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SIMULTANEOUS HYDROLYSIS-LEACHING OF SYNTHETIC MANGANESE ORE USING BAMBOO SAW DUST AND COMPUTATIONAL ANALYSIS USING ANSYS.

By

SUCHITRA A/P PERUMAL

SUPERVISOR: DR. SUHAINA BT ISMAIL

CO – SUPERVISOR: DR. MUHAMMAD KHALIL ABDULLAH

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation titled **"Simultaneous hydrolysis-leaching of synthetic manganese ore using bamboo saw dust and computational analysis using ANSYS"**. I also declare that it has not been previously submitted for the award of any degree or diploma or other title of this for any other examining body or University.

Name of student : Suchitra A/P Perumal Signature :

Date :

Witnessed by,

Supervisor : Dr Suhaina Bt Ismail Signature :

Date :

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LIST OF SYMBOLS AND ABBREVIATION

ANOVA	Analysis of Variance
BSD	Bamboo Sawdust
°C	Degree Celsius
DOE	Design of Experiment
FRIM	Forest Research Institute of Malaysia
ICP-OES	Inductive Couple Plasma - Optical Emission Spectrometry
K	Kelvin
LOI	Loss on Ignition
µm	Micrometer
mL	Millilетre
M	Molar
%	Percent
rpm	Rotation per Minute
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

HIDROLISIS-PENGURASAN REDUKTIF SERENTAK PADA SINTETIK BIJIH MANGAN DAN ANALISIS PENGIRAAN MENGUNAKAN ANSYS.

ABSTRAK

Kajian ini dijalankan untuk mengkaji kesan utama dan kesan interaksi antara kepekatan asid sulfurik dan kelajuan rotasi pengaduk pada SMO dengan menggunakan minitab 18 dan mengkaji kelakuan aliran udara, suhu, BSD, SMO dan asid sulfurik menggunakan perisian ANSYS Fluent. Sebelum kerja eksperimen, penyediaan sampel dan kajian pencirian dijalankan pada BSD dan SMO. Saiz zarah BSD dan SMO dikurangkan kepada -75 µm. Analisis XRF menunjukan bahawa SMO mempunyai Mn (68.490 %), dan Fe (0.06 %) sebagai elemen terbanyak dan elemen terendah ialah Ca (0.00393 %) dan K (0.000623 %). Dari hasil XRD, BSD didapati mempunyai 41.01% kristalografi. Proses hidrolisis-peleburan reduktif SMO dijalankan dengan reka bentuk faktorial penuh 2^2 + 5. Kajian ini mempunyai dua factor iaitu kepekatan asid sulfuric dan kelajuan rotasi pengaduk. Tahap tinggi, sederhana dan rendah ditunjukkan oleh +1, 0 dan -1 masing-masing. Lima titik pusat berfungsi sebagai pengukuran dalam kestabilan proses dan memeriksa kelengkungan. Pemulihan Mn ditentukan dengan menggunakan ICP-OES. Kemudian, kesan utama dan kesan interaksi pemboleh ubah pada kerja eksperimen dianalisis dengan menggunakan Minitab 18. Untuk kerja pengkomputeran,model tindak balas telah direka menggunakan Solid Works 2013. Model ini diimport ke ANSYS Fluent 15.0. Tingkah aliran fasa udara, pepejal dan cecair semasa proses hidrolisis-peleburan reduktif dianalisis pada kelajuan pengaduk yang berlainan. Model matematik yang dihasilkan menggunakan ANOVA menunjukkan tiada kesan penting ditunjukkan antara pemboleh ubah utama. Walau bagaimanapun, kesan interaksi antara pembolehubah utama agak ketara. Dari analisis komputasi, tingkah aliran pada 400 rpm adalah lebih bergolak dan fasa pepejal dan cecair teragih dengan baik daripada 200 rpm. Tahap pengedaran sederhana ditunjukkan pada 300 rpm.

SIMULTANEOUS HYDROLYSIS-LEACHING OF SYNTHETIC MANGANESE ORE USING BAMBOO SAW DUST AND COMPUTATIONAL ANALYSIS USING ANSYS.

ABSTRACT

This research is carried out to investigate the main effect and interaction effect of sulphuric acid concentration and rotation speed of stirrer on SMO by using Minitab 18 and to study the flow behaviour of BSD, SMO and sulphuric acid using ANSYS Fluent software. Prior to the experimental work, sample preparation and characterization studies are carried out. The BSD and SMO particle size were reduced to -75 µm. XRF analysis indicates that the major elements present in SMO are Mn (68.490 %), and Fe (0.06 %) while the minor elements are Ca (0.00393 %) and K (0.000623 %). From the XRD result, BSD is found out to have 41.01 % of crystallinity. Simultaneous hydrolysis-leaching process of SMO is conducted with full factorial design of $2^2 + 5$. The two factors are studied in this research which are the concentration of sulphuric acid and rotation speed of stirrer. High, medium and low level of the variable are indicated by +1, 0 and -1 respectively. Five centre points are added in this design as a measurement in process stability and to check curvature. The Mn recovery from the leached liquor is determined by using ICP-OES. Then, main effect and interaction effect of the variables on experimental work is analysed by using Minitab 18. For the computational work, first reaction flask model were designed using Solid Works 2013. This model was imported into ANSYS Fluent 15.0. The flow behaviour of air, solid and liquid phases during simultaneous hydrolysis-leaching were analysed at different stirring speed. The mathematical model generated using ANOVA shows no significance effect was shown between the main variables on the experimental work. However, the interaction effects between main variables are quite significant. From the computational analysis, flow behaviour at 400 rpm is more turbulent and the solid and liquid phases are well-distributed than at 200 rpm. Medium level of distribution is shown at 300 rpm.

CHAPTER 1

INTRODUCTION

1.1 Significance of research work

Manganese plays crucial role in both metallurgical and non-metallurgical industries. Manganese is mainly use as an alloy composition for deoxidizing and desulphurizing addictive in steel industry. Moreover, manganese is quite significant as alloy for aluminium, and copper. In non-metallurgical industry, manganese is highly preferred in dry cell, glass and chemical industry. However, the shortage and low grade of manganese carbonate ores have become the main problem that restrict the sustainable development of manganese industry (Li *et al.*, 2015).

Hydrometallurgical processing of complex ores and concentrates is becoming increasingly significant as the mining industry seeks to exploit mineral deposits that are difficult to treat using conventional mineral processing (Dreisinger, 2009) . Extraction of manganese must be carried out under reducing conditions since Manganese oxide ore is stable in acid or alkaline conditions (Wu *et al.*, 2014). Moreover, different hydrolysis-leaching method does not have a significant effect on the overall reductive leaching of synthetic manganese ore. Approximately 99% of manganese can be recovered from simultaneous hydrolysis and leaching of synthetic manganese ore using bamboo saw dust as reducing agent (Ismail *et al.*, 2013, Kimberley, 2017).

Research have been done for reductive leaching of manganese ore using biomass as reducing agents such as corncob, sawdust ,cane molasses ,molasses alcohol wastewater, waste tea and cornstalk. This is because biomass is non-hazardous, and has good reactivity, availability and low cost and is used under mild conditions (Tang *et al.*, 2014).

1.2 Problem Statement

Various hydrometallurgical process are available for the extraction of Mn from reductive leaching of Mn ores. These methods are various in the usage of different types of reducing agent. Previous researchers have conducted the study of reductive leaching using SO_2 as reducing agent. However, some of the reducing agent can be dangerous to the environment, Thus, more focus should be given in the usage of environmental friendly reducing agent such as carbohydrates. Glucose, sucrose, lactose, BSD and oxalic acid are some of the examples of carbohydrates that can be used as reducing agent (Furlani, Pagnanelli and Toro, 2006, Hariprasad *et al.*, 2009).

Apart from that, the flow behaviour of solid, liquid and air phases during the leaching process is critical for improving the performance of the system. Such behaviour cannot be identified by naked eyes. . The hydrodynamics of stirred tanks can be resolved using computational fluid dynamics (CFD). The flow generated by the impellers complex and modelling it in the presence of high solid concentration is challenging. However with the advances in CFD models, such as turbulence and particle-fluid interactions, have made modelling of such flows feasible (Wadnerkar, Pareek and Utikar, 2015).

Plenty of previous studies have been conducted to study the effects of acid concentration and stirring speed on the SMO extraction using different types of carbohydrates as reducing agent. However, very little attention is given to study the flow behaviour of solid, liquid, and air phases in reductive leaching process.

1.3 Objectives of Research Work

I. To investigate the main effects and interaction effects of concentration sulphuric acid and stirrer speed rate on SMO using Minitab 18.

II. To study the flow behaviour flow behaviour of air, BSD, SMO and sulphuric acid during the simultaneous hydrolysis-leaching using ANSYS Fluent software.

1.4 Scope of Study

This study involves experimental work and followed by simulation work. Prior to experimental work, sample preparation and characterization study is carried out on the raw materials. Sample preparation is to prepare the raw materials so that it follows the requirements for experimental work. Characterization study is carried out to study further the raw materials used in this research work such as the surface morphology, elements present in the raw materials and its phase.

A total of nine experiments were carried out based on the DOE of this research which is the full factorial of 2^2+5 centre points. All the nine experiments are simultaneous hydrolysis-leaching with sulphuric acid concentration and rate of stirring as the variables. Once the experimental work is done, the recovery of Mn is determined by ICP-OES.

As for computational part, the design of simultaneous hydrolysis-leaching is carried out using solid works. This is followed by simulation work using ANSYS Fluent 15 software. Simulation work is carried out to study the flow behaviour of BSD, SMO, and sulphuric acid.

1.5 Thesis Organization

This research paper is consists of five chapters with references and appendices. The chapters included are introduction, literature review, methodology, results and discussion, and conclusion and recommendation. The chapters are arranged according to the numbering order such as Chapter 1, Chapter 2, Chapter 3, Chapter 4, and Chapter 5.

Chapter 1 covers the introduction of the research work. In this chapter, the significance of this research work, problem statement, objectives, scope of study and thesis organization are explained in detail.

Chapter 2 discuss about literature review related to this study. Articles and journals related to this work by previous researches are briefly explained. Chapter 3 focuses on the methodology. This chapter explains thoroughly the steps taken for sample preparation, characterization studies conducted on raw materials, arrangement of experimental work and the method chosen for analyse data obtained.

Chapter 3 is followed by Chapter 4 which covers results and discussion of sample preparation, characterization studies, experimental and simulation work. The results from this research are properly tabulated and interpreted, based on previous studies and engineering knowledge.

Lastly, Chapter 5 concludes the overall findings obtained from this research work. This chapter includes the conclusion of each objectives and recommendation for future research on this related field to improvise the findings.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discuss a detailed literature review of studies related to this research work. This chapter begins with the literature of the characteristics of raw materials which are BSD and SMO, followed by hydrolysis, reductive leaching and finished off with ANSYS Fluent for simulation. The topic includes a brief introduction of particular subject, summary of previous works related to the field, and substantive findings.

BSD and SMO are the raw materials studied in this research work. This chapter discuss the research background of the BSD and SMO in general. Previous studies on the type, characteristics, and significant usage of these raw materials are analysed and discussed in this Chapter. Apart from that, the composition of these raw materials and the related technology are also analysed.

Studies of raw material were followed by the method used for analysing. Hydrolysis and reductive leaching are used to extract reducing sugar from BSD and to extract Manganese from SMO respectively. Chapter 2 includes literature review of various studies with different parameters and the effectiveness of the experiment on the recovery of the ore.

This Chapter also includes the studies about the software used for the simulation work, ANSYS Fluent. Literature review on the principle and fundamental of ANSYS Fluent as well as the previous studies regarding the analysis of phases are discussed.

2.2 Bamboo

Bamboo belongs to the Gramineae family and sub-family of Bambuseae. It is also known as a perennial woody grass and distributed widely all around the world (He *et al.*, 2014). Bamboo is the common term applied to around 1250 species of large woody grasses, with maximum of 40 m in height. it shares a number of common characteristics of fuel with other bioenergy feed stocks, namely alkali index and low ash content (Scurlock, Dayton and Hames, 2000).

Gigantochloa scortechinii is a type of bamboo that found in central and northern Peninsular Malaysia, in Sumatra, Indonesia, and in southern Thailand. This species is the most popular in Peninsular Malaysia region. In this research, *Gigantochloa Scortechinii* is used in the form of saw dust during experimental work.

Throughout the world, bamboo is included in everyday uses of 2.5 million people, which is about 20 million ton per annum. Bamboo is mostly used in construction and reinforcing fibres, paper, textiles and board, as a source of food, for combustion and for other bioenergy applications. The high utilisation of bamboo in bioenergy applications is due to the diminishing fossil resources. Thus, sustainable and clean renewable energy and bio-based chemicals from lingo cellulosic feed stocks are considered as promising alternatives to petroleum-based products (Yuan, Wen and Kapu, 2018).

Over 90% of the total mass of bamboo culms are cellulose, hemi-cellulose and lignin. According to Mohan, Banerjee and Goud (2015), cellulose is the primary constituent in any biomass to produce oligosaccharides and monomeric sugars which are glucose and fructose. Hemicellulose is the secondary most abundant polymer in biomass that produce pentose sugars, arabinose and hexoses. Cellulose is the most abundant organic compound and commonly act as a renewable source for chemicals and energy. Moreover, cellulose is the primary component of lingo cellulosic biomass (Binder and Raines, 2010). The minor constituents of bamboo are resins, tannins, waxes and inorganic salts. Bamboo contains other organic composition besides than cellulose and lignin. It have 6% starch and protein, 2% deoxidized saccharide, and 4% fat (Sun *et al.*, 2016).

2.3 Synthetic Manganese Ore

Manganese is a transition metal with atomic number of 25. Manganese is located in group 7 and period 4 in periodic table. This element is found as a free element in nature, often in combination with iron, and in many minerals. A total 380 million metric tons is the estimated world ore reserves of manganese. The leading producers of manganese are Australia, Gabon, South Africa, China, Brazil, and Ukraine.

According to the Department of Mineral and Geoscience, Malaysia, local production of manganese ore in 2016 increased by 41.8 per cent to 681,667 tonnes from 480,727 tonnes produced in 2015. Kelantan, Terengganu, Pahang and Johor are where manganese deposits is locally located. In Malaysia, the grades of Manganese are mostly below 50 percentage.

Manganese is found in more than hundred minerals. However, it does not occur naturally in its native state as a base metal. Common manganese-containing minerals are Oxides, carbonates, and silicates. Pyrolusite is the common manganese mineral. This mineral has about 63 % of manganese. This element also occurs as rhodonate, manganese silicate and rhodocrosite, manganese carbonate. Mostly manganese occur in iron ores or in nodules on the bottom of the ocean. Ruch *et al.* (1973) stated that manganese content in coal is 6 to100 µg/g. In crude oil, manganese is found as a natural trace element over a high concentrations (Šarć and Lucchini, 2007).

The usage of manganese is pretty common in cast iron production and steel as an alloying addition. Manganese is also used for non-metallurgical applications for the production of battery cathodes, as water treatment chemicals, as well as a colorant for bricks in construction industry.

2.4 Hydrolysis

Hydrolysis is a process which involves breaking down biomass polymers into fermentable sugars. Hydrolysis can takes place either by using acids as catalysts, or using enzymes called celluloses. Individual sugar molecules are obtain by breaking down cellulose or hemi cellulose in biomass by dilute or concentrated acids ,which later can be fermented into ethanol (Wyman, 1994). While, enzymatic hydrolysis is the conversion process of lignocellulose that utilizes enzymes to depolymerize lingo cellulosic biomass (Modenbach and Nokes, 2013).

Hydrochloric and sulphuric acids are the most common catalysts for hydrolysis process of lingo cellulosic residues. However, phosphoric acid can be more advantageous for hydrolysis. This is because, phosphoric acid is less aggressive than other acids such as furfural or acetic acid (Billies, 2014).

The advantages of acid hydrolysis are that pre-treatment is unnecessary for the acid to penetrate lignin, higher rate of acid hydrolysis than enzyme hydrolysis, and glucose also degrades rapidly under acidic conditions. Dilute acid causes the hydrolysis reaction to be very complex because the substrate and the catalyst are in different phases where substrate is in a solid phase while catalyst is in a liquid phase. The reaction rate of hydrolysis depends on temperature, acid concentration, reaction time, and substrate composition (Lenihan*et al.*, 2010).

In bio-refinery operation, enzymatic hydrolysis is a key process. The rate of enzymatic hydrolysis, final carbohydrate conversion, and concentration affect the techno-economic feasibility of commercial operations in bio-refinery operations. The operating costs can be reduced by 19% when the insoluble solids is increase to 8% during a simultaneous saccharification and fermentation process to ethanol (Geng*et al.*, 2015).

Hydrolysis of cellulose is affected by various variables includes the surface area accessibility of the waste materials, cellulose fiber, crystallinity, and the presence of lignin and hemicellulose. Lignin and hemicellulose makes the access of cellulase enzymes to cellulose tough, thus reduce the efficiency of the hydrolysis (Sun and Cheng, 2002). This is why, prior to the enzymatic process, feedstock pre-treatment is necessary to remove lignin and enhance the porosity of the lingo cellulosic materials (Verardi *et al.*, 2012).

Pre-treatment must meet certain requirements such as improve the formation of sugars or the ability to subsequently form sugars by enzymatic hydrolysis, avoid the degradation or loss of carbohydrate, avoid the formation of by product inhibitory to the subsequent hydrolysis and fermentation processes, and be cost-effective (Sun and Cheng, 2002). According to Converse *et al.* (1989) they are some requirements that must be satisfied by a technically successful pre-treatment. These requirements are removal of the xylan, preservation of the glucan, preservation of the xylose produced and melting and partial removal of the lignin.

Physical, physico-chemical, chemical, and biological processes have been used for pre-treatment of lingo cellulosic materials (Sun and Cheng, 2002).Physical pre-treatment are mechanical comminution, and pyrolysis, while physico-chemical are steam explosion (auto-hydrolysis), Ammonia fibre explosion (AFEX) and CO2 explosion. Chemical pre-treatment are Ozonolysis, Acid hydrolysis, Alkaline hydrolysis, Oxidative delignification, and Organosolv process. Finally, In biological pre-treatment processes, microorganisms such as brown, white and soft-rot fungi are used to degrade lignin and hemicellulose in waste materials.

Key factors for an effective pre-treatment of lingo cellulosic biomass are minimum heat and power requirements, lignin recovery, fermentation compatibility, obtaining high sugar concentration, effectiveness at low moisture content,non-production of solid-waste residues, operation in reasonable size and moderate cost reactors, high yields for multiple crops, sites ages, harvesting times, highly digestible pre-treated solid, no significant sugars degradation., minimum amount of toxic compounds, and biomass size reduction not required (Alvira, Ballesteros and Negro, 2010).

Main factors that influence the enzymatic hydrolysis of cellulose in lingo cellulosic feed stocks can be divided in two groups which are enzyme-related and substrate-related factors, though many of them are interrelated during the hydrolysis process. Composition of the liquid fraction and solid process streams resulting from different pre-treatment approaches can be widely different. These differences will have a great influence on the requirements for effective enzymatic saccharification in subsequent processing steps (Alvira, Ballesteros and Negro, 2010).

2.5 Reductive Leaching

Reductive leaching is a hydrometallurgical process which is commonly used for the extraction metal from metal bearing materials, in an acid media with the presence of reducing agent. In the leaching of manganiferrous ores containing tetravalent manganese a reducing agent is necessary to reduce Mn (IV) to soluble Mn (II) (Furlani, Pagnanelli and Toro, 2006). Reducing agents applies to natural and secondary resources such as laterite ores and deep sea manganese nodules and recycled materials such as spent batteries with high-valence metal oxides of manganese, cobalt, and iron to leach metal values .

Low-grade manganese ores can be treated either by reduction roasting followed by acid leaching or directly by reductive acid leaching using different acidic reducing agents and acids, such as hydrochloric acid and pyrite, iron(II) sulphate, aqueous sulphur dioxide , hydrogen peroxide in acidic medium ,mixed methanol sulphuric acid solution, an aqueous alcoholic-HCl acid mixture , sulphuric acid and oxalic acid , non-aqueous dimethyl sulfoxide, mixed sucrose-sulphuric acid solution and glucose in acidic medium (Su*et al.*, 2008).

Commonly the leaching of low grade manganese is carried out using various acids namely sulphuric acid, oxalic acid, nitric acid, citric acid and hydrochloric acid (Das *et al.*, 2012).Several researches have been carried out on reductive leaching of manganese using biomass includes cane molasses (Su *et al.*, 2008),corncob (Tian *et al.*, 2010), cornstalk (Cheng, Zhu and Zhao, 2009), sawdust (Feng, Zhang and Li, 2016), waste tea (Tang *et al.*, 2014) and waste cellulosic (Hariprasad *et al.*, 2009) as reductant. Biomass has attracted attention for manganese ore extraction since it is low cost, renewable, non-hazardous and an abundant renewable resource. Biomass materials has high demand as a reductant in the mineral industry .This is because it can partially solve the universal problem of global warming as it is green, and have pollution-free characteristics (Feng, Zhang and Li, 2016).

In a study on manganese recoveries from low-grade ores using organic acids as reducing agents, acid leaching potential by oxalic citric acid were analysed. Various acid concentrations were used to study the efficiency of the acids. From the research, it was concluded that manganese recovery of 66% can be obtained by oxalic acid at 2 M concentration whereas citric acid shows recovery of 40 % in 6 days making it to have less effect on manganese leaching (Das *et al.*, 2012).

A research carried out by Haifeng Su on reductive leaching of manganese from low-grade manganese ore in H2SO4using cane molasses as reducing agent as it is a low cost rich resource, containing renewable and non-hazardous reducing agents compared to other raw materials available for manganese leaching under mild acidic conditions. In this study the leaching efficiencies of Mn, Fe and Al during the leaching process analysed .The result shows the leaching efficiencies of 97.0% for Mn, whereas 21.5% for Al and 32.4% for Fe, respectively (Su *et al.*, 2008).

Manganese recovery from medium grade ore using a waste cellulose were studied by D Hariprasad. The aim of this study was to investigate the effectiveness of lingo-cellulosic base wastes such as used newspaper as a reducing agent. The parameters studied were sulphuric acid, temperature, reductant to ore ratio and ore particle size .Based on this study, the optimum conditions to obtain more than 90% of extraction were by using 5% H2SO4, reductant to ore ratio of 0.5, 8 hours of reaction time, 10% pulp density and -100 µm of ore particle size. Moreover, newspaper was found to be equally effective as a reducing agent for low grade ore (Hariprasad *et al.*, 2009).

In another study, manganese leaching and recovery from low-grade pyrolusite ore using sulphuric acid (H_2SO_4) as a leachant and pyrolysis pre-treated sawdust as a reductant were studied. The parameters investigated in this study were the effects of the dosage of pyrolysis pre-treated sawdust to pyrolusite ore, the concentration of sulphuric acid, the liquid/solid ratio, the leaching temperature, and the leaching time on manganese and iron leaching efficiencies. This study concluded that using pyrolysis-pre-treated sawdust from biomass waste in the leaching of manganese is environmentally and economically beneficial (Feng, Zhang and Li, 2016).

A study on the kinetics of reductive leaching of manganese from a low grade ore in dilute nitric acid with molasses is conducted. In this study, reductive leaching is carried out in dilute nitric acid because it extract high manganese and low iron extraction with less moles of acid. The leaching process follows the kinetic model 1- 2/3X- (1- X)2/3=kt with an apparent activation energy of 25.7 kJ/mole. This study concluded that the concentration of molasses and HNO_3 as well as temperature are the significant factors which influence the leaching rate. A reaction order of 1.2 for acid concentration and 1.9 for molasses concentration were obtained from this research (Lasheen, El Hazek and Helal, 2009).

Table 2-1 shows the brief explanation of previous research works done on similar experimental work to simultaneous hydrolysis and leaching of synthetic manganese ore using bamboo saw dust.

2.6 ANSYS Fluent

ANSYS Fluent is one of the powerful software under computational fluid dynamics (CFD), which plays significant role in industries to optimize a process performance. It is an engineering analysis software that deals with the finite element analysis, structural analysis, computational fluid dynamics, explicit and implicit methods and heat transfer.

ANSYS Fluent is preferred world widely as it have well-validated physical modelling capabilities to deliver fast, accurate results across the widest range of CFD and multi-physics applications includes predict impact of fluid flow. Fluid flow problems include incompressible and compressible, laminar and turbulent can be analysed using ANSYS Fluent as it provides comprehensive modelling capabilities for a wide range. Steady-state or transient analyses also can examine using this software. Apart from that, ANSYS Fluent also widely used for transport phenomena. This is because, it have a broad range of mathematical models which are capable to model complex geometries.

According to ANSYS Fluent theory guide, 2013, this software is useful for modelling multiple stages in turbo machinery applications, as such, is also provided, along with the mixing plane model for computing time-averaged flow fields as well as a time-accurate sliding mesh method.

The changes in the system can be observed and predicted by applying this computational model.

The time averaged continuity equation (Bakker & Akker, 1994),

$$\vec{\nabla}.(\vec{u}\vec{u}) = -\vec{\nabla}.\left(\frac{p}{\rho}\vec{\vec{I}}\right) + \vec{\nabla}.(\nu(\vec{\nabla}\vec{u} + (\vec{\nabla}\vec{u})^T)) - \vec{\nabla}.\overline{\vec{u}'\vec{u}'}$$

The first term on the right hand of this equation denotes the divergence of the pressure, the second term is the divergence of the various stresses and the third term is the divergence of the Reynolds stress tensor (Bakker & Akker, 1994).

2.7 Multiphase flow

Multiphase flow is the instantaneous flow of mixture of different phases. Sometimes multiphase can also be referred as multicomponent flow where a substance do not have a distinguished phase but it is a uniform thorough out its existence. Multi-phase flow occurs when more than one material is present in a flow field and the materials are present in different physical states of matter or are present in the same physical state of matter but with distinct chemical properties. The materials present in multiphase flow are often identified as belonging to the primary or secondary phases. The primary phase is defined as the phase that is continuous or enveloping the secondary phase. The secondary phase is the material that is distributed throughout the primary phase. Normally primary phases are gas or liquid while secondary phases are solids or liquids (Smith, 2012).

Factors influencing multiphase flow are boundary conditions such as either stationary or rotating wall, fluid characteristics such as density, viscosity, specific heat, and thermal conductivity, flow rate and cross section. In nuclear plant, the study of multiphase flow is significant because the chemical and flow properties vary strongly over the flow regime which accounts for the design and safety of the subsystems in the plant (Bandaru and Singh, 2017) .

In this study, multiphase flow is analysed using ANSYS Fluent to improve leaching performance. ANSYS Fluent have varies multiphase models. These models are lagrangian dispersed phase model (DPM), dense dispersed phase model (DDPM), volume of fluid model (VOF), eulerian model, mixture model and immiscible fluid model. The choice of the models are depends on few important criteria of the particular problem in concern such as whether the flow is dispersed, presence of immiscible phases, and inertia of dispersed phase. DPM, DDPM are suitable models to use for dispersed multiphase flow while VOF, immiscible fluid models are for non-dispersed multiphase flow.

Mixture multiphase model is the simplification of eulerian model and applicable when inertia of dispersed phase is small. This model is similar to VOF as both uses a single fluid approach. However, mixture model allows the phases to be interpenetrating, thus the volume fractions can vary from 0 to 1. Besides that, it allows the phases to move at different velocities using the concept of slip velocities. If the phases are assumed to move at same velocity than the mixture model is reduced to homogeneous multiphase model. Mixture model is applicable for non-homogeneous mixture model, low particle relaxation times, one continuous phase and N dispersed phases (Smith, 2012).

Table 2-2 shows the summary of previous research works on the computational fluid dynamics.

2.8 Research Background

2.8.1 Research Background of Experimental work

Table 2-1: Research background on the hydrolysis and leaching of Manganese.

Journal Title	Research Sample	Operating Conditions	Results
Reductive acid leaching of manganese dioxide with glucose: Identification of oxidation derivatives of glucose (Furlani, Pagnanelli and Toro, 2006)	Glucose	H_2SO_4 concentration: 2 % Temperature:90°C Rate of agitation: 200 rpm	Glucose is oxidized by mono-carboxylic polyhydroxy acids and formic acid. Formic acid was quantified as the major component.
Reductive leaching of manganese from low-grade manganese ore in H2SO4using as reductant.(Su*et al.*,	Cane molasses	H_2SO_4concentration: 1.9 mol/L Temperature:90°C Rate of agitation: 200 rpm	The leaching efficiencies were 97.0% for Mn, whereas 21.5% for Al and 32.4% for Fe, respectively

Reductive leaching of manganese from low-grade manganese dioxide ores using corncob as reductant in sulphuric acid solution (Tian*et al.*, 2010)	Corncob	H_2SO_4concentration: 1.9 mol /L Temperature:85°C Reaction time:60 min	The leaching efficiency of manganese reached 92.8% while iron dissolved was 24.6% under the optimal condition.
Study in reduction-roast leaching manganese from low-grade manganese dioxide ores using cornstalk as reductant (Cheng, Zhu and Zhao, 2009)	Cornstalk	H_2SO_4concentration: 3.0 mol /L Temperature:50°C Reaction time:40 min	The leaching recovery of manganese reached 90.2% under the optimal condition when manganese dioxide ore to cornstalk weight ratio of 10:3
Leaching of pyrolusite using molasses alcohol wastewater as a reductant (Su*et al.*, 2009)	Molasses alcohol wastewater	H_2SO_4concentration: 1.9mol /L Temperature:90°C Reaction time:120 min	Leaching yields of 93% for Mn, with relatively low recoveries of 37% for Fe and 25% for Al.

2.8.2 Research Background of Simulation

Table 2-2: Research background on simulation work

Title / Objective:	Objective	Methodology	Results	Recommendation/Comment
CFD modelling of stirred tanks Numerical considerations By Deglon ,D.& Meyer,C (Deglon and Meyer, 2006)(Deglon and Meyer, 2006)	Demonstrate that the Multiple Reference Frames (MRF) impeller rotation model and the standard k–e turbulence model can accurately model turbulent fluid flow provided very fine grids coupled with higher-order discretization.	CFD software Fluent 6 is used to simulate flow in a small baffled tank	Turbulent kinetic energy predictions are strongly influenced by both the grid resolution and discretization scheme	Poor predictions of turbulence obtained using the k–e turbulence model, often noted in the literature, may be due to numerical errors rather than inadequacies in the turbulence model

Multiphase flow analysis of hydrodynamic journal bearing using CFD coupled FSI considering cavitation By D.Y. Dhande , D.W. Pande (Dhande and Pande, 2016)	Study of bearing with and without effects of cavitation	Mixture model is used to model cavitation in the bearing and parametric modelling is used for modifying the flow domain due to deformation.	The oil vapour distribution goes on increasing with the increase in shaft speed, thus lowering the magnitude of the pressure build up in the bearing.	Multiphase study of bearings with cavitation hence becomes extremely important in case of bearings operating with higher speeds

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This Chapter focuses on the method adopted by this study. Moreover, this Chapter covers the particular of raw materials used, chemicals used, sample preparation method, characterization studies, experimental design, experimental set-up and procedure. Finally, ANSYS simulation conducted to study the flow of solid, liquid, and air phases on a reaction flask.

The raw materials used in this experiment are BSD and SMO. Prior to experimental work, sample preparation and characterization studies are conducted on raw materials .Sample preparation mainly to prepare raw materials of size less than 75 micron for experimental work. This followed by characterization studies to understand about the details of raw materials. The experimental design used in this experiment is 2^2+5. Thus, nine experiments were conducted with different acidic concentrations and rotation per minute of stirrer.

This Chapter also focuses on the experimental procedure and parameters used during this study .The experimental procedure involve simultaneous hydrolysis and leaching where the reducing sugar from the hydrolysis of bamboo saw dust is used for reductive acid leaching of synthetic manganese ore. The parameters involve for simultaneous hydrolysis and leaching were sulphuric acid concentration and rotation of stirrer. This followed by ICP analysis of liquors collected during the course of experiments to determine Mn, Fe and Al recovery.

Finally, the discussion of simulation work using ANSYS also included in this Chapter. The overall flow chart is illustrated in Figure 3-1.

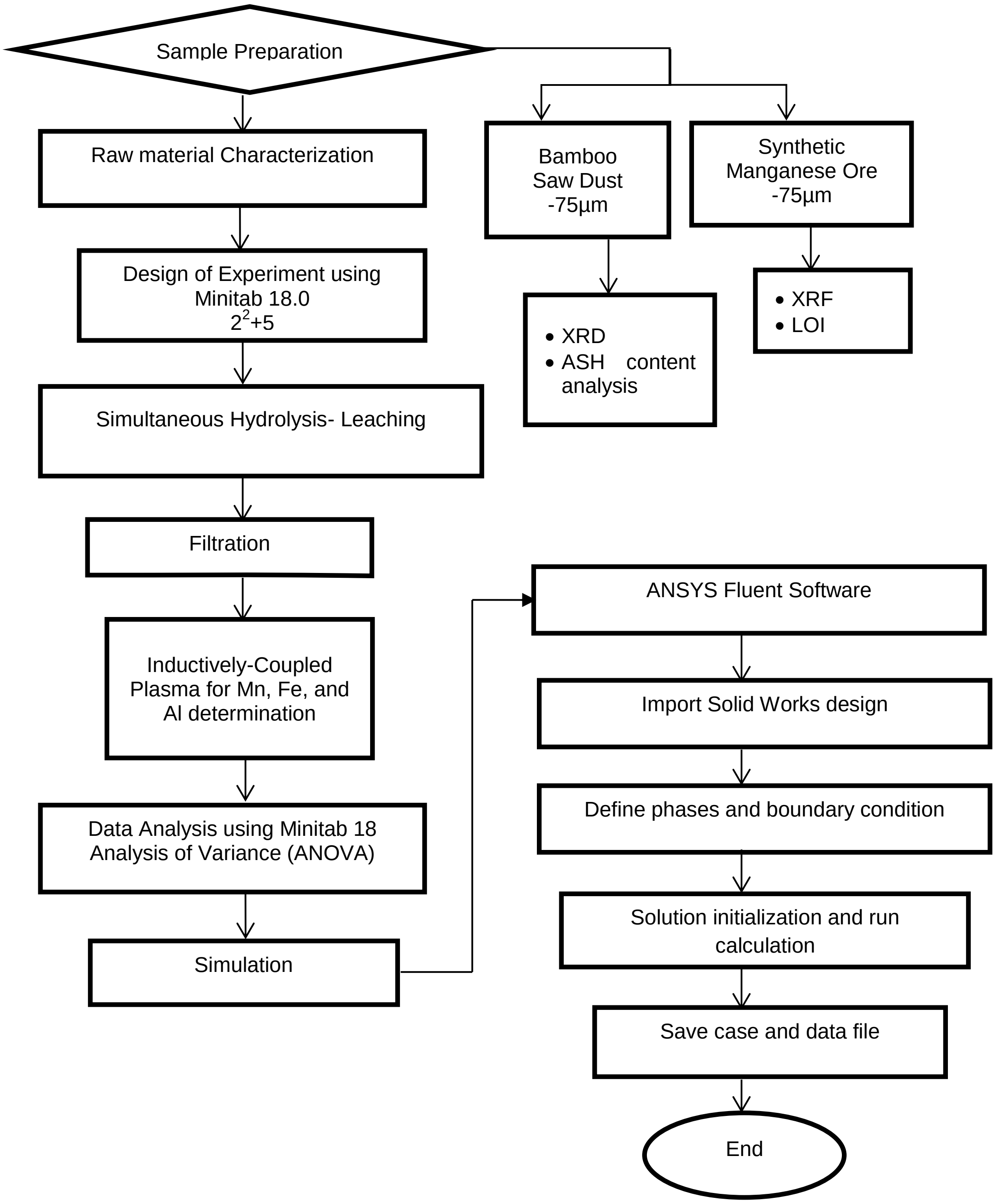

Figure 3-1: Overall work chart of experimental and simulation part

3.2 Raw Materials

The raw materials used for experimental work are bamboo saw dust and synthetic manganese ore. Bamboo sawdust is used to produce reducing sugar by hydrolysis process where this reducing sugar is used for the reductive leaching of synthetic manganese ore.

3.2.1 Bamboo Saw Dust (BSD)

For this research work, *Bamboo Gigantochloa Scortechinii* from Forest Research Institute Malaysia (FRIM) is utilized. The total weight of bamboo saw dust after drying is 556.30 g. Drying of bamboo saw dust is crucial to remove moisture content. After drying completed, BSD stored in an air-tight container, wrapped with aluminium foil. This is to prevent further moisture absorbance by the bamboo particles. For this experimental work, about 200g of BSD of -75 µm is prepared.

3.2.2 Synthetic Manganese Ore (SMO)

Synthetic manganese ore used for this studies is from *Acros Organics* at -230 mesh with 99% purity. SMO is further reduced in size to -75 micron for X-ray Fluorescence analysis (XRF) and to use in experimental work. During sample preparation, about 200 g of synthetic manganese ore of -75 µm is prepared for reductive leaching process.

3.3 Chemicals

The extraction of manganese is carried out by reductive acid leaching. Thus, various chemicals are used in this study. The chemicals used in simultaneous hydrolysis and leaching of synthetic manganese ore are sulphuric acid (H_2SO_4), and nitric acid (HNO_3).

Sulphuric acid is used as medium for simultaneous hydrolysis and leaching process of SMO. A total of nine experiments is carried out with acid concentration of 3.0

M, 3.5 M and 4.0 M. Moreover, nitric acid is crucial in this study to preserve the leached liquor collected at time intervals and at the end of leaching process. Nitric acid of 1% and 10 % concentration is used in this study. The former concentration of nitric acid is used for cleaning lab apparatus while the latter concentration is used for preserve heavy metals after leaching.

3.4 Sample preparation

3.4.1 Sample preparation for Bamboo Sawdust

BSD is prepared prior to the experimental work. Figure 3-2 shows the sample preparation steps for bamboo sawdust.

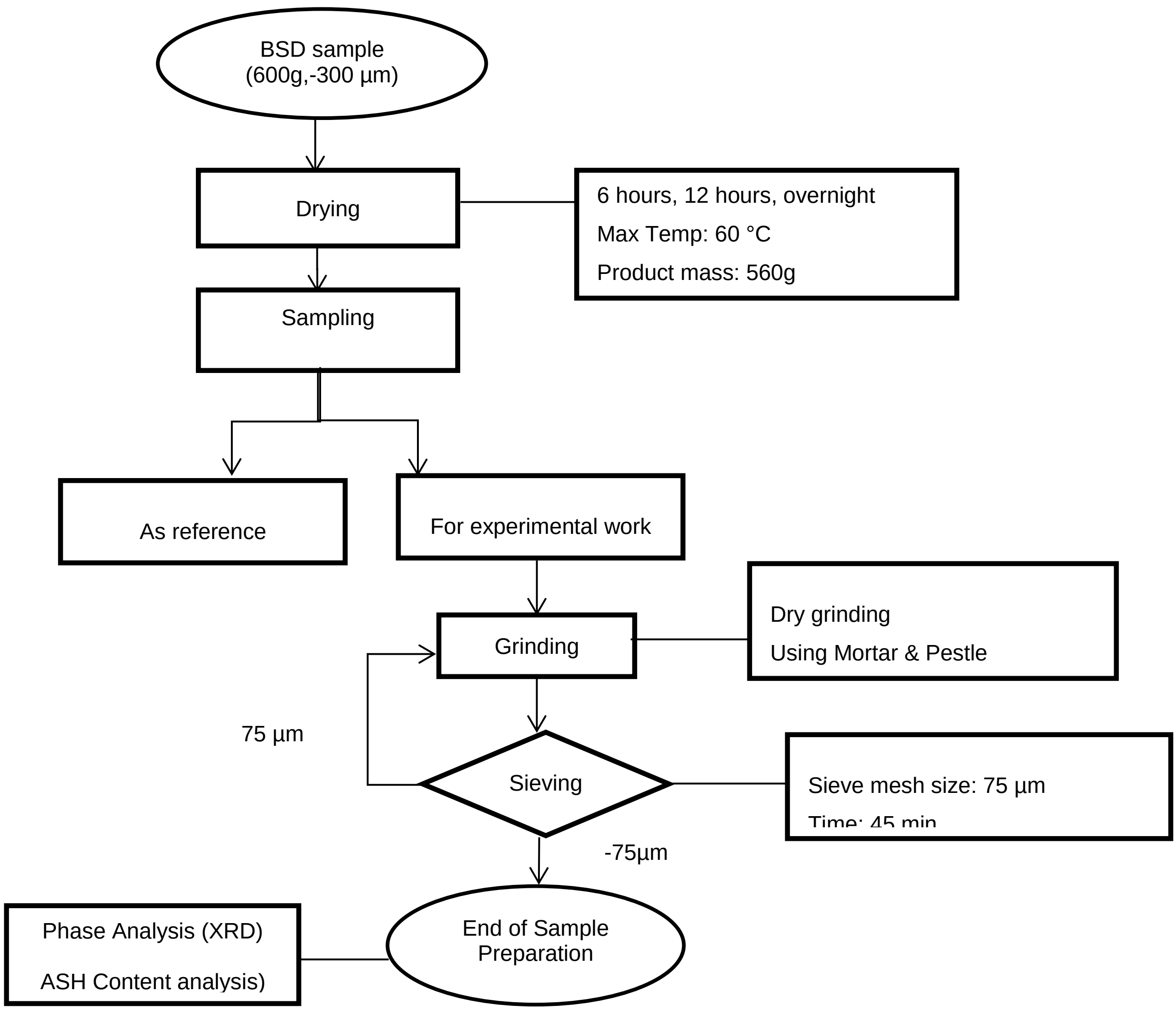

Figure 3-2: Sample preparation of BSD

As shown in Figure 3-2, the raw BSD used in this research work is of size -300µm and about 600 g. The raw BSD from FRIM is oven dried with maximum temperature of 60 °C in the time interval of 6 hours, 12 hours and overnight. After the drying completed for each period, the dried mass of BSD is recorded. Drying is done until constant mass of BSD is obtained. The dried sample is stored in an air-tight covered with aluminium foil to prevent the sample from excess exposure of light. BSD is very sensitive to heat and moisture. Drying at extreme temperature can cause the organic matter of BSD to destroy and leads to failure in producing reducing sugar.

Drying of BSD is followed by sampling of the dried sample .Sampling is done by using splitter where half of the sample is kept as reference while another half is used for further processing. The sample from latter is sent for dry grinding process. Since the original sample provided is very fine, grinding of BSD is carried out using blender and mortar and pestle. Figure 3-3 shows mortar and pestle used to grind the BSD. The purpose of grinding is to reduce BSD of size to -75 µm. Grinding of BSD using blender take place for 6 minutes with 20 g of feed each time while for mortar and pestle, BSD of 200 g is grinded for 15 minutes.

Then, the sample is sieved to obtain the distribution of BSD size. Sieving is conducted for 30 minutes with amplitude of 6. The sieve used is of mesh size 75 µm. The product of -75 µm is chosen for experimental work. While oversize particles (+75 µm) is re-grinded. The final step of sample preparation of BSD is the ash content analysis of BSD. This is to measure the inorganic matter present in the sample. The grinded sample of -75 µm are then analysed for characterization study and used for experimental work.