Investigation of Levoglucosan Production from Pyrolysed Rubber Seed Kernel

by

Ariff Shah Bin Ismail

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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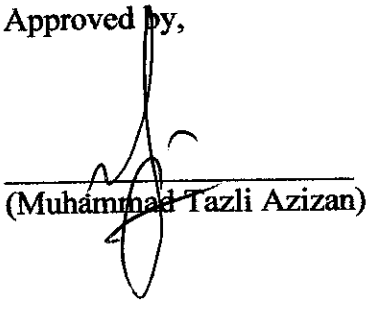
Approved by,



(Muhammad Tazli Azizan)

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TRONOH, PERAK

January 2009

CERTIFICATION OF ORIGINALITY

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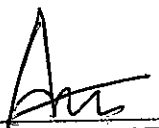

ARIFF SHAH BIN ISMAIL

ABSTRACT

The project objective is to investigate *Levoglucosan Content in Pyrolysed Rubber Seed Kernel*. The price of levoglucosan and other raw chemical components are increasing from time to time. This has put some pressure for the industry to find a way to control the price and ensuring continuous supply of the chemical. The reduction of crude oil price has provided us some space to control the chemical price. Before the crude oil price increase again, the industry must start looking the possibility of adding new resources of chemical, instead of crude oil. Levoglucosan is an expensive chemical. It is widely used in large scale polymer production likes resin, sealant, adhesive and coating and many more. Unfortunately, however, as presently available, pure levoglucosan is very expensive. Further, presently known processes for providing levoglucosan give levoglucosan in a form that is contaminated by impurities. The introduction of rubber seed kernel as new source of levoglucosan could control the price and increase the use of levoglucosan in manufacturing industry. The project scope includes the investigation of best operating condition for high levoglucosan yield. The rubber seed kernel will undergo pyrolysis process and yield bio-oil that contains levoglucosan. The experimental works proved that levoglucosan present in bio-oil (maximum yield is around 5%). The levoglucosan content is high whenever the sample size is 250 UM and the temperature is more than 300 °C. This dissertation summarizes works and research that had been done since the project started and propose methodologies to extract levoglucosan from pyrolysed rubber seed kernel.

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The author would like to take this opportunity to thank all parties involved in making the Final Year Research Project, a great educational session. Deepest gratitude to Allah the Almighty, for the wisdom and strength given in completing this Final Year Research Project, despite all the challenges and hardship experienced throughout this one year project. Heartfelt appreciation goes to Mr. Mohammad Tazli bin Azizan, Final Year Research Project Supervisor for the continuous support and guidance. The author would also like to thank the following fellows for their respective professionalism and contribution to the research:

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Biomass refers to living and recently dead biological material that can be used as fuel or for industrial production. Instead of common thought that the scope of biomass technology refers to plant matter grown to generate electricity or produce biofuel, the scope also extend to the plant or animal matter used for production of fibers, chemicals or heat. Another example of extension of biomass technology is utilization of biodegradable waste as fuel. It excludes organic material which has been transformed by geological processes into substances such as coal or petroleum. One seventh of total energy consumption is from biomass which is the main energy resource for over 1.5 billion people in the world. According to rough estimation by the researches, about 120 billion tons of biomass is formed each year by means of photosynthesis. This is five times the total present energy consumption in the world.

A lot of researches and developments had been made only in developing biomass as renewable energy. Biomass energy itself is the only one which has both the property of fossil fuel and characteristics which mean that it can be stored, renewed and transferred to useful thermal energy, electrical energy and fuel energy. The conversion of biomass using pyrolysis technologies to produce bio-char, bio-oils and gaseous products is one of the most promising alternatives under study nowadays to convert biomass into useful products and energy. (M. Garcia-Perez, 2006) Biochar is a charcoal produced from biomass that can store carbon. Meanwhile bio-oils are composed of water, organics and a small amount of ash. According to (D., 1999) bio-oil globally represented as approximately 20% water, 40% GC-detectable compounds, 15% non-volatile HPLC detectable compounds and around 15 mass% high molar mass non-detectable compounds.

China is relatively rich in biomass energy resources. Five billion tons of biomass can be produced in the whole country annually, among which 700 million tons of it is from the agricultural sector. In rural energy consumption in China, biomass energy takes up about 70%. In biomass conversion systems, each linkage can bring benefit to human beings. It has the characteristics of a good all round system. The cloths, food, residence and travel of human beings rely on it. Its waste material can be used as energy and the final residue can be returned to fields as humus, especially the photosynthesis of green plants can improve the worsening environment resulting from over-emitted carbon dioxide, which is the feature that other energy resources cannot reach. (Suzhen, 1994)

As the world keeps moving and the technology is developing rapidly, the agriculture development is left behind. Due to the concern, the developing countries are looking for technical measures that could be helpful for sustainable agriculture development, such as adopting multiple-level utilization technology of matter, realizing "no-waste production", improving resource using efficiency and reaching good circulation of agricultural ecology. Instead of only using biomass as the renewable energy resource, the author would like to extent the research to use the biomass as the chemical resources.

1.2 PROBLEM STATEMENT

Chemical raw materials nowadays have become important commodity in the global market. This industry is well known tightly depended on the oil and gas market. As the crude price was soaring from day to day once upon a time ago, the chemical raw materials prices also experience the same trend. Fortunately, the price of crude has decrease recently. The ample time before the crude oil hit up again must be used wisely. The key point to control the chemical industry is by ensuring availability of the chemical in large amounts and at acceptable prices. Definitely the chemical have to be produced in a simple and low cost process. Besides that, the adverse effect on the environment should be considered as the top priority. If the industry can ensure that the production processes could be versatile and modifiable

according to various circumstances, the direct effect of oil and gas market on the industry could be reduced.

Levoglucosan is only one of the expensive biochemical. The price of levoglucosan is around RM165 per gram, which is very high. The interesting part on levoglucosan research is, the price (even though is high) is maintained for such a long time. This is a result of instable demand on the levoglucosan. According to (Balodis, 2004), the demand is unstable due to the expensive price of levoglucosan. Thus, there is a lot of opportunity in levoglucosan. The author acknowledges that very few research projects that had been done to extract the biochemical from biomass components especially in Malaysia. If anybody could just find another source of levoglucosan and optimize the operating condition to produce high yield of levoglucosan, the demand will be stable and hence the price may be higher. Malaysia is well known as one of the biggest natural rubber supplier. Hence, a lot of big scale rubber plants could be found in Malaysia. In 2007, the total planted rubber plant in Malaysia was 1229.74 million hectares. The author sees possibility of using rubber seed that is available in Malaysia in a huge quantity as the raw material for the project.

1.2.1 Significant of Project

The agriculture sectors all over the world provide large quantities of biomass residue. The biomass residue if not been utilized and converted to valuable products will be waste crops and might cause pollutions to the environment. The rubber seed kernel is plenty in amount and locally available. Thus, the study on the extraction of levoglucosan from pyrolysed rubber seed kernel is necessary to see the potential of using rubber seed kernel as agriculture-base chemical. If the rubber seed kernel could produce levoglucosan, several key-questions must be answered through further research and study. What are the best operating conditions that produce high yield of levoglucosan? What is the best way to extract levoglucosan from bio-char and bio-oil? The study gives thorough understanding on the effects of particle size, heating rate and pyrolysis temperature on the yield of fuel oil

produced from biomass under study. The findings reveal the potential of the abundant agriculture-based material as the agriculture base chemical.

1.3 OBJECTIVES

- To identify the existence of Levoglucosan in rubber seed kernel.
- To investigate and adjust the parameters of pyrolysed rubber seeds kernel to obtain high yield of levoglucosan.
- Pre-develop the experimental setup to extract the levoglucosan from bio-oil

1.4 SCOPE OF STUDIES

- Study on the chemistry and nature of levoglucosan and its industrial applications.
- Study on rubber seed kernel, the availability in the local market.
- Study on the concept, principle and parameters of pyrolysis process and possibility of applying the process on rubber seed kernel.

1.5 RELEVENCY OF PROJECT

Present chemical used in the industry is largely dependent on crude oil, which has limited the future sustainable development. The future availability of crude oil is uncertain. A pure speculation on crude oil in the market could have major impact on the chemical price. Therefore, the chemical industry is instable. This project is a platform of revealing option of chemical sources. The prospect of extracting chemical in substantial quantities from agriculture residues is now arousing interest world wide stimulated by increasing concern over the environmental consequences of conventional fossil and nuclear fuel use. The study on potential use of rubber seed kernel as raw material for levoglucosan is a significant milestone to produce agro-based chemical.

1.6 FEASIBILITY OF THE PROJECT WITHIN THE SCOPE AND TIME FRAME

The duration set for the project is 32 weeks. The time constrain always become a major limitation in reaching the goal of the project. However, the author believed that with proper planning and smart time management, the objectives of the project could be achieved. Besides that, the semester break had been used to conduct the experiment and more research. The effort is worthy as the objectives were achieved within the time frame.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 PYROLYSIS

Pyrolysis is a thermochemical conversion of biomass in the absence of oxygen that produces three main products. The products are bio-oil (liquid), bio-char (solid) and gas. It is a popular process of converting woody biomass into fuel and extractable chemical product. Pyrolysis and gasification, both are option for recovering valuable product from biomass and agriculture residue. Gasification is the breakdown of hydrocarbons into a syngas by carefully controlling the amount of oxygen present such as the conversion of coal into town gas. The main benefits of the pyrolysis process compared to combustion and gasification is that a liquid fuel is easier to transport then either solid or gaseous fuel. This factor is important in determining the location of the pyrolysis plant. The pyrolysis process can involve a range of different processes, including bubbling fluidised bed, rotating cone reactor and mechanical or centrifugal ablative process. (Winsley, 2007) It involves trade-offs between the production of bio-char and gas. The process can be calibrated to maximise the output of different products, depending on economic factors.

Table 1: Typical Product Yield (dry wood basis)

Mode	Conditions	Bio-oil	Biochar	Gas
Fast	Moderate temperatures (500°C) for 1 second	75%	12%	13%
Intermediate	Moderate temperatures (500°C) for 10–20 seconds	50%	20%	30%
Slow (carbonisation)	Low temperature, (400°C), very long solids residence time	30%	35%	35%
Gasification	High temperature, 800°C, long vapour residency time	5%	10%	85%

Source: International Energy Agency (2007)

Pyrolysis of lignocellulosic materials is complex since their major constituents, namely cellulose, hemicellulose and lignin, show different reactivities.

(P. R. Bonelli, 2000) The pyrolysed material properties are very much depending on temperature and overall conversion level as different reactions associated to thermal decomposition of each constituent occur. Interactions between constituents and minute amounts of mineral matter naturally present in whole biomass samples, that catalyze numerous reactions taking place during pyrolysis (Antal Jr, 1995) and (Caballero et al., 1997), introduce additional factors of complexity, making it difficult to achieve a generalized knowledge of pyrolysis of any lignocellulosic material.

2.1.1 Bio-oil and Bio-char

The yield of products from pyrolysis varies heavily with temperature. The lower the temperature, the more char is created per unit biomass. (Winsley, 2007) Pyrolysis is classified into two categories which are fast pyrolysis and slow pyrolysis. Most commonly, fast pyrolysis take few seconds and yields 60% bio-oil, 20% biochar, and 20% syngas. Meanwhile, slow pyrolysis can be optimized to produce substantially more char (~50%), but takes several hours to complete. For typical inputs, the energy required to run a "fast" pyrolyzer is approximately 15% of the energy that it outputs. (Laird, 2008) Modern pyrolysis plants can be run entirely off of the syngas created by the pyrolysis process and thus output 3-9 times the amount of energy required to run. The experimentation of bio-char and bio-oil typically had been on wood because of its consistency as material and its low ash content. (Winsley, 2007)

The liquid product produced through the operation of fast pyrolysis always in the form of aerosols rather than a true vapour. This has become a great challenge to the operation of fast pyrolysis. Quenching, that is the contact with a cooled liquid is effective with a careful design and temperature control to avoid blockage from differential condensation. ((Dilla, 2006)

Safety is an important consideration in any large scale production. At the present, there has not been any clear case and claim that shows that pyrolysis

process could cause any harm. However, according to (Diebold, 1999), there had been found a limited degree of mutagenecity and teratogenicity from the fast pyrolysis liquid. It is claimed that the effects depend on the chemical composition and dosage of the pyrolysed liquid. The bad effect (if it is persist) could be avoided by using protective gloves, clothing and safety glasses.

The bio-oil or pyrolysis oil is used as a fuel, after removal of valuable bio-chemicals that can be used as food additives or pharmaceuticals. It has only 42% of the energy content of fuel oil on a weight basis and 61% on a volumetric basis. (Winsley, 2007) Bio-oil contains organic acids which are corrosive to steel containers, has a high water vapor content which is detrimental to ignition, and contains some biochar in the liquid which can block injectors. (Yaman, 2003) The bio-oil cannot be used directly in most car engines. The produced oil is composed of a very complex mixture of oxygenated hydrocarbons, and like crude fossil oil can be used in refining to produce a range of chemicals, fuels and fertilizers. The present of water in bio-oil lowers its heating value but improves its flow characteristic, which is beneficial for combustion (pumping and atomisation). The emission of nitrous oxide also could be reduced. Bio-oil can be used as a basis for higher-value extract and by products such as acetic acid, resins, food flavouring, agrichemicals, fertilisers and emission-control agents.

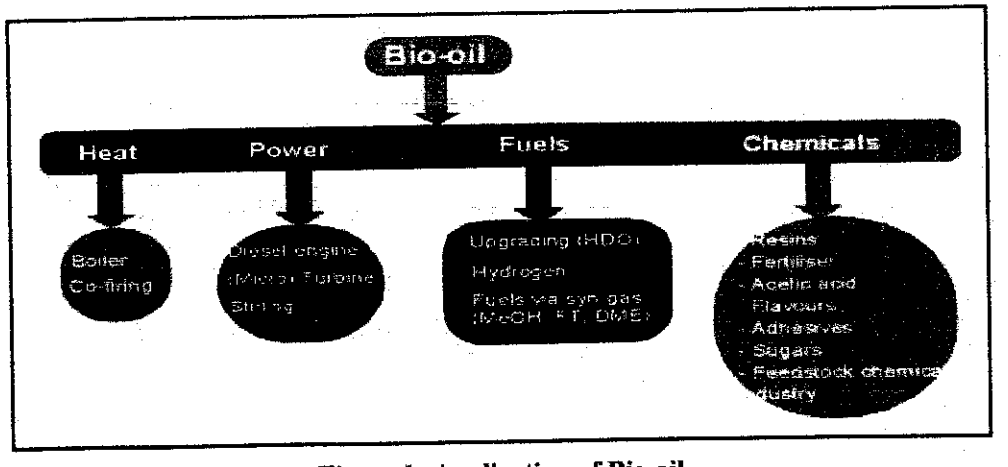


Figure 1: Application of Bio-oil

Biochar can be used as a soil amendment to increase plant growth yield. Besides that biochar could improve water quality, reduce soil emissions of GHGs, reduce leaching of nutrients, reduce soil acidity, and reduce irrigation and fertilizer requirements. The key factors to biochar properties are very dependent on regional conditions including soil type, condition (depleted or healthy), temperature, and humidity. Study found that appropriate additions of biochar to soil could reduce N2O emissions by up to 80% and completely suppress methane emissions If biochar is used for the production of energy rather than as a soil amendment, it can be directly substituted for any application that uses coal. Pyrolysis also may be the most cost-effective way of producing electrical energy from biomaterial. (Bridgwater, 2003)

2.1.2 Pyrolysis System

Currently, most research is focusing on maximizing the yield of liquid product as opposed to char. The liquid pyrolytic product can be easily stored and transported, readily upgraded and refined to produce high quality fuels and may contain chemicals in economically recoverable amounts (Karaosmanoglu et al., 1999). There are three primary methods for deploying a pyrolysis system.

1. Built a centralized system where all biomass in the region would be brought to a pyrolysis plant for processing.
2. Use a lower-tech pyrolysis kiln for small scale plantation.
3. Use a mobile system where a truck equipped with a pyrolyzer would be driven around to pyrolyze biomass. It would be powered using the syngas stream, return the biochar to the earth, and transport the bio-oil to a refinery or storage site.

The selection of pyrolysis system must be based on technical and economical feasibility. The cost of transportation of the liquid and solid by-products, the amount of material to be processed in a region, and the ability to feed directly

into the power grid are all factors to be considered when deciding on a specific implementation.

2.2 *RUBBER SEED AS RAW MATERIAL*

Table 2: Rubber Plantation in Malaysia

Year	Peninsular Malaysia		P. Malaysia Total	Sabah		Sarawak		Sabah & Sarawak Total	Malaysia Total		Grand Total
	Estates	Smallholdings		Estates	Smallholdings	Estates	Smallholdings		Estates	Smallholdings	
1998	175.60	1,107.51	1,283.11	4.10	85.90	0.22	170.29	260.51	179.92	1,363.70	1,543.62
1999	147.72	1,064.64	1,212.36	3.21	85.01	0.22	163.95	252.39	151.15	1,313.60	1,464.75
2000	121.16	1,063.79	1,184.95	2.40	85.01	0.22	158.10	245.73	123.78	1,306.90	1,430.68
2001	93.64	1,058.78	1,152.42	1.88	85.16	0.00	149.86	236.90	95.52	1,293.80	1,389.32
2002	84.28	1,054.86	1,139.14	0.53	62.89	0.00	146.25	209.67	84.81	1,264.00	1,348.81
2003	77.93	1,027.06	1,094.99	0.53	63.89	0.00	145.55	209.97	78.46	1,236.35	1,314.81
2004	64.22	993.11	1,057.33	0.20	64.57	0.00	145.90	220.67	64.42	1,203.58	1,268.00
2005	57.17	991.81	1,048.98	0.20	65.28	0.00	144.65	210.13	57.37	1,201.74	1,259.11
2006	54.04	988.55	1,042.59	0.11	65.28	0.00	143.14	208.53	54.15	1,196.97	1,251.12
2007	53.25	968.18	1,021.43	0.09	65.28	0.00	143.14	208.51	53.34	1,176.60	1,229.94

Table 1 showed the planted hectare of Natural Rubber in Malaysia. The table can be divided into two parts which are estate and smallholdings plant. In 2007, total rubber plantation was 1.229 mil. Hectare. It is estimated that each hectare could produce 800 kg – 1200 kg of rubber seed per year. In number, Malaysia has 1.229 mil tonnes of rubber seed per year. Each rubber seed could yield 42 wt% of bio-oil (Ramadhas, 2005) Therefore, there is a huge amount of resources available for this project.

Figure 2: Rubber Seed Kernel

Figure 3: Rubber Seed (inside)

A seed is a small embryonic plant enclosed in a covering called the seed coat, usually with some stored food. 50% – 60% of rubber seed is its part called kernel. Kernel is the outer shell of the seed that contain 40% - 50% brown oil. Rubber seeds are

ellipsoidal, variable in size, 2.5–3 cm long, mottled brown, lustrous, weighing 2–4 g each. The kernel and seed could be separated by breaking the capsules. Recently, there was a finding that the rubber seed could produce biodiesel oil. The Star on 6th January 2008 reported the success of a lecturer from Universiti Teknologi PETRONAS, Mr. Tazli Azizan to conduct in-situ transesterification process to produce biodiesel from rubber seeds.

2.3 CHEMISTRY OF LEVOGLUCOSAN

Necessity of developing alternative sources of energy and chemical feedstock is gaining renewed interests in pyrolytic conversion of biomass, especially cellulosic materials. (Joong Kwon, 2007) An important aspect of cellulose pyrolysis is the formation of 1,6-anhydro-b-D-glucopyranoside (levoglucosan, LG), presumably as primary degradation product. (Joong Kwon, 2007) Levoglucosan is used in various fields of chemistry and engineering, such as pyrolysis and fire-retardants research, organic synthesis, biofuel research, biology, and as a biomass burning tracer in sediment analysis for the paleorecord.

The chemistry of 1,6-β-D-anhydroglucopyranose (levoglucosan) has long been known and its multiple reaction possibilities have been well examined. (Stanek, 1977) It is a product of cellulose combustion. As the cellulose is heated at high temperature (more than 300degC), it will undergo various pyrolytic processes. Then, a combustible solid called char will be formed and it contains high concentration of levoglucosan. However, massive industrial utilisation of this product was not realised because there is no simple production means in a larger scale.

Due to the presence of 1, 6-anhydrorings capable of breaking and three secondary hydroxyl groups, LG can be used for the synthesis of different low and high-molecular compounds. The introduction of levoglucosan into polyesters could improve the number of operation characteristics such as heat stability and rigidity; to extend the source of raw material for polyatomic alcohols; to reduce the expenditure of food-stuffs i.e. glycerol and xylitol.

2.4 PAST RESEARCH ON LEVOGLUCOSAN

2.4.1 Rapid cooling, continuous-feed pyrolyzer for biomass processing Preparation of levoglucosan from cellulose and starch

Joong Kwon (2007) suggested the use of special type continuous pyrolyzer for biomass processing. The pyrolyzer was developed for efficient collection of primary degradation product from biomass. Besides chemical and enzymatic conversion of cellulose into glucose, the pyrolytic process has been pursued for commercial-scale production of fuel and chemicals. (D.S. Scott, 1984) Many studied were been reported, giving levoglucosan yield of 30-60% from pure cellulose. Unfortunately, the ability to obtain high yield of levoglucosan were obtained only in small-scale, batch type process. To fulfil the market need, the process must be continuous and efficient process. According to (Joong Kwon, 2007), conventional methods of pyrolysis of solid materials employed heating of the material from the bottom, or introducing the material to a uniformly heated area. These methods when applied to cellulose pyrolysis will lead to levoglucosan's secondary decomposition. (Joong Kwon, 2007) claimed that the continuous pyrolyzer provides capabilities of continuous feed and scaling up for practical processes.

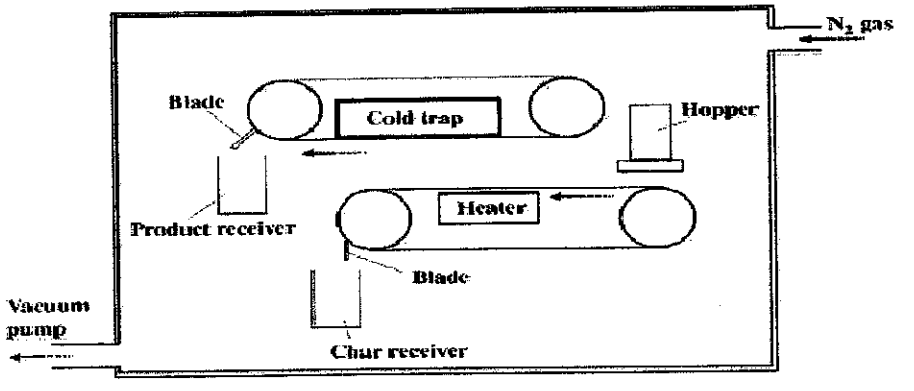


Figure 4: Schematic Design of Continuous - Feed Pyrolyzer

The team had conducted experiments using cellulose (430°C) and corn starch (410°C). It was learnt from their previous research that higher temperature from this (for respected cellulose and corn starch) will lead to lower yield of syrups. Using the invented pyrolyzer, they managed to obtain 80% to 99% bio-oil for cellulose and 90% to 99% bio-char. The chromatography test was conducted and the result was shown in figure 5. The interesting finding was at t = 5.8 min, levoglucosan appeared to be the major component of pyrolyzates.

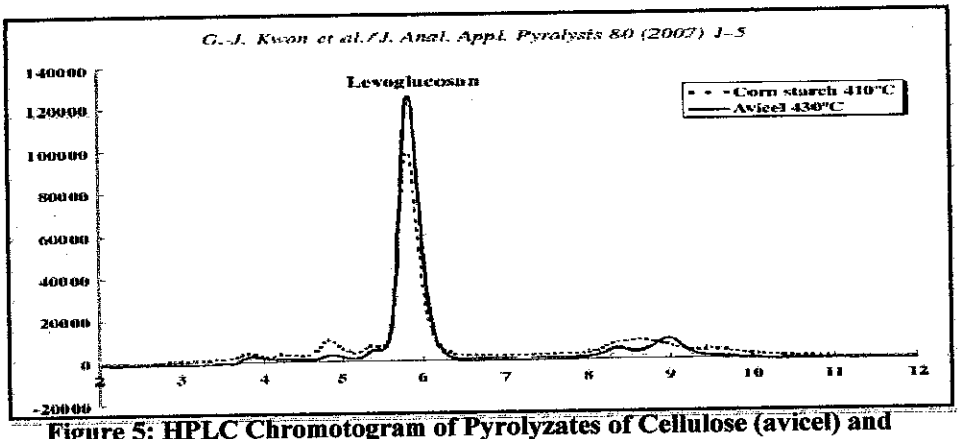


Figure 5: HPLC Chromotogram of Pyrolyzates of Cellulose (avicel) and Corn Starch at 5 kPa

The relation of bio-oil yield and pyrolysis temperature and residual pressure was showed in Fig. 4. The highest bio-oil yield for cellulose was 96% and was achieved at 1 kPa and 430°C. Meanwhile for starch, the highest bio-oil yield was 87% and was achieved at 5 kPa and 430°C.

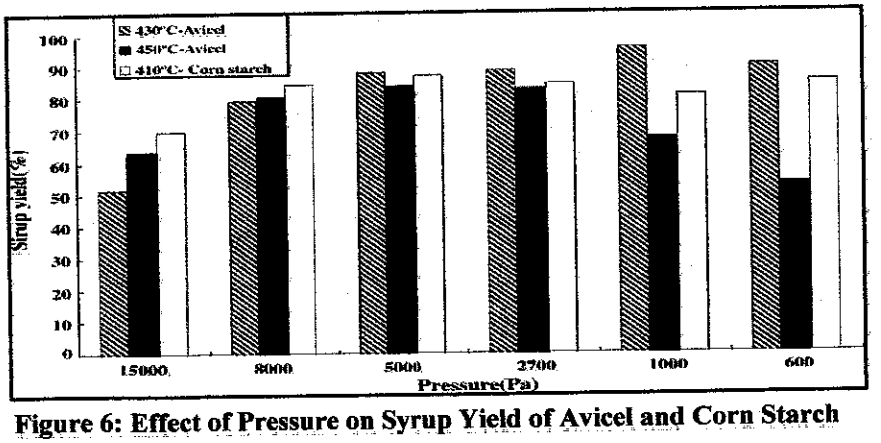


Figure 6: Effect of Pressure on Syrup Yield of Avicel and Corn Starch

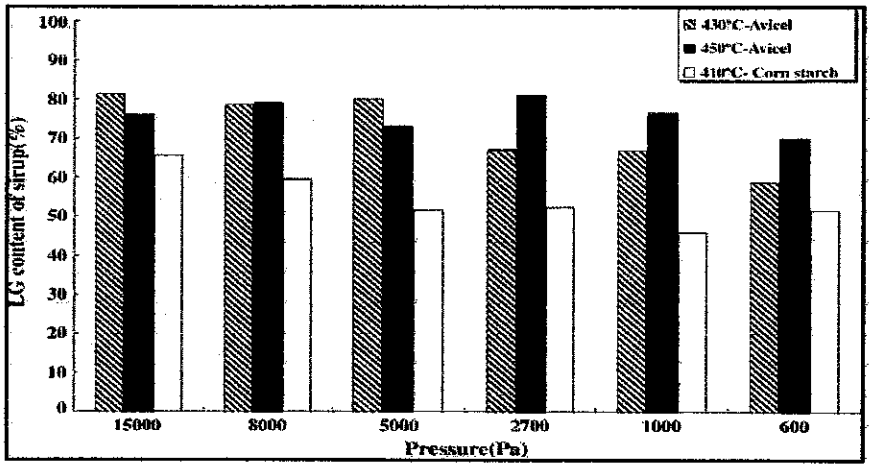


Figure 7: Effect of Pressure on Levoglucosan Content of Avicel and Corn Starchtent of Avicel and Corn Starch

Fig. 5 shows the levoglucosan content of bio-oil from cellulose and corn starch for varied pressure. The value ranged 59–81% for cellulose, and 46–66% for corn starch. The highest values were around 80% for Avicel at 2700–15,000 Pa. Multiplying the values in Figs. 4 and 5 we obtain the levoglucosan yield of 40–70% of the cellulose and corn starch. This was clearly shown in Figure 6.

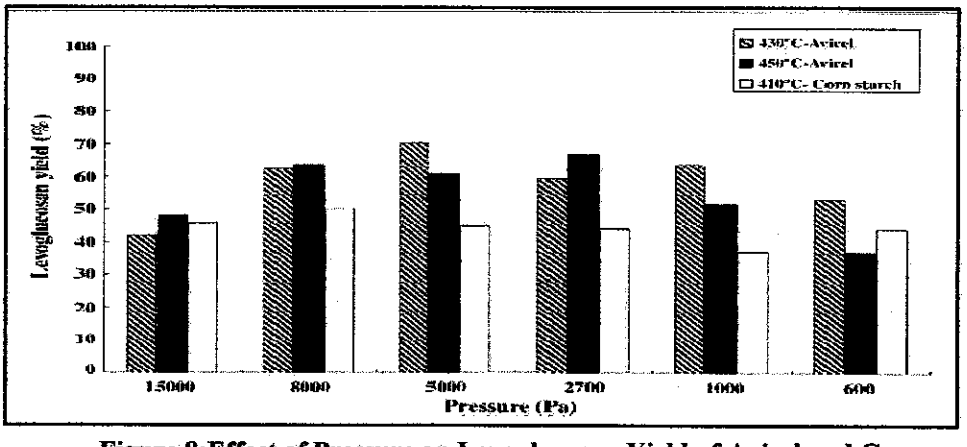


Figure 8:Effect of Pressure on Levoglucosan Yield of Avicel and Corn Starch

(Joong Kwon, 2007) claimed that they managed to obtain the highest ever achieved of levoglucosan yield. The highest value was 70.1%, for cellulose (430 8C, 5 kPa) well exceeds 58% reported by (F. Shafizadeh, 1979) and 61% by Essig (1989).

CHAPTER 3

ECONOMIC POTENTIAL ANALYSIS

3.1 REPRESENTATIVE OF BIO-BASED PRODUCT OPPORTUNITIES

Table 3: Bio-based Product Opportunities

BIOBASED PRODUCT	CLASSIFICATIONS	MARKET OPPORTUNITY	MARKET SIZE
Bio-oil, whole or residual	Liquid Fuel	Pyrolytic bio-oil has been used commercially for industrial heat since the early 1990's,[3] has been successfully tested as a boiler fuel,[2] and is being tested as fuel for diesel transportation and stationary turbine and diesel power.[3]	
Various extracted chemicals	Resins	Petroleum derived phenol-formaldehyde resin is used in plywood, oriented strand board, and other wood composites. Resin from pyrolysis bio-oils could replace up to 50 percent of the phenol-formaldehyde. Ensyn has developed several natural resin products that are produced from bio-oil.[3]	3.9 billion pounds per year at $0.30 per pound[4]
Various extracted chemicals	Food Additives	Extracted additives impart "smoked", "roasted" and "grilled" flavors to food products. Commercialization by Red Arrow Food Products Company of Wisconsin (www.redarrowusa.com) using bio-oil from the Ensyn fast pyrolysis process.[3]	Specialty market
Levoglucosan	Polymers, Pharmaceuticals, Pesticides, Surfactants	Levoglucosan is considered a potential building block for synthesis of polymers, pharmaceuticals, pesticides, and surfactants.[5] Microorganisms have been identified that can ferment levoglucosan to citric acid and itaconic acid.[5]	Large

Table 5 is cited from www.wisbiorefine.org (retrieved on 28/04/2009). Levoglucosan is considered as a potential building block for synthesis of polymers, pharmaceuticals, pesticides and surfactants. (Brown, 2003) According to (Sturlz, 2004), after removing the value added chemical i.e. levoglucosan, the residual bio-heating values are reported to be approximately the same or slightly higher. Therefore, extracting levoglucosan from rubber seed oil will not diminish other potential use of rubber seed oil.

3.2 RUBBER SEED OIL

Rubber seed kernel contains 42 wt% of bio-oil, which is semi drying type oil. Normally, the produced oil is yellow in color but it vary according to freshness of the rubber seed. According to (Ramadhas, 2005), at present, rubber seed oil has not found any major application and hence the natural production of seeds remain underutilized. Therefore, he had started extensive research in the potential used of rubber seed oil as fuel in the compression ignition engines. Complete characterization on physical and chemical properties of rubber seed oil was discovered and cited below in page xx;

3.3 INDUSTRIAL APPLICATION OF RUBBER SEED OIL

Studies on practical utilization of rubber seed oil revealed that it has strong potential to substitute linseed oil in alkyd production. (A Coomarasamy, 1975) Besides that, rubber seed oil was used as soap. According to (Gandhi, 1990), rubber seed oil does not contain any unusual fatty acid it was a rich source of essential fatty acid. Its digestability was found to be 97% compared to 94%. Therefore, the rubber seed oil could be considered for edible use. Another important use of rubber seed oil is in alkyd resins, which are used in large amounts in paint manufacturing. Others applications;

- Leather industry
- Preparation of grease
- Fuel for diesel engines
- Pharmaceutical industry
- Polymer industry i.e. adhesive, fire retardant

3.4 LEVOGLUCOSAN ECONOMIC ANALYSIS

According to literature review on rubber plantation, Malaysia has 1.229 mil. Hectare of rubber plantation in 2007. It is estimated that each hectare could produce 1000 kg of rubber seed per year. Each gram of rubber seed kernel could produce 42 wt% rubber seed oil. Based on the experimental works, the levoglucosan content in bio-oil (in lab scale pyrolysis setup) could reach up to 8 wt%. The levoglucosan price in local market is RM 165.00 per gram. Assuming the real price without considering packing and shipping price is 0.5 x RM165.00, the real price is RM82.50. The economic potential (EP1) for 100 g of levoglucosan is shown below;

EP1 = 100 g x RM82.50 – 100 x 1/0.42 x 1/0.08 x RM3 per 1000 g

= RM8, 241 profit per 100 g

For 1kg, the profit will be RM82, 410

CHAPTER 4

METHODOLOGY

4.1 PREPARATION OF RAW MATERIAL

1. Rubber seed kernel (RSK) was collected and stored in the lab.
2. Then, RSK was washed to separate the sample from physical impurities and volatile component.
3. The sample was heated inside at a temperature of 110°C for 12 hour to remove water content inside the sample and weighted regularly to determine the moisture content of the sample after being heated for few hours. The temperature of drying process is control in the range of 110°C to 120°C to avoid damaging the sample.
4. Step 3 was repeated until the weight of the sample is constant. If the weight is not constant after 12 hours, the sample had to continue undergone the drying process. This was done in order to make sure all the moisture content was dried out.
5. Samples were blended and sieved using sieve shaker ranging from 125μm to 1mm and screened into fraction.
6. The various particle sizes of RSK was grouped into 3 groups.
7. RSK was stored in air tight containers such as desiccators to maintain low moisture content of the samples.

Figure 9: Dried Rubber Seed Kernel

Figure 10: : Meshed Rubber Seed Kernel

4.2 EXPERIMENTAL PROCEDURE USING FBAU

4.2.1: Study the effect of temperature on the product yield

1. 250μm sample was weighted 50 g.
2. Reactor outlet tube was untied to place in the sample from the bottom.
3. Sample was positioned in the middle of the tube where the heated coil was located to ensure a complete and homogeneous burning.
4. The reactor outlet tube opening was closed tightly to ensure no gas or liquid will be released from the reactor.
5. Fixed Bed Activation Unit power supply is switch on.
6. Nitrogen gas cylinder was connected to the nitrogen gas inlet of Fixed Bed Activation Unit.
7. Valve 1 and valve 5 green buttons were switch on indicating that these valve are opened.
8. Valve 2, 3 and valve 4 on the panel remain closed by switching off the buttons.
9. Nitrogen gas flow was controlled at 0.1 ml/min by using flow meter controller attached to the panel.
10. Once the nitrogen flow was stable, the reaction temperature was set to 300°C.
11. Step 11 was repeated with temperature of 400°C, 500°C and 600°C.
12. Once the reaction has reached it desired reaction time, the sample was pinched down to room temperature. The cooling process takes about 12 hours.
13. After the temperature has cooled down, the reactor outlet tube was untied and the liquid in the reactor was collected in a beaker which will be transfer to the COD bottle for storage.
14. The ash produced from the pyrolysis process was weighted to determine the weight loss of the sample.
15. Finally the levoglucosan concentration in each product samples was tested in GC-MS. The data was recorded.

4.2.2: Study the effect of sample size on the product yield

1. 250μm sample was weighted 50 g.
2. Reactor outlet tube was untied to place in the sample from the bottom.
3. Sample was positioned in the middle of the tube where the heated coil was located to ensure a complete and homogeneous burning.
4. The reactor outlet tube opening was closed tightly to ensure no gas or liquid will be released from the reactor.
5. Fixed Bed Activation Unit power supply is switch on.
6. Nitrogen gas cylinder was connected to the nitrogen gas inlet of Fixed Bed Activation Unit.
7. Valve 1 and valve 5 green buttons were switch on indicating that these valve are opened.
8. Valve 2, 3 and valve 4 on the panel remain closed by switching off the buttons.
9. Nitrogen gas flow was controlled at 0.1 ml/min by using flow meter controller attached to the panel.
10. Once the nitrogen flow was stable, the reaction temperature was set to 300°C.
11. Step 11 was repeated with sample size of 500 μm and >1000μm.
12. Once the reaction has reached it desired reaction time, the sample was pinched down to room temperature. The cooling process takes about 12 hours.
13. After the temperature has cooled down, the reactor outlet tube was untied and the liquid in the reactor was collected in a beaker which will be transfer to the COD bottle for storage.
14. The ash produced from the pyrolysis process was weighted to determine the weight loss of the sample.
15. Finally the levoglucosan concentration in each product samples was tested in GC-MS. The data was recorded.

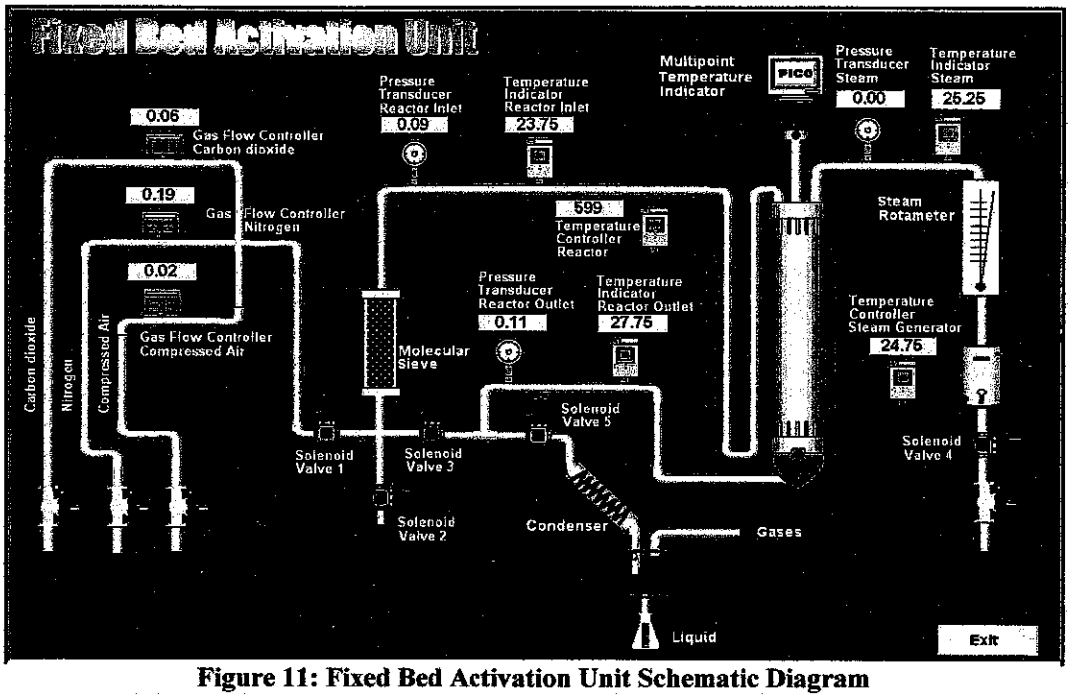


Figure 11: Fixed Bed Activation Unit Schematic Diagram

4.3 EXPERIMENTAL PROCEDURE USING SELF-DEVELOPED PYROLYSIS SETUP

1. Meshed rubber seed kernel was put into the container.
2. The equipment was assembled according to Figure xx.
3. The tab water's tube was allowed to circulate along the condenser.
4. The nitrogen gas's tube was calibrated at 0. 1 ml/min and connected to the equipment.
5. The heating mantel was switched on and digital temperature indicator was monitored.
6. When the temperature reached 300 C, the product beaker was changed and the bio-oil was stored in tight container. Then the new beaker was employed.
7. Step 6 was repeated at each temperature increment of 100 C.
8. The experiment stopped at 600 C and the equipment was pinched out for 5 hours.

9. The bio-char remained in the beaker was weighed and recorded.
10. Step 1-9 was repeated with sample size 500 μm and >1000 μm.

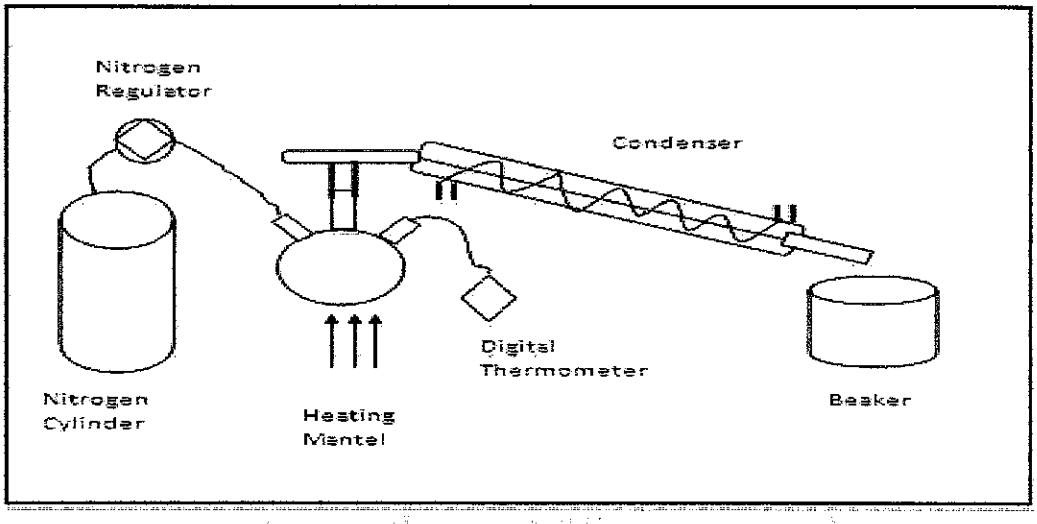


Figure 12: Schematic Diagram of Self-Developed Pyrolysis Setup

4.4 SAFETY CONCERN

The self-developed pyrolysis setup is less protective on human health especially for those who have serious asthma. The vapour produced during pyrolysis process flowed into condenser and the condensed liquid flowed into designated beaker. A huge portion of the vapour was not condensed at release to the atmosphere. The odour was bad and may cause inhalation problem. Therefore, the self-developed pyrolysis setup must be operated in the fume cupboard.

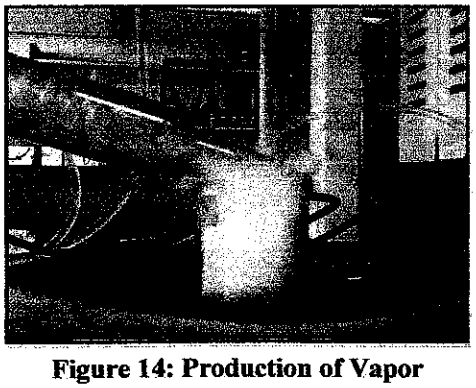


Figure 14: Production of Vapor

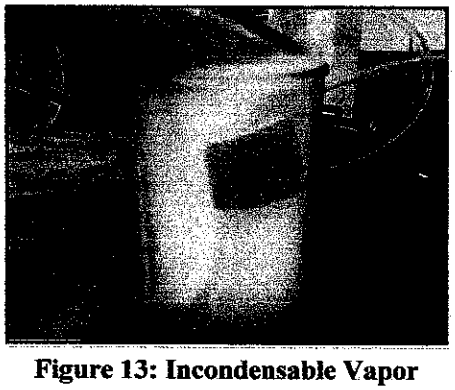


Figure 13: Incondensable Vapor

4.4 BIO-OIL ANALYSIS USING GC-MS

1. 1 gram of GC-MS standard was weighed in a small container.
2. 9 gram of de-ionized water was added to the container. A standard of 10 wt% levoglucosan was ready.
3. The standard was diluted into 5 wt%, 2.5 wt% and 1.25 wt% GC-MS standard. Each standard was kept in small container.
4. Each standard was diluted 10 times of previous concentration.
5. The diluted standards were injected into GC-MS and the standard's characteristics were recorded.
6. Sample of bio-oil was diluted 10 times of initial concentration.
7. The sample of bio-oil was injected and levoglucosan concentration was observed at time 4 minutes – 6 minutes. A clear and sharp peak appeared on graph indicating the levoglucosan present.
8. The graph was compared with standard graph and the concentration of levoglucosan was obtained.
9. Step 6 – 8 were repeated for each sample of bio-oil.

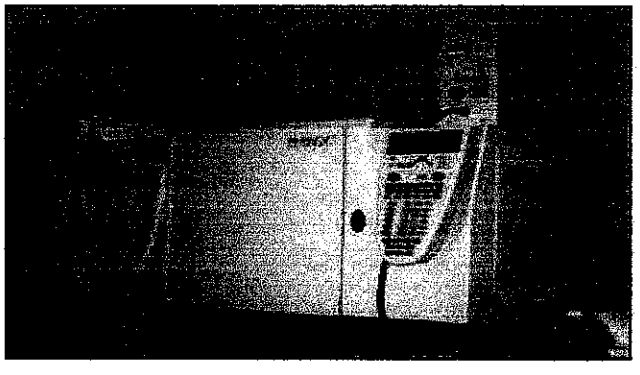


Figure 15: GC-MS Equipment Equipment

4.5 LIQUID CHARACTERIZATION

4.5.1 Determination of density

There are two ways to determine the density of bio-oil, using digital density meter and mathematical approach. However, a minimum of 10 ml bio-oil

needed if the digital density meter is to be used. The author prefers mathematical approach;

$$\rho = \frac{m}{V}$$

Where:

m = mass of liquid

V = volume of liquid

4.5.2 Determination of viscosity

Viscosity is determined using viscometer. Similarly, the viscometer needs 10 ml of bio-oil each time it is used. Therefore, the viscosity test was not done in this project. However, there are a lot of literatures describe the viscosity of the rubber seed oil.

4.5.3 Determination of pH

Determination of pH is important to classified either the rubber seed oil is acidic or alkaline. The pH paper was used and dipped into the rubber seed oil. The pH paper color would change and the paper was compared with pH scale. The use of digital pH analysis requires huge amount of bio-oil and therefore not possible.

4.5.4 Determination of calorific value

According to (Singh, 1988), the calorific value of pyrolysis liquid was determined using Dulong Formula. Bomb calorimeter was not possible to be emplotyed due to high water content in the pyrolysis oil. First, the CHNS is used to quantify the amount of carbon, hydrogen, and sulphur in the rubber seed kernel. Then, the value is plugged into Dulong formula and the calorific value is obtained.

$$Q_{GCV}\ (\text{MJ/kg}) = 33.83C + 144.3\left(\frac{H - O}{8}\right)$$

Where:

C: mass fraction of carbon

H: mass fraction of hydrogen

O: mass fraction of oxygen

4.6 PROXIMATE ANALYSIS

4.6.1 Determination of Percentage of Moisture

The percentage of moisture in the analysis sample is calculated as follows;

$$\text{Percentage of moisture} = \frac{A - B}{B - C} \times 100$$

where;

A: mass of container and wet sample, g

B: mass of container and dry sample, g

C: mass of container, g

5.6.2 Determination of Ash content

The percentage of ash in the analysis sample is calculated as follows;

$$\text{Percentage of ash} = \frac{A - B}{C} \times 100$$

where;

A: weight of capsule, cover and ash residue, g

B: weight of empty capsule and cover, g

C: weight of analysis sample used, g

4.6.3 Determination of Percentage of Lost

The percentage of volatile matter is determined as follows;

$$\text{Percentage of weight loss} = \frac{A - B}{A} \times 100$$

where;

A: weight of sample used, g

B: weight of sample after heating, g

C-D :Percentage of volatile matter

C = percentage of weight loss, %

D = percentage of moisture, %

4.7 KEY MILESTONES

Appendix 1

4.8 GANT CHART

Appendix 2

4.9 LISTS OF EQUIPMENTS

Appendix 3

CHAPTER 5

RESULT AND DISCUSSION

5.1 SAMPLE PRETREATMENT STEP

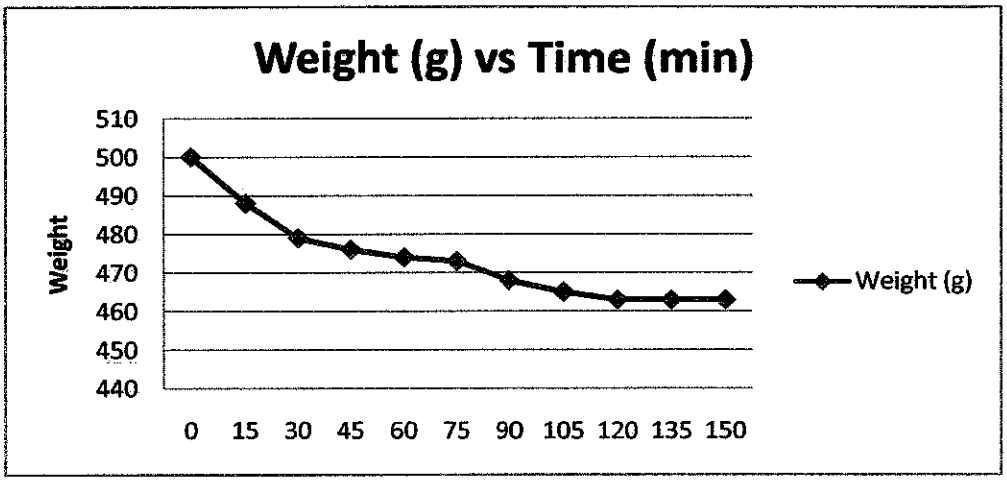


Figure 16: Rubber Seed Weight vs Heating Time

The drying process was conducted by using drying oven in the laboratory at 110 °C. Every 15 minutes, the rubber seed kernel was weighed. The drying process is important to ensure efficient and reliable pyrolysis process. Water and moisture in the sample will evaporate during pyrolysis process and the vapor will be flowing into condenser. The warm vapor will intact with the cold water and it will be condensed. Therefore, the quality of bio-oil produced will be bad and levoglucosan content would be reduced. The graph shows that the weight of rubber seed kernel was decreasing with time until a constant weight was achieved. Significant decrease in weight indicated that some of free water in the rubber seed kernel had been evaporated. It was found that after two hours, the weight of the dried rubber seed kernel was not changing anymore. It can be concluded that the water and moisture that was in the rubber seed kernel was fully evaporated within 2 hours of drying in the oven.

According to (Alves, 1989), when heat is applied into wood particles, the particles begin to dry more intensely at the outer boundary as the temperature is higher. When the liquid in the outer boundary is evaporated, the liquid in the inner part of the particle will move to the outer boundary through diffusion and convection mechanism. The liquid will be heated and evaporated. However, some of the inner liquid might be able to escape and move to colder part (inner part of the particle) and condensation may occur there. It is worth to know that as heating process continued, the particle resistance to heat will become harder. The heat penetration will not be as good as before. Thus, continue supplying the heat may not help in removing the free water and moisture in the particle.

5.2 COLOUR ATTRIBUTES BEFORE AND AFTER PYROLYSIS PROCESS

The initial appearance of rubber seed kernel was yellowish powder. After undergone pyrolysis process, the colour of remaining rubber seed kernel (called bio-char) change to black. Similarly, the bio-oil produced was also dark in colour.

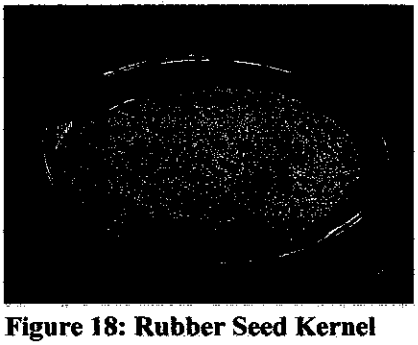


Figure 18: Rubber Seed Kernel

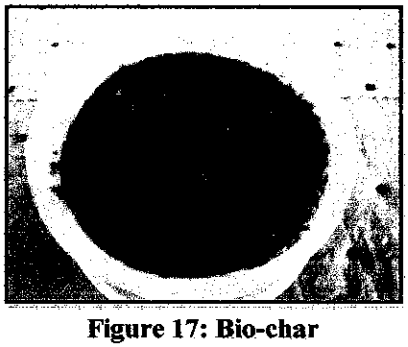


Figure 17: Bio-char

Figure 19: Rubber Seed Oil

5.3 GC-MS STANDARD ANALYSIS

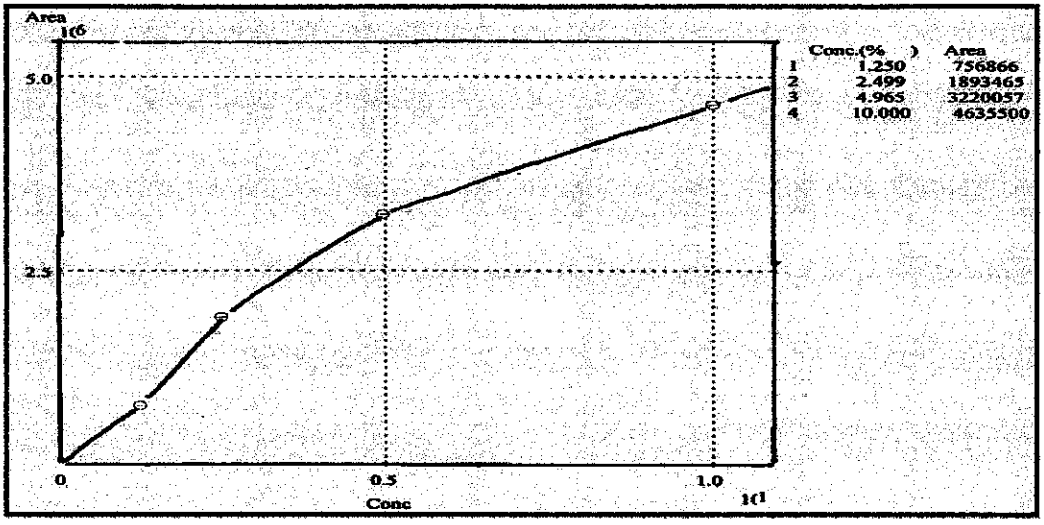


Figure 20: GC-MS Standard Curve

The GC-MS Levoglucosan Standard bought from Germany was in solid phase. The GC-MS equipment uses liquid standard. Thus, the standard needs to be diluted with any solvent that could dissolve levoglucosan. The solvent used in this project was de-ionized water. Four GC-MS standards were prepared (1.25 wt%. 2.50 wt%, 5 wt%, 10 wt %) and injected into GC-MS. After calibration, the above graph was obtained. The y-axis represents intensity while the x-axis represents the levoglucosan concentration. It can be concluded here that the relationship of levoglucosan concentration and intensity is not linear. In the nutshell, if the levoglucosan concentration exceeds 10 wt%, i.e. 40%, new standard shall be prepared and injected into GC-MS. Assuming linear relationship is not permissible. This is important finding in this experiment before real test is made.

5.4 EXPERIMENTAL RESULTS

5.4.1 Temperature Profile and Product Yield

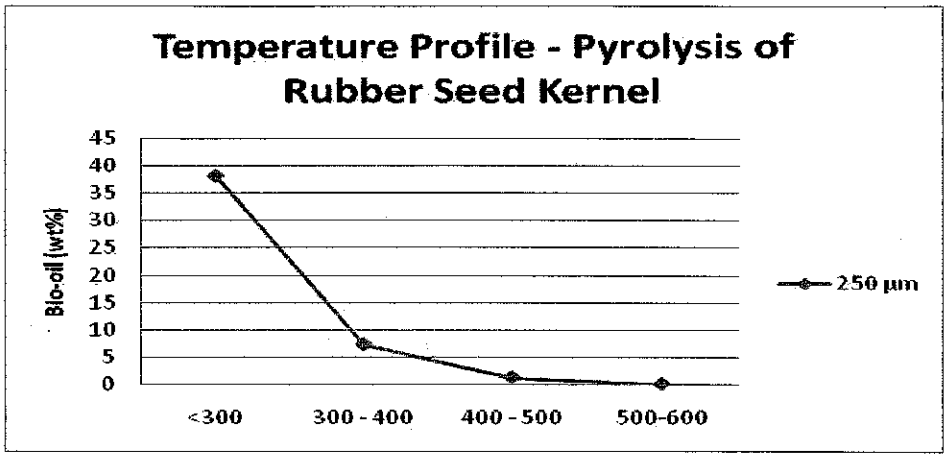


Figure 21: Temperature Profile and Bio-oil Yield - Sample Size 250 um

Observation

The graph shows the temperature profile of pyrolysed rubber seed kernel (250 µm) and the produced bio-oil in wt%. The pyrolysis process started at 27 °C and the nitrogen gas was supplied at 0.1 cm^3/s. After 19 minutes of heating, the temperature was 200 °C. At 220 °C, a lot of vapor produced and bio-oil began to form. As the vapor produced, the temperature increased quickly. Within 8 minutes, the temperature reached 300 °C. At the same time, a lot of bio-oil produced. The amount of bio-oil produced when the temperature was less than 300 °C was 38.28 wt%. The heating process continued and temperature reached 400 °C within 10 minutes. Another sample was collected and the amount of bio-oil produced was 7.192 wt%. The vapor came out from experimental setup was reducing with time. After temperatures exceeded 400 °C, the production of vapor and bio-oil stopped.

Temperature Increment, Heating Time and production of Vapor

The heating time and temperature increment are related each other. At the beginning, the temperature was 27 °C and 19 minutes was needed to reach 200 °C. Next, the temperature increment was so quick and 8 minutes was needed to reach 300 °C. As expected, more time was needed to heat the

rubber seed kernel in the glassware in the early stage of pyrolysis process. The hot vapor produced (after temperature was 220 °C) had increased the temperature quickly and reduced the heating time. This was conformed as the temperature increment reduced back when the production of vapor was less (after the temperature was approaching 400 °C)

Temperature Increment, Heating Time and production of Bio-oil

The production of bio-oil was encouraging in the early stage of pyrolysis process. 38.28 wt% of bio-oil produced when the temperature was less than 300 °C. The volume reduced to 7.192 wt% as temperature reached 400 °C and nothing produced after temperature reached 400 °C. It is concluded that all sample of rubber seed kernel was burnt with nitrogen before temperature reached 400 °C, resulting no bio-oil produced after that. To obtain the sample of bio-oil (when the sample size is 250 μm), it is recommended to use Fixed Bed Activation Unit (FBAU). The yield produced by using FBAU is not accurate but FBAU still could give bio-oil at high temperature.

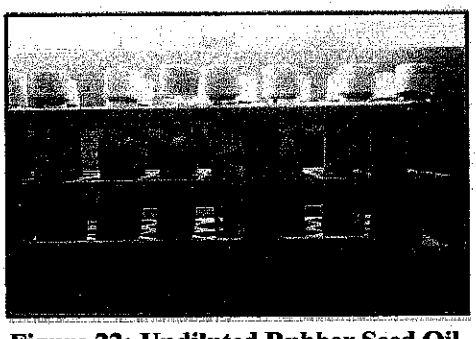


Figure 22: Undiluted Rubber Seed Oil

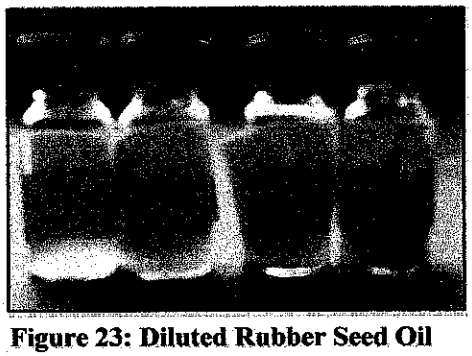


Figure 23: Diluted Rubber Seed Oil

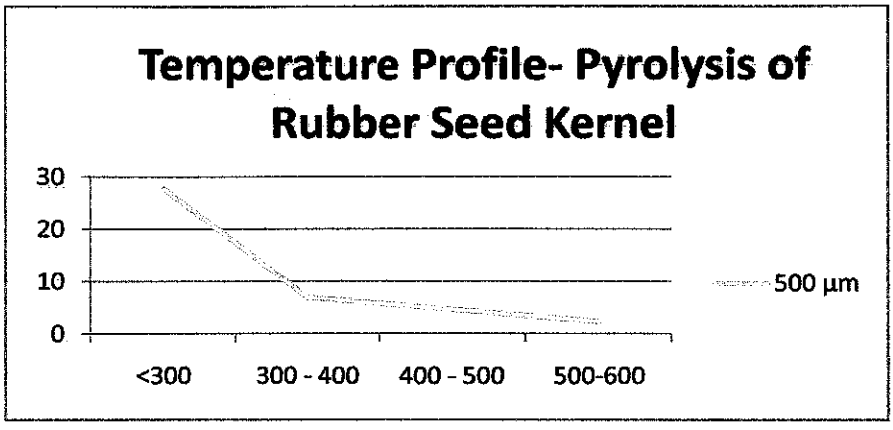


Figure 24: Temperature Profile and Bio-oil Yield – Sample Size 500 um

Observation

The graph shows the temperature profile of pyrolysed rubber seed kernel (500 µm) and the produced bio-oil in wt%. The pyrolysis process started at 27 °C and the nitrogen gas was supplied at 0.1 cm3/s. After 26 minutes of heating, the temperature was 240 °C. At 240 °C, a lot of vapor produced and bio-oil began to form. Similar with previous observation on 250 µm, the temperature increased quickly after the vapor produced. Within 6 minutes, the temperature reached 340 °C. The increment was too sudden and first bio-oil sample was collected at temperature of 340 °C. The amount was 27.72 wt%. It is worth to note that previously the first sample of bio-oil was collected at 300 °C. To standardize the result of experiment with previous experiment, the production of bio-oil during 300 °C – 340 °C was assumed negligible. The validness of this assumption will be further discussed later. The heating process continued and temperature reached 400 °C within 8 minutes. Another sample was collected and the amount of bio-oil produced was 6.96 wt%. The vapor came out from experimental setup was reducing with time. After temperatures exceeded 400 °C, the production of vapor and bio-oil was slowing down. At 500 °C, 4.64 wt% of bio-oil collected and at 600 °C, 2.32 wt% of bio-oil collected. Almost none of vapor produced after temperature reached 530 °C.

Temperature Increment, Heating Time and production of Vapor

Similarly, the heating time and temperature increment are related each other. Unlike previous experiment, the temperature took longer time to reached 240 °C. The production of vapor was also a bit late compare to previous experiment. But the temperature increased quickly after 300 °C. This was difference with previous experiment where the temperature increment was highest in the early stage of pyrolysis process. This observation was in line with the theory relating the contact surface and reaction efficiency. Compare to previous experiment, the total contact surface between sample and heat was less. Previously, the sample size was 250 μM, allowing bigger contact surface. Therefore, now the pyrolysis process took longer time to increase the sample temperature and production of vapor was less at the beginning. However, after the temperature reached 300 °C, a lot of vapor started to come out, and the vapor had increased the temperature quickly. It was observed that the process had shifted forward. The vapor was still produced at 400 – 600 °C, which was unlikely to be happened in previous experiment.

Temperature Increment, Heating Time and production of Bio-oil

The production of bio-oil was encouraging in the early stage of pyrolysis process. 38.28 wt% of bio-oil produced when the temperature was less than 340 °C. Before this, to standardize the result, it was assumed that the production of bio-oil when temperature was 300 °C – 340 °C was negligible. Therefore, in the record, production of bio-oil at T<300 was 27.72 wt%. However, according to the theory of contact surface, supposedly the production of bio-oil should be less than previous experiment. It was unrealistic to say that no vapor was produced at 300 °C – 340 °C as lot of vapor was coming out at that time. The author concluded that the assumption was invalid. The result of 38.28 wt% was too high and it was an error. The volume reduced to 6.96 wt% as temperature reached 400 °C. At 500 °C, 4.64 wt% of bio-oil collected and at 600 °C, 2.32 wt% of bio-oil collected. Unlike previous experiment, the production of bio-oil continued at higher

temperature. It can be concluded that bigger sample size need more time and heat to be completely pyrolysed. This sample size (500 μM) is recommended for high temperature pyrolysis process.

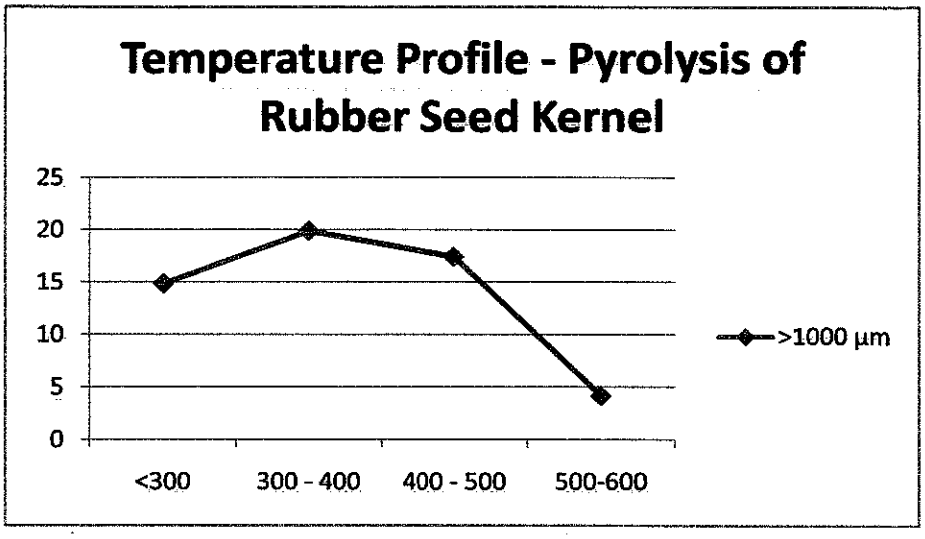


Figure 25: Temperature Profile and Bio-oil Yield – Sample Size >1000 um

Observation

The graph shows the temperature profile of pyrolysed rubber seed kernel (>1000 μm) and the produced bio-oil in wt%. The pyrolysis process started at 26 °C and the nitrogen gas was supplied at 0.1 cm^3/s. After 23 minutes of heating, the temperature was only 200 °C. But a lot of vapor produced and bio-oil began to form. Similar with previous observations, the temperature increased quickly after the vapor produced. Within few minutes, the temperature reached 300 °C. It was also noted that the increment was not sudden as previous experiment. The first bio-oil sample was collected at temperature of 300 °C. The amount was 14.848 wt%. The heating process continued and temperature reached 400 °C within 7 minutes. Another sample was collected and the amount of bio-oil produced was 19.592 wt%. The vapor came out from experimental setup was maximum during 300 °C – 400 °C. At 500 °C, still a lot of bio-oil collected and the amount was 17.4wt%. After 500 °C, the production of vapor and bio-oil reduced. At temperature more than 500 °C, only 4.176 wt% of bio-oil was collected.

Temperature Increment, Heating Time and production of Vapor

Similarly, the heating time and temperature increment are related each other. Unlike previous experiment, the temperature took longer time to reached 200 °C. The production of vapor was also a bit late compare to previous experiment. But the temperature increased quickly after 300 °C. It can be concluded that the process had shifted. (Backward, needing longer heating time)This was difference with previous experiment where the temperature increment was highest in the early stage of pyrolysis process. This observation was in line with the theory relating the contact surface and reaction efficiency. Compare to previous experiment, the total contact surface between sample and heat was less. Previously, the sample size was 250 µM and 500 µM, allowing bigger contact surface. Therefore, now the pyrolysis process took longer time to increase the sample temperature and production of vapor was less at the beginning. However, after the temperature reached 300 °C, a lot of vapor started to come out, and the vapor had increased the temperature quickly. The vapor was abundantly produced at 300 °C – 400 °C and 400 °C – 500 °C. Compare to previous case, the vapor was maximized only at 300 °C – 400 °C.

Temperature Increment, Heating Time and production of Bio-oil

Compare to previous experiments, the production of bio-oil was **less** encouraging in the early stage of pyrolysis process. Only 14.48 wt% of bio-oil produced when the temperature was less than 300 °C. This amount was logical when compare to experiment of 250 µM. At temperature less than 300 °C, the amount of bio-oil produced was lower than first experiment on 250 µM sample size. This was in line with the theory of contact surface. Another sample was collected at 400 °C and the amount 19.852 wt%. This was the first time that the amount of bio-oil produced at 300 °C – 400 °C exceeded the amount produced at lower temperature. At 500 °C, 17.4 wt% of bio-oil collected and this was a decrease to previous value. But the value was big enough compare to previous sample sizes. In the nutshell, sample size of >1000 µm is suitable for higher operating temperature. Meanwhile, at 600 °C, only 4.176 wt% of bio-oil collected, indicating the pyrolysis process was

almost completed. Similar to previous experiment (500 μM), the production of bio-oil continued at higher temperature. It can be concluded that bigger sample size need more time and heat to be completely pyrolysed. This sample size (1000 μm) is recommended for high temperature pyrolysis process.

5.4.2 Effect of sample size on product yield

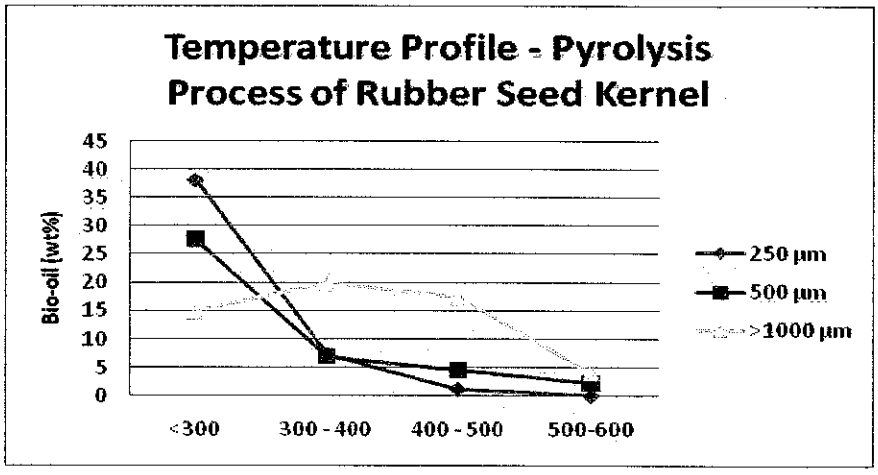


Figure 26: Temperature Profile and Bio-oil Yield - Effect of Sample Size

The graph shows the temperature profile of pyrolysis process of rubber seed kernel for all experiments and sample sizes. Details description of the process had been discussed previously. From this graph, few conclusions could be made;

1. Sample size of 250 μM has biggest contact surface and it is suitable for low temperature pyrolysis process. It will quickly burn and the process takes less time to be completed. This is well explained and easily understood when one understand the theory of contact surface. The drawback is the pyrolysis process will be so quick and completed before reaching 400 °C. Therefore, if anybody expected a product at higher temperature such as 500 °C, this sample size is not recommended.

2. Sample size of 1000 μm has difference characteristic with 250 μM. The surface contact is less compare to 250 μM of sample size. It will take longer time to produce bio-oil and most of the bio-oil is produced when temperature is higher than 400 °C. The theory of surface contact explained this

observation. Therefore, it is recommended to use this sample size if higher pyrolysis temperature has become our priority.

3. Sample size of 500 μM is the intermediate of both previous sample sizes. The pyrolysis characteristic of this sample sizes is the intermediate characteristics of previous sample. The surface contact is greater than >1000 μm sample size but lesser than 250 μM sample size. Most of bio-oil is produced when temperature is less than 300 °C. However, at higher temperature, the bio-oil is still produced though the volume is not much.

5.4.3 Temperature Profile and Levoglucosan Yield

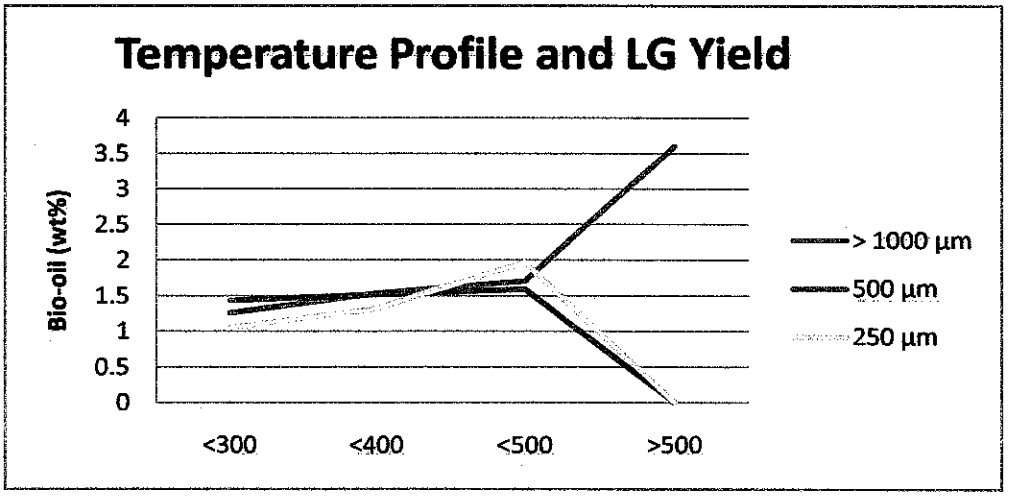


Figure 27: Temperature Profile and Levoglucosan Yield

Observation

The graph shows the temperature profile of pyrolysed rubber seed kernel (250μm, 500μm,>1000μm) and the produced levoglucosan in wt%. It was observed that at temperature lower than 300 °C, the levoglucosan yield was approximately 1.052 wt%, which the lowest value. The value increased slowly with temperature until the temperature reached 400 °C. As the temperature approaching 500 °C, the levoglucosan yield increased significantly and reached highest value ever. At temperature more than 500 °C, the production of levoglucosan stopped. The levoglucosan yield (wt %) trend for 500 μm was

similar to 250 μm. It was observed that the levoglucosan yield was 1.435 wt% when the temperature was below 300 °C. As the temperature increased, the levoglucosan increased slowly and reached 1.52 wt%. Above 500 °C, the production of levoglucosan yield was zero. The trend of levoglucosan yield (wt%) for sample size >1000 μm slightly different from previous sample size. The levoglucosan yield was 1.706 wt% whenever the temperature was below 300 °C. As the temperature increased up to 400 °C, the levoglucosan yield started to increase significantly. At 500 °C, the levoglucosan yield was 1.706 wt%. The distinguishing characteristic of >1000 μm with previous samples was on the levoglucosan yield whenever the temperature passed 500 °C. The recorded levoglucosan yield was 3.6 wt%, which is the highest values at all temperatures and sizes.

Result Analysis

The graphs describe the characteristics of levoglucosan yield with respect to heating temperature. For all sample sizes, the levoglucosan yield was at lowest value when the temperature was below 300 °C. In addition, the value slightly increased when the temperature was increased to 400 °C. The pattern was uniform for all sample sizes. This is in line with research done by (Joong Kwon, 2007) that stated the levoglucosan yield increases with temperature. He also found that the maximum yield of levoglucosan was achieved at temperature of 430 °C and 5 kPa. However, the self- developed equipment only operated at atmospheric condition. Therefore, at atmospheric pressure, the author estimated that the maximum yield of levoglucosan will be at higher temperature than 430 °C. This was proved to be a good assumption as the result showed that maximum yield of levoglucosan was achieved at temperature above 500 °C (sample size >1000 μm). The levoglucosan yield at that time was 3.6 wt%. On the other hand, (Steve Helle, 2007) summarized the effect of temperature and acid concentration on hydrolysis of levoglucosan. He found that the hydrolysis of levoglucosan into glucose is increasing with temperature and acid sulphuric. Therefore, the author concluded that there is a peak point of temperature where the levoglucosan yield will start to decrease. The reduction is most probably due to hydrolysis of levoglucosan into glucose

and the peak point is yet to be determined. Question may rises on the levoglucosan yield at high temperature for sample size of 250 μm and 500 μm. Both sample sizes yield 0 wt% of levoglucosan at T > 500 °C. Before this, the author had discussed that small sample sizes will not yield bio-oil at higher temperature. Therefore, the levoglucosan production stopped together with bio-oil production.

5.4.4: Effect of sample size on Levoglucosan yield

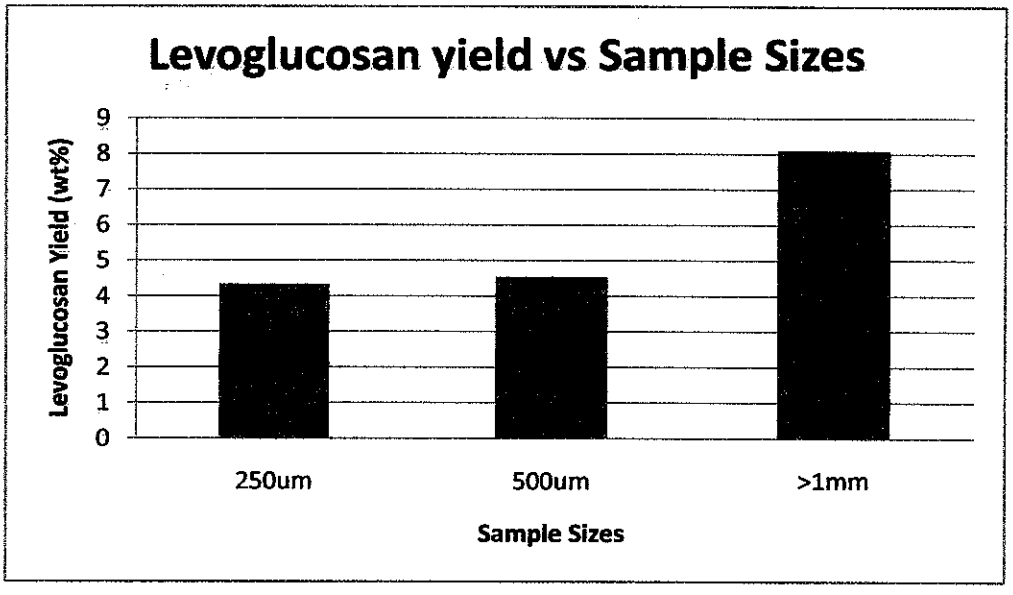


Figure 28: Levoglucosan Yield vs Sample Size

Observation

Several experiments were conducted to determine the effect of sample size on the levoglucosan yield. Initially, it was presumed that the levoglucosan yield will increase with the decrease of the size of samples. However, the result was opposed to the assumption and maximum yield of levoglucosan was achieved when the sample size was >1000 μm. The maximum yield was found to be 8.098% while the minimum yield found to be 4.339 wt% (sample size 250 μm). On the other hand, the levoglucosan yield for 500 μm was 4.547 wt%.

Result Analysis

Previously, the author had discussed on the bio-oil yield with respect to sample sizes. In previous cases, the bio-oil yield was found to be maximum when sample size >1000 µm and minimum when sample size was 250 µm. Similar thing was observed here as the levoglucosan yield is maximum for sample size >1000 µm. Definitely, both cases had relation to each other. The bio-oil contains levoglucosan. When less bio-oil is produced, less levoglucosan will be produced. This is the first and simple reason why levoglucosan yield for 250 µm is very low. The second deduction that could be made is on the characteristic of levoglucosan. Levoglucosan and cellobiosan can be used as tracer compounds to determine smoke distribution. (Simoneit, et al., 1999) It is worth to note that levoglucosan is in gaseous form when it is pyrolysed. Effective condensation mechanism will has big impact on the levoglucosan yield. The vapor produced during pyrolysis of small sample size was vigorous and the self-developed equipment was ineffective to condense the quick and rapid vapor. Meanwhile, for big size sample, the vapor was not really vigorous and most of the vapor was condensed into bio-oil. The author believed that if the efficiency of condenser of FBAU or self-developed equipment could enhanced, more bio-oil and levoglucosan could be collected.

5.4.5: Comparison of Fixed Bed Activation Unit and Self-Developed Equipment

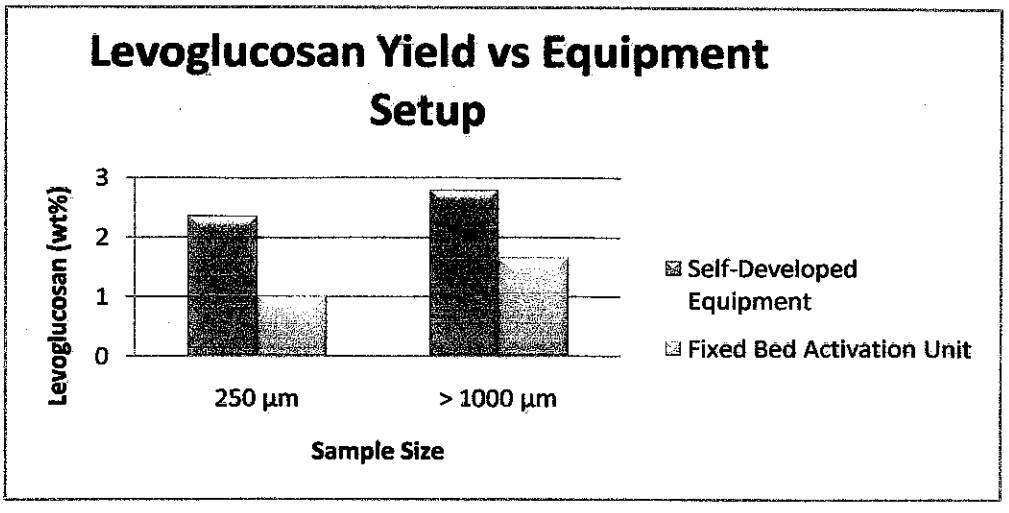


Figure 29: Levoglucosan Yield vs Equipment Setup

Four experiments were conducted to compare the efficiency of Fixed Bed Activation Unit (FBAU) and self-developed pyrolysis setup. The results show that self-developed pyrolysis setup is better than FBAU in producing levoglucosan. FBAU was damaged last year and could not condense the vapor into bio-oil. The bio-oil that was collected by the author was the liquid that contain in the reactor arm of FBAU. The bio-oil may be contaminated. Besides that, FBAU itself had been utilized in many researches and experiments. Some of the raw materials such as Empty Fruit Bunch (EFB), coffee powder, and activated carbon were left sticking in the inner side of the reactor. These things may have contaminated the bio-oil such that the levoglucosan is converted into other compound. According to Helle et. al (2007), the acid hydrolysis of levoglucosan will lead to formation glucose which is undesirable. Thus, acidic environment in FBAU will damage the bio-oil and levoglucosan. The self-developed pyrolysis setup was a dedicated setup for this project. Therefore, it was clean and the levoglucosan content was better.

5.5 PROXIMATE ANALYSIS

Table 4: Proximate Analysis Table

Temp	Sample Size	Weight		Weight loss	Liquid volume	Liquid weight	Char Yield	Liquid yield
		Start, w_1	End, w_2					
°C	µm	g	g	wt%	ml	g	wt%	%
<300	250	50.00	13.92	72.16	16.47	19.10	27.84	38.20
	500	50.00	15.45	69.10	11.95	13.86	30.90	27.72
	>1000	50.00	16.64	66.72	6.40	7.42	33.28	14.85
300 - 400	250	50.00	13.86	72.28	3.07	3.56	27.72	7.12
	500	50.00	15.31	69.38	3.00	3.48	30.62	6.96
	>1000	50.00	16.07	67.86	8.56	9.93	32.14	19.86
400 - 500	250	50.00	13.44	73.12	1.00	1.16	26.88	2.32
	500	50.00	14.60	70.80	2.00	2.32	29.20	4.64
	>1000	50.00	15.57	68.86	7.50	8.70	31.14	17.40
> 500	250	50.00	13.44	73.12	0.00	0.00	24.35	0.00
	500	50.00	14.60	70.80	1.00	1.16	27.90	2.32
	>1000	50.00	15.57	68.86	1.80	2.09	29.83	4.18

5.6 CHARACTERIZATION OF PYROLYSIS LIQUID

Table 5: Rubber Seed Oil Properties

Property	Rubber Seed Oil
Density	1.16
Viscosity mm	66
Flash point	198ºC
Fire Point	210º C
Calorific Value	37.5
Saponification Value	206
Acid Value	34

Source: Handbook of Plant-Based Biofuel
Ashok Pandey (2008)

The water content test of rubber seed oil was not conducted in this project. The information on the water content of rubber seed oil was obtained from literature. The existence of water influences the performance of rubber seed oil. High water content causes a decrease in viscosity of the oil which can facilitate transport, pumping and atomization. Besides that, it improves stability, lowers the combustion temperature and as a consequence, it may cause a reduction of the NOx emission. (Dilla, 2006) For the purpose of extracting levoglucosan, the water in the bio-oil must be removed to obtain high purity of levoglucosan. However in most cases, the water content in bio-oil cannot be removed by conventional methods like distillation. (Dilla, 2006) The proposed method to remove the water content from bio-oil is by using azeotrophic distillation or rotary evaporator. The limitation in using azeotropic distillation must be considered as azeotropic distillation requires large volume of solvent and bio-oil. Thus, it is not suitable for lab scale experiment. The use of rotary evaporator is justified to be suitable.

The density of rubber seed oil is 1.16 kg/m^3 and determined using mathematical approach. This value is higher than fuel oil density, 0.85 kg/m^3. This has implications on the design and specification of equipment such as pumps and atomisers in boilers and engines.

CHAPTER 6
CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

Levoglucosan ia one of chemical materials for fire retardant and wood adhesive industry. As the fire retardant price is increasing from day to day, the availability of levoglucosan in the market is important. The unavailability of cheap and efficient process to extract the levoglucosan keep levoglucosan price high in the chemical market. On the other hand, rubber seed kernel is available in huge quantity in Malaysia. The project's objective is to investigate the levoglucosan content in pyrolysed rubber seed kernel. The main scope of the project is to conduct experiments that led to the optimization of operating condition for pyrolysis process. The effect of temperature; sample size and type of equipment on levoglucosan yield were studied during this project. The levoglucosan yield was found to be increased with temperature. The maximum yield of levoglucosan was obtained at temperature above 500 C. Besides that the maximum yield of levoglucosaan (3.6 wt %), was obtained for >1000 μm sample size, using self-developed pyrolysis setup. The self-developed equipment was found to be better in all cases than FBAU as it is uncontaminated with anything that harm the bio-oil produced. Based on the experimental works and results obtained, the author concluded that levoglucosan present in the pyrolysed rubber seed kernel and could be further optimized.

6.2 RECOMMENDATION

The author realizes that the project has promising potential to be further developed. The main limitations in this project were on the equipments, required chemicals and

time constraint. In reality, the experimental works started late due to these factors. Nevertheless, it still produced good result. The following are the recommendation that can be made to increase the quality of the product and the outcome of the project.

6.2.1 Fixed Bed Activation Unit (FBAU)

- Initially, high expectation was put onto FBAU. However, the condenser was damaged and jeopardizes the product. In reality, FBAU is good equipment due to the ability to increase the temperature up to 600 C within short time. Therefore, it is recommended to fix the condensing part of FBAU so that pure and clean bio-oil could be produced. The use of vacuum condenser could be considered here.
- Current FBAU is not feasible enough especially during depositing the sample into reactor. Most of the rubber seed kernel spill down during depositing step. Sample support leg could be relocated to ease the depositing sample work.
- A quick and efficient mechanism is needed to remove the bio-char and ash from the reactor. Currently, the char existed in the cooled bio-oil and damage the quality of the product.

6.2.2 Self-developed Pyrolysis Setup

- The self-developed pyrolysis setup could be improved by introducing cold water as condensing liquid. The production of vapour especially for small sample was so rapid that the normal water could not fully condense the vapour. The bio-oil and levoglucosan yield would be much higher if all the vapour could be condensed.
- Another point of improvement necessary for this setup was on the heating mechanism. Currently, the heating process takes long time to reach high temperature i.e. 500 C. The author noticed that for small sample, the production of vapour stopped before reaching 500 C, thus, no production of

bio-oil. If the heating process takes shorter time, the author believes that for small size sample, the bio-oil could be obtained at temperature above 500 C.

6.2.3 Development of the Project

- The project scope for this semester focused on optimizing the levoglucosan and bio-oil yield. The next step was to identify if any other parameter that could enhance the levoglucosan yield. (Joong Kwon, 2007) claimed that pressure and temperature are determining parameters on levoglucosan yield. Therefore, if the project is to be extended, the impact of pressure on levoglucosan yield could be investigated and optimized pressure point must be obtained.
- The biggest challenge in levoglucosan production is in extracting the chemical from bio-oil. The project only beneficial if complete extraction procedures could be developed and tested. The author had developed the procedures to extract the levoglucosan from bio-oil. Due to time constraint and unavailability of chemicals, the procedures have not been tested. Any researcher that continue this project could refer to the procedures in appendix 5.

References:

A Coomarasamy, M. R. (1975). *Rubber Reseach Institute of Sri Lanka, Annual Review.* Cylon: Rubber Research Institute of Sri Lanka.

Alves, S. a. (1989). A model for Pyrolysis for wet wood. *Chemical Engineering Science* , 2861 - 2869.

Antal Jr, M. a. (1995). Cellulose pyrolysis kinetics: the current state of knowledge. *Ind. Eng. Chem. Res* , 703–71.

Balodis, J. (2004). Levoglucosan from Biomass as a Raw Material for New Materials and Technologies.

Bridgwater, A. V. (2003). A techno-economic comparison of power production by biomass fast pyrolysis with gasification and combustion. *6 Renewable & Sustainable Energy Rev. 181* , 231.

D., M. (1999). New Methods for chemical and physical characterization and round robin testing. In B. A., *Fast pyrolysis of biomass: a handbook* (pp. p.92–101). Newbury: CPL Press.

D.S. Scott, J. P. (1984). Can. J. Chem. Eng.

Diebold, J. (1999). A review of the toxicity of biomass pyrolysis liquids formed at lower temperatures. In A. C. Bridgwater, *Fast pyrolysis of biomass: A handbook.* Newbury: CPL Press.

Dilla, F. (2006). *Intensification of Biodiesel from Rubber Seed Kernel.*

F. Shafizadeh, R. F. (1979). J. Appl. Polym. Sci. 23.

Gandhi, C. M. (1990). Journal of AMerican Oil Chemist Society. 67(11), 883.

Joong Kwon, D. Y. (2007). Rapid-cooling, continuous-feed pyrolyzer for biomass processing. *Preparation of levoglucosan from cellulose and starch* .

Laird, D. (2008). The Charcoal Vision: A Win–Win–Win Scenario for Simultaneously Producing Bioenergy. *Permanently Sequestering Carbon, while Improving Soil and Water Quality* .

M. Garcia-Perez, A. C. (2006). Characterization of bio-oils in chemical families.

P. R. Bonelli, P. A. (2000). Effect of pyrolysis temperature on composition, surface properties and thermal degradation rates of Brazil Nut shells.

Ramadhas, J. M. (2005). Characterization and effect of using rubber seed oil as fuel in compression ignition engines . *International Journal of Renewable Energy* , 795 - 803.

Simoneit, B. R., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., et al. (1999). Atmospheric Environment.

Singh, G. S. (1988). *Commercial scale bunch mulching of oil palm.* K.Lumpur: The Incorp. Soc. of Planters.

Stanek, M. C. (1977). *Adv. Carbohydr. Chem. Biochem'.* New York, San Fransisco, London: Academic Press.

Steve Helle, a. N. (2007). A kinetic model for production of glucose by hydrolysis. *Carbohydrate Research 342* , 2365–2370.

Suzhen, W. M. (1994). A potential renewable energy resource development and utilization of biomass energy.

Winsley, P. (2007). Biochar and bioenergy production for climate change mitigation. *NEW ZEALAND SCI. REV. 5,* .

Yaman, S. (2003). Pyrolysis of biomass to produce fuels and chemical feedstocks. *45 Energy Conversion & MGMT* , 651.

APPENDIX

Appendix 1: Key Milestone

1.1 Key Milestone (Semester 1)

1.1.1 Submission of Preliminary Report in Week 4

1.1.2 Submission of Progress Report 1 in Week 8

1.1.3 Submission of Final Interim Report in Week 13

1.1.4 Final Oral Presentation in Week 14

1.2 Key Milestone (Semester 2)

1.2.1 Preparing of samples and apparatus in Week 1

1.2.2 Submission of Progress Report 1in Week 4

1.2.3 Submission of Progress Report 2 in Week 10

1.2.4 Poster Exhibition in Week 11

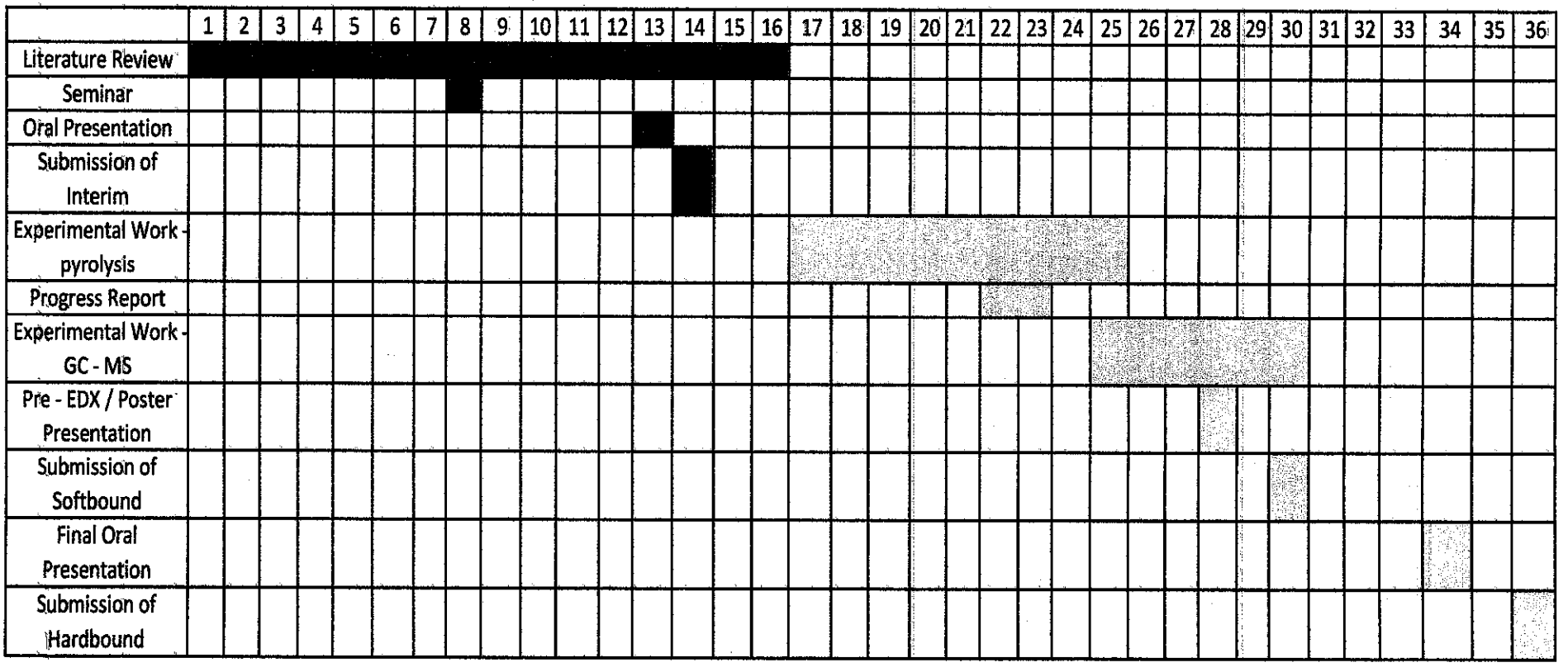
1.2.5 Engineering Design Exhibition in Week 12

1.2.6 Submission of Dissertation in Week 14

1.2.7 Oral Presentation in Week 18 and Week 19

1.2.8. Submission on Final Dissertation in Week 20

Appendix 2; Gant – chart



Appendix 3: List of Equipments

1. Fixed Bed Activation Unit (FBAU)
2. Heating mantel
3. 3 – neck Soxhlet and connectors
4. Digital thermometer
5. Condenser
6. Gas Chromatography – Mass Spectrometry and apparatus
7. Heating oven
8. Beaker

Appendix 4; GC-MS Results

1. 50 g of Rubber Seed Kernel, size of 1000 µm.

T < 300 °C

```
*** CLASS-5000 *** Report No. = 78  Data : ARIFF5S.D09  09/04/03 10:17:56

Sample          : sample < 300 deg C
ID              : ariff
Method File Name : ARIFF5S.MET


*** Peak Report ***
 PKNO R.Time  I.Time - F.Time        Area %Total Name
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*** Quantitation ***
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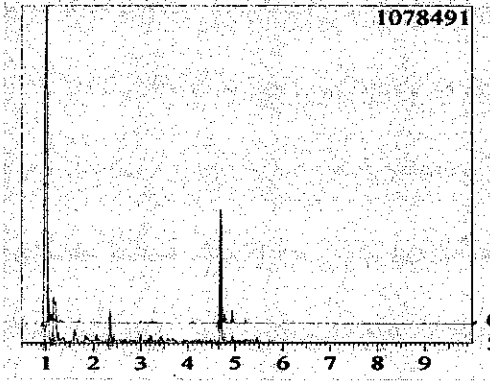


```
ID   : 1   M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.710
Area : 765593
Conc. : 1.259%

   M/Z      Area      %Rel.Int.to Target
1  57.00    349976    46
```

T < 400 °C

```
*** CLASS-5000 *** Report No. = 79  Data : ARIFF5S.D10  09/04/03 10:43:32

Sample          : sample < 400 deg C
ID              : ariff
Method File Name : ARIFF5S.MET


*** Peak Report ***
 PKNO R.Time  I.Time - F.Time        Area %Total Name
--- No data exists ! ---

*** Quantitation ***
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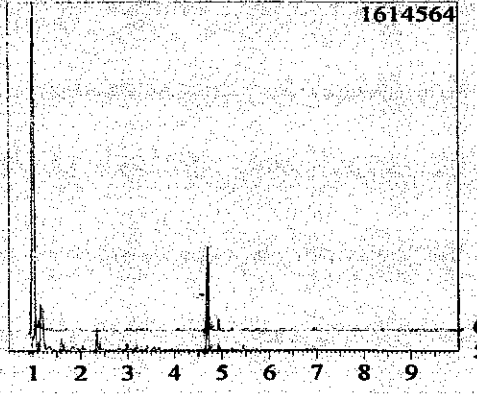



```
ID   : 1   M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.707
Area : 1015039
Conc. : 1.533%

   M/Z      Area      %Rel.Int.to Target
1  57.00    463758    46
```

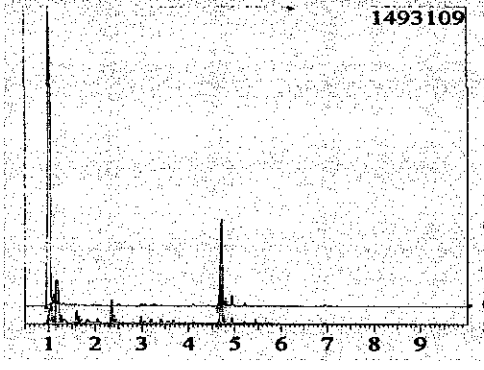
T < 500 °C

*** CLASS-5000 *** Report No. = 76 Data : ARIFF5S.D07 09/04/02 17:02:01

Sample : sample < 500 deg C
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.714
Area : 1172037
Conc. : 1.706%

	M/Z	Area	%Rel.Int.to Target
1	57.00	529056	45

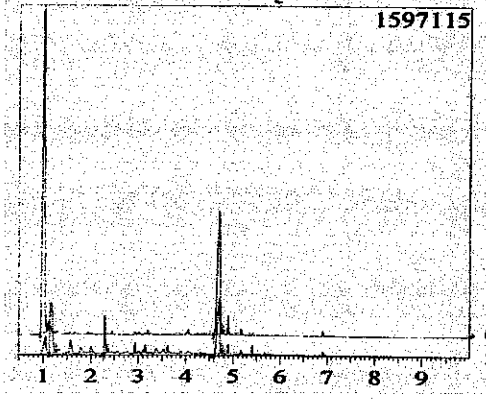
T > 500 °C

*** CLASS-5000 *** Report No. = 77 Data : ARIFF5S.D08 09/04/02 17:22:36

Sample : sample > 500 deg C
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.715
Area : 2485610
Conc. : 3.600%

	M/Z	Area	%Rel.Int.to Target
1	57.00	1129617	45

2. 50 g of Rubber Seed Kernel, size of 500 µm

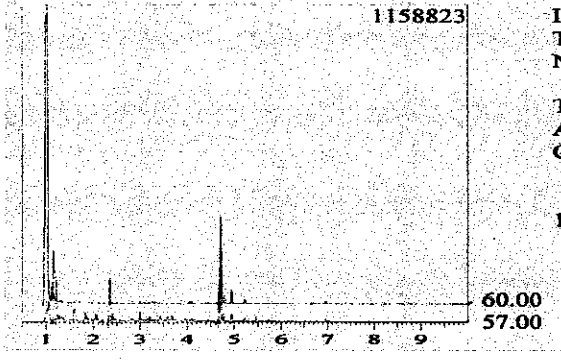
T < 300°C

*** CLASS-5000 *** Report No. = 86 Data : ARIFF5S.D17 09/04/06 12:19:01

Sample : sample <400 deg C exp 2
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.717
Area : 714629
Conc. : 1.180%

	M/Z	Area	%Rel.Int.to Target
1	57.00	327644	46

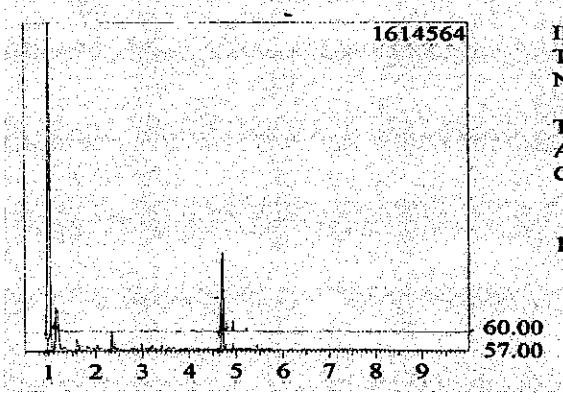
T < 500°C

*** CLASS-5000 *** Report No. = 79 Data : ARIFF5S.D10 09/04/03 10:43:32

Sample : sample < 400 deg C
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.707
Area : 1015039
Conc. : 1.533%

	M/Z	Area	%Rel.Int.to Target
1	57.00	463758	46

3. 50 g of Rubber Seed Kernel, size of 250 µm

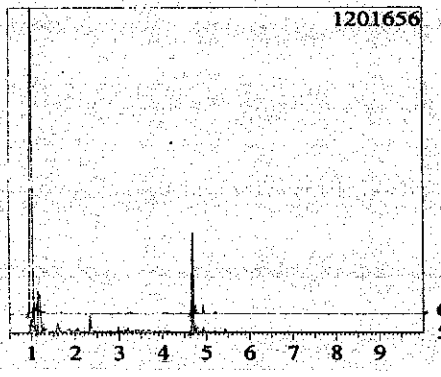
T < 300 °C

*** CLASS-5000 *** Report No. = 80 Data : ARIFF5S.D11 09/04/03 11:09:15

Sample : sample < 300 deg C 6th
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.689
Area : 637237
Conc. : 1.052%

	M/Z	Area	%Rel.Int.to Target
1	57.00	287087	45

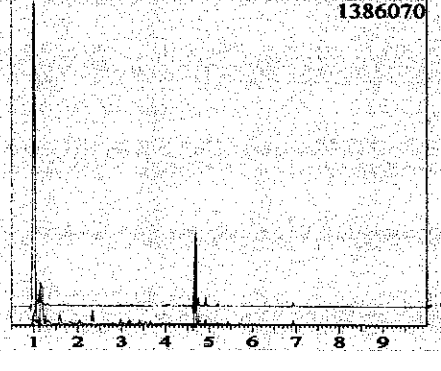
T < 400 °C

*** CLASS-5000 *** Report No. = 81 Data : ARIFF5S.D12 09/04/03 11:33:10

Sample : sample < 400 deg C 6th
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.688
Area : 819797
Conc. : 1.319%

	M/Z	Area	%Rel.Int.to Target
1	57.00	374524	46

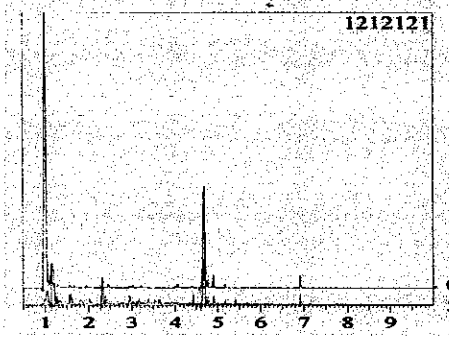
T < 500 °C

*** CLASS-5000 *** Report No. = 82 Data : ARIFF5S.D13 09/04/03 11:54:27

Sample : sample > 400 deg C 6th
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.691
Area : 1409884
Conc. : 1.968%

	M/Z	Area	%Rel.Int.to Target
1	57.00	638900	45

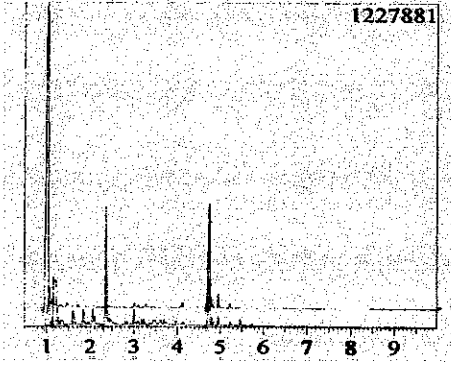
4. 50 g of Rubber Seed Kernel, >1000 µm, 400 °C (FBAU)

*** CLASS-5000 *** Report No. = 90 Data : ARIFF5S.D21 09/04/06 14:56:07

Sample : sample FBAU exp 9/7
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.750
Area : 1126797
Conc. : 1.656%

	M/Z	Area	%Rel.Int.to Target
1	57.00	511583	45

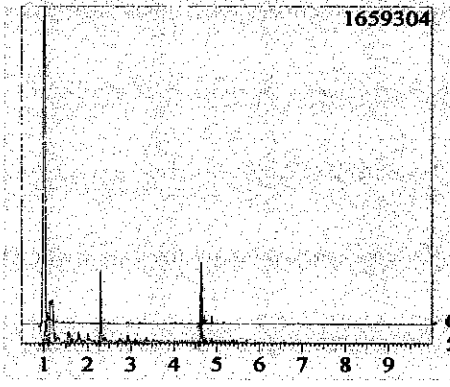
5. 50 g of Rubber Seed Kernel, 250 µm, 400 °C (FBAU)

*** CLASS-5000 *** Report No. = 83 Data : ARIFF5S.D14 09/04/03 12:14:49

Sample : sample FBAU exp 9 400 deg C
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.643
Area : 611689
Conc. : 1.010%

	M/Z	Area	%Rel.Int.to Target
1	57.00	276122	45

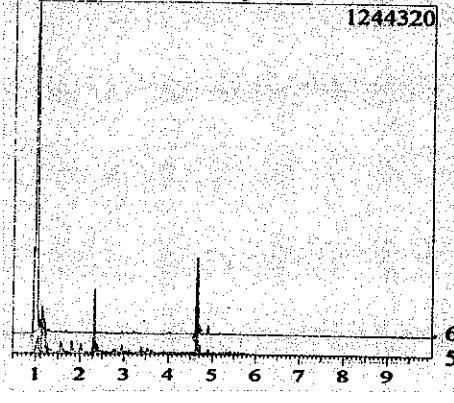
6. 50 g of Rubber Seed Kernel, 250 µm, 400 °C (FBAU)

*** CLASS-5000 *** Report No. = 89 Data : ARIFF5S.D20 09/04/06 14:11:38

Sample : sample FBAU exp 5
ID : ariff
Method File Name : ARIFF5S.MET

*** Peak Report ***
PKNO R.Time I.Time - F.Time Area %Total Name
--- No data exists ! ---

*** Quantitation ***



ID : 1 M/Z : 60.00
Type : Target
Name : levoglucosan

Time : 4.660
Area : 543251
Conc. : 0.897%

	M/Z	Area	%Rel.Int.to Target
1	57.00	246551	45

Appendix 5: Experimental Procedures for Extraction of Levoglucosan from Pyrolysed Rubber Seed Kernel (for future use)

1. Pyrolysis oil in COD bottles will be obtained from previous pyrolysis experiment.
2. The GC-MS records for each bottle will be interpreted and the bottle with the highest concentration of levoglucosan will be selected.
3. The selected sample will be divided into five (5) groups.
4. The pyrolysis oil obtained will be diluted with water. Calcium hydroxide will be add (the mixture need to be stir vigorously during the process) to control the pH of the pyrolysis oil in the range of 12 – 12.5. Based on literature, 4g of Calcium hydroxide is needed for 30g of pyrolysis oil.
5. As the pH is controlled at 12-12.5, more calcium hydroxide will be added to the solution to remove most of the coloured material from the pyrolysis oil. It is estimated that the calcium hydroxide needed is 1.5 to 2.5 times of the undiluted pyrolysis oil.
6. The aqueous mixture is then will be dried with methyl isobutyl ketone (MIBK) by azeotropic distillation. Water will be removed here.
7. The insoluble solid will be further dried by evaporation process to remove all traces of MIBK and brown-yellow solid will be formed.
8. The solid will be grounded to a fine powder. Soxhlet apparatus and ethyl acetate solvent will be used to extract the levoglucosan. The duration needed is estimated around 24 hours to 48 hours. Levoglucosan-rich extract will be formed.
9. The ethyl acetate will be removed from the levoglucosan-rich extract by crystallization with reduce pressure.
10. The re-crystallization with acetone could be done if necessary if more impurities need to be removed.
11. Step 4 to 10 should be repeated with calcium oxide replacing calcium hydroxide and ethanol replacing MIBK.
12. The results will be recorded and discussed.

Appendix 6 : Kinetic Study on Levoglucosan

Steve Helle et al (2007) investigated the acid hydrolysis of two common anhydro sugars in wood pyrolysis oils, levoglucosan and cellobiosan. The acid hydrolysis of levoglucosan will lead to formation of glucose which is undesirable. Thus, understanding the kinetic of the hydrolysis reaction could help to stop the levoglucosan from been hydrolysed. Meanwhile, the hydrolysis of cellobiosan will lead to formation of levoglucosan and glucose. Levoglucosan hydrolysis to glucose follows a first-order reaction, with activation energy of 114 kJ mol (Steve Helle et al., 2007) Levoglucosan and cellobiosan are among the organic compounds formed from the burning of biomass and present in biomass pyrolysis oils (bio-oil). Both levoglucosan and cellobiosan can be used as tracer compounds to determine smoke distribution. (Simoneit et al., 1999) The good thing is levoglucosan does not undergo acid-catalyzed hydrolysis under typical atmospheric conditions. (Fraser et al., 2000)

A major challenge of producing renewable chemical from biomass is to extract and process the cellulose to glucose. The pyrolysis of biomass provides alternate method to acid and enzymatic hydrolysis to overcome the challenge. Adding dilute acid to the levoglucosan will lead to the formation of sugar. In addition, study had shown that the addition of sulphuric acid to bio-oil generated more glucose than could be accounted for by the amount of levoglucosan present. (Gao, 2003) In this study, Steve Helle et al (2007) had investigated the rates of levoglucosan and cellobiosan hydrolysis in water, sulfite pulp mill pulping liquor, and in pyrolysis oil extract. . Spent sulfite liquor contains the hemicellulose sugars and the lignin that are removed from the wood during the sulfite pulping process. Several experiments were conducted in spent sulfite pulping liquor, water extract of pyrolysis oil and spent sulfite pulping liquor extract of pyrolysis oil with and without acid condition. It was also found that the activation energy for hydrolysis in spent sulfite liquor or pyrolysis oil extract was 87 kJ mol~1. This is lower than the activation energy of hydrolysis of levoglucosan in dilute acid. Compare to the levoglucosan hydrolysis rate in dilute sulphuric acid, the levoglucosan hydrolysis rate was greater in spent sulfite liquor (pure levoglucosan added to spent sulfite

liquor), spent sulfite liquor pyrolysis oil extract, or water pyrolysis oil extract. (Helle et al., 2007)

Levoglucosan Hydrolysis

Levoglucosan hydrolysis follow first-order kinetics.

$$\text{Levoglucosan } (A) \xrightarrow{k_1} \text{Glucose } (D) \qquad (1)$$

Equation 2 and 3 describe the rate of disappearance of levoglucosan and rate of production glucose.

$$\frac{dA}{dt} = -k_1 A \qquad (2)$$

$$\frac{dD}{dt} = k_1 A \qquad (3)$$

A = molar concentration of levoglucosan

D = molar concentration of glucose

Ki = first order rate constant

Assuming initial glucose and levoglucosan are zero, equation 1 and 2 become,

$$\frac{A}{A_0} = e^{-k_1 t} \qquad (4)$$

$$\frac{D}{A_0} = (1 - e^{-k_1 t}) \qquad (5)$$

Steve Helle et al (2007) summarized the effect of temperature and acid concentration on hydrolysis of levoglucosan in graphs below; the hydrolysis of levoglucosan into glucose is increasing with temperature and acid sulphuric concentration.

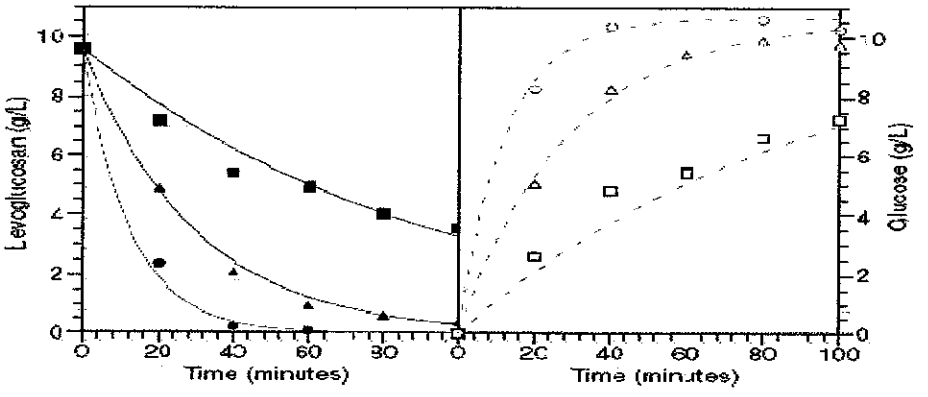


Fig. 30: Effect of temperature on levoglucosan kinetics. Hydrolysis at 90~C (■), 100~C (●), and 110~C(▲). All hydrolyses at 500mM sulfuric acid

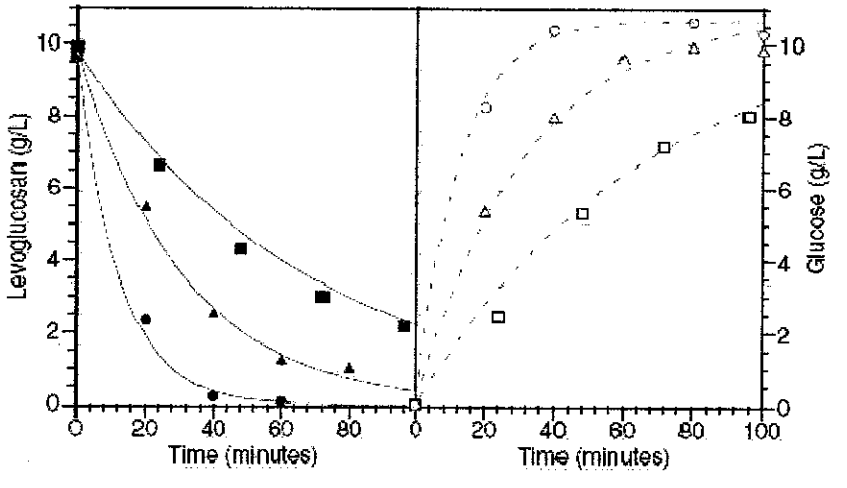


Fig. 31: Effect of sulfuric acid concentration on levoglucosan kinetics. Hydrolysis at 120mM H2SO4 ( ) 250mM H2SO4 ( ), and 500mM H2SO4 ( ) . All hydrolyses at 110 ~C.

The following equation is used to relate the hydrolysis with temperature and sulphuric acid concentration; where $[H_2SO_4]$ is the acid concentration in mmol L^{-1}, n and A are constant, R is universal constant of 8.314 J mol^{-1} K^{-1}. E is the activation energy (in J mol^{-1}) and T is temperature in Kelvin.

I

$$k_1 = [H_2SO_4]^n A e^{-E_1/RT} \qquad (6)$$

Based on the experiment that had been conducted, the activation energy was 114 kJ mol^{-1} and A was 1.0×10^{-11}.

Cellobiosan hydrolysis kinetics

Cellobiosan hydrolysis will yield cellobiose, ***levoglucosan***, and glucose. According to Steve Helle et al (2007), there are no other product been formed. They had developed a reaction scheme to describe the overall reaction kinetic. It is shown in figure 11. The initial hydrolysis reactions may be either the hydrolysis of cellobiosan to form levoglucosan and glucose or the hydrolysis of levoglucosan to produce cellubiose.

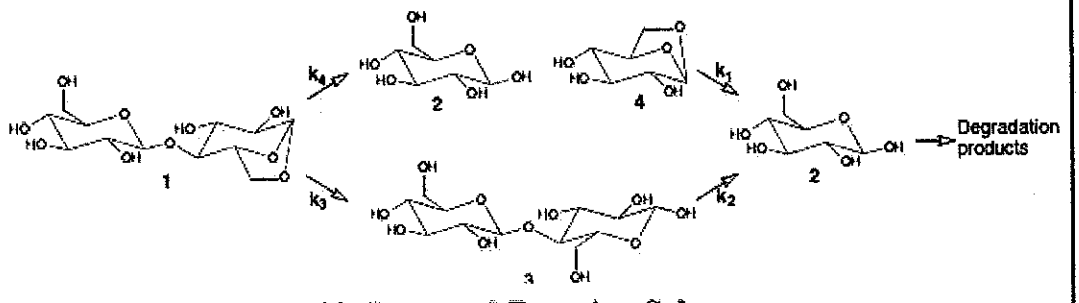


Fig. 32: Proposed Reaction Scheme

where (1) is cellobiosan hydrolysis scheme, (2) is cellubiose, (3) is glucose, (4) is levoglucosan.

All hydrolysis process was modelled into 1st order reaction. Based on the proposed reaction scheme, rate equation was developed;

$$\frac{dA}{dt} = -k_1 A + k_4 B \qquad (7)$$

$$\frac{dB}{dt} = -k_3 B - k_4 B = -(k_3 + k_4)B = -k_5 B \qquad (8)$$

$$\frac{dC}{dt} = k_3 B - k_2 C \qquad (9)$$

$$\frac{dD}{dt} = k_1 A + k_4 B + 2k_2 C \qquad (10)$$

K1 = reaction constant of levoglucosan hydrolysis into glucose

A = Levoglucosan concentration

K2 = reaction constant of cellubiose hydrolysis into glucose

B = Cellobiosan concentration

K3 = reaction constant of cellobiosan hydrolysis into cellobiose

C = Cellobiose concentration

D = Glucose concentration

K4 = reaction constant of cellubiosan hydrolysis into levoglucosan and glucose

The experimental efforts that had been done had given valuable results and references for the author. The reaction rates constant were obtained as below;

K1 = 0.000539 $^{s-1}$

K2 = 0.000218 $^{s-1}$

K3 = 0.000158 $^{s-1}$

K4 = 0.000158 $^{s-1}$

K5 = 0.000342 $^{s-1}$

Based on the reaction rates constant, it is concluded that the levoglucosan hydrolysis rate was two and half times greater than the cellobiose hydrolysis rate. Besides that, the levoglucosan hydrolysis is also one and a half times greater than cellobiosan hydrolysis rate.The hydrolysis of cellobiosan to cellubiose proceed at greater rate than hydrolysis to levoglucosan and glucose. In the nutshell, the greater rate of cellobiose formation and slower levoglucosan formation reaction resulted in bigger accumulation of cellobiose than levoglucosan.