the raw materials. (wt% of dry basis)

Element / Run	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
1	47.61	6.413	1.461	0.141	43.38
2	43.98	5.714	1.345	0.049	45.8
3	46.4	6.166	1.309	1.429	47.25
Average	**45.99**	**6.098**	**1.372**	**0.538**	**45.487**

From Table 4.3, we can see that dry leaves contain high carbon and oxygen. It is mainly derived from cellulose and lignin which contains carbon and oxygen mostly.

4.2 Degree of Extent of Liquefaction

4.2.1 Effect of Reaction Temperature and Solvent

Mass of Dry Leaves	: 5 g
Mass of Solvent	: 10 g
Mass of Sulfuric Acid	: 0.4 g
Reaction Time	: 2 hrs

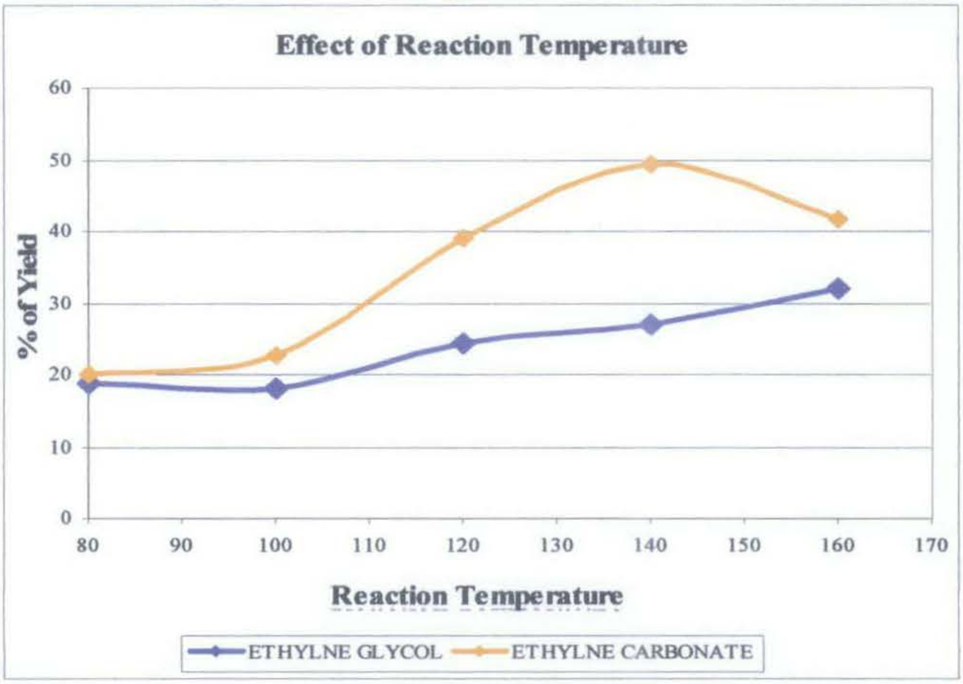


Figure 4.1 : Effect of Reaction Temperature to Percentage of Yield

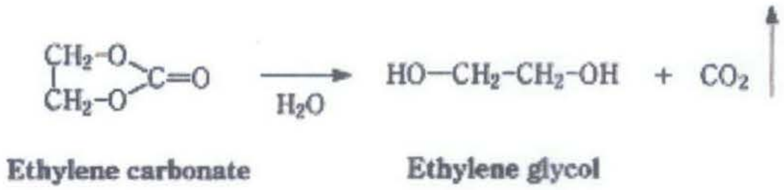
To investigate the effect of reaction temperature on the yield of the heavy oil, experimental measurements were taken at five different temperatures. The experiment results for the yield of heavy oil dependency on the reaction temperature shown in Figure 4.1. From Figure 4.1, the yield of heavy oil strongly depends on the reaction temperature at 140°C for ethylene carbonate (EC) and while 160°C for ethylene glycol (EG). It can be seen that the heavy oil yield increasing with increasing reaction temperature first and then is followed with decrease with further increasing reaction temperature. The curve looks like a bell shape curve. This is due to the competition of two reaction involved in the liquefaction, that is, hydrolysis and repolymerization. At the initial stage, biomass is decomposed and depolymerized to small compound and these compounds may rearrange through condensation, cyclization and polymerization to form new compounds. The highest heavy oil yield is 32% for ethylene glycol and 41.6% for ethylene carbonate.

It can also be seen that EC give higher yield compared to EG in the experiment. These finding indicate that EC are quite effective liquefying reagents for cellulose liquefaction as stated in literature review.

EC has been used as effective solvents in the field of electrical engineering due to high permittivity value with 89.9 (40 °C) (Riddick et al.,1986). It has been known that, for an acid catalyzed reaction in non-aqueous solvent, the acid potential depends on the permittivity of the solvent. In general, the higher the premitivity of solvent is, the higher the potential acidity is (Yoshino,1989). Taking this concept into account, the liquefaction of cellulose by EC in the presence of acid catalyst, acid catalyzed degradation of cellulose would be satisfactory because of its high permittivity and could lead to complete liquefaction in a short time.

It has been known that EC is transformed into EG with a release of carbon dioxide at elevated temperature in the presence of acid catalysts as shown in Scheme 1 (Peppel, 1958). This reaction may have occurred during liquefaction of lignocelluloses in this study. The considerable bubbles observed in the flask were probably due to generation of carbon dioxide.

However, at the end of liquefaction, EC would be transformed into ethylene glycols. Ethylene glycols produced by EC would give almost the same product.



Scheme 1: .Decomposition reaction of ethylene carbonate.

4.2.2 Effect of Reaction Time

Mass of Dry Leaves : 5 g
Mass of Solvent : 10 g
Mass of Sulfuric Acid : 0.4 g
Reaction Temperature : 140°C

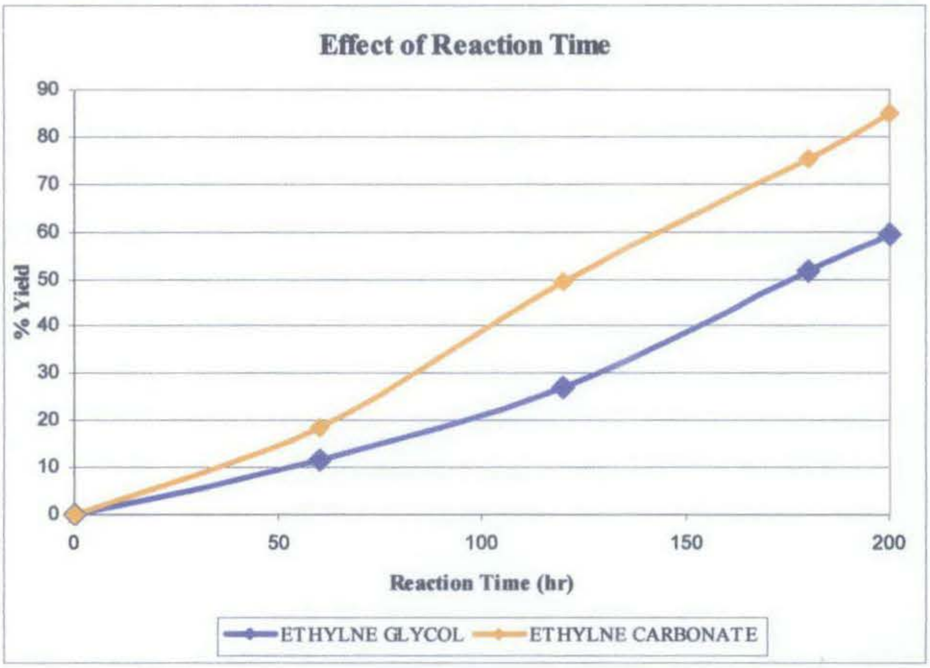


Figure 4.2 : Effect of Reaction Time with Percentage of Yield

The percentage of yield as a function of time is shown in figure 4.2. Four experiments were carried out for each plot in order to examine variation. In the case of ethylene glycol (EG), the liquefaction is sufficiently slow that only 27% of yield at 120min. On the other hand, cellulose was liquefied very rapidly and almost completely at 200min when ethylene carbonate was used.

The liquefaction rate constants of cellulose liquefactions were shown in Table 4.4. There rate constants values were calculated from the slope line at the early stage of liquefaction as shown in Appendix A. It is implies that from the figure that the liquefaction of cellulose follows the pseudo-order reaction during the early stage.

Table 4.4: Liquefaction rate constants of cellulose liquefaction with various liquefying reagent

	EC	EG
Rate Constant	0.5803	0.2752
Standard Error	0.9934	0.9735

Rate constant (k) is calculated from figure in appendix B, y=100 exp (-kx)
From table 4.4, we can see that EC gives approximately 2 times faster liquefaction rate than EG.

4.3 Liquid Product Analysis

4.3.1 Density Determination

From literature review, the densities of bio oil are above 1200 kg/m^3. The density of bio oils from the experiment were shown in Appendix D. From the table, the bio oil from the experiment is between 1173 to 1317 kg/m^3 with different parameters. This shows that the experiment density is feasible.

4.3.2 Viscosity Determination

The viscosity of bio oil is between 25 to 1000 centi poise depending on which raw material was used. The viscosity of bio oils from the experiment were shown in Appendix D. From the table, the bio oil from the experiment of this project is 27 to 43 centi poise. This shows that the experiment viscosity is in the range of bio oil viscosity.

4.3.3 pH Measurements

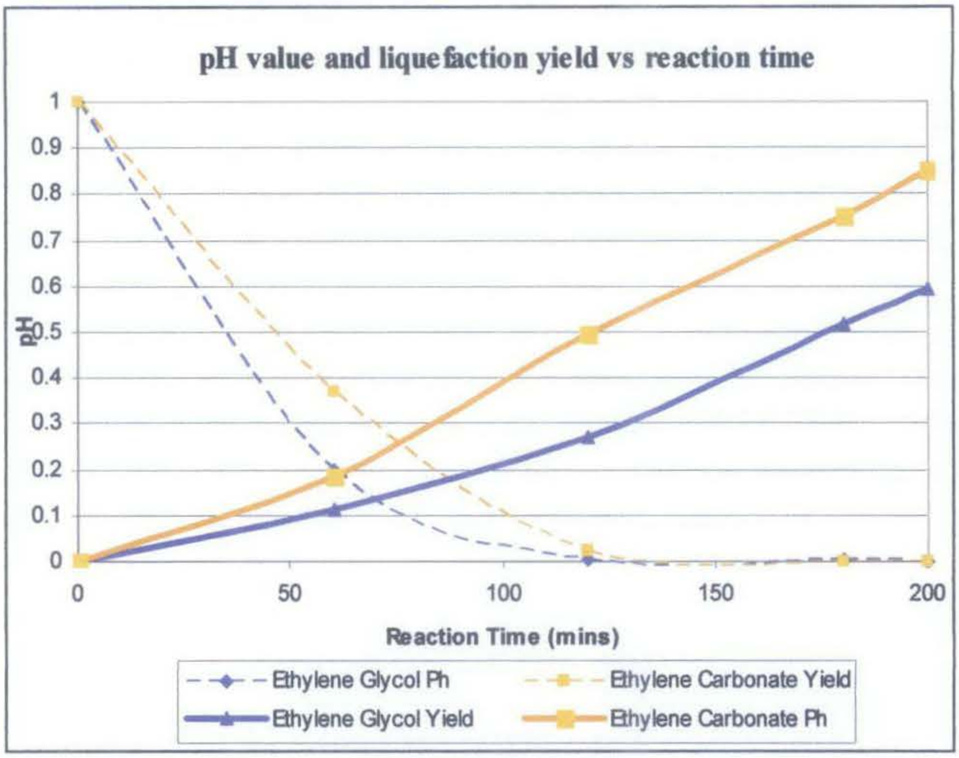


Figure 4.3 : Evolutions of yiled in liquefied cellulose and acid concentration.

The reactivity's of each basic component, cellulose, hemicellulose and lignin, are very different during solvolysis. In the presence of a strong acid, such as sulphuric acid, the linkage between glycosidic units of cellulosic compounds are subjected to hydrolytic cleavage. This is not the case with lignin, which even tends to give a precipitate at a low pH level. Moreover, synergies between basic components of dry leaves are difficult to take into account during the liquefaction reaction. Samples of micro-crystalline celluloses were liquefied in ethylene glycol and ethylene carbonate acidified with H_2SO_4, in the experimental conditions above described for dry leaves. The concentrations in H^+ ion were measured by pH-metric analysis. Figure 4.3 show the simultaneous evolution of liquefied cellulose yield and the normalised acid concentration during the solvolysis: $[H^+]/[H_{t=0}^+]$. The yield in liquefied cellulose increases, while the acidity of the solvent medium drastically drops to an almost null value. The change in acidity could thus be explained. The H^+ ions released from sulphuric acid are consumed by hydrolytic reactions.

From the figure 4.3 and Appendix D, we can see that only ethylene carbonate which gives the higher yield gives high value of pH which is 3.618 and 3.875. This concludes that acid donates for H+ ion in the presence of ethylene carbonate more which leads to high liquefaction yield percentage.

4.3.4 GC-MS Analysis

Table in appendix E presented the identified compounds in the oil obtained from biomass liquefaction in the two solvents with different temperature and time. The area% for each compound identified (defined by the percentage of the compound's chromotograhic area out the total area) and the total area% for all the listed compounds were also shown in the tables. It can be seen that the product categories and abundance were greatly affected by the solvent type.

According to literature review (BREW Project, 2008), the hydrolysis conversion products will be as in figure 4.4.

C2	**C3**	**C4**	**C5**
o Ethanol o Acetic Acid Glyoxylic Acid o Oxalic Acid	o Lactic Acid o 3-Hydroxypropionic Acid o Glycerol o 1,2-Propanediol o 1-3-Propanediol o Propionic Acid o Acetone	o Fumaric Acid o Succinic Acid o Malic Acid o Butyric Acid o 1-Butanol o 2,3-Butanediol o Acetoin o Aspartic Acid o 1,2,4-butanetriol	o Itacomic Acid o Glutamic Acid **C6** o Citric Acid o Lysine o Cis-cismuconic acid o Gluconic Acid o Kojic Acid

Figure 4.4 : Hydrolysis Conversion Products

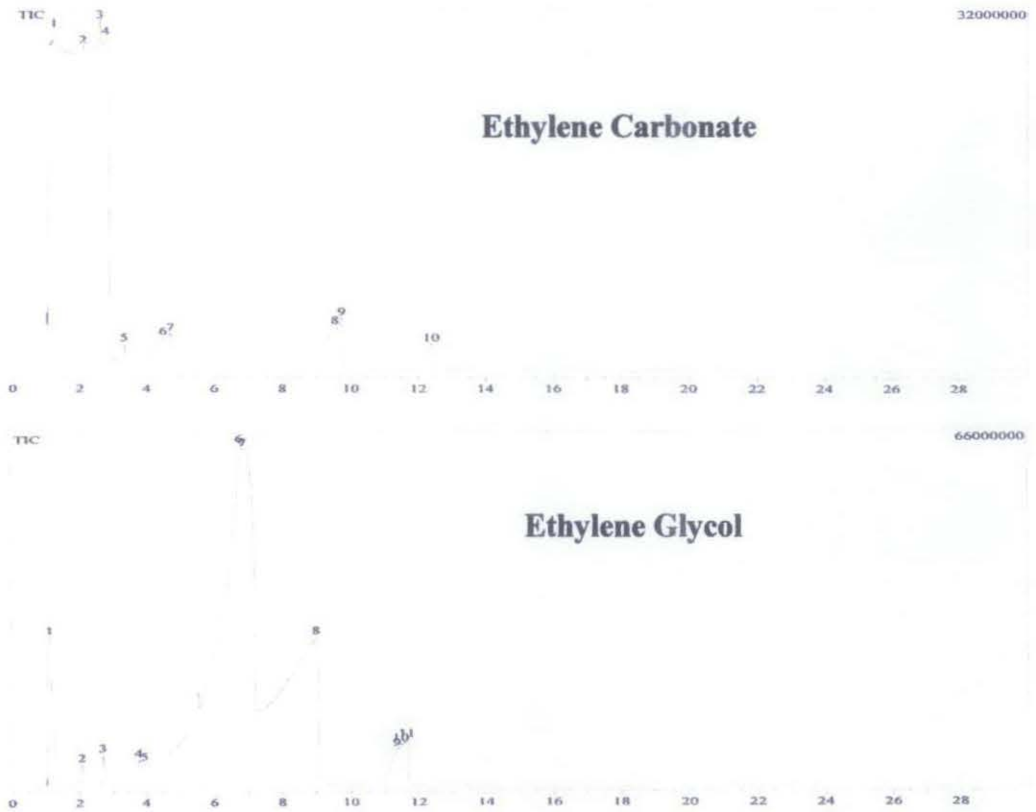


Figure 4.5 : GC-MS spectra of oil produced from the tested solvents. Condition: temperature 140°C, reaction time 200 min.

From figure 4.5, ethylene carbonate liquefaction products, three major peaks appeared at about 1.26, 1.99 and 2.75 min identified as butyric acid, gluconic acid and glycolic acid respectively and these compounds accounted for about 95.2% of total peak area. Butyric acid, gluconic acid and glyconic acid is the hydrolysis conversion products from the literature review. The trace of this compound concludes that dry leaves can be converted to bio oil.

Meanwhile the major compound for ethylene glycol liquefaction appeared at 1.11, 1.99, 4.02, 7.25, 8.73, 11.78 min identified as gamma-Valerolactone, Butyric Acid, Succinic acid, methyl carbonate, 1,3,5-Trioxane and Butane-1,2,4-triol respectively and these compounds accounted for 65.38% of total peak area. Butryric acid and succinic acid is also the product from hydrolysis conversion from literature review.

From both GC-MS analysis, 95.2% of total area from liquefaction products of ethylene carbonate is from literature review while only 1.63% totals area from ethylene glycol liquefaction product from literature review. This can conclude that ethylene carbonate may yield more conversion products of bio oil.

It is also worthily noted that less compounds with nitrogen and sulfur atom were detectec in the oils obtained in the present study. The lower heteroatom content may relate to the optimum temperature which gave rise to thorough decomposition containing polymer (e.g protein) and the elimination of hero atoms like nitrogen, sulphur and so on.

4.4 Residue Content Analysis

4.4.1 Fourier Transform Infra-Red (FTIR) Spectra

ETHYLNE CARBONATE

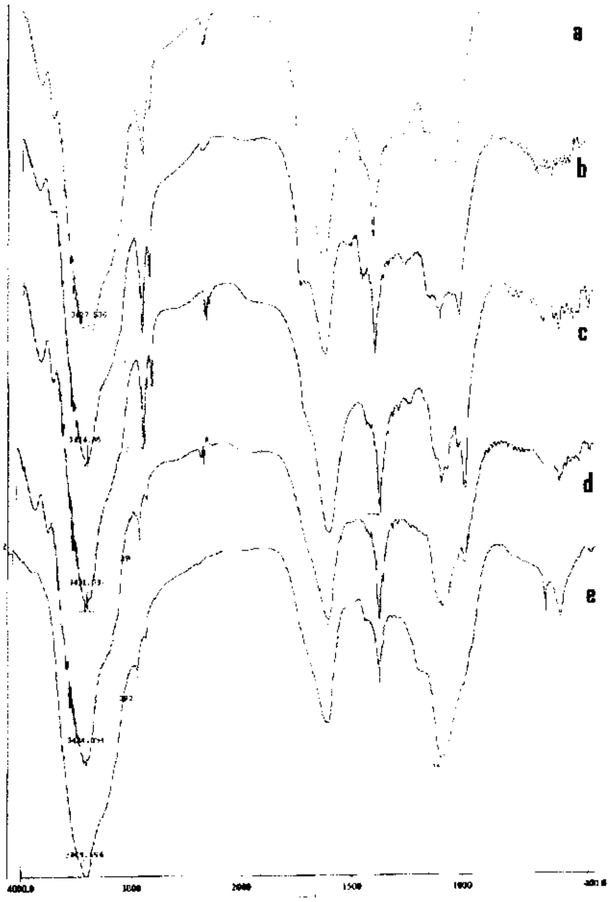


Figure 4.6 : IR Spectra of (a) Raw Dry Leaves (b) EC liquefaction of dry leaves (60 minutes) (c) EC liquefaction of dry leaves (120 minutes) (d) EC liquefaction of dry leaves (180 minutes) (e) EC liquefaction of dry leaves (200 minutes)

The insoluble residues from dry leaves were analyzed by FTIR. The IR spectra of the residues during the EC liquefaction of dry leaves together with raw dry leaves are shown in Figure 4.6. According to the literature review, the bands at 3420 cm^{-1} was caused by –OH in dry leaves and water. Absorption at 2913 cm^{-1} was attributed to the symmetric CH3-vibration of methoxy group and the band at 1020 cm^{-1} represented the C-O stretch vibration for the O-CH2. The band at 1630 cm^{-1} belonged to the aryl group. The reason for the broad bank at 3420 cm^{-1} was contributed to the combination and overlap of absorption of aliphatic and aromatic O-H, Ar-H, =C-H and N-H stretching.

The peaks between 1000 cm^{-1} and 600 cm^{-1} were from the out-of-plane vibrations of methyl or other alkyl constituents on the aromatic group. The dry leaves is mainly constituted of cellulose, hemicellulose and lignin. From the analysis, it can be concluded that the band at 1620 (C=O) represents the hemicellulose. The absorption at 1020 cm^{-1} represents the cellulose (β glycosidic bond) and absorption at 1400 cm^{-1} and 1600 cm^{-1} represents lignin.

The band at 1630 cm^{-1} decrease and band at 1020 cm^{-1} is almost disappeared as retention time of liquefaction increase. This shows that cellulose and hemi cellulose decomposition.

The IR spectrum of the residue at the initial stage (liquefaction at 60 minutes) is similar to that of raw, while the spectra of residues at 120 minutes, 180 minutes and 200 minutes differ from the raw material. Previous studies indicate that the band at about 1400 cm^{-1} may represent both the overlapping of symmetric carboxyl stretching vibrations from un-ionized carboxylates and C–O–C stretching vibrations from esters. Thus it is possible that these residues would mainly be derived from lignin.

It has been reported that delignification of dry leaves is more difficult than wood in organic acid cooking because of the condensation reaction of lignin. Under strong acidic conditions, the condensation reaction occurs between carbonium cations at the α-position and electron-rich aromatic ring carbons of lignin compounds, leading to a diphenylmethane structure. The structure formed from guaiacyl lignin's is reported to be more persistent in acid catalyzed degradation as compared with that syringyl lignins (Shimada et al 1997). This mechanism might be interpreted as the liquefaction of dry leaves nit be as thorough.

ETHYLNE GLYCOL

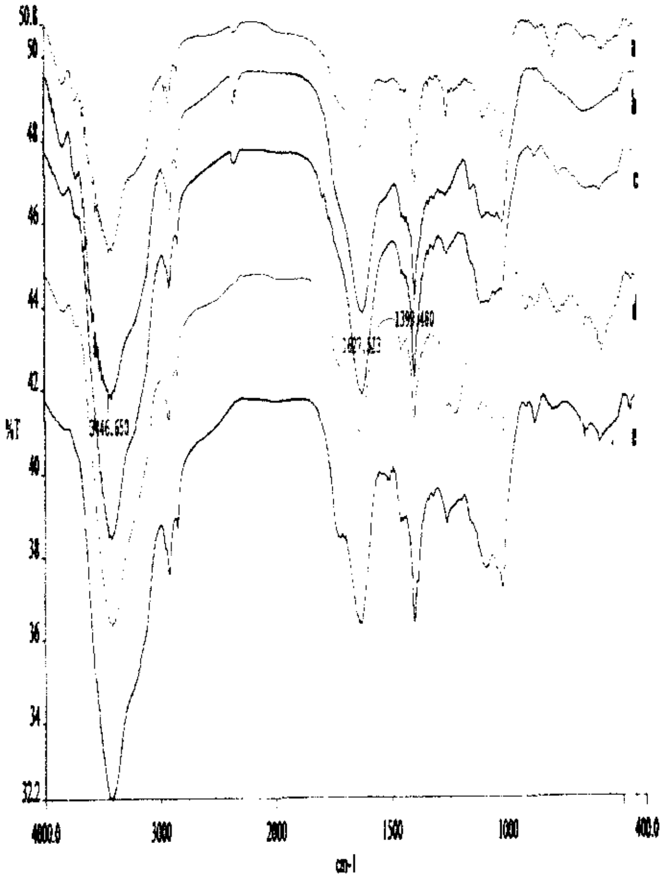


Figure 4.7 : IR Spectra of (a) Raw Dry Leaves (b) EG liquefaction of dry leaves (60 minutes) (c) EG liquefaction of dry leaves (120 minutes) (d) EG liquefaction of dry leaves (180 minutes) (e) EG liquefaction of dry leaves (200 minutes)

From Figure 4.7, the intense broad band between 3370 cm^{-1} and 3410 cm^{-1} indicates the presence of OH groups in large quantities in dry leaves. It can also be seen that the band at 1620 cm^{-1} show the residue obtain at 60 minutes still have cellulose and lignin. But the intensity of these bands decreased. Therefore, dry leaves biomass cannot be liquefied completely at reaction 60 minutes.

It can bee seen that the four kinds of residue from different reaction time have the similar functional groups. From the spectral difference of FTIR spectra of these heavy oils and raw material, the absorbance peak appeared on the range 1600-650 cm^{-1}. It is showed that the aromatic ring start to recombine at this time.

From figure 4.7, those between 930 cm^{-1} and 684 cm^{-1} respectively, indicate the presence of the aromatic double bonding. Those at 746 cm^{-1} and 706 cm^{-1} respectively are due the presence of O-substituted benzene ring. These bands in the liquefied dry leaves spectrum indicate the presence of the aromatic lignin based components.

In comparison between FTIR spectrum between ethylene glycol and ethylene carbonate, it can be seen that the band at 1630 cm^{-1} strongly decrease and band at 1020 cm^{-1} in ethylene carbonate. This shows that ethylene carbonate give high decomposition compared to ethylene glycol.

From figure 4.6 and 4.7, it can also be seen that there is very strong band at 1400cm^{-1} that indicated carboxylic acid in ethylene carbonate compare to ethylene glycol. This can conclude that ethylene carbonate give higher yield or conversion from cellulose to carboxylic acid compared to ethylene glycol.

4.5 Mechanism of cellulose solvolysis

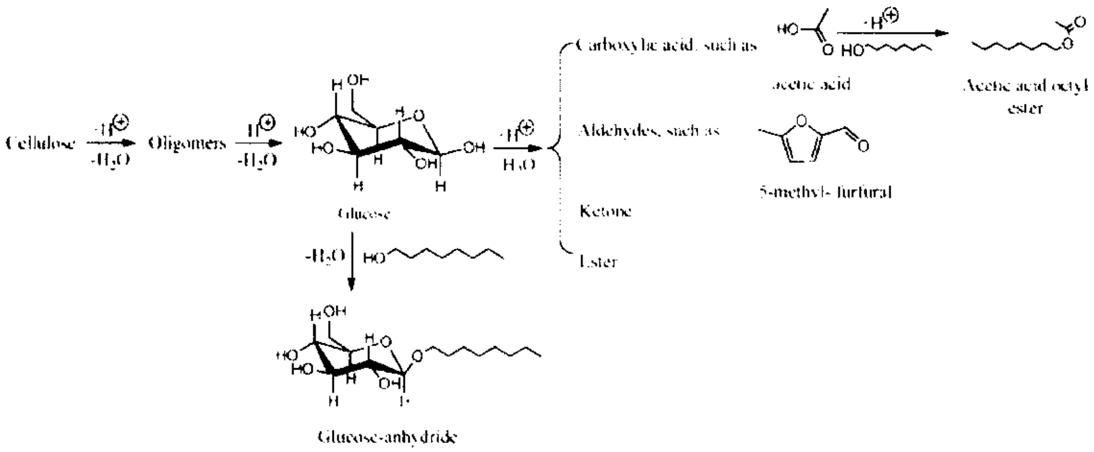


Figure 4.8 : Cellulose alcoholysis pathways catalyzed by acid.

It is well-known that cellulose, hemicellulose, and lignin are the three main components of biomass. These components can be alcoholized with acid as a catalyst according to the pathways shown in Figures 4.8. The intermediates include glucose and xylose from cellulose and hemicellulose degradations, denoted as C-OH, and also include the fragments A and B from lignin degradation, designed as L-OH. These intermediates can react further with alcoholic solvents according to the literature review.

When using ethylene glycol a single molecule of polyhydric alcohol can be combined with multi-molecular C-OH. As a result, the molecular weight of products is increased and the formation of heavy oil and residue is promoted with polyhydric alcohols.

In the literature review, the conversion product of liquefaction ethylene carbonate and ethylene glycol is levulinic acid. Although there is no trace on levulinic acid for this project, the decomposition and degradation of cellulose will be discussed.

We earlier reported that when using EG as a solvolysis reagent, cellulose was degraded and produced a considerable amount of EG glucosides at the early stage of the reaction; then the glucosides decomposed into a large quantity of levulinates. Even in the case of using EC, because EC decomposes into polyalcohols under acidic conditions, glucosides are produced at the early stage of the reaction, after which the glucosides decompose into a levulinic acid structure as in figure 4.9

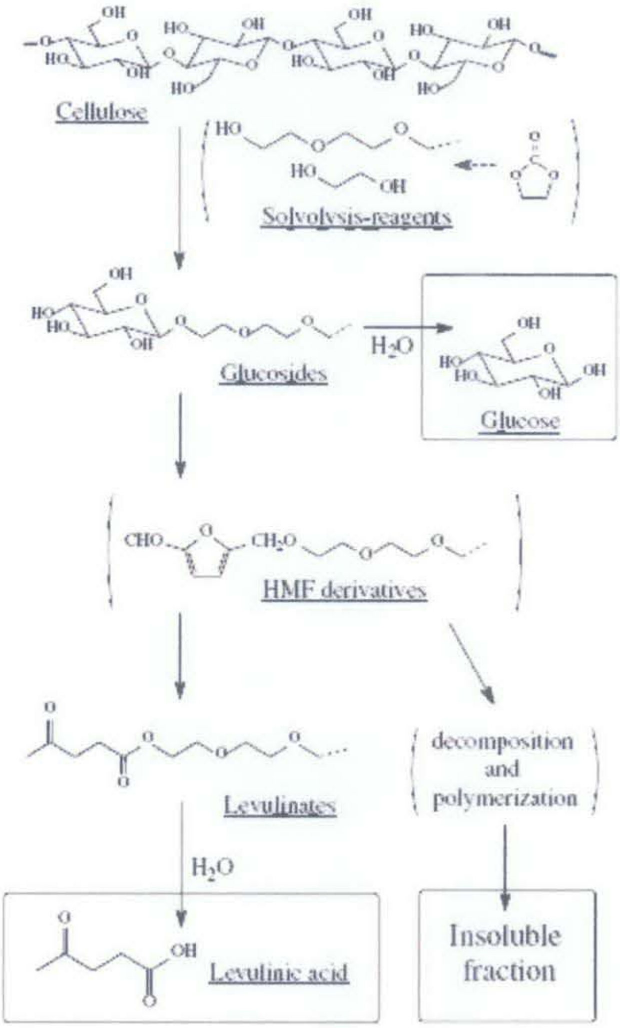


Fig. 4.9. Mechanism of cellulose degradation and decomposition during the solvolysis reaction, and the solvolyzed product analysis

This project describes a method for analyzing the degraded cellulose in the solvolyzed products. Glucose content was measured by hydrolysis treatment of the liquid product , and was defined as the glucoside content of the solvolyzed products.. The reaction conditions for the hydrolysis were optimized to give the highest yield of hydrolysis product.

CHAPTER 5

CONCLUSION

Liquefaction of biomass with proper solvent is a process that can promise fully be integrated with optimized conditions to simultaneously produce fuel addictives and valuable chemicals. In this study, rapid liquefaction of lignocellulosic material such as cellulose was achieved by using EC and EG as novel liquefying reagents. The liquefaction of cellulose follows the pseudo-first order reaction in the early stage. EC gave almost 2 times faster liquefaction rate compared to EG. EC is an effective liquefying reagent for cellulose liquefaction due to its permittivity value.

The product distribution was also strongly affected by the solvent. The major hydrocarbons were identified as butyric acid, gluconic acid and glycolic acid in the case of EC liquefaction process. The composition of oil from EG liquefaction process consisted mainly, gamma-Valerolactone, Butyric Acid, Succinic acid and Butane-1,2,4-triol. The study has shown that employing different solvents could change the distribution and relative abundance of produced compounds.

The effect of reaction temperature also plays a big role in liquefaction process. Optimum temperature will give the highest percentage yield. The study shows that, for EC liquefaction process, the highest percentage yield is at 140°C while for EG liquefaction process, the highest percentage yield is at 160°C.

CHAPTER 6

RECOMMENDATION

For this Project:

1. The future experiment will be conducted using different amount of catalyst. It is known that the more acid used, the more solvolysis reaction will take place, the higher liquefaction yield percentage.
2. The energy of the residue shall be observed using bomb calorimeter in order to find the energy content in it.
3. The composition of carbon, hydrogen, sulfur and nitrogen of liquid product should be analyzed using CHNS equipment.

For this course:

1. **Academic syllabus**

   The current evolution of green technology or productions of energy from renewable natural resources are now aware by the people around the globe. But the main concern is on how much they do know about them definition of green technology, the effect of the technology to the nature, the current technology on green engineering and the importance of it to the future generation. In concern with this matter, the author would like to suggest for the environment conserving technology to be added into the syllabus of students in UTP. This syllabus shouldn't be a pre-requisite for one course only to graduate, but it has to be a compulsory subject to all the engineering students

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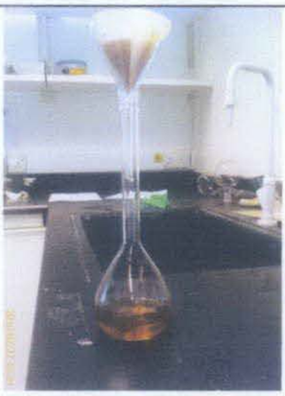
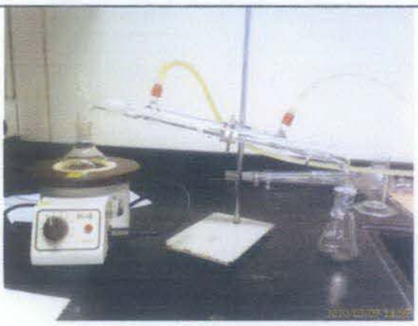
APPENDIX A
METHODOLOGY

A. Preparation of Raw Material

Dry leaves collected and gathered.	
Dry leaves were dried in the oven for 105°C overnight.	
Dried dry leaves were blend into small particles.	

B. Liquefaction Process

Mixture of liquefying reagents, ethylene carbonate/ethylene glycol with 0.15g of 97% sulfuric acid at 140-150°C were preheated and mixed into the flask.	
The liquefaction was conducted at 150°C. The mixture is then diluted with 1,4 dioxane.	
The product of liquefaction filtrated using filter paper	
The mixtures of 1,4-dioxane and water were separated using distillation method.	

The solvolyzed product was diluted with distilled water	
Ethylene carbonate and ethylene glycol with water is separated using separating funnel.	

APPENDIX B

RESULTS OF PERCENTAGE YIELD FOR LIQUEFACTION

A. Effect of Reaction Temperature

ETHYLNE GLYCOL

Sample	Temperature	Initial Solid Mass	Resiude Mass	Percentage of Yield
A	80	5	4.06	18.8
B	100	5	4.10	18
C	120	5	3.78	24.4
D	140	5	3.65	27
E	160	5	3.40	32

ETHYLNE CARBONATE

Sample	Temperature	Initial Solid Mass	Resiude Mass	Percentage of Yield
F	80	5	4.00	20
G	100	5	3.87	22.6
H	120	5	3.05	39
I	140	5	2.53	49.4
J	160	5	2.92	41.6

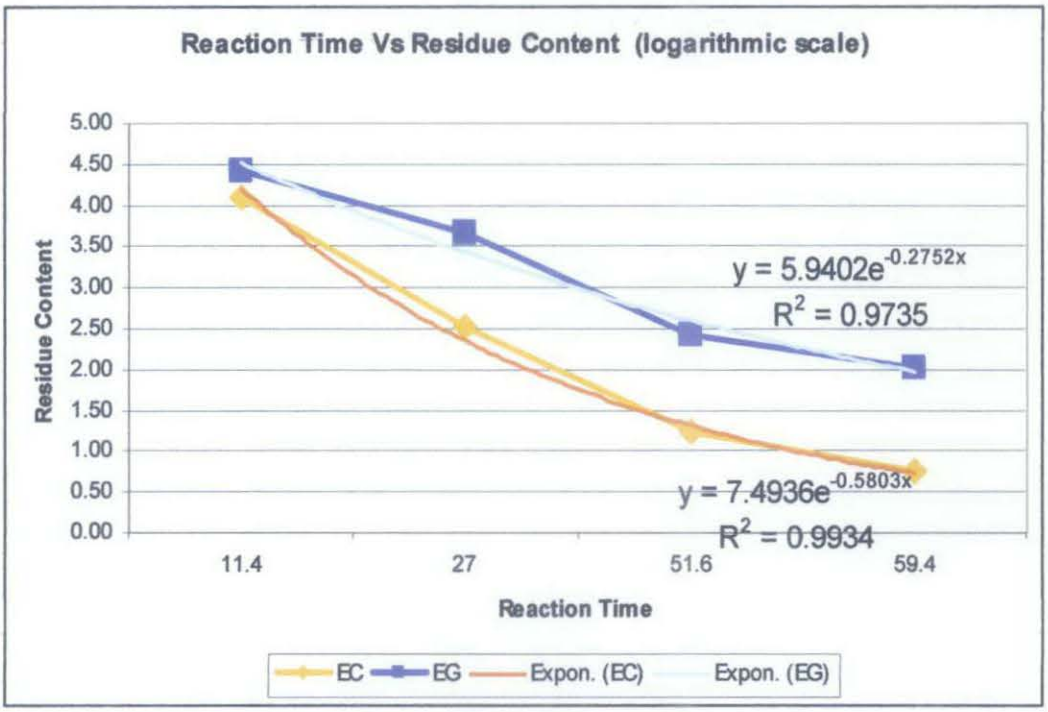
B. Effect on Reaction Time

ETHYLNE GLYCOL

Sample	Time	Initial Solid Mass	Resiude Mass	%of yield
	0	**0**	**0**	**0**
K	60	5	4.43	11.4
D	120	5	3.65	27
L	180	5	2.42	51.6
M	200	5	1.76	64.8

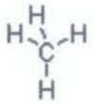
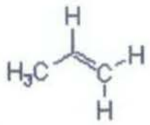
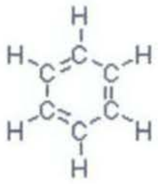
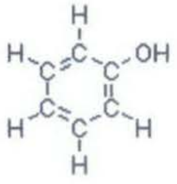
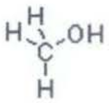
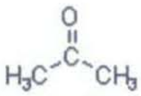
ETHYLNE CARBONATE

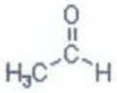
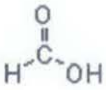
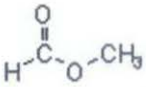
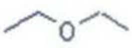
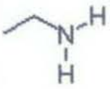
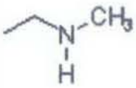
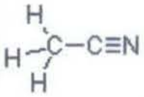
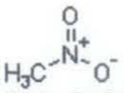
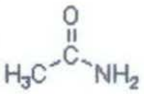
Sample	Time	Initial Solid Mass	Resiude Mass	%of yield
	0	**0**	**0**	**0**
N	60	5	4.08	18.4
I	120	5	2.53	49.4
O	180	5	1.23	75.4
P	200	5	0.75	85


Reaction Time Vs Residue Content (logarithmic scale)
Residue Content
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
11.4
27
51.6
59.4
Reaction Time
$y = 5.9402e^{-0.2752x}$
$R^2 = 0.9735$
$y = 7.4936e^{-0.5803x}$
$R^2 = 0.9934$
EC
EG
Expon. (EC)
Expon. (EG)

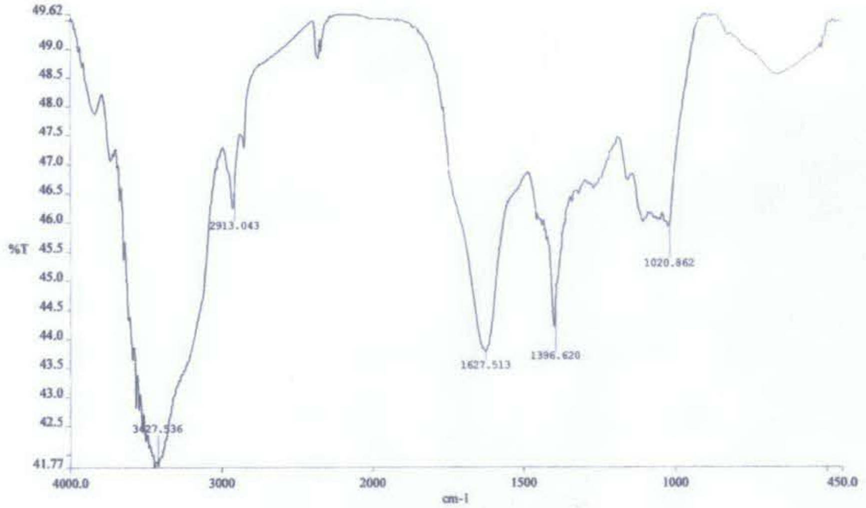
APPENDIX C

FTIR RANGE FOR RESIDUE CONTENT

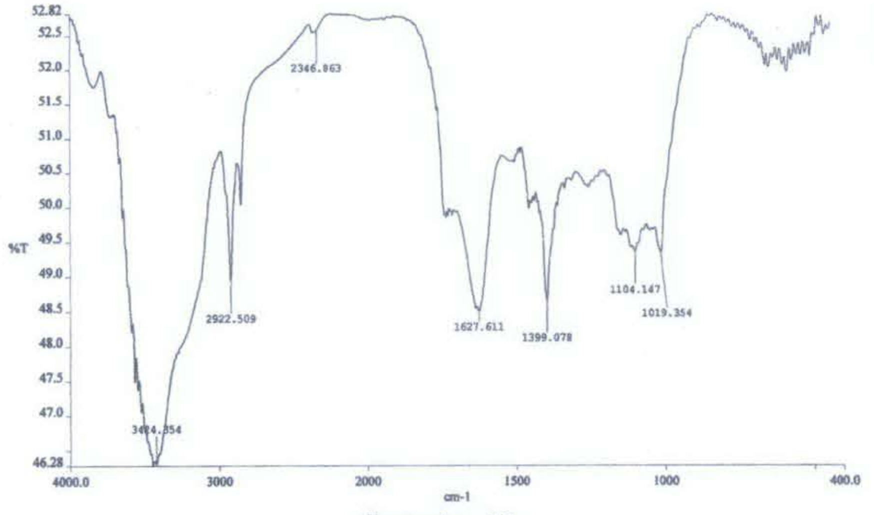
Functional Group Names **&** **Example Compounds**	**Absorption Ranges Frequency (cm^{-1})**	**Type of Vibration (causing IR absorption)**
Alkanes:  Methane	**3000-2800** (Note: The absorptions can be seen a several distinct peaks in this region.) **1500-1450**	C-H Stretch C-H Bend
Alkenes:  1-Propene	**3100-3000** **1675-1600**	=C-H Stretch C=C Stretch
Alkynes: $HC\equiv C-CH_3$ Propyne	**3300-3200** **2200-2100**	≡C—H Stretch C≡C Stretch
Aromatic Rings:  Benzene	**3100-3000** **1600-1580** **(1300-1000)**	=C-H Stretch C=C Stretch C=C Stretch
Alcohols, Phenols:  Phenol  Methanol (Alcohol)	**3600-3100** **(Note: Phenols MUST have Aromatic Ring Absorptions too.)** **1500-1450**	H-bonded O-H Stretch (C - O Stretch)
Ketones:  Acetone	**1750-1625**	C=O Stretch

Aldehydes:  Ethanal	**1750-1625** **2850-2800** **2750-2700**	C=O Stretch C-H Stretch off C=O C-H Stretch off C=O
Carboxylic Acids:  Formic Acid	**3400-2400** (Note: This peak always covers the entire region with a VERY BROAD peak.) **1730-1360**	H-bonded O-H Stretch C=O Stretch
Esters:  Methyl Formate	**1300-1000**	C - O Stretch
Ethers:  Diethyl Ether (aka-Ethyl Ether)	**(1300-1000)**	(C - O Stretch)
Amines: Primary  Ethylamine	**3500-3200** **(TWO PEAKS!)** **1640-1560**	N-H Stretch N-H Bend
Amines: Secondary  N-Methylethylamine	**3500-3200** **(ONE PEAK!)** **1550-1450**	N-H Stretch N-H Bend
Nitriles:  Methanenitrile	**2300-2200**	C≡N Stretch
Nitro Groups:  Nitromethane **(Note: Both peaks are < 200 cm^{-1} apart.)**	**1600-1500** **1400-1300**	N=O Stretch N=O Stretch
Amides:  Methanamide	**3500-3100** **1670-1600** **1640-1550**	N-H Stretch C=O Stretch N-H Bend

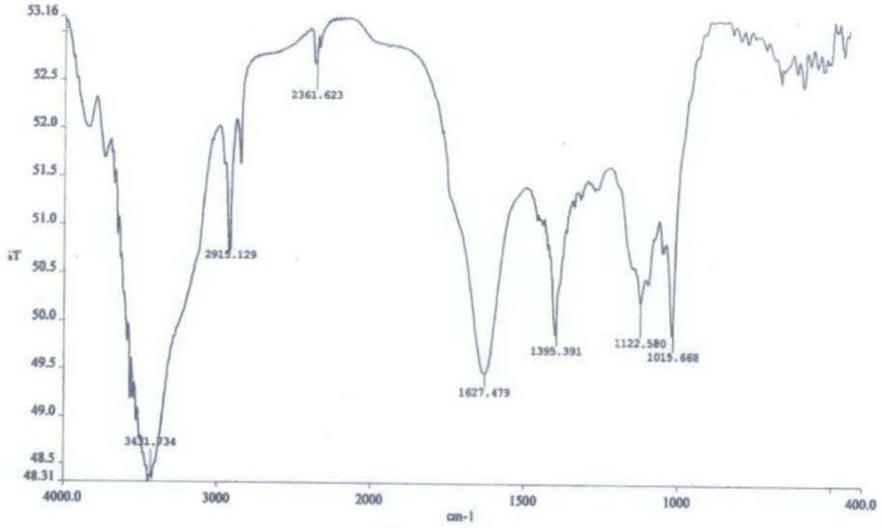
ETHYLENE CARBONATE



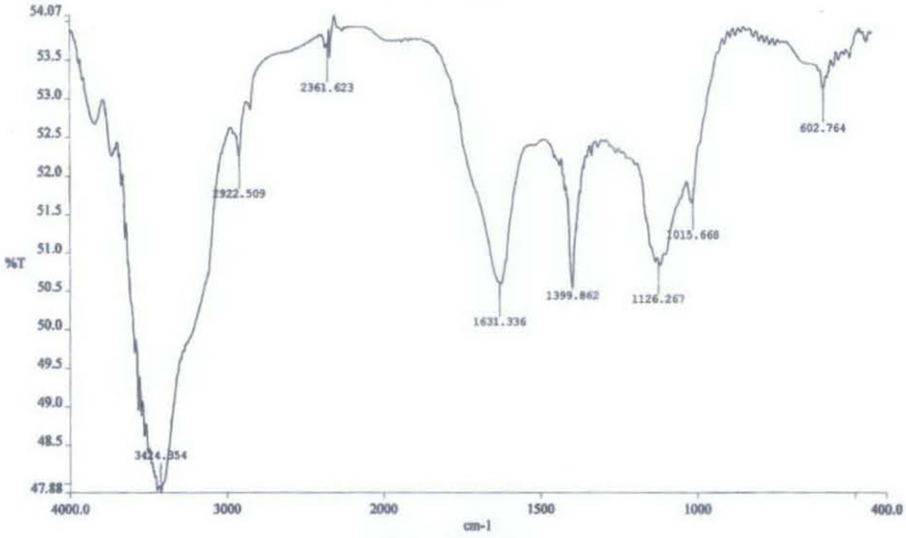
Sample : Raw Material



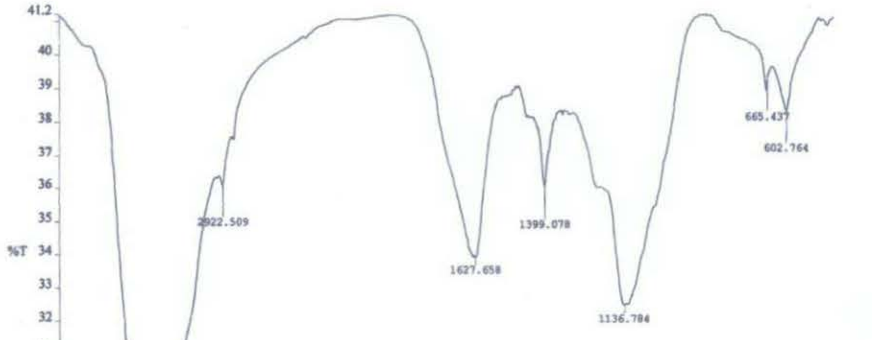
Sample : N



Sample : I

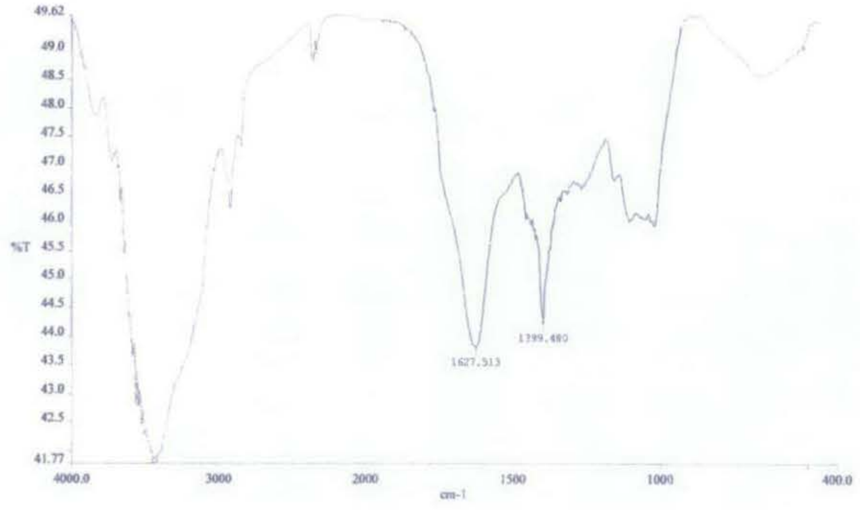


Sample : O

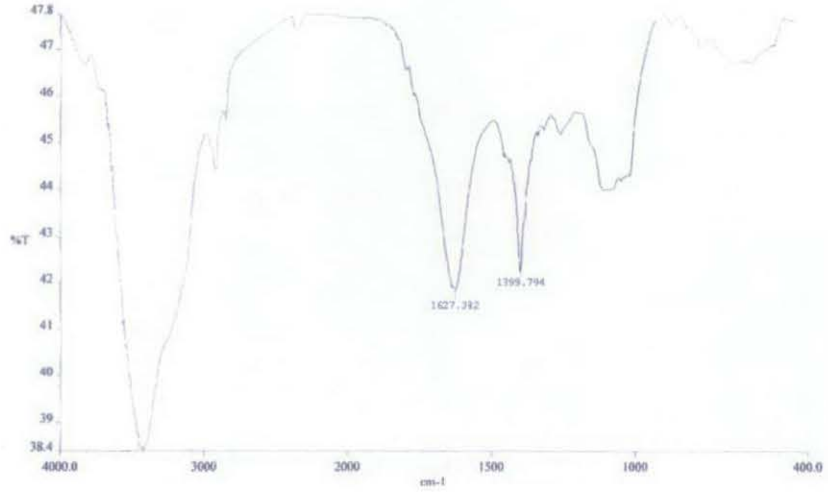


Sample : P

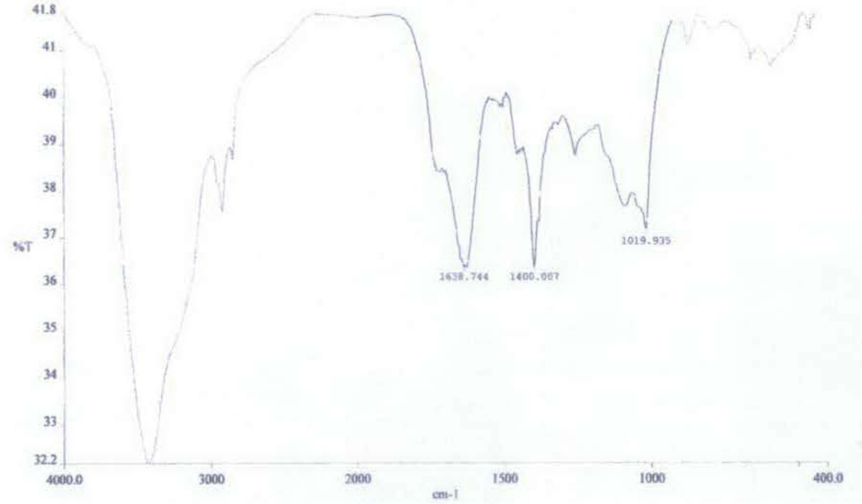
ETHYLENE GLYCOL



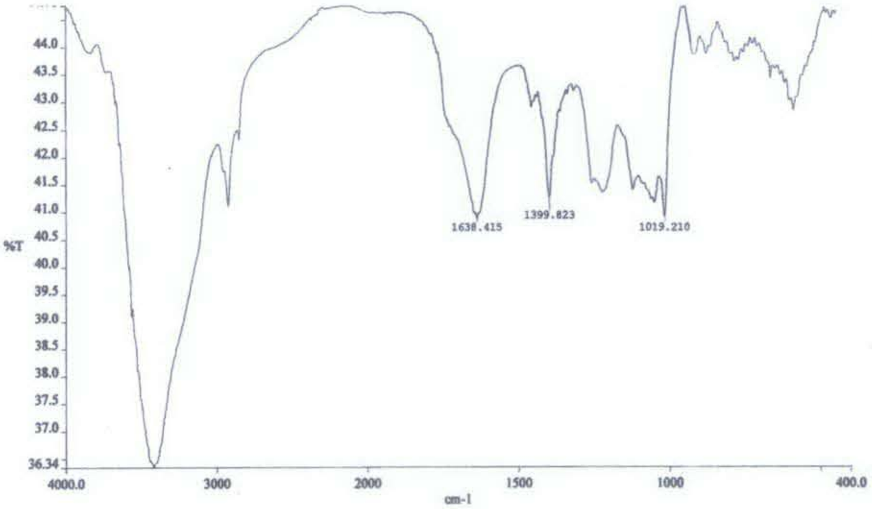
Sample : K



Sample : D



Sample : L



Sample : N

APPENDIX D

ANALYSIS RESULT FOR LIQUID PRODUCT

A. Density Measurements

Actual Sample	Mass (kg)	Volume (m3)	Density (kg/m3)
A	0.00089	0.0000012	1325.000
B	0.00273	0.00000285	1203.509
C	0.00148	0.0000017	1282.353
D	0.00032	0.0000004	1300.000
E	0.0013	0.0000016	1250.000
F	0.00398	0.000004	1170.000
G	0.00143	0.0000017	1252.941
H	0.00044	0.0000006	1233.333
I	0.00168	0.0000019	1252.632
J	0.00308	0.0000032	1181.250
K	0.00107	0.000001	1770.000
L	0.00489	0.0000047	1189.362
M	0.00149	0.0000017	1288.235
N	0.00213	0.0000023	1230.435
O	0.00514	0.0000052	1123.077
P	0.00522	0.0000055	1312.727

B. Viscosity Measurements

Actual Sample	Viscosity
A	34.50
B	31.50
C	39.00
D	27.80
E	43.50
F	33.00
G	30.90
H	26.70
I	36.00
J	26.20
K	30.80
L	27.80
M	30.80
N	33.80
O	29.30
P	32.20

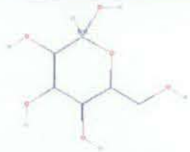
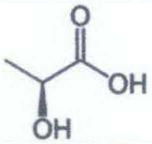
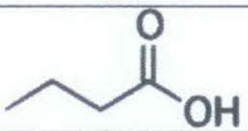
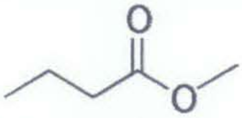
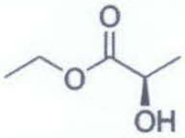
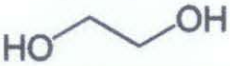
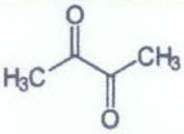
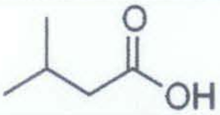
C. pH Measurements

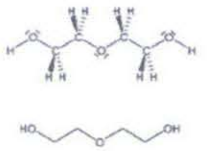
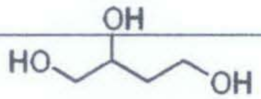
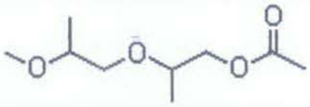
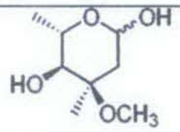
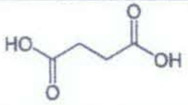
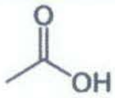
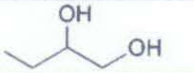
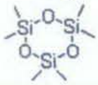
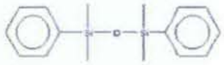
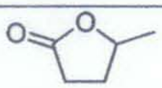
Sample	**Ph**
A	1.583
B	1.391
C	1.330
D	2.263
E	0.940
F	0.411
G	0.426
H	0.758
I	1.654
J	0.868
K	0.698
L	2.635
M	2.826
N	0.432
O	3.613
P	3.875

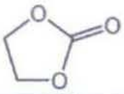
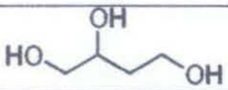
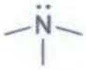
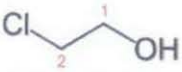
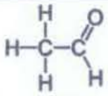
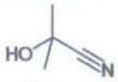
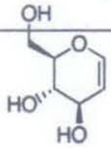
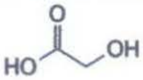
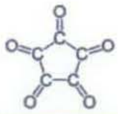
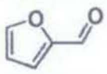
APPENDIX E

GC-MS ANALYSIS RESULT FOR LIQUID PRODUCT

A. Compounds found in GC-MS

No	Name of Compound	Molecular Formula	Molecular Weight	Molecular Sturcture
1	6-(hydroxymethyl)oxane-2,3,4,5-tetrol	$(C_6H_{10}O_5)_n$		
2	2-hydroxypropanoic acid (Lactic Acid)	$C_3H_6O_3$	90	
3	1-Propanecarboxylic acid (Butyric Acid)	$C_4H_8O_2$	88	
4	Methyl butanoate	$C_5H_{10}O_2$	102	
5	Ethyl (S)-2-hydroxypropanoate	$C_5H_{10}O_3$		
6	Methyl Vinyl Ether	C3H6O	58	**$H_3C\text{-}O\text{-}CH{=}CH_2$**
7	1,3-dioxolane	$C_3H_6O_2$	74	
8	Acetone	C_3H_6O	74	 
9	Ethylene Glycol	C2H6O2	62	
10	2,3-butanedione	$C_4H_6O_2$	86	
11	3-Methylbutanoic acid	$C_5H_{10}O_2$	102	

12	(2-hydroxyethoxy)ethan-2-ol (Diethylene glycol)	$C_4H_{10}O_3$	106	
13	Benzo[b]thiophene	C_8H_6S	134	
14	1,2,4-Butanetriol	$C_4H_{10}O_3$	106	
15	Dipropylene glycol methyl ether acetate	$C_9H_{18}O_4$	206	
16	4-Methoxy-4,6-dimethyl-tetrahydropyran-2,5-diol	$C_8H_{16}O_4$	176	
17	Dihydroxyacetone	C3H6O3	90	
18	Butanedioic acid (Succinic acid)	C4H6O4	118	
19	Acetic Acid	$C_2H_4O_2$	60	
20	methyl carbonate	$C_3H_6O_3$	90	
21	Butane-1,2-diol	$C_4H_{10}O_2$	90	
22	1,3,5-Trioxane	$C_3H_6O_3$	90	
23	Hexamethylcyclotrisiloxane	$C_6H_{18}O_3Si_3$	222	
24	1,1,3,3-Tetramethyl-1,3-diphenyldisiloxane	$C_{16}H_{22}OSi_2$	286	
25	5-Methyldihydrofuran-2(3H)-one (gamma-Valerolactone)	$C_5H_8O_2$	100	
26	2-fluoro-1-ethanol	C2H5FO	64	

27	Ethylene carbonate	$C_3H_4O_3$	88	
28	Butane-1,2,4-triol	$C_4H_{10}O_3$	106	
29	Trimethylamine	C_3H_9N	59	
30	2-Chloroethanol	C_2H_5ClO	80	
31	Acetaldehyde	C_2H_4O	44	
32	ethanethioic S-acid	C_2H_4OS	76	
33	Acetone cyanohydrin	C_4H_7NO	85	
34	2-(Hydroxymethyl)-3,4-dihydro-2H-pyran-3,4-diol (glucal)	$C_6H_{10}O_4$	146	
35	oxolane-2,5-dione	$C_4H_4O_3$	100	
36	dimethyl (E)-but-2-enedioate	$C_6H_8O_4$	144	
37	3,4-diethoxycyclobut-3-ene-1,2-dione	$C_8H_{10}O_4$	170	
38	glycolic acid,	$C_2H_4O_3$	81	
39	leuconic acid	C_5O_5	140	
40	1,3,2-dioxathiolane 2,2-dioxide	$C_2H_4O_4S$	124	
41	Furan-2-carbaldehyde	$C_5H_4O_2$	56	

B. Molecular Formula and Relative Content in Bio-Oil

NO	RT	Compound	Formula	Mw	A	B	C	D	E	G	H	I	J	K	L	M	N	O	P
1	1.08	Ammonia	H3N	17	-	-	-	-	-	-	-	-	-	2.96	-	-	-	-	-
2	1.11	5-Methyldihydrofuran-2(3H)-one (gamma-Valerolactone)	$C_5H_8O_2$	100	-	-	4.95	4.61	4.12	-	-	8.06	-	-	-	-	6.9	8.75	-
3	1.16	Carbon Dioxide	CO2	44	-	5.86	-	-	-	-	-	-	-	-	-	-	-	-	-
4	1.2	Sulfur Dioxide	SO2	64.1	-	-	-	-	-	-	-	-	-	-	18.6	22.79	-	-	-
5	1.216	Water	H2O	18	-	0.49	-	-	-	7.69	12.08	-	-	0.92	10.68	-	-	-	-
6	1.23	Methyl Vinyl Ether	C3H6O	104	-	-	12.64	12.9	-	28.26	-	-	30.05	-	-	-	0.16	-	-
7	1.25	Trimethylamine	C_3H_9N	59	56.93	-	-	-	7.49	-	-	-	-	-	-	-	-	-	-
8	1.26	glycolic acid,	$C_2H_4O_3$	81	-	2.43	-	-	-	-	-	-	-	-	-	-	-	-	14.28
9	1.36	Methylene Chloride	CH2Cl2	84.9	-	6.72	-	-	-	-	-	-	-	0.46	-	-	-	-	-
10	1.999	Butyric Acid	C4H8O2	60	-	0.07	0.05	-	-	-	0.42	0.15	1.91	0.87	37.19	44.09	-	1.34	62.87
11	2.33	Dihydroxyacetone	C3H6O3	90	-	-	-	-	-	-	0.05	0.5	-	-	-	-	-	0.29	-
12	2.384	Methyl butanoate	C5H10O2	118	7.76	-	2.49	-	10.16	5.42	-	4.75	10.5	0.02	-	-	-	-	-
13	2.51	1,5-Pentanediol	$C_5H_{12}O_2$	104		-		25.18						-	-	-	-	-	-
14	2.688	Ethyl (S)-2-hydroxypropanoate	C5H10O3	94	-	-	-	-	-	-	-	-	14.16	-	-	-	-	-	-
15	2.73	1,4-dioxane	C4H802	60	-	-	-	-	-	-	0.45	0.17	-	-	28.65	-	-	-	-
16	2.75	leuconic acid	C_5O_5	140											-	29.56	-	-	18.05
17	3.886	Lactic Acid	C4H8O3	90	0.3	-	-	0.66	-	-	-	-	1.74	0.07	-	-	0.66	-	-
18	4.017	Butanedioic acid (Succinic acid)	C4H6O4	118	-	-	0.44	-	-	-	0.06	-	-	-	-	-	-	0.29	-
19	4.55	2-fluoro-1-ethanol	C2H5FO	64	-	-	-	-	-	-	-	0.06	-	-	-	-	-	-	-
20	5.01	Furan-2-carbaldehyde	$C_5H_4O_2$	56	-	-	-	-	-	-	-	-	-	-	0.1	-	-	-	-
21	5.684	Acetone	$C_3H_6O_2$	74	-	-	-	-	-	0.8	0.06	-	1.98	0.03	-	-	-	-	-
22	5.71	2-Chloroethanol	C_2H_5ClO	80	-	-	-	-	2.41	-	-	-	-	-	-	-	-	-	-

23	6.16	Acetaldehyde	C_2H_4O	44	-	-	-	0.05	6.57	-	-	-	-	-	-	-	-	-	-
24	6.529	Acetic Acid	$C_2H_4O_2$	60	-	-	-	0.04	-	-	8.17	-	-	-	0.22	0.14	-	-	0.21
25	6.811	Ethylene Glycol	C2H6O2	62	1.92	84.35	79.42	56.18	31.06	0.19	24.55	82.85	3.98	93.76	0.1	0.31	92.24	34.33	3.54
26	7.01	ethanethioic S-acid	C_2H_4OS	76	-	-	-	-	12	-	-	-	-	-	-	-	-	-	-
27	7.248	methyl carbonate	$C_3H_6O_3$	90	-	-	-	-	-	-	32.04	-	-	-	-	-	-	47.49	-
28	7.466	Butane-1,2-diol	$C_4H_{10}O_2$	90	-	-	-	-	-	-	20.5	-	-	-	-	-	-	-	-
29	8.73	1,3,5-Trioxane	$C_3H_6O_3$	90	-	-	-	-	-	-	-	-	-	-	-	-	-	3.77	-
30	9.4	Ethylene carbonate	$C_3H_4O_3$	88	-	-	-	-	26.2	57.44	-	0.69	-	-	1.53	0.71	-	-	0.31
31	10.5	2,3-butanedione	$C_4H_6O_2$	86	-	-	-	-	-	-	0.04	-	0.37	-	-	-	-	-	-
32	11.35	Hexamethylcyclotrisiloxane	$C_6H_{18}O_3Si_3$	222	-	0.08	-	-	-	-	0.06	-	-	-	-	0.26	-	-	-
33	11.78	Butane-1,2,4-triol	$C_4H_{10}O_3$	106	0.73	-	-	0.2	-	-	-	2.46	-	0.9	-	-	0.05	3.61	-
34	12.169	3-Methylbutanoic acid	$C_5H_{10}O_2$	102	-	-	-	-	-	-	-	-	0.35	-	-	-	-	-	-
35	12.38	2-(Hydroxymethyl)-3,4-dihydro-2H-pyran-3,4-diol (glucal)	$C_6H_{10}O_4$	146	14.86	-	-	-	-	-	-	-	-	-	-	-	-	-	-
36	12.65	1,3,2-dioxathiolane 2,2-dioxide	$C_2H_4O_4S$	124	-	-	-	-	-	-	-	-	-	-	1.9	2.13	-	-	0.74
37	12.684	1,2,4-Butanetriol	$C_4H_{10}O_3$	106	5.24	-	-	-	-	-	-	-	0.24	-	-	-	-	-	-
38	13.236	1,4,7,10-tetraoxacyclododecane-2-methanol	C9H18O5	206	-	-	-	0.04	-	-	-	-	0.96	-	-	-	-	-	-
39	14.577	Tridecane	C13H28	184	3.46	-	-	-	-	-	-	-	6.91	-	-	-	-	-	-
40	14.867	Benzo[*b*]thiophene	C_8H_6S	134	0.92	-	-	-	-	-	-	-	0.75	-	-	-	-	-	-
41	16.25	dimethyl (E)-but-2-enedioate	$C_6H_8O_4$	144	-	-	-	0.04	-	-	-	-	-	-	-	-	-	-	-
42	17.967	(2-hydroxyethoxy)ethan-2-ol (Diethylene glycol)	$C_4H_{10}O_3$	106	5.66	-	-	-	-	-	1.4	-	21.5	-	-	-	-	-	-
43	20.35	3,4-diethoxycyclobut-3-ene-1,2-dione	$C_8H_{10}O_4$	170	-	-	-	0.04	-	-	-	-	-	-	-	-	-	-	-

44	20.285	Dipropylene glycol methyl ether acetate	$C_9H_{18}O_4$	206	-	-	-	-	-	-	-	-	0.53	-	-	-	-	-	-
45	22.25	oxolane-2,5-dione	$C_4H_4O_3$	100	-	-	-	-	-	0.21	-	-	-	-	-	-	-	-	-
46	23.386	2-[2-(ethenyloxy)ethoxy]-	C6H12O3	132	2.21	-	-	-	-	-	-	-	3.79	-	-	-	-	-	-
47	24.803	4-Methoxy-4,6-dimethyl-tetrahydropyran-2,5-diol	$C_8H_{16}O_4$	176	-	-	-	0.05	-	-	-		0.28	-	-	-	-	-	-
48	25.86	1,1,3,3-Tetramethyl-1,3-diphenyldisiloxane	$C_{16}H_{22}OSi_2$	286	-	-	-	-	-	-	0.13	-	-	0.03	-	-	-	-	-
					99.99	100	99.99	99.99	100	100	100	99.69	100	100	98.97	99.99	100	99.87	100