SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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DETERMINING EXTRACTIVE CONTENTS OF DIFFERENT TYPES OF HARDWOOD BIOMASS- EFFECT ON PARTICLE SIZE

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Determining Extractive Contents Of Different Types Of Hardwood Biomass-Effect On Particle Size**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title for any other examining body or university.

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TABLE OF CONTENTS

Contents | **Page**

LIST OF TABLES

LIST OF FIGURES

Page

PENENTUAN EKSTRAKTIF KANDUNGAN DARI PELBAGAI BIOMASS KAYU KERAS- EFEK SAIZ ZARAH

ABSTRAK

Kajian ini dilakukan untuk menentukan kandungan ekstraktif jenis biojisim kayu keras dan saiz kesan zarah. Interaksi antara jenis biojisim yang digunakan dan saiz zarah yang berbeza dengan tindak balas kepada peratusan selulosa disiasat dan dikenal pasti dengan menggunakan reka bentuk eksperimen (DOE). Terdapat tiga jenis pencirian dilakukan ke atas jenis-jenis sampel biomass, Mikroskop Imbasan Elektron (SEM) untuk pemerhatian morfologi, X-Ray Diffraction (XRD) untuk penghabluran dan Karbon Hidrogen Nitrogen Sulphur (CHNS) analyzer untuk menentukan karbon, hidrogen dan nitrogen kandungan. pencirian itu dilakukan untuk mengenal pasti dan membezakan perbezaan antara biojisim yang berbeza dan dengan julat saiz yang berbeza. Kajian morfologi oleh SEM menunjukkan perbezaan dalam struktur tiga sampel biojisim yang berbeza dengan tiga pelbagai saiz yang berbeza manakala XRD menunjukkan perbezaan dalam penghabluran setiap sampel biojisim berkenaan dengan pelbagai saiz mereka. Model matematik adalah plot dari penggunaan ANOVA, dengan menggunakan kepentingan dan interaksi faktor-faktor yang telah dimanipulasi semasa proses hidrolisis sampel biojisim yang berbeza dengan yang berbeza pelbagai saiz zarah. Dari keputusan yang diperolehi, kedua-dua jenis sampel biojisim dan pelbagai saiz zarah menunjukkan sedikit interaksi antara satu sama lain dan didapati bahawa jenis biojisim mempunyai faktor penting yang lebih tinggi sedikit kepada peratusan selulosa.

DETERMINATION OF EXTRACTIVES CONTENT FROM DIFFERENT TYPES OF HARDWOOD BIOMASS- EFFECT ON PARTICLE SIZE

ABSTRACT

This research is done to determine extractive contents of different types of hard wood biomass and its effect particle size. The interaction between the type of biomass used and the different particle sizes with response to cellulose percentage is investigated and identified by using Design of experiment (DOE). There were three types of characterization done on the types of biomass sample, Scanning Electron Microscope (SEM) for morphology observation, X-Ray Diffraction (XRD) for crystallinity and Carbon Hydrogen Nitrogen Sulfur (CHNS) analyser to determine the carbon, hydrogen and nitrogen content. The characterization was done to identify and differentiate the differences between the different biomass and with different size ranges. The morphology study by SEM shows the difference in structure of the three different biomass sample with three different size range while the XRD shows the difference in crystallinity of each biomass sample with respect to their size range. A mathematical model was plot from the use of the ANOVA, by using the significance and interaction of the factors that was manipulated during the hydrolysis process of different biomass samples with different particle size range. From the results obtained, both type of biomass sample and particle size range shows little interaction with each other and it was found that type of biomass has a slightly higher significant factor to percentage of cellulose.

CHAPTER 1

INTRODUCTION

1.1 Significant of research work

Biomass has always been an alternative energy source to replace for the depleting non-renewable fossil fuel etc. Due to the advancement of technology and research in the biomass sector, it has been adapted in many industries serving a purpose of decreasing the harmful gasses that is released by burning of fossil fuels. A study of utilizing biomass to replace metallurgical coke as a reducing agent to produce pig iron was conducted by (Srivastava et al. 2013). Their research has shown that not only can biomass be successfully used as a reducing agent, it also shows that the carbon emissions are reduced to almost 50% when using biomass as a reducing agent.

A reducing agent for the mining industry typically has to be able to release CO and H_2 for it to reduce another metal composition. Certain biomass store carbon and hydrogen in the form of carbohydrates by utilizing atmospheric CO_2 for plant growth and converting it. Upon thermal decomposition, biomass can further be decomposed to produce CO and H_2 to reduce iron oxide into metallic iron.(Srivastava et al. 2013)

As to why the use of hardwood biomass rather than softwood would also be related to the emission of CO and lignin content. Softwood biomass has a relatively higher amount of lignin content which in turn give a lower emission of CO emission rate when burning and contribute a higher generation of CO2 gas compared to hardwood biomass (Amaral et al. 2014). As supported from recent studies, reducing agents has to be able to release CO gas for reduction which means hardwood biomass would have a higher advantage in this particular sector.

Reduction is a process of known in the mineral industry to obtain a more purify form of metal from a specific ore. For manganese ore reduction process is necessary to recover manganese as such a reducing agent is needed to optimize the process. The application of the agricultural biomass has been investigated by several researcher with relatively high Mn recovery in standard conditions (Ismail et al. 2015). The use of biomass as reducing agent research has also extended to the possibility of making use of what was previously known to be of lower grade manganese ore to be economically mined (Ismail et al. 2016).

1.2 Problem Statement

The problem of extracting from biomass is the lignin layer that exists in every plant biomass particle. The sugar monomers that is needed to extract are tightly bounded to the lignin. Various study regarding the relationship of lignin with sugar extraction has been done and one example is the study of a few scholars from China (Si et al. 2015) which studied the effect on lignin extraction on biomass enzymatic saccharification. It was found that lignin extraction greatly enhances biomass saccharification. First step to be taken is having to breakdown the lignin for the extractive content but lignin has high resistance towards degradation. The experiment will touch on how the particle size affect the extractive content of the biomass particles, as the smaller the particle size the more lightly lignin will breakdown. This study aims to determine at which size the lignin breaks down for future use of biomass extraction.

1.3 Research objectives

- To determine the extractive content of different type of hardwood biomass.
- To study the effect of particle size on the hydrolysis of biomass.

1.4 Scope of work

For this research, the work done will be focused on determining extractive contents on various types of hardwood biomass. The hardwood biomass chosen are rubber tree type sample, bamboo tree type sample and rattan type sample, all three are obtained from different places of origin as raw product.

The next factor to be considered are particle size range. The raw biomass samples are categorized to three different particle size ranges to determine the relationship between effect of particle size on determination of extractive content. The three different size ranges start from (-212+75)µm followed by the middle size range of(-75+53)µm and finally the smallest size range of (-53)µm.

A number of characterization method was employed for further understanding of the biomass sample. The surface morphology of the biomass sample with each respective size range was determined using SEM, the crystallinity index was calculated by XRD analysis and finally the contents of carbon, hydrogen and nitrogen was obtained using CHNS elemental analyser.

The relationship between particle size and type of hardwood biomass with the extractives content determination is calculated using ANOVA.

1.5 Thesis Organization

This thesis is composed of 5 main chapters including the current chapter 1 which is introduction followed by literature review in chapter 2, methodology in chapter 3, results and discussion in chapter 4 and is completed by chapter 5 containing conclusion and recommendation for future research.

For chapter 1, the general background of the research is discussed, an overview of the whole project which discusses on the problem statements, the objectives regarding the significance of the project and the scope of work.

Chapter 2 is about the literature review where several articles and journals are studied and discussed. This chapter also focuses on the problems faced by previous scholars in their studies beside the objective of this research paper.

In the next chapter, methods and materials used to complete each task in completing this research is discussed thoroughly. Information gathering from previous studies regarding this topic is crucial to avoid redundant testing or analysis in the experimental work.

The most important part of the experiment is discussed in chapter 4, where all experimental results are compiled and discussed properly with knowledge from previous engineering studies. The outcome of the experiment is discussed and evaluated.

The final chapter in this paper ends by writing a compact summary about the conclusion of the overall discussed results. The summary also includes all the achievements from the stated objective earlier in the introduction chapter of this paper. A recommendation is also given to discuss suggestions as how we can improve the research work in future studies for this particular field in order to achieve better outcomes.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The mining industry has had its fair share in contributing Global warming and increasing demand for fossil fuels used as reducing agent for producing pure metals from its constituent metals. The use of fossil fuel in our industry has not only create enormous amount of pollution, it also uses high amount of energy and create significant amount of heat making the reducing process costly. They are the main driving forces for developing a more techniques and materials for reduction which are more environmentally friendly at a much lower cost. One of the most recent researches done are by substituting fossil fuel reducing agent with biomass pellets. One of the best choice was by using Lignocellulosic biomass which is an abundant, renewable, non-food source for the production of biomass pellets.(Mirmohamadsadeghi et al. 2016).

Many past investigators has focused on reducing ores such as manganese by organic reductants of manly carbohydrates like glucose11-13, sucrose14, lactose15, oxalic acid16 etc. This is mainly due to the fact that manganese usually exists in pyrolusite (MnO_2) and the biggest complication with this particular ore is that it is stable in acid or alkaline oxidizing agent therefore need to be carried out under reducing conditions. The previous reducing agents had been used under dangerously harmful acidic media with hazardous reducing agents such as SO_2 , which is why the attention has turned to using carbohydrates as reductants. Carbohydrates are non-dangerous and low cost reducing agents that may be used either in pure form or as industrial wastes. The revealed ponders demonstrate that the sugars are successful reductants under mellow temperature conditions (<90°C). Ligno-cellulose based waste materials such as sawdust and bagasses are potential reductants for acid leaching of manganese ores.

2.2 Hardwood and softwood biomass

Biomass in layman's term means waste that will be used for energy. More specifically, this paper will discuss how the burning of biomass will provide energy for it to release its reducing gas for reduction process that can be useful in the mining field, biomass is said to be one of the promising sustainable energy sources and is being used widely due to its availability and environmentally-friendly nature(Tilman et al. 2006). The most common type of biomass to be used as a reducing agents are agricultural biomass. Agricultural waste has been used widely as feedstock for energy (Pasangulapati et al. 2012). Agricultural biomass comes in two form, either hardwood or softwood. Of the two it can be said that softwood in general is cheaper mainly due to the fact that it grows faster which is pretty much the main difference between the two category of agricultural biomass.

Although Hardwood biomass is said to be named such because it is much denser and harder compared to softwood,that is not the case all the time. Some hardwood (eg: balsa wood) is categorized as a hardwood but in reality is lighter, and less dense than other type of woods, including softwood. The classification between the two types of woods are based on their basis of reproduction rather than weigh or density. Hardwood are from an angiosperm tree, comes with a covering while softwood is from a gymnosperm, comes without covering.

For industrial purposes, softwood are generally less dense ergo will have to occupy a larger volume compared to hardwood which means more storage space would be needed to house a store full of softwood biomass for further processing. Hardwood was proven to release a higher level of CO emission and lower level of CO_2 emission compared to softwood (Amaral et al. 2014) which is more favourable for use as a reducing agent in the mining industry and is why this paper focused on hardwood biomass instead.

As explained earlier all three of the sample chosen namely bamboo, rattan and rubber tree are an angiosperm ass all hardwoods are but they differ in structure. Rubber are dicotyledonous tree, has round shaped leaves flowers, seed come in a pod shape structure called nuts and is pretty much basic tree with a stem or a trunk which provides nutrients to other parts of the plant and acts as a support structure. Bamboo are flowering plants of the grass family, inter nodal regions of the stem are usually hollow, absent of a dicotyledonous woody xylem causing them to be columnar rather than tapering. Rattans are have slender stems, vine like structure, scrambling over other vegetation and unlike hollow bamboo, rattan are solid need structural support and cannot stand on their own.

2.3 Commercial application

Rattan are vines that grow in tropical forests, although mainly used in the furniture industry, rattan has other uses including in traditional medicine, food and construction materials(Rachchh et al. 2014). The fruit of rattan produces a red resin known as red dragon which is thought to have medicinal properties. Rattan is used primarily in furniture both outdoor and indoor type due to its durability and versatility. Rattan furniture is also easily maintained and available in various shapes and sizes and colour. Rattan has many different species which fits into specific uses. Some of the smaller diameter rattans are often used for baskets and the furniture industry make use of this rattan by weaving. The other larger diameter of rattan was used for poles and stripped for weaving(Myers 2015). Rattan was also used as toughness modifiers and reinforcing fillers. Cellulose material used as fillers in plastics and cement was proven to be lightweight, enhanced mechanical properties and free of health hazards compared to synthetic fillers which is costly and also requires more energy in production. It was also stated that natural fibres such as rattan has emerged as a renewable and cheaper substitute to synthetics such as glass and carbon in making structural components. Natural fibres have the advantage that they are renewable resources and have marketing appeal. For over 2000 years natural fibres such as rattan has been around and used to reinforce materials as they are cost effective and superior substitute to glass fibres in composites (Rachchh et al. 2014). Rattan is also famous for being used to make handicraft and art pieces. Aside from the importance of its durability, the resistance it has to splintering allows sections of the rattan to be used in martial arts, as staves or canes. It is also common material used for the handles in percussion mallets, walking sticks and high end umbrella.

Rubber trees can reach up to 100 feet in the wild. Two main nation are leaders of rubber producers namely Malaysia and Indonesia and it is safe to safe that rubber tree can be found in abundance in this two states. Rubber trees are mainly grown for the tapping of the latex but it could also be used for timber when the tree reaches age of 25-30 years in which case the latex production of the tree pretty much ceases, the woods can be harvested for furniture making and other vast range of products as substitute wood from natural forests (Gouvêa et al. 2013). The white or yellow latex usually occurs in latex vessels in the bark, outside the phloem and comes out of the tree in sap form. The latex is a sticky, milky colloid acquired by making incisions on the bark and collecting the milky fluid in a vessel. The whole process to obtain latex fluid is called tapping. The older the tree, the more sap is produced until it reaches 25 years and above where latex production stops. In plantations, trees are normally smaller due to the fact that they grow slower when tapped for latex. The process of tapping does not occur until the tree reaches the age of five to six years. Raw rubber tapped from the trees consists of polymers of the organic compound isoprene with minimal impurities of other compounds and water. The natural rubbers made from forms of polyisoprene (Havanapan et al. 2016) are classified as elastomers. After acquiring the latex, refining process take place for rubber to be ready for commercial processing where latex is allowed to coagulate. After coagulation, lumps are collected and processed for marketing purposes. The use of rubber is extensive due to its large, appealing properties such as stretch ratio, high resilience and waterproof qualities and others. There are many types of rubber that exists due to further processing which gives additional properties to it. For example uncured rubber is used for cements, friction tapes etc. Resistance to abrasion also gives softer rubbers a rather valuable use like for tires and conveyor and hard rubber valuable for piping to handle abrasive sludge. The flexibility if rubber also gives an advantage to make products like hoses and rollers. The diversity of equipment produced by rubber even extends to top end latex products like condoms, gloves and so on.

Bamboo has been an important part in millions of human beings for the past millennium and has been the centre of scientific study for ages since its considered to be one of the most versatile and fastest growing plants on the earth. Over the past recent years, exploitation on bamboo plants increased with a new purpose, a substitute for timber and bamboo are found in rapidly developing areas where timber is usually limited. Bamboo is an anisotropic plant which means it has different mechanical properties in the longitudinal, radial and transverse section which is one of the feature for its usefulness and also prove to be one of the difficulties in construction making. The mechanical properties of bamboo has already been acknowledged to have tremendous potential as a structural material but is susceptible to environmental degradation which can be reduced by further treatment (Lakkad & Patel 1981). The growing interest for development in bamboo product are mainly due to the fact that bamboo products are sustainable, cost effective and ecologically responsible alternative construction material (Sharma et al. 2015). For construction purposes, the harvest can only start once the culms reach their greatest strength and contain lowest level of sugar in their sap as high sugar content gives rise to pest infestation. Besides construction, bamboo is also for culinary purposes, weapons, musical instruments and other art forms.

2.4 Lignocellulosic plants

The term lignocellulosic feedstocks refer to the inedible stems and leaves of the above-ground plant body. Lignocellulosic crops has been used widely as biofuel due to its capability to adapt to barren land and is associated with high input and output energy efficiency and fairly low cost of handling. Plant biomass are made of complex materials, they generally have 3 major organic components which are the lignin, cellulose and hemicellulose as mentioned in the name itself, lignocellulosic plants.

Lignin has high molecular-weight structure with cross-linked polymers of phenolic monomers and have generally complex structures. Lignin gives structural support, impermeability and resistance against microbial attacks in the cell wall.

Cellulose is composed of long chains of cellobiose units that are linked to D-glucose subunits through β-(1,4)-glycosidic bonds and are the main structural constituent in cell walls. Hydrolysis catalysed by cellulose or acid can can be used to break these linkage bonds.

Hemicellulose are composed of branches of short monosaccharides such as pentose (xylose, rhamnose, and arabinose), hexose (glucose, mannose, and galactose), and uronic acid.

These components occur in the cell wall where cellulose are packed into mcrofibrils by cellulose polymers linked by both var der Waals and hydrogen bonds, they are then protected by the hemicellulose and lignin. The processing cost of lignocellulosic crops are high due to these features on the structural component of the plant. Lignin seal is broken and the crystalline structure of cellulose are broken by using pretreatment on the lignocellulosic crops. Since the features of lignin prove to make the crops quite challenging to process, naterials with low lignin and high cellulose and hemicellulose contents are more desired for future biomass processing and production (Jung et al. 2015).

2.5 Reducing agent

Reduction in mining industry are usually the step where oxidized metal becomes the elemental metal with the aid of a reducing agent. Reducing agents helps facilitate and speeds up the process. In the process of reducing manganese ore, the reductants used are usually coal, graphite and pyrite. Coal was used as a reductant to transform manganese dioxide to manganese oxide in traditional technology (Sahoo & Rao 1989) but these reductants however generate plenty of smoke dust and requires high temperatures for reaction to occur. Which means processing manganese ore requires high production cost energy consumption and serious environmental pollution (LI et al. 2015). The use of biomass as a reductant in has gathered more attention and was able to achieve a rather high recovery efficiency at a fairly regulated temperature by using corncob to extract low grade manganese dioxide ores in sulfuric acid solutions (Tian et al. 2010).

CO_2 emissions is very high from production of pig iron using coke as a reducing agent. By producing biomass reducing pellets as reducing agent, the CO_2 emission was managed to be decreased considerably. The total iron obtain also had very minimal loss in weight and the other advantageous aspect of using biomass rather than fossil fuel derived agents are the lower energy consumption needed since it need a lower temperature to operate (Srivastava et al. 2013).

2.6 Hydrolysis process

Hydrolysis is a procedure to hydrolyze the natural material utilizing the corrosive. Hydrolysis handle normally used to remove the decreasing sugar that contains in the BSD. The diminishing sugars that may contain in the bamboo sawdust are the sucrose, lactose, glucose and substantially more. In this review, hydrolysis process is done to distinguish the impacts of picked parameters towards the BSD in delivering diminishing sugars.

Physical, compound or physicochemical pretreatment is utilized to separate the hemicellulose and lignin structure to enhance the hydrolysis rate (Zhang et al. 2007). The pretreatment methodologies are the steam blast, weaken corrosive and lime for hydrolysis (Zhang et al. 2011). The pretreatment utilizing weaken sulfuric corrosive, H_2SO_4 (corrosive hydrolysis) is the destined to use as it is having high effectiveness in the isolating procedure of cell divider parts bringing about hemicellulose hydrolysate and cellulignin (Dussán et al. 2014)

Other than that, weaken corrosive hydrolysis likewise is a broadly utilized technique contrasted with another hydrolysis strategy. This technique is compelling and modest with a solitary stage hydrolysis. Corrosive go about as an impetus in the corrosive hydrolysis of lignocellulosic biomass that delivered xylose from hemicellulose, while cellulose and lignin part stay unaltered (Suharti & Sakinah 2015).

Hemicellulose is anything but difficult to corrupt amid corrosive hydrolysis because of its formless, brunched structure contrasted with cellulose which needs serious treatment conditions because of its crystalline nature (Parajó et al. 1995).

2.7 Hydrolysis parameters

Parameter configuration is a technique for choosing nominal esteems for the arrangement of working factors. It can be embraced to upgrade strength or to streamline the nominal reaction (Frey et al. 2003).

It was likewise shown that the measure of sugar discharged amid hydrolysis relied on upon the kind of raw material and working states of the analysis, for example, temperature, corrosive fixation and living arrangement time (Pessoa et al. 1996). Amid hydrolysis, the acid concentration was observed to be the most critical parameter influencing the sugar yield, while temperature demonstrated the most astounding effect on the arrangement of sugar degrradation items (Neureiter et al. 2002)

The real drawback of acid hydrolysis is that it creates a hydrolysate that contains the sugar required for bioconversion as well as sugar and lignin degradation items and in addition acetic acid that could slow down or prevent the bioconversion of xylose (Parajo et al., 1995). Hence, the optimize condition of acid hydrolysis can amplify the biomass degradation while limiting the undesirable items.

These discoveries proposed that the increasing H_2SO_4 concentration required a shorter residence time to get the most astounding recovery of xylose in the subsequent hemicellulosic hydrolysate (Rafiqul & Mimi Sakinah 2012). Unmistakably the response time and acid concentration are the central point which impact the resulting products (Akpinar et al., 2009).

The pH of the hemicellulosic hydrolysate was changed to 6.0 by including CaO powder followed by filtration, to expel the precipitate formed. The filtrate was put away at 4°C and analyzed for xylose, glucose, furfural, and acetic acid (Rafiqul and Sakinah, 2011).

Keeping in mind the end goal to decide the correct response time, the response of the hydrolysis must be halted straight away after the hydrolysis procedure. Isolate between the lixiviant and the buildup after the procedure and neutralize the reaction. The response of sulphuric acid towards the bamboo sawdust will never stop even at the low temperature. The hydrolyzed response must be ceased by neutralizing it and keep in a chiller before the analysis procedure. Acid concentration may influence the hydrolysis procedure, as the higher grouping of corrosive can give more demolition towards the BSD surface. The blending time likewise can be diminished since the bamboo effortlessly hydrolyzed in the high concentration hydrolysis acid

Aside from that, the speed of stirrer additionally assumes an essential part to guarantee the BSD and the hydrolysis acid is all around mixed. Along these lines, all BSD can have the equivalent opportunities to hydrolyze in the acid. The density of the BSD is not as much as the density of the acid, so it tends to skim close to the surface. This stirrer can help in the hydrolysis procedure to empower all bamboo to hydrolyzed in the acid. A decent mixing outcome is vital for limiting venture and working costs, giving exceptional returns when the mass exchange is restricting and consequently upgrading productivity, as indicated by handbook of modern blending, by Edward et al., 2004.

In this exploration think about, the hydrolysis procedure of bamboo sawdust conditions is fluctuated in regards to sulphuric acid, H_2SO_4 concentration and stirrer speed rotation, at 6 hours response time and 100ºC brooding temperatures. The investigations are completed utilizing a 200ml reaction flask, which is firmly fixed and drenched in a silicone bath given electrical heating. Since this work is an open system, the opening window of fum cupboard is kept at a consistent height. This activity is to control the others variables which are hard to control; that may influence the hydrolysis procedure. Other than that, it is one of the answers for counteract significant losses in the hydrolyzed liquor due of to evaporation.

2.8 CHNS elemental analyser

Classic chemical techniques has always been used to detect basic elements such as Carbon, hydrogen, nitrogen and sulfur in organic compounds. Although the relevant chemical reaction used to determine such elements are highly accurate, these techniques are usually focused on one element, takes a long period of time to be completed and is labor intensive.

Given with the technology we have nowadays, companies have made a number of automated element analysis devices to promote automation and to expedite the element analysis of organic compounds as it is one of the crucial steps in analysis of various organic compounds containing samples. The devices mentioned works on the catalysed high temperature decomposition of analysed material in the oxygen medium, then gas chromatography analysis takes place on the resulting gas products. Manufacturers provides reactors that contain both the oxidation zone represented by the tungsten oxide and the reduction zones represented by the copper wire.

This kind of analysis takes a rather short amount of time compared to the other more traditional method, it is even considered to be able to give instant results as this analysis only takes a few minutes. Therefore the main reason why element analyzers in the single reactor mode is use widely is due to the high speed of simultaneous detection of C, H, N and S (Eksperiandova et al. 2011).

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter discusses the overview of methods used from the start of the research until the end. Firstly it will include the general explanation of raw materials used such as where it was obtained and the size etc. Next would be the list of chemicals used then followed by the preparation done to the raw samples for further processing which mainly leads to obtaining the reduced size of each sample from approximately ± 500 µm to three size ranges namely (-212+75)µm, (-75+53)µm and (-53)µm. Once the sample is prepared, then follows the characterization of samples which includes morphology observation by using Scanning Electron Microscope (SEM), crystallinity index analysis with the aid of X-Ray Diffraction (XRD) and carbon, hydrogen and nitrogen content analysis by using Carbon Hydrogen Nitrogen Sulfur (CHNS) elemental analyser.

After characterization of sample occurs, the hydrolysis experimental process is carried out by using design of experimental (DOE) sequential design. The design chosen to fit this research is 3^2 fractional factorial design with two factors, particle size of biomass sample, and type of biomass sample. The hydrolysis experiment carried out was to determine the extractives content, lignin content, cellulose content, hemicellulose content and holocellulose content of each biomass sample with respect to each sample size. The sequence of methodology is as represented in figure 3.1 below.

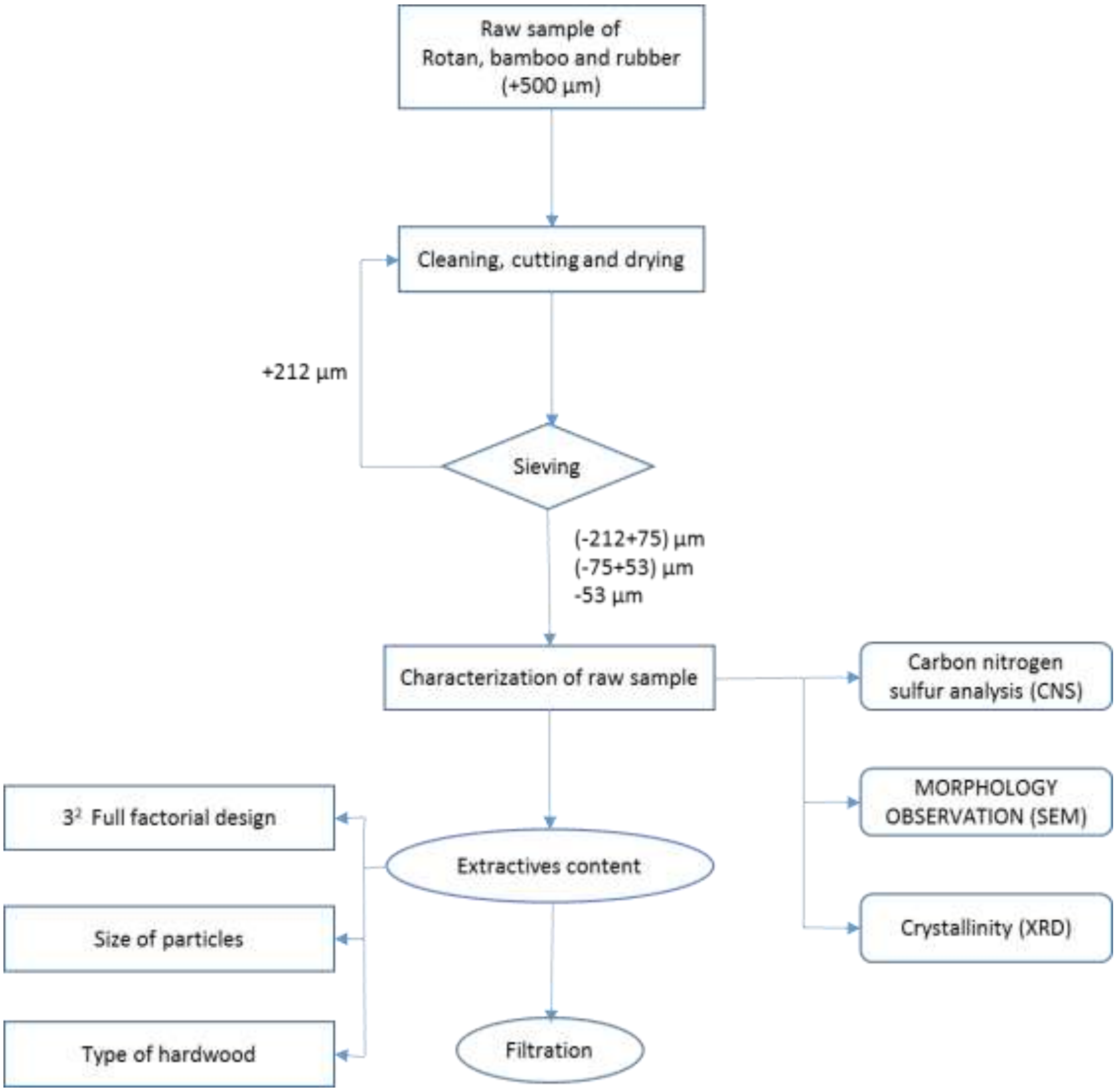

Figure 3.1: Flowchart to show overall work progress

3.2 Raw material

Ample research could be found about the use of bamboo biomass in the mineral industry as reducing agent. This research paper aims to study about other types of hardwood biomass that might prove to be as useful aside from the proven bamboo biomass for the use in the reducing agent sector of mining. For the raw sample, the hardwood chosen was bamboo, rubber and rattan for comparative reasons. Bamboo biomass was obtained from the Forest Research Institute Malaysia (FRIM) in Kepong, Kuala Lumpur. Rubber sample was found from private properties near Sungai Bakap, Penang and was given under consent from the owner of land. Lastly rattan sample was obtain from a nearby factory, at Jawi, Penang where it was used mainly for furniture production. All this sample, bamboo, rattan and rubber was of size +500 μm and weighs approximately 3.01 kg, 0.9 kg and 1.1 kg respectively in their natural plant form but was cut down into smaller manageable pieces. This particular samples was chosen for it is found in abundance in our country, Malaysia.

Figure 3.2 samples obtained from their respective places (a) bamboo (b) rattan (c) rubber

3.3 Chemicals used

The chemicals used for this research are listed in table 3.1 below.

Table 3.1: chemical used in hydrolysis of biomass samples.

Types Of Chemicals	Molecular Formula	Molecular Weight (g/mol)	Percent (%)	Supplier
Ethanol	CH_3CH_2OH	46.07	98	Merck
Nitric acid	HNO_3	63.01	65	Merck
Sulfuric acid	H_2SO_4	98.08	98	Merck
Acetic acid	CH_3COOH	60.05	98	Merck

3.4 Sample Preparation

Regarding Figure 3.2, a total of 3 samples was collected (bamboo, rattan and rubber) and then cleaned of any impurities from their previous place of processing. The samples was then allowed to be dried outdoors, directly under the sun for at least a day until no moisture is visible or felt, samples are then oven dried in a Memmert oven at 60 ^{o} C. Drying process continues until constant weight is obtained. The dried samples then proceed for cutting. The equipment use for cutting is a CB 75F band saw machine and is used to obtain a size dimension of approximately ± 6cm x 2cm (height x base) for all sample. This particular dimension is for it to accommodate the necessary feed size of the next process, which is grinding. The equipment used for grinding is a mini grinder with filter of -250µm. After grinding, the three sample is then sieved for the specific sizes needed of (-212+75)µm, (-75+53)µm and (-53)µm. Sieve shaker with those specific mesh limits are selected, the sieve shaker used was an Octagon Digital Sieve Shaker with 1.5 amplitude. Since there is three samples chosen with three different sizes to work with, 9 samples are prepared. The specific sizes of the grinded biomass is then stored separately in a dark, airtight container stored at room temperature. The procedure of size reduction of the three biomass sample is shown in figure 3.3.

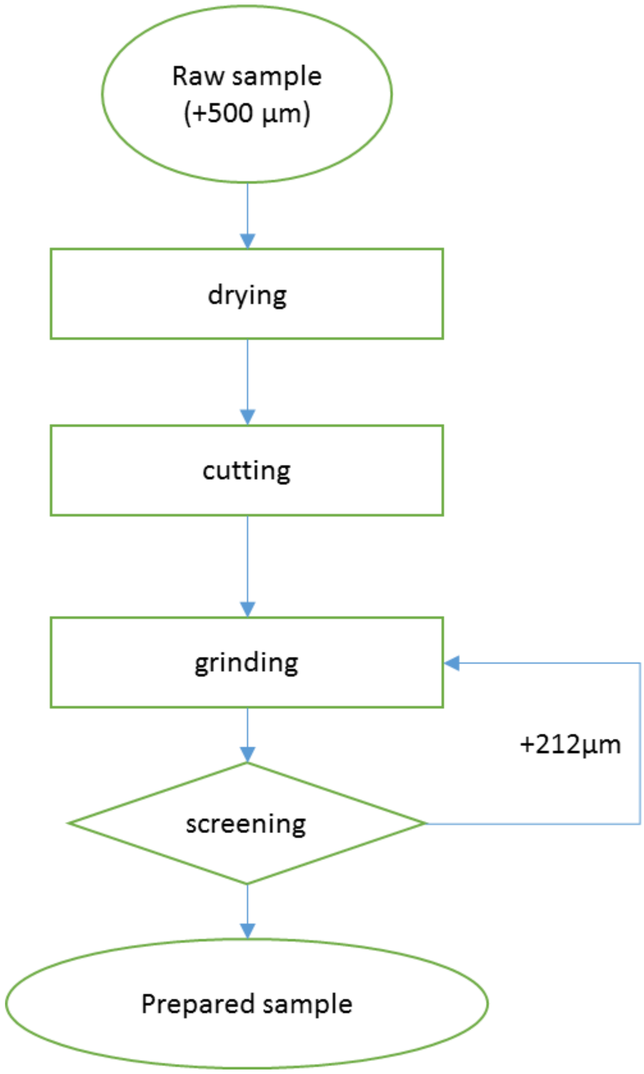

Figure 3.3: Flowchart of procedure of biomass sample preparation

Figure 3.4: Equipment used for sample preparation (a) Memmert oven (b) CB75F band saw (c) Mini grinder

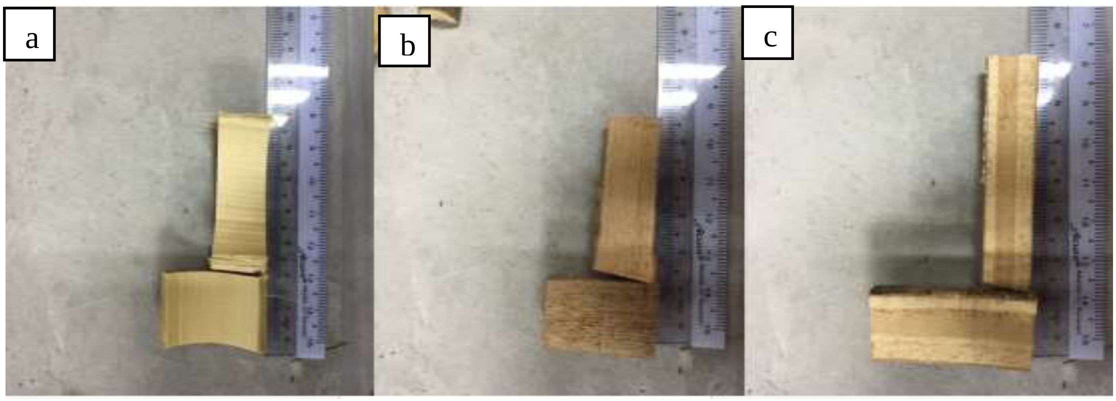

Figure 3.5: Size dimensions before grinding (a) bamboo sample (b) rattan sample (c) rubber sample

3.5 Characterization of raw sample

3.5.1 Carbon, nitrogen, and sulfur content

Approximately 2.5g of sample was taken from the three type of hardwood, bamboo, rattan and rubber for determining their carbon, nitrogen and sulfur content and place in a sample bag. Then undergoes a carbon, hydrogen, nitrogen and sulfur, CHNS/O Series II Perkin Elmer analyzer. Firstly, in the combustion process (furnace at 1000°C), carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of nitrogen and sulphur to sulphur dioxide. If other elements such as chlorine are present, they will also be converted to combustion products, such as hydrogen chloride. A variety of absorbents are used to remove these additional combustion products as well as some of the principal elements, sulphur for example, if no determination of these additional elements is required. The combustion products are swept out of the combustion chamber by inert carrier gas such as helium and passed over heated (about 600° C) high purity copper. This copper can be situated at the base of the combustion chamber or in a separate furnace. The function of this copper is to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen to nitrogen gas. The gases are then passed through the absorbent traps in order to leave only carbon dioxide, water, nitrogen and sulphur dioxide. Detection of the gases can be carried out in a variety of ways including a GC separation followed by quantification using thermal conductivity detection a partial separation by GC ('frontal chromatography') followed by thermal conductivity detection (CHN but not S) a series of separate infra-red and thermal conductivity cells for detection of individual compounds. Quantification of the elements requires calibration for each element by using high purity 'micro-analytical standard'