# CATALYTIC POTENTIAL OF NATURAL ZEOLITES AND SELECTED METALIC ORES IN PYROLYSIS OF GROUNDNUT SHELLS FOR BIO-OIL PRODUCTION

## BY

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# DECLARATION

I, KALEGA IVAN FREDRICK, hereby declare that the dissertation titled "**Catalytic Potential of natural zeolites and selected metallic ores in pyrolysis of groundnut shells for bio-oil production"** is my original work and has not been submitted to this or any other institution for an academic award.

**Signed**‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗

**Date** ‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗‗

# APPROVAL

The dissertation of KALEGA Ivan Fredrick was developed under our supervision and is hereby cleared for submission to Graduate School and Senate of Kyambogo University with our approval.

**Signed:** _____

**Dr. Aldo Okullo**

**Date:** _____

**Signed:** _____

**Dr. William Wanasolo**

**Date:** _____

# DEDICATION

I dedicate this work to all my friends and family members.

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The Swedish Embassy in Uganda for availing the research fund under Mak-Sida project 2015/2020

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# ABSTRACT

Catalytic pyrolysis is a promising thermochemical method of conversion of biomass to chemicals and fuels compatible with current petrochemical engines. Catalytic modification of pyrolyzed bio-oils are geared towards the elimination and substitution of oxygen and oxygen containing functionalities in addition to increasing hydrogen to carbon ratio in the final product. Recent progress has focused on both hydrodeoxygenation and hydrogenation of bio-oil using a variety of metal catalyst in the production of aromatic compounds from bio-oil using catalytic pyrolysis. However, current effectiveness of catalysts and conversion efficiency remain a challenge. In this study five naturally occurring inorganic materials from Usuuku rock, Kilembe mines rock, Tiira soil, Katwe salt and Manafwa river zeolites, having traces of transition metal elements were investigated for their influence on H/C and O/C ratio of bio-oil produced by pyrolysis of groundnut shells. The results showed bio-oil catalysed by zeolitic with metallic ore in the framework had a high H/C ratio and generated are hydrocarbons, that is, paraffins, olefins and aromatics than those without catalyst. Basing on the results of the study, it was concluded that different catalysts have impact on product composition, with catalysts of highest $SiO_2/Al_2O_3$ producing more light gases. This result agrees with Cheng et al. (2000) who studied furan conversion to aromatics and olefins using HZSM-5.

It was also concluded that the natural catalytic materials enhanced yields of the petroleum like compounds mentioned above, i.e., Kilembe ore for benzofuran; Katwe salt for aromatics; and Manafwa catalyst for olefins, CO and aromatics. This was based on eraspec fuel analyser and showed that the materials selected had catalytic potential for pyrolysis of groundnut

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background

The major source for energy and fuel is from non-renewable fossil sources, i.e., crude oils, coals and natural gas. Currently, they have received considerable attention due to their depletion, rising cost, uncertainty of supply, and issues with safe storage and transportation. However, environmental concerns about fossil fuel have taken the centre of stage in the last few decades because of global concern about climate change due to increasing greenhouse gases and acid rain from the use fossil fuel (J. J. Conti et al., 2014). The recovery of energy from a renewable source like biomass involves chemical, biochemical and thermochemical processes, depending on the nature of the source.  The utilization of biomass for energy generation has led to reduced carbon dioxide and Sulphur dioxide emissions and importantly reduced greenhouse effect and acid rain. The net flow of carbon dioxide to the atmosphere, and thereby the global warming, is reduced when fossil fuels are replaced with readily available biomass. Consumption of agricultural residues for energy production would also reduce environmental damage.

Owing to various advantages, the use of biomass feedstock for renewable energy has been considered globally. Numerous techniques for converting biomass to biofuels have been investigated(Mortensen *et al.,* 2011). Gasification of biomass is a relatively old technology to produce syngas (CO+ $H_2$) which can be used for heat and electricity generation(Goyal *et al.,* 2008). Fast pyrolysis and liquefication of biomass could be used for production of bio-oil(Yakovlev *et al.,* 2009)

Pyrolysis bio-oil is a renewable liquid produced from biomass pyrolysis. It has different compositions due to different feedstocks and process conditions and can be used as a source of high-quality chemicals. In addition, pyrolysis bio-oil can be used as an alternative fuel directly or generally after application of some purifying and improving processes. Some properties of bio-oils can result in several significant problems during its use as fuel in boiler, engine and gas turbine equipment constructed for combustion of petroleum-derived fuels (Amadi *et al.,* 2004). This is because bio-oils have poor volatility, high viscosity, coking and corrosiveness compared to petroleum-derived fuel (Akia *et al.,* 2014). It is necessary to describe important physical and chemical properties of bio-oils, but mostly fuel properties.

Catalyst fast pyrolysis is a technique that involves pyrolysis of biomass in the presence of catalyst in an inert environment at atmospheric pressure. The advantage of catalytic fast pyrolysis is that it can turn biomass into gasoline ranged aromatics in a single step(Carlson *et al.,* 2008). When biomass is subjected to extreme heating temperatures (550-600°C) the typical products formed include; solid charcoal (biochar), liquid product (bio-oil) and gas mixture (pyrolysis gas). However, the bio-oil is not miscible with the fossil fuel, but is miscible with water up to 35%-40% and gradually ages as the polyphenols polymerize, leading to variable viscosity ranging from 10 to 10,000 centipoise(Yildiz *et al.,* 2013). The rate of ageing increases with the exposure to light, oxygen or heat above 80°C leading to storage issue(Owczuk & Kołodziejczyk, 2015). The pH is relatively low due to the presence of organic acids, further increasing corrosion and storage issues (Owczuk & Kołodziejczyk, 2015). To overcome these issues, bio-oil must be modified chemically or upgraded by removal and modification of unwanted compounds, most of which contains oxygen. In most cases, the final product is evaluated by its oxygen to carbon ratio (O/C) and hydrogen to carbon ratio

(H/C). With lower O/C and high H/C ratio indicating a higher quality liquid product (Özçimen & Karaosmanoğlu, 2004). These ratios are especially important if the bio-oil is to be used as substitute for demanding petrochemical applications such as transportation fuels that needs clean, homogenous fuel stream (Özçimen & Karaosmanoğlu, 2004). To achieve these results, biomass is pyrolyzed in the presence of catalysts that affect the desired changes before the initial condensation generally referred to as catalytic fast pyrolysis. In the catalytic fast pyrolysis, lignocellulosic biomass decomposes into small oxygenated molecules. These small molecules could fit perfectly into catalyst pores to form hydrocarbon pools. In the presence of the catalyst the generated molecules undergo a chain of rearrangement. The aromatics and the olefins are formed on the active sites of the catalyst and oxygen is removed in form of $CO$, $CO_2$ and $H_2O$. Ideally a single reactor would fulfil all process requirements and produce quality liquid fuel from biomass(Zhang *et al*., 2007). Due to its potential in wide variety of situations, many consider catalytic fast pyrolysis to be the most promising way to improve the final, liquid composition.

The challenge is to design a catalyst that positively affects all the over 300 volatilized, organic compounds through various cracking and reforming reactions. This is vital for biorefineries and cost-effective with current infrastructure. The advantage of fast pyrolysis of biomass are: It is able to convert biomass in single reactor and eliminates the oxygenates as carbon dioxide ($CO_2$) and carbon monoxide $CO$ whereas in slow pyrolysis the oxygenates are eliminated as$CO_2$, $CO$ and $H_2O$, therefor reducing on the hydrogen content in the pyrolysis favouring formation of aromatics from olefin (mainly ethylene and propylene) under oligomerization process. Examples of catalytic pyrolysis reaction are:

**Dehydration of ethanol on zeolite catalyst**

$$C_2H_5OH$$

**De- polymerization**
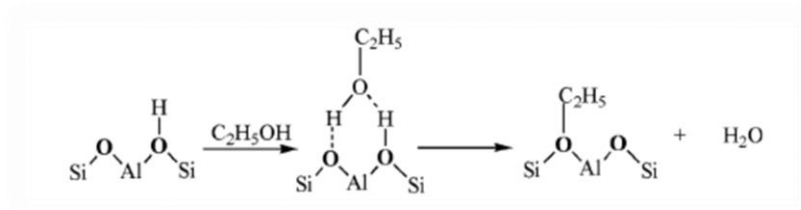
$$n \; H_2C=CH_2 \rightleftharpoons \; * \left[ \begin{array}{cc} C & C \\ H_2 & H_2 \end{array} \right]_n *$$
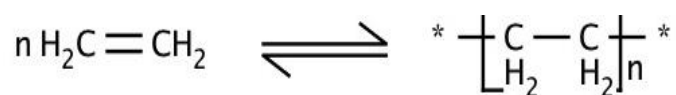
**Fragmentation**
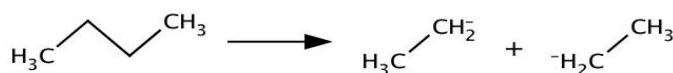
**Rearrangement**
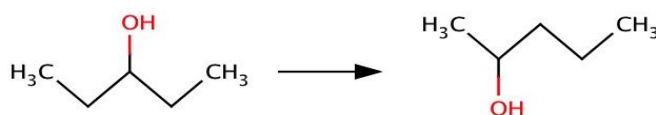
source; (Dickerson & Soria, 2013)

**Figure 1.1; Pyrolysis reactions**

In the process of upgrading the raw bio-oil, tar tends to poison the catalyst. Tar is a complex mixture of considerable hydrocarbons including aromatic compounds of single ring to 5-ring along with other oxygen-containing hydrogen compounds and complex polycyclic aromatic hydrocarbon (PAHs). This makes the catalyst inactive

(not being in position to work on the oil vapours) and compromises on the quality of the final product(bio-oil). The poisoning of the catalyst increases the cost of production. This is because more of the fresh catalysts would be required in order to upgrade the oils.

The biomass under study is the groundnut shell, which is a residue after separation of the groundnuts. It is available in copious amount in the Eastern part of Uganda. The crop residue is of low value and generally used in the burning and gasifier as fuel. The residue contains 54.4% total carbohydrate content (dry weight) as its cell wall(Wang et al., 2014)

## 1.2 Problem statement

Literature(Venderbosch, 2015) has shown that most used catalysts for pyrolysis are conventional catalysts(synthetic) and easilypoisoned during the pyrolysis process which makes them inactive and expensive.In addition,not available on local market in Uganda. To overcome the challenges associated with the use of conventional catalysts,the currentstudy considered investigating the potential of abundant and natural materials available locally for catalytic potentialin the pyrolysis of groundnut shells for bio-oil production.The study alsoaimedat identifying natural catalytic materials that can be utilisedas catalystin removing oxygenated compounds via catalytic pyrolysis. Preliminary studies on groundnut shells showed that they can generate bio-oil via pyrolysis. The groundnut shells are abundant and locally available in most part of Uganda

## 1.3 Objectives

The general objective of the study was to investigate the catalytic potential of selected naturally occurring inorganic ores in Uganda for their influence on H/C and O/C ratio

of bio-oil produced by pyrolysis of groundnut shells as alternatives to conventional (synthetic) catalysts in.

### 1.3.1   Specific objectives

The specific objectives were to:

1. Characterize thebiomass (groundnut shells) and catalysts (zeolitic materials and the selected metal ores of Tiira gold mine soil, Usuuku rock, Manafwa riverbanks zeolite, Kilembe mine rock and Katwe salt) intended to produce bio-oils by catalytic pyrolysis

2. Carry out pyrolysis reactions withHZSM-5- a synthetic catalyst -and naturally selected activated local catalysts

3. Establish the effect of the catalysts on the distinctive properties of the bio-oils produced.

### 1.4 Research questions

1. What is the chemical composition of the selected natural available catalytic materials intended for groundnut shell pyrolysis?

2. Can the selected inorganic ores act as catalysts for biofuel production from biomass?

### 1.5 The scope

The study concentrated on selected naturally occurring inorganic ores with catalytic potential. The identification of these minerals was based on survey done by the Department of Geological Survey and Mines, Entebbe, Uganda 2009 as shown in **Figure 1.2**below

**Figure 1.2 Sampling locations**

Figure 1.2 shows the location of the different suspected catalytic inorganic ores in Uganda namely: Manafwa river zeolite, Tiira gold mine, Usuuku rock ( Ca, Fe, P and alumina silicates), Kilembe copper mine rock ( Cu, Co, Ca and alumina) and Katwe salt mine ( Na, K, Ca and alumina).The biomass was collected from Kumi district.

## 1.6 Justification

Catalytic pyrolysis is a promising thermochemical conversion route for lignocellulosic biomass that produces chemicals and fuels compatible with current, petrochemical infrastructure. Catalytic modifications to pyrolysis bio-oils are geared towards the elimination and substitution of oxygen and oxygen-containing functionalities in addition to increasing the hydrogen to carbon ratio of the final products. Recent progress has focused on both hydrodeoxygenation and hydrogenation of bio-oil using a variety of metal catalysts and the production of aromatics from bio-oil using cracking zeolites. Research is currently focused on identifying naturally occurring ores that benefit from the advantages of zeolite cracking. Development of robust, highly selective catalysts will help achieve the goal of producing drop-in fuels and petrochemical commodities from lignocellulosic biomass streams.

**1.7 Significance**

The findings of this study were expected to;

1.      Process locally available naturally occurring zeolites and metallic ores as catalysts for pyrolysis of groundnut shells into useful biofuel precursors and chemical feedstocks that could offer a cheaper and an abundant supplement to Uganda's fuel and chemical needs.

2.      Increase literature on the presence of catalytic materials that can be used in the pyrolysis of Ugandan agricultural wastes for uses such as value addition into useful chemical feedstocks and fuels.

3.      The utilization of natural catalytic materials for would reduce foreign currency used time spent when importing the synthetic catalyst.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Introduction

The demand for energy is growing faster due to rapid industrialization and social growth. Conventional energy sources, such as coal, Crude oil, and natural gas, have limited reserves that are expected not to last for an extended period(Akia *et al.,* 2014). Consequently, energy management will be difficult for the coming generations (Adhikari *et al.,* 2006) and in addition, environment-related problems associated with conventional energy sources are continuously increasing. Over the last half century, a trend toward continuous increases in  average atmospheric temperature has been observed, totalling a half degree centigrade (Goyal *et al.,* 2008). This trend may lead to natural calamities such as excessive rainfall and consequent floods, droughts, and high local temperatures. With increasing energy demand, the emerging alternative and renewable energy resources are expected to play an increasing role in future energy consumption, at least to reduce the environmental concerns. In contrast to conventional energy sources, nonconventional energy sources such as wind, sunlight, water, and biomass have been used since ancient times. Biomass is now being considered as an important energy resource all over the world and is being used to meet a variety of energy needs, including generating electricity, fuelling vehicles, and providing process heat for industrial facilities. Among all the renewable sources of energy, biomass is unique as it effectively stores solar energy. It is the only renewable source of carbon that can be converted into convenient solid, liquid, and gaseous fuels. Biomass is the fourth largest source of energy in the World, accounting for about 15% of the world's primary energy consumption and about 38% of the primary energy consumption in

developing countries(J. Conti et al., 2011).Most types of biomass have cellulose as the largest fraction, about 40 to 50% by weight, followed by hemicellulose about 20 to 40%. Besides these, biomass also has other components such as sulphur with negligible content and, therefore, do not contribute to the emission of sulphur dioxide, which causes acid rain. The combustion of biomass produces less ash than coal combustion. Moreover, the ash produced can be used as soil additive on farms(Bridgwater, 2012). Biodiesel as one of the biomass derived fuel has shown great potential worldwide as a clean alternative fuel for diesel engines because of its reduced emission pollutants, sustainability, biodegradability, and usability in conventional diesel engines without significant modifications. With the increasing need for alternative fuel, many biomass conversion technologies have been developed as shown in the chart. The different biomass conversion technologies show that biomass has great potential for generation of hydrocarbon fuels like crude oil fuels.
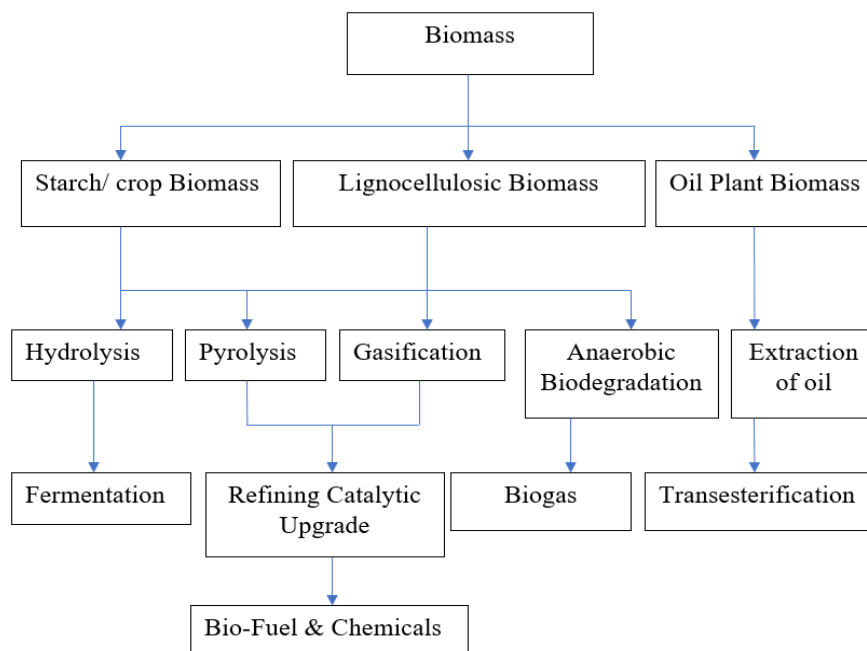


**Figure 2.1; Biomass conversion technologies,**

## 2.2 Pyrolysis

Pyrolysis is the thermochemical decomposition of biomass at temperatures between 400 and 650°C in the absence of oxygen which results in the production of bio-oils, biosynthetic gas and char. The decomposition process release volatile species, while the solid, non-volatiles are collected as bio-char (Yaman, 2004). A portion of the gas-phase volatiles condense into a black, viscous fluid termed as bio-oil that has variety of synonyms including pyrolysis oil, bio-crude oil, bio-oil (Westerhof *et al.*, 2008). Pyrolysis methods differ in their residence time, temperature, and heating rate, which in turn affect greatly the percentages of gas, char and the liquid products. Depending on the operating conditions, the pyrolysis process can be divided into two sub classes; slow pyrolysis (carbonization) and fast pyrolysis.

## 2.2.1 Slow pyrolysis

Slow pyrolysis processes are performed at a low-heating rate of 0.1- 1°C/s, a long residence time in hours and a temperature ranging between 400-600°C. The long residence times can cause secondary cracking of the primary products reducing yield and adversely affecting oil properties. In addition, a low heating rate and long residence time may increase energy input. These are not attractive for commercial application of liquid fuel production. At present, the preferred technology for production of pyrolysis oil products is fast pyrolysis at high temperatures with very short residence times. The pyrolysis oil from biomass waste has been reported to be highly oxygenated and has a complex mixture of large amounts of different molecular compounds because of fragmentation reactions of the cellulose, hemicellulose and lignin polymer and is chemically unstable. Thus, the liquid products still need to be upgraded by lowering the oxygen content and removing residues. Decades of research to optimize yield of liquid and gases has resulted in the adaption of fast pyrolysis process.

## 2.2.2 Fast pyrolysis

This is a relatively new, promising technology involving a high liquid yield achieved through rapid heating rates of 10 to >1000 °C/s, short residence times of <2 s, temperatures of 400–650 °C, and rapid quenching of the vapours.(Balat et al., 2009). The very short vapour resident times are used to produce liquid and gaseous products. With fast pyrolysis, the aim is to maximize the production of the liquid from biomass, to yields up to 75 *wt*.%, as postulated by Bridgwater(Bridgwater, 2012). However, bio-oil produced by fast pyrolysis poses some undesirable properties including; low heating values, high viscosity, corrosive, incomplete volatility and thermal instability (Dynamotive, 2007). These liquid characteristics stem from the presence of oxygenated organic compounds in the feed, including phenols, carboxylic acid, aldehydes, ketones, aromatics, carbohydrates and alcohols. These compounds readily polymerize during storage resulting in an increase in viscosity and average molecular weight thus it is important to chemically upgrade the pyrolysis products. The chemical upgrade processes include hydro-deoxygenation and catalytic cracking of the pyrolysis vapours with zeolites which eliminate oxygen as CO and $CO_2$.*(Brown & Holmgren, 2009)*

Figure 2.2 shows the different steps for the fast pyrolysis of lignocellulosic biomass, mainly wood. In a primary phase, decomposition of the macro biopolymers within the biomass particles takes place resulting in char and vapours(Venderbosch & Prins, 2010). Part of the primary vapours will condense into the final bio-oil, but another fraction of the vapours can undergo additional cracking to non-condensable gases, heavy tars and/or bio-char. The aim of fast pyrolysis is to maximize the quantity and optimize the quality of the pyrolysis oil.(Venderbosch & Prins, 2010)**.**
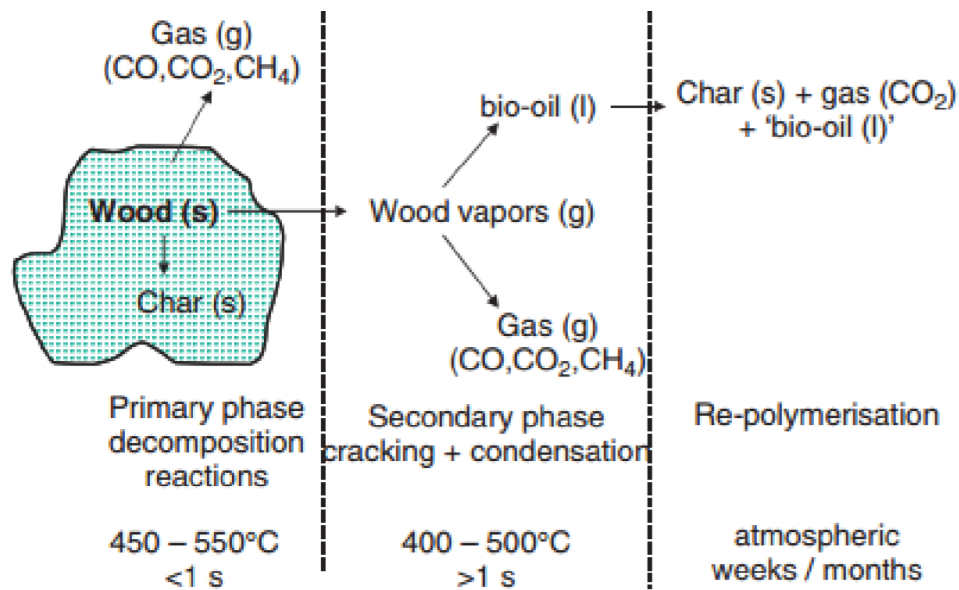
Source: Mohan *et al,* (2006)

**Figure 2.2; Reaction pathways for wood pyrolysis.**

The type of biomass used determine the quality and quantity of bio-oil yield. From an ecological and economical point of view, it is more attractive to use waste streams having no further use in already existing application (Venderbosch, 2015*)*. Other conditions that may influence the amount of liquid are temperature, residence time of biomass and vapours, and pre-treatment of the feedstock. With wood as biomass, observed oil yields ranged from 55 to 70 wt.% (on dry-feed basis) (Venderbosch & Prins, 2010). Some articles report higher yields but those are rather exceptional and could only be produced in laboratory scale. Theoretically, the share of the solid and gaseous phases account for 12 and 13 wt.%, respectively. In practice, these values are higher because it is not always feasible to meet the required process conditions for fast pyrolysis. Mohan *et al.* (2006) reported the yields of char and non-condensable gases are approximately between 15 - 25 wt.% and 10 - 20 wt.%, respectively. This implies that biochar and non-condensable gas form a significant part of the product *(*Mohan *et al.,* 2006*)*

**2.3Catalysts**

Catalysis as one of the most frequently observed natural phenomena is the basic form of chemical reactions proceeding at a high rate in nature as well as in different fields of practical activities. Catalysis is the most powerful method of controlling and directing chemical reactions. Competent international forecasts place catalysis among the most promising fields of basic research (Linck *et al.,* 2014). The successes of basic research in the field of catalysis have a direct effect on solving many fundamental technological, environmental and social problems that face humanity(Yildiz *et al.,* 2013). These include efficient utilization of raw materials and formation of new sources of raw materials, invention of new materials and substances with pre-programmed properties, development of efficient systems for environmental protection, mastering of new sources of energy and improvement of existing ones, and development of new processes and technologies in chemistry and biology(Amadi *et al.,* 2004).

**2.3.1 Synthetic Catalysts**

Catalysts belong to the group of so-called performance chemicals. They have a complex composition (often supported on carriers or dissolved in solvents) and are added to the reaction mixture to enhance processing of other chemicals. In most of the cases, industrial catalysts contain three groups of components: catalytically active materials, catalyst supports, and promoters. Catalytic processes form the fundamentals of modern chemical and petrochemical industries (Petrov, 1998). Over 70% of the processes in these industries are catalytic, while for the newly introduced ones this percentage is over 90. In the developed countries catalytic processes create about 20% of the Gross Domestic Product (GDP). Catalysis is one of the top priority issues of chemical science and many countries have founded specialized institutes and laboratories for basic research and applied studies in the field of catalysis (Petrov, 1998). Effective

application of the existing catalysts and development of new types need precise and fast information about their catalytic properties. The determination of catalytic activity, selectivity and lifetime of an industrial catalyst for a certain catalytic process is a difficult, expensive and time-consuming task(Hartmann et al., 2016).Therefore, identification of simple and non-expensive catalyst materials can be of importance to the industry

### 2.3.2 General aspects

The main reason to use catalysts in fast pyrolysis research was to selectively remove oxygen prior to condensation of the gases to improve the oil quality. This type of reaction is heterogeneous catalysis because it made use of a solid catalyst facilitating its separation and recycling(Yildiz *et al.*, 2017). It was claimed that Catalytic fast pyrolysis (CFP)possesses several interesting characteristics compared to other upgrading techniques. These include possibility to execute the experiment in one single reactor (for in-situ mode); the use of relatively cheap and readily available catalysts like zeolites; the handling of an attractive range of feedstock biomass and the production of bio-oil blend with current fuels(Yildiz *et al.*, 2013). In practice, there are two operating modes for Catalytic fast pyrolysis: in-situ and ex-situ catalysis. In the in-situ type, biomass is pyrolyzed in a reactor in which the heterogeneous catalyst is also present and vapours diffuse into the catalytic pores where they are reformed (Figure2.3(a) and (b). In the ex-situ mode, created vapours come out of the pyrolysis reactor and contact with the catalyst in a second, separated reactor where the vapours are upgraded (Figure 2.39(c) and (d)(Yildiz et al., 2013).
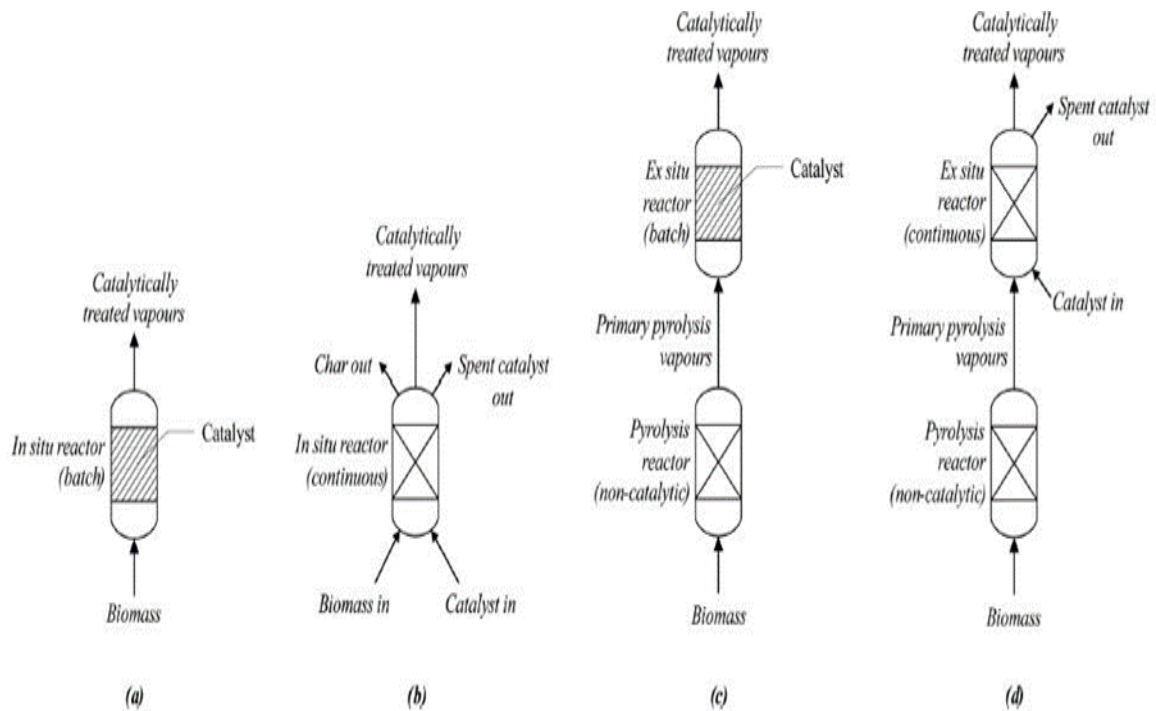
Source: Yildiz et al., (2017)

**Figure2.3Operational modes of catalytic fast pyrolysis(a): in situ, (b): in situ (continuous), (c): ex-situ and (d): ex-situ.**

### 2.3.3Natural catalyst materials

A great number of natural materials of different nature exhibit catalytic activity in one or more catalytic reactions but, only few of them are suitable for preparation of industrial catalysts. There is a substantial difference between catalytically active materials and industrial catalysts. The catalytically active material is a precursor of an industrial catalyst that has to undergo many transformations and treatments to become a real industrial catalyst. Catalytically active materials usually possess appropriate catalytic properties (activity and selectivity) which are required for industrial catalysts (Petrov, 1998). The effective industrial catalysts are products which possess different properties and should be selected using the following criteria: high catalytic activity, high selectivity, proper pore structure, long lifetime, high resistance to deactivation and

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catalytic poisoning, easy regeneration, low operation and light-off temperature, high thermal stability, high thermal conductivity, high mechanical strength,  high resistance to attrition and low price (Petrov, 1998). It is impossible, however, to prepare a catalyst that meets strictly all the above requirements. In order to obtain the best performance, it is necessary to make a compromise for the extent to which all necessary requirements are satisfied. The typical groups of catalytically active materials involve metals, oxides, acids and bases, chlorides, carbides, nitrides, borides, silicide, phosphides, molten salts, anchored homogeneous catalysts (Stefanidis *et al.*, 2016).  As mentioned before, the most suitable natural catalyst material must be selected for every process for example, the medium acidity HZSM-5 Zeolite ($SiO_2$/$Al_2O_3$ 25-30) can be prepared with the use of expensive and corrosive organic template reducing the total cost of the catalyst and improving on the overall sustainability of the process(Narayanan *et al.,* 1995). The process over zeolite is deteriorated by the carbon deposition (coke formation) as a result of coke precursor such as methoxy phenols and hydrogen depleted atmosphere that result in the formation of compound with lower H/C ratio that tends to be on the catalyst and polymerize blocking of the active sites and pores of the catalyst.(Narayanan *et al.*, 1995). The extensive research has been carried out on the effect of alkali metals on the decomposition of the biomass under pyrolysis and the alkali have been found to strongly favour the formation of lower molecular weight compound by conversion of levoglucosan in biomass pyrolysis (Fahmi et al., 2007)

### 2.3.4 Catalytic upgrade

The oil upgraded by hydrodeoxygenation can be produced at a very competitive price compared to other biomass conversion technologies. The catalytic treatment can either be in situ (adding catalyst particles to the reactor) or ex-situ (secondary conversion of the produced pyrolysis vapour fraction). The desired function of the catalyst is in both

cases the removal of oxygen containing compounds and the catalytic cracking of high molecular weight compounds. The main chemical reactions are hydrocracking, decarboxylation, hydrodeoxygenation, cracking, and hydrogenation(Zhang *et al.,* 2007).

**2.3.5 Choice of catalyst**

In the search for the proper catalyst, some parameters must be considered. Catalysts keeping their activity and selectivity over an extended period, are favoured. A stable catalyst will change very slowly over the course of time. Porosity can also have a significant effect on catalytic properties (Lin & Huber, 2009). Besides, the catalysts must be thermally and mechanically stable, robust and resistant against deactivation (Mohan *et al.*, 2006). The current research used natural zeolites as a catalyst in pyrolysis of groundnut shells.

**2.3.6 Catalyst cracking**

Catalyst cracking occurs via decarboxylation and dehydration reactions at atmospheric pressure. Typically, the acidic and hydrophobic catalyst ZSM-5 is used for those type of reactions. The formed products are hydrocarbons, water and oil soluble organics, $CO$, $CO_2$ and coke. Due to the high temperatures, bonds in the larger molecules are cleaved and deoxygenation of the compounds takes place (Gollakota *et al.,* 2016)

$$xCH_3OH \xrightarrow[\text{Catalyst}]{\text{Zeolite}} (CH_2)_x + xH_2O$$
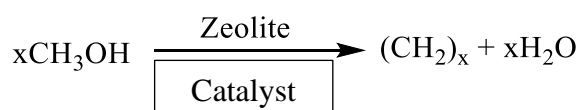
**Figure 2.4; Dehydration of methanol to form hydrocarbons.**

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General disadvantages of hydrotreating and catalytic cracking are the low yield of upgraded bio-oil and catalyst deactivation. This arises from the production of coke, char and tar (Junming *et al.*, 2008). This first issue can partially be solved by co-feeding hydrogen gas or hydrogen donors (methanol, tetralin or decalin) as well as modifications to the reactor systems themselves (Jacobson *et al.,* 2013).

**2.3.7 Catalytic fast pyrolysis**

Catalytic Fast pyrolysis (CFP) removes oxygenated compound via $CO_2$ and CO while slow Catalytic pyrolysis (SCP) remove the oxygenated compound via $H_2O$. The CFC tends to increase hydrogen while SCP reduce on hydrogen and increase on the volume of water in bio-oil(Yakovlev *et al., 2009*).The efficiency of a CFP system can depend on: operating temperature of the catalyst; the relative rate of the catalyzed vapour phase reactions; heating rate and residence time of the feedstock. High biomass heating rates are essential to suppress coke formation (Yildiz *et al., 2017*).High value ratio of mass flow rate of biomass to the mass of catalyst are preferable in order to lower the formation of coke and polycyclic aromatics as well as to improve process economics by reducing the amount of used catalyst (Mante *et al., 2013*), In catalytic experiments, high-lignin-low-ash-biomass like woody variants are preferred (Hayes, 2013).

**2.3.8 Metal oxides**

Metal oxides particularly transition metal oxides, have been widely used as heterogeneous catalysts in various reactions (Jakab *et al., 2010)*. Generally, metal oxides possess either redox properties due to their multivalent nature and/or certain acid–base properties which could potentially catalyze the thermal decomposition of lignocellulose and/or the reaction of pyrolysis intermediates to form more stable products. Various metal oxides, including MgO, NiO, $Al_2O_3$, $ZrO_2$, $TiO_2$, $MnO_2$, $CeO_2$, $Fe_2O_3$, and their mixtures, have been tested as catalysts for CFP. Acidic metal oxides

such as $Al_2O_3$, $SiO_2$, and $SiO_2$–$Al_2O_3$ as well as the sulfated metal oxides such as $SO_4^{2}$ /$TiO_2$, $SO_4^{2}$ /$ZrO_2$, and $SO_4^{2}$ /$SnO_2$ have been investigated as catalysts in CFP(Stefanidis *et al.,* 2016). The presence of acidic metal oxides also changes the composition of bio-oil. For $Al_2O_3$-catalyzed pyrolysis, there were many more aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH) in the organic products. The $SiO_2$ with weak acidity and medium porosity is active in removing oxygenated compounds such as acids, ketones, and aldehydes and in inhibiting coke and polycyclic aromatic compound formation in CFP of Jatropha residue (Vichaphund et al., 2015) Acidic metal oxides also catalyze the decarbonylation reactions and lead to the increase of CO. Meanwhile the yields to $C_1$–$C_4$ hydrocarbons are also greatly increased (Stefanidis *et al.,* 2016)

**2.3.9 Catalytic cracking with zeolites**

Zeolites are complex, three-dimensional porous structures with varying elemental compositions that exhibit catalytic activity in up to 50% of their volume. Cracking and dehydration are the main reactions seen. Adsorption of the oxy compound occurs on an acid site. This is followed by either decomposition or bimolecular monomer dehydration, as determined by pore size (Mortensen *et al.*, 2011). As with sulfide/oxide and transition metal catalysts, the acidity of the zeolite affects the reactivity and yields, with high acidity leading to a higher affinity for C and water formation(Aho *et al.,* 2007). In HZSM-5, one of the most widely used zeolites, acidity is linked to the Si/Al ratio, with a low ratio indicating high acidity. Pore blockage from polymerization and polycondensation reactions causes deactivation of the catalyst. Zeolites should have correct pore size and acidic sites to promote desired reactions while minimizing carbon

formation. The presence of [AlO$_4$]- in the zeolite structure introduces a negative charge which is compenseted by proton leading to the formation of strong Bronsted acid sites.
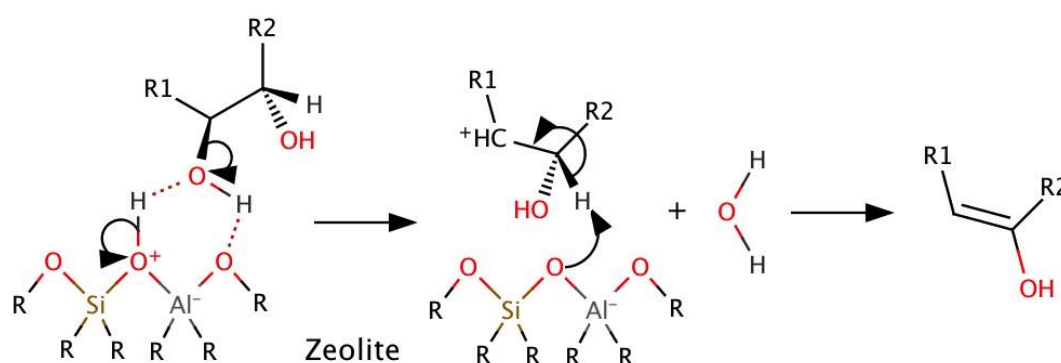


Sourece: Dickerson et al (2013)

**Figure 2.5; Aluminosilicate zeolite dehydration of model compound**

Zeolites produce aromatics at atmospheric pressures without hydrogen requirements. The final product generally has a low heating value. This is due both to its low H/C ratio and high O/C ratio as compared to hydro-deoxygenated pyrolysis oils (Bridgwater, 2012; Mortensen *et al.,* 2011). Research is generally conducted at temperatures from 350 to 600 °C. For HZSM-5, yields are in the 15% range with predictions of 23% *(A. Bridgwater, 1996)*. Excessive carbon production and therefore catalyst coking is a problem. In one study, coke deposition at all temperatures led to a decrease in the catalytic activity after only 30 min time on stream(Huber & Dumesic, 2006). Furthermore, coke has been shown to significantly increase at temperatures above 400 °C (Gayubo et al., 2004) Some coke can be burned off, but irreversible dealumination and loss of acid sites occurs at temperatures as low as 450 °C in the presence of water (Gayubo et al., 2004) Research on the reduction of coking is important, with a variety of approaches showing a promising result. For example, the recycling of non-condensable gases into a catalytic reactor has the potential to reduce char/coke yields while increasing oil yields.(Adjaye & Bakhshi, 1994).The elemental composition of the

fast pyrolysis bio-oil feedstock, as measured by its Hydrogen to Carbon effective ($H/C_{eff}$) ratio has been determined to have a large impact on the production of olefins, aromatics, and coke. Experiments have shown that pyrolytic bio-oil feedstocks with a ratio of at least 1:2 or higher perform better in zeolite pyrolysis upgrading (Zhang *et al.*, 2011). Yields of olefins and aromatics increased while coke production decreased with increasing $H/C_{eff}$ ratios. Catalyst life increased as coke yield decreased. This suggests that it may be beneficial to increase the $H/C_{eff}$ ratio to1:2 through hydrogenation of the bio-oil feedstock before upgrading with a zeolite catalyst. Another method of effectively increasing the $H/C_{eff}$ ratio is to co-pyrolyze a hydrogen donor such as methanol. (DeSisto et al., 2010) Desisto studied the pyrolysis of wood waste in a dual zone, fluidized bed reactor. The results showed an overall increase in hydrocarbon products, including alkylated phenols and aromatics. The alkylated products are thought to compete with the production of polyaromatic hydrocarbons (PAHs) that are not desirable and therefore explain the corresponding decrease in 3-, 4-, and 5-ring PAHs.

**2.3.9.1 Synthetic Zeolites**

They are aluminosilicates, composed primarily of Si, Al and O, and another metal including Ti, Sn, Zn and others, with the general formula: $\{[M^{n+}]_{x/n} \bullet [H_2O]_m\}\{[AlO_2]x[SiO_2]_y\}^{x-}$, where $M^{n+}$ cations and $H_2O$ bind inside the cavities, or pores of the Al-O-Si framework. Like the natural zeolite, the syntheticzeolites have a microporous extended framework whose surfaces extend deep inside the solid, small neutral molecules such as $CO_2$, $NH_3$, and hydrocarbons can adsorb to the internal surfaces of the zeolites, some zeolites for which $M = H^+$ are strong acids and catalyze a variety of reactions in the petrochemical industry. For example: Isomerization of m-xylene (a) to p-xylene (b)
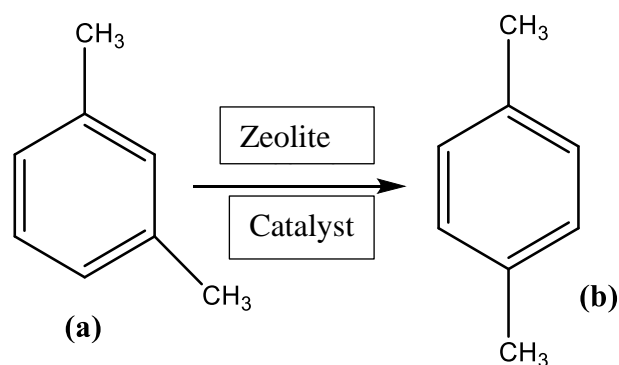
**Figure 2.6: Isomerization of m-xylene (a) to p-xylene (b)**

Zeolites with a specific composition and structure can perform selective catalysis because only molecules with a certain size can enter and exit the porous framework in which the catalysis occurs, there is also shape selectivity, Ion exchange capacity and separation of molecules by their size.

**2.3.9.2 Structure for synthetic Zeolites**

These are crystalline microporous silica based materials with a well-defined and ordered pore structure (Jacobson *et al.,* 2013). Synthetic zeolites are used in selective adsorbing, petroleum refining and purification processes (Bartholomew & Farrauto, 2011)**.**
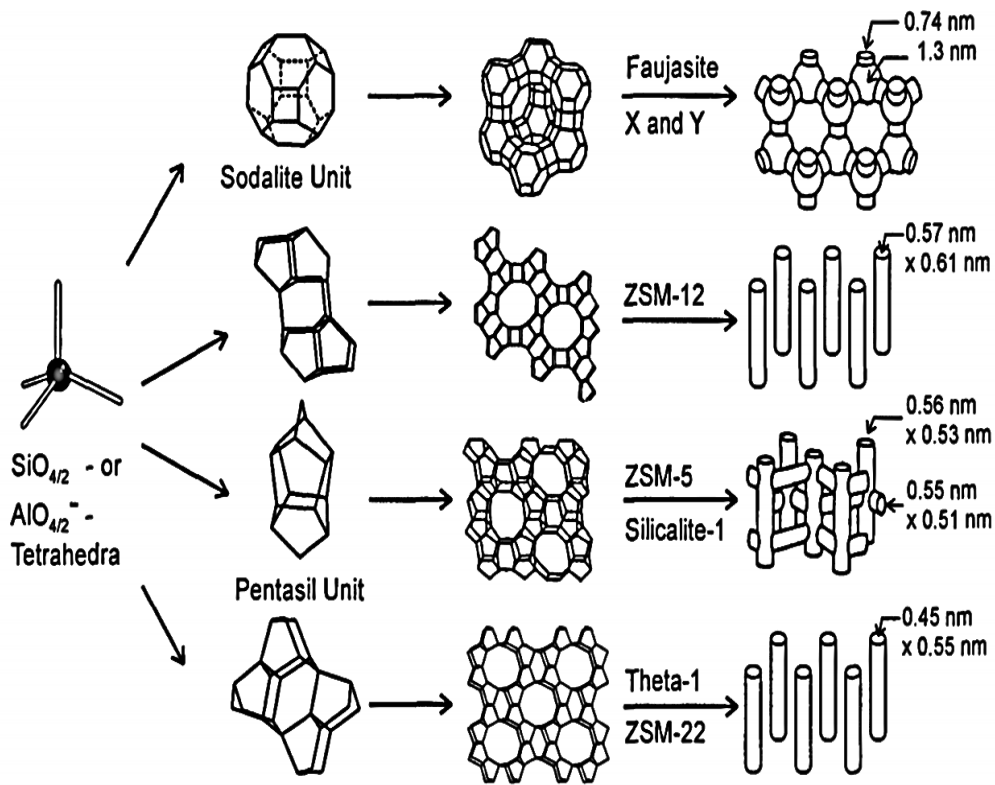
Source; Jacobson *et al.,* 2013

**Figure 2.7: Structure of the four synthetic zeolites**

From top to bottom faujasite or Zeolite X, Y; Zeolite ZSM 12; Zeolite ZSM 5 or Silcalite-1; Zeolite Theta-1 or ZSM 22 and their micropores system and dimension. In that category, the (H)ZSM-5 is the most well-known member.
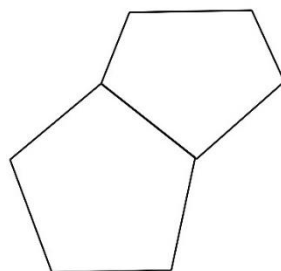


Source; Morris, (2011)

**Figure 2.8: The pentasil unit for HZSM-5.**
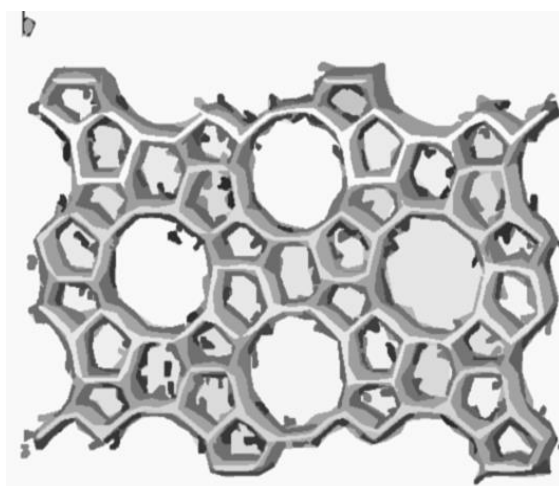
Source; Morris, (2011)

**Figure 2.9: 3D-structure of HZSM-5(Morris, 2011).**

The secondary structure of HZSM-5 is pentasil units. These units are attached to each other to form pentasil chains, and ten pentasil units can form a 3D-structure, as shown in Figure 2.9 below. The created cavities have a size between 5.4 and 5.6 Å ($10^{-10}$ m).(Jacobson *et al.,* 2013)

The aluminosilicate materials can be built with units of $SiO_4$ and $AlO_4$, linked together with a common oxygen atom. The net negative charge is brought into an equilibrium by the presence of a cation (Morris, 2011). Zeolites contain acid sites and have very small pore sizes so only small molecules will diffuse through. They promote cracking reactions and selective deoxygenation of pyrolytic vapours.(Yildiz *et al.,* 2013). Acid catalysts show excellent properties like tenable acidity, superior water tolerance and high thermal stability (Engtrakul *et al.*, 2016).The acidity of the catalyst expressed as the $SiO_2/Al_2O_3$-ratio (SAR) has also its influence on the product selectivity (Engtrakul et al., 2016). The more aluminium (III) oxide incorporated in the ZSM-5, the lower the ratio of Brønsted/Lewis acid sites. A higher SAR means a decrease in number of acid sites and apparently a lower total acidity. Engtrakul*et al*., (2016) investigated different ratios, ranging from a SAR of 23 to 280. With a higher acidity, more unsubstituted aromatics benzene, naphthalene and anthracene were created at the expense of alkylated

aromatics such as xylene, dimethyl naphtalene and methylanthracene. This is related to the relative cyclisation and alkylation rates within the zeolite. Within a more acidic catalyst, the acid sites are more concentrated to each other and additional cyclisation reactions occur at a higher rate than alkylations (Engtrakul *et al*., 2016).The Bronsted acid site contain an oxygen atom in its framework that is protonated, resulting in a hydroxyl group donating its hydrogen to the adsorbed molecule, while by the Lewis acid site, electron pairs are transferred from the adsorbed molecule to the solid surface (Jacobson *et al.,* 2013*)*. Zeolites with a lower acid site density tend to deactivate faster and generate more hydrocarbons such as paraffin, olefins and aromatics in total. A high SAR leads to the production of more aliphatic alkanes and alkenes, while more benzene containing compounds are produced with a lower ratio. A low SAR means high acid strength sites facilitating the dehydrocyclisation of alkanes/alkenes to aromatics.
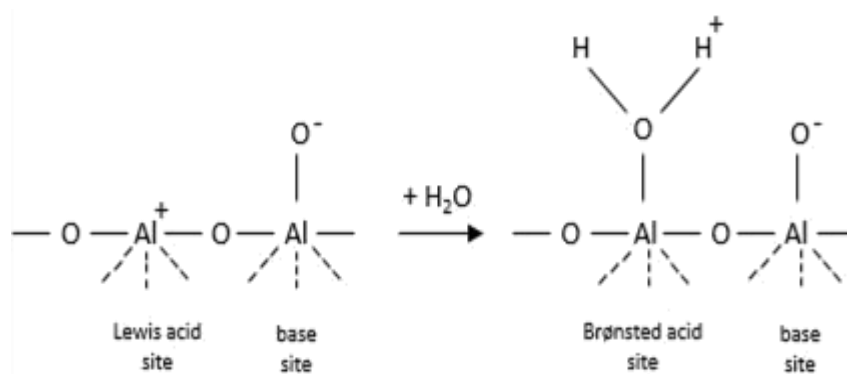


Source: Engtrakul et al. (2016)

**Figure 2.10:TheBrønsted acid site reactions**

The prepared catalysts are used in reaction mechanism of Catalytic Fast Pyrolysis is shown in figure 2.10. Cellulose is converted into hydro-sugars like 1,6-anhydro-β-D-glucofuranose (AGF), 1,4:3,6-dianhydro-α-D-glucopyranose (DGP), levoglucosenone(LGO) and levoglucosan (LGA) due to the removal of water. Those intermediates can be transformed into furans by an acid catalysed dehydration or

decarbonylation/decarboxylations steps. Furans are also formed out of hemicellulose while losing water, and with the same reactions that occur during the conversion of anhydrosugars to furans, a pool of hydrocarbon compounds is created. When lignin is subjected to non-catalytic depolymerisation, monomeric phenols are created, which can be further converted into monoaromatics (MAHs) and eventually in a second phase to polyaromatic hydrocarbons (PAHs). From all those intermediates, heterogeneous coke can be formed on the catalyst (Yildiz *et al.,* 2017).
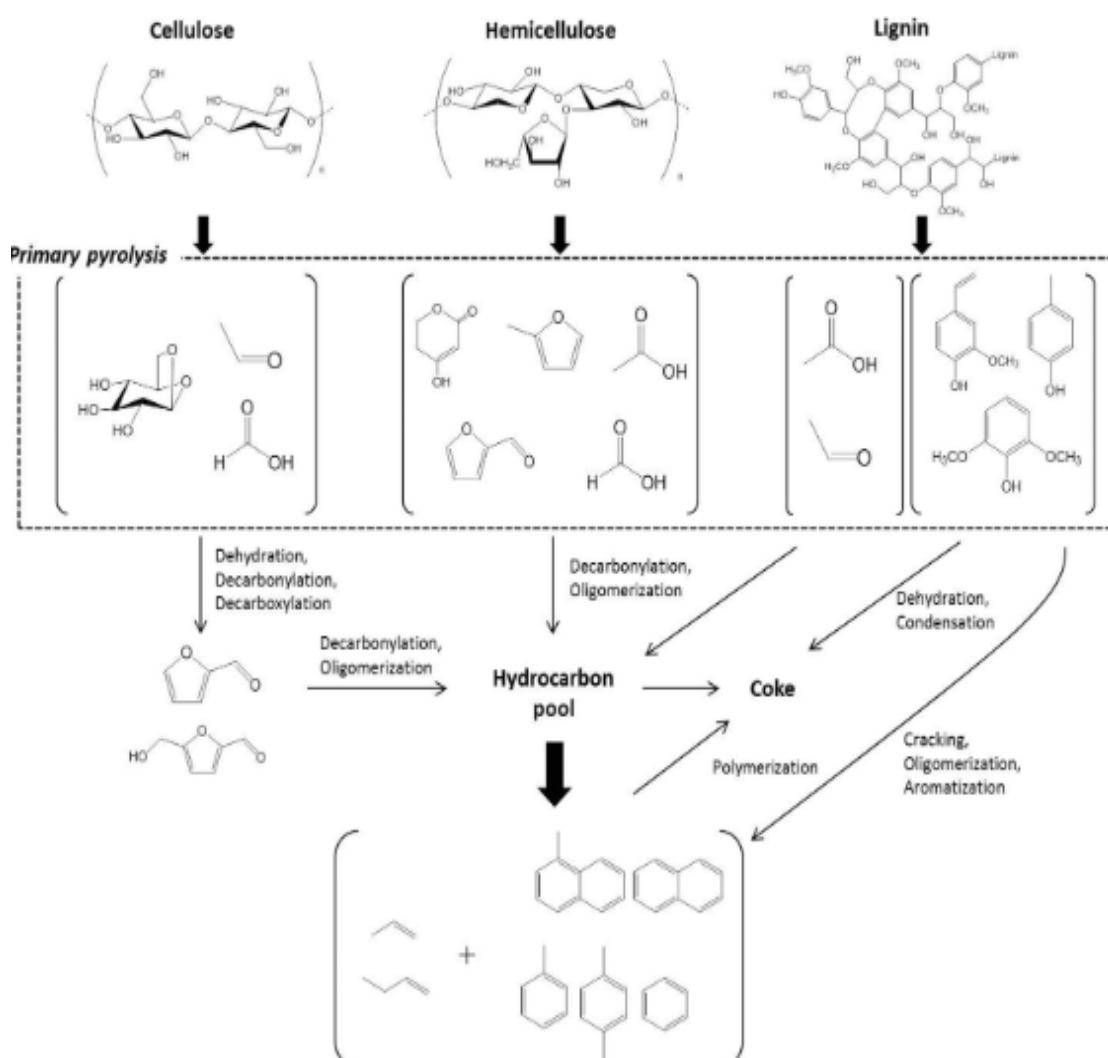


**Figure 2.11; Chemical conversion of cellulose, hemicellulose and lignin**

The general conceptual reaction describing the several deoxygenation reactions during the pyrolysis process is as shown in figure 2.11 above

## 2.4 Bio-oil: properties and applications

The interesting product of fast pyrolysis is bio-oil. Although producing it with maximal yields is one of the purposes, the quality of the bio-oil predominates as the main aim of the fast pyrolysis. A critical factor in that regard is the amount of oxygen and its functionality in the bio-oil. Its relatively high oxygen content is one reason why it cannot be used as a direct substitute for heating fuels or for power production in boilers. Oxygen functionalities are present in more than 300 different compounds in the liquid examples. carboxylic acids, alcohols, ketones, aldehydes, ethers and esters. In that way, bio-oil may have some potential, but its complex composition makes it challenging to create a valuable and profitable product out of it(Oasmaa *et al.,* 2009)

The physicochemical properties of the bio-oil compared with those of conventional fuel oil. Typically, the liquid colour is deep brown (Oasmaa & Peacocke, 2001). Its elemental composition corresponds quite well with that of the original biomass. Bio-oil has a distinctive acid, smoky smell due to the volatile, low molecular weight acids and aldehydes and it can irritate the eyes after prolonged exposure. The oil can corrode materials such as aluminium and carbon steel (Soltes & Lin, 1984). Polyolefins and stainless steel are more resistant to the liquid and should be usedin handling and storing bio-oil. The pH results from the high concentration of organic acids such as formic and acetic acid in the bio-oil(Bridgwater, 2012)

Another drawback is the relatively low higher heating value (HHV). A low HHV means that the product is less suited as a direct fuel. As the produced oil contains water as well as organic compounds, phase separation may occur at a certain water/organic - ratio (Westerhof *et al*., 2008). At rather low water concentrations in bio-oil (between 15 – 25

%), water is usually miscible due to the presence of other polar hydrophilic constituents such as short alcohols, ketones or aldehydes. Water in bio-oil is partly derived from moisture in the feed material (usually feedstocks with a maximum moisture content of 15 wt.%) and dehydration reactions occurring during catalytic fast pyrolysis (Elliott & Water, 1994). To remove all the water out of the pyrolysis oil, the liquid must be heated to at least 100 °C, which is also above the boiling point temperature of some light oxygenates in bio-oil(Bridgwater, 2012). Sometimes, water is added to the bio-oil to reduce the viscosity and to improve the stability.

The properties of the liquid mixture can change over time. This process is known as aging and involves an increase of the viscosity and average molecular weight, possibly accompanied with a phase separation. When the bio-oil is held at room temperature instead of kept refrigerated, more secondary reactions (including polymerization reactions) will appear, affecting the quality of the bio-oil. This can be controlled by adding alcohols (methanol or ethanol), that solubilize the less-soluble constituents and lower the reactivity of certain compounds in the bio-oil(Diebold, 1999).

# CHAPTER THREE

# MATERIALS AND METHODS

This chapter considers the materials and methods used in the study,the analytical methods and equipment used in characterization, preparation of biomass samples;and quantification of bio synthetic gas and bio char yields.

## 3.Materials

The materials used in this study were groundnut shells which is agricultural waste material collected after de-shelling of the groundnut. The catalysts were zeolitic materials with traces of transitional metals and equipment that were used to treat biomass to bio-oil was a pyrolizer.

## 3.1.1 Collection of groundnut shells

The biomass used was groundnut shells collected from Ngora District in the Eastern Region of Uganda. Biomass was Sun-dried, then milled using the Ping Laboratory Mill (Model No. 386, Made in China).

## 3.1.2 Catalyst

Basing on information from Geological Survey and Mines, Ministry of Energy and Mineral Development Entebbe, natural zeolites were sampled from Manafwa District along the Manafwa river. TheTiira gold mine rock and Usuuku rock from Tororo district. The charcoalpyrite samples were obtained from Kilembe, and Katwe salt from lake katwe, both in Kasese District. The choice of minerals was based on the presence of zeolitic nature, transitional elements, alkaline earth, alkali metal element in the minerals.

### 3.1.3 Equipment

Electric oven Kentong 202-AU; Pottery craft Muffle furnace P59101; Electronic balance Hangping FA1104, Roll mill, Xinkyo Batch pyrolizer SK2-2-12TPA2; Oil, char and gas sample containers, storage containers and sealable Ziplock plastic bags; PS-80 grinder; International standard test sieves 3.35mm, 2.36mm, 0.71mm, 1mm, 0.3mm and 0.425mm mesh sizes,Nitrogen cylinder, EralyticEraspec -fuel Analyzer-FTIR,Thermo Scientific Nitron XL5,Flash 2000 organic elemental Analyser from Thermo Scientific.

### 3.2 Methods

This section includes the methods used in analyzing data that was generated after the experiment.

## 3.2.1: Proximate and ultimate analysis of biomass

The parameters for proximate analysis were moisture content, volatile matter, ash, and fixed carbon. The proximate analysis of different materials was done according to ASTM test methods - ASTM E871-82 2013for measuring moisture content; ASTM 1755(E. ASTM, 1755) for determining ash content; E872-82 (E872-82, 2013)for determining volatile matter, respectively. Fixed carbon was calculated as (100- (Ash content + Volatile matter).

The milled groundnut shells were screened to 2 mm particle size. 100g air-dry weight (Wa) of screened groundnut shells sample was weighed using electronic balance Model: FA1104 and placed in the oven in aluminium container of known weight at $105^{\circ}C$ for 24hours. After 24 hours, the oven was switched off and left to cool. The oven dried sample was weighed and the new weight (Wb) recorded.

NB: The weight of the Aluminium foil used in weighting was the same for all experiment

Percentage moisture content % $= \frac{Wa-Wb}{Wa} \ x \ 100$%,…………………Equation 3. 1

Where:**Wa** = Air dry weight, **Wb** = oven dry weight.

## 3.2.2 Ash Content

Ash content was performed according to ASTM procedure E1755, with the help of Equation 3.2. 100g sample of oven air dry groundnut shells were burnt in the fume cupboard to reduce on the mass to ash. The pre-burnt ash was placed in crucibles and transferred into the muffle furnace (Model: P59101). The sample was then ignited in the furnace to 500ºC for 1hr in order to burn off all organic matter in the sample. The ash was removed from the furnace and placed in the desiccator for 30mins to prevent re-absorption of moisture.

Ash content % $= \frac{Wn-Wf}{100} \ 100$% ……………………………………. Equation 3. 2

Where:**Wn**– Weight of crucible and Ash, **Wf**– weight of crucible

## 3.2.3 Volatile matter

The volatile matter of the groundnut shell was estimated with ASTM procedure E872 and Equation 3.3. The 100g of sample was heated (carbonised) in a covered crucible to 950ºC and kept at this temperature for 7 minutes

Loss of weight % $= \frac{100g-Weight \ of \ Ash \ only}{100g}$X 100%

Volatile matter = Loss of weight – Ash content ………………………… Equation 3. 3

## 3.3 Physical characterization of bio fuel precursors

Elemental analysis included the quantitative determination of carbon, hydrogen, nitrogen, sulfur and oxygen within a fuel material. Almost all the heat being formed from combustion of biomass products was obtained from carbon and hydrogen burning. For this reason, characterizing the elemental composition of products from biomass pyrolysis was important to evaluate the fuel potentials. Furthermore, measuring nitrogen and sulfur contents in the structure of fuels was crucial for environmental pollution, since nitrogen and sulfur oxides were formed because of the nitrogen and sulfur in the structure of fuel when fuel is burned. Elemental analysis of the biochar and bio-oil products was performed according to 5373 and 5291(D. ASTM, 1996) standard test methods. The composition was determined according to 3176(D. ASTM, 1989). Empirical formula, H/C and O/C molar ratios were calculated from elemental composition. Oxygen content of bio-oil was generally calculated as;

$$O\% = 100 - (ash\,\% + moisture\,\% + C\,\% + H\,\% + S\,\%\,)\ldots\ldots\ldots \text{ Equation 3. 4}$$

The total sulfur of biochar and bio-oil samples was determined according to 3177(D. ASTM) and 4294(D. ASTM, 2010), respectively.

### 3.3.1 Determination of the amount of Carbon, hydrogen, nitrogen and oxygen

The elemental composition (that is Carbon, hydrogen and nitrogen) of the biomass was determined with the elemental analyser (Flash 2000 organic elemental Analyzer from Thermo Fischer Scientific) while the oxygen content was calculated by using Equation 3.5.

$$O_{content}\,\% = 100\% - \%C_{content} - \%H_{content} - \%\,N_{content}, \text{------------------ Equation 3. 5}$$

### 3.3.2 Biomass calorific values

The higher heating value on dry basis (HHV$_{dry}$) was calculated basing on elemental analysis results obtained using a correlation developed by Channiwal and Parikh (Channiwala & Parikh, 2002)as shown in Equation 3.6.

$$HHV\ dry\ \left(\frac{MJ}{Kg}\right) = 0.3491C + 1.1783H + 0.1005S - 0.10340O - 0.015N - 0.0211A$$

---------- Equation 3. 6

Where, C- Carbon, H- Hydrogen, S- Sulphur, O- Oxygen, N- Nitrogen, A- Ash

### 3.3.3 Hydrogen to carbon ratio (H/C)

This was calculated basing on the Equation 3.7

$$H/C = \frac{MMC\ x\ MGH}{MGC\ x\ MMH},$$ ……………………………………………... Equation 3. 7

Where, MMC-Molar Mass of Carbon, MGC- Mass of Carbon recorded from the machine, MGH- Mass of Hydrogen recorded from the machine, MMC- Molar Mass of Hydrogen

### 3.3.4 Oxygen to carbon ratio (O/C)

This was calculated using equation 3.8

$$O/C = \frac{MMC\ x\ MGO}{MGC\ X\ MMO},$$ …………………………………………… Equation 3. 8

Where, MMC-Molar Mass of Carbon, MGC- Mass Given of Carbon, MGO- Mass Given of Oxygen, MMO- Molar Mass of Oxygen

### 3.3.5 Empirical formula

The Equations equation 3.9 was used to deduce the molecular formula of the biomass as follows:

Empirical Formula $= CH_{H/C} O_{O/C},$ …………………………………... Equation 3. 9

## 3.4  Catalyst preparation

In this research selected metallic ores and natural zeolite catalytic materials were collected across the country as shown in Figure 1.1.

### 3.4.1 Catalytic materials activation

The catalytic materials were crushed and sieved with 250 µm sieve. 30g of each catalytic material was weighed, then washed with distilled water and dried in an oven at 110°C for 2 hours. Afterwards, it was submerged in 3M HCl solution of concentration 48 hours. The mixture was filtered and washed with distilled water until neutral (pH = 7), dried in an oven at 110°C for 3 hours. The dried solid powder were active catalysts and ready to be used as adsorbent.

### 3.5 Determination of inorganic content in the catalysts and biochar

The inorganic contents of the catalysts and ash were quantified using the X-ray fluoresce Instrument at Department of Geological Survey and Mines – Entebbe.

Calculation of silica to Alumina ($SiO_2/Al_2O_3$) ratio:

$SiO_2/Al_2O_3 = \dfrac{\% \; of \; SiO2 \; x \; Molecular \; weight \; of \; Al2O3}{\% \; of \; Al2O3 \; x \; Molecular \; weight \; SiO2}$…………………… Equation 3. 10

## 3.6 Biomass pyrolysis run

This was carried out in the pyrolizer in ex-situ batch system as shown in Figure 3.1
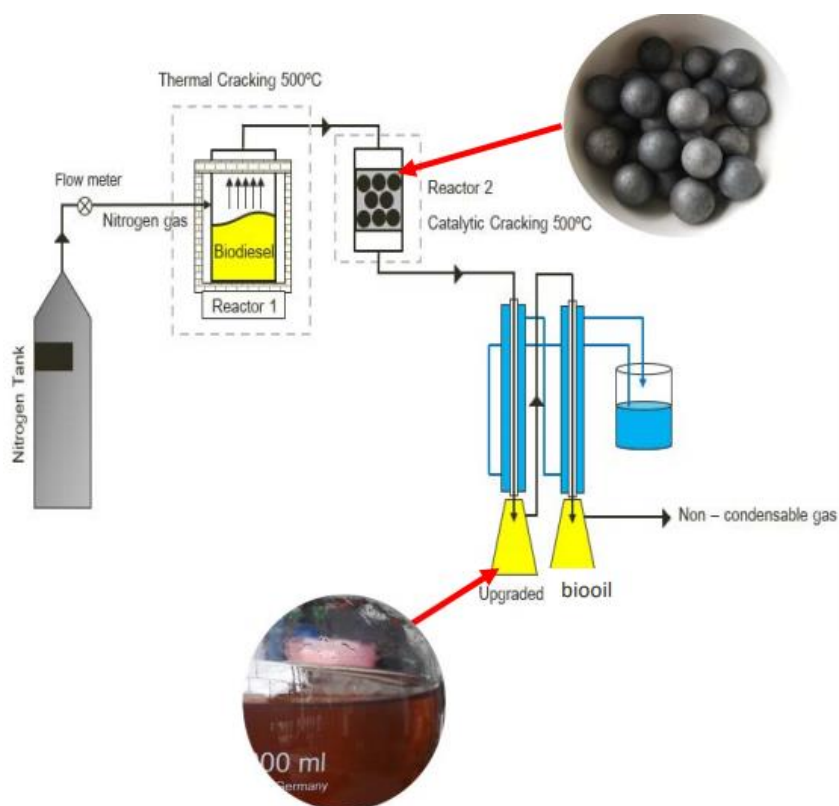


**Figure 3.1: Experimental setup**

The pyrolysis experiments were carried out in the double fixed bed quartz reactors with dimensions, length- 300 mm, internal diameter- 150 mm and outer diameter- 160 mm for thermal cracking and catalytic cracking with dimension, length- 150 mm, internal diameter- 50 mm and outer diameter- 60 mm. The reactor was heated externally by an electric furnace, with the temperature being measured by a Cr-Al: K type thermocouple fixed inside the reactor, and temperature was controlled by an external PID controller. A 300 g of groundnut shell sample was loaded in pyrolysis reactor for each test. The condensable liquid product was collected through the condenser and weighed. After pyrolysis, the solid residue left inside the reactor was weighed. The weight of gaseous/volatile product was calculated from the material balance.

### 3.6.1: Biomass pyrolysis run

A sample of 300g of groundnut shells powder (200 micron) was loaded in the thermal cracking chamber and 20g powder of natural or synthetic catalyst were loaded in the catalytic chamber. The PID controller was switched on with temperature raising at intervals of 25°C/min to 500°C in the Catalytic reactor chambers and afterwards the thermal reactor switched on with the same temperature profile. Nitrogen was used as a carrier gas. Prior to each run, the entire pyrolysis set up was purged with nitrogen at 100ml/min flow rate for 30min to ensure an inert atmosphere was achieved. Pyrolysis was carried out for 40 minutes with flow rate of 100ml/min. The evolved bio-oil was condensed in the two condensers loaded with dichloromethane and placed in ice bath. The bio-char and liquid products were directly weighed, and the gas yield was measured as the difference. Reproducibility was ensured with replicated runs and the experimental error ranged between ±5% of the average value. The bio-oil was separated from dichromethane by distillation. The bio-oil fraction obtained was further analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to determine the organic content of the bio-oil.
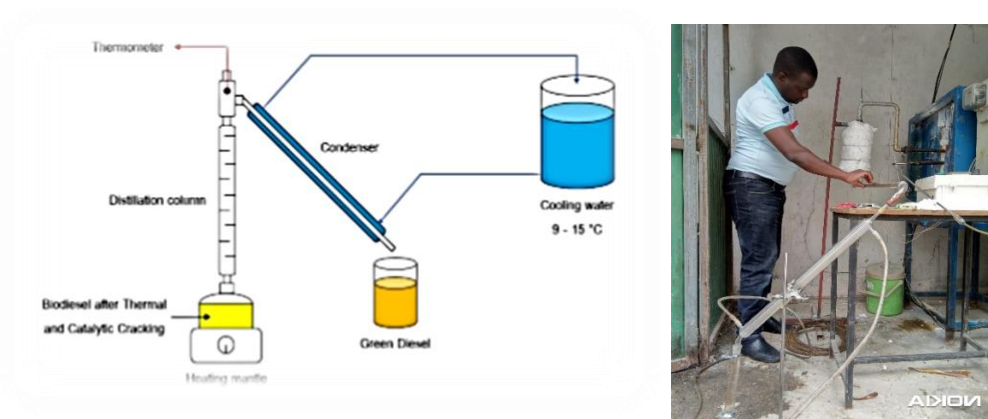


**Figure 3.2: Fractional Distillation Unit**

**3.6.2: Determination of the density and organic content present in the bio-oil**

The characterization of the bio-oils was carried out using Eraspec Fuel analyser FTIR (Eralytic Instruments Austria) equipped with a patented mid FTIR interferometer laser and temperature-controlled detector that detected various characteristic functional groups available in the bio-oil. The interaction of an infrared light with bio-oil make the chemical bond to stretch, contract, and absorb infrared radiation in a specific wavelength range in the presence of the rest of the molecules. Based on this, the principle functional groups present in the bio-oil were identified. The FTIR spectra was collected generally in the range of 400-4000 $cm^{-1}$ region with 8$cm^{-1}$ resolution. All compounds except for elemental diatomic gases such as $N_2$, $H_2$ and $O_2$, had infrared spectra and most components present were analyzed by their characteristic infrared absorption. Other components present in the sample also absorbed at the analytical wavelength, so the FTIR spectrometer was calibrated for cross sensitivities.

**3.6.3 Determination of density and pH of the bio-oil**

The determination of density of oil was done using the hydrometer of range 0.900 - 1.50g/ml and the pH was determined using a pH meter by Ohaus St series Pen

# CHAPTER FOUR

# RESULTS AND DISCUSSION

In this chapter, density, heating value, pH value, elemental analysis, ash and metals, Fourier Transform Infrared Spectroscopy (FTIR) analysis, standards applied to the bio-oil products was presented in this section and results obtained under objective one, two and three respectively alongside the discussion of all corresponding outcomes, in line with some of the established findings in literature.

## 4.1 Proximate analysis results

The proximate results obtained in laboratory analysis of samples of groundnut shells that were intended for pyrolysis are as shown in the tables below:

**Table 4. 1: Proximate analysis of biomass.**

| Component | Average Weight % |
|---|---|
| MC | $6.68 \pm 0.05$ |
| AC | $6.8\ 5\pm 0.40$ |
| VM | $66.95 \pm 0.53$ |
| FC | $19.53 \pm 0.14$ |

MC-Moisture Content, AC- Ash Content, VM- Volatile matter, FC-Fixed Carbon

Fixed carbon = 100% - (Volatile matter + Ash content)

The proximate analysis shows that groundnut shells had a lot of volatile matter. Therefore, a high bio-oil yield was expected as the volatile matter is the combination of non-condensable gas and the bio-liquid.

**Table 4.2: Elemental composition of the biomass (Ultimate Analysis)**

| Component | Average Wt.% |
|---|---|
| Carbon | 44.265±0.52 |
| Hydrogen | 7.028±0.88 |
| Nitrogen | 1.284±0.12 |
| Sulphur | 0.0 2± 0.01 |
| Oxygen | 47.423 ± 0.60 |
| H/C | 1.90 ± 0.21 |
| O/C | 0.803±0.01 |
| Molecular formula | $CH_{1.9}O_{0.803}$ |
| HHV(MJ/Kg) | 18.669 |

**HHV-**High heating value **H/C-**Hydrogen/ carbon ratio O**/C**- Oxygen carbon ratio

From the ultimate analysis of the biomass, the sum of carbon and hydrogen represented more than 50% of the total mass. This implied that hydrocarbon recovery was predicated to be high. The high H/C ratio also implied the good bio-oil properties expected.

**Table 4. 3:Mineral Composition of the biochar**

| Element | Average |
|---|---|
| Magnesium (Mg) | 01.83 ± 0.02 |
| Aluminium (Al) | 11.61 ± 0.05 |
| Silica (Si) | 18.26 ± 0.14 |
| Phosphorous (P) | 00.95 ± 0.03 |
| Chlorine (Cl) | 00.71 ± 0.02 |
| Potassium (K) | 09.33 ± 0.02 |
| Calcium (Ca) | 04.55 ± 0.02 |
| Iron (Fe) | 8.46±0.0387 |

## 4.2 Characteristics of natural zeolites and metallic ore

In order to determine the basic characteristic of natural zeolites several measurements were carried out.

### 4.2.1 X-ray fluoresce analysis of catalysts

X-ray fluoresce analysis was used to determine the chemical composition of different Catalysts that were used in the experiment. The elemental composition was used to determine the silicate /aluminate ratio.

**Table 4. 4: Mineral composition of selected zeolites and metallic ores**

| Elements | Rock salt Katwe wt% | Manafwe river side zeolite wt% | Kilembe rock wt% | Usuuku rock wt% | Tiira rock wt% |
|---|---|---|---|---|---|
| $Al_2O_2$ | $9.45 \pm 0.05$ | $6.58 \pm 0.05$ | $9.45 \pm 0.03$ | $11.15 \pm 0.06$ | $14.47 \pm 0.05$ |
| CaO | $1.26 \pm 0.02$ | $3.51 \pm 0.10$ | $1.26 \pm 0.10$ | $0.49 \pm 0.1$ | $<0.01 \pm 0.01$ |
| FeO | $0.96 \pm 0.02$ | $5.0 \pm 0.02$ | $0.96 \pm 0.005$ | $6.48 \pm 0.04$ | $20.28 \pm 0.01$ |
| MgO | $2.17 \pm 0.2$ | $3.0 \pm 0.20$ | $2.17 \pm 0.20$ | $3.23 \pm 0.20$ | $1.97 \pm 0.2$ |
| MnO | $0.01 \pm 0.03$ | $0.12 \pm 0.003$ | $0.01 \pm 0.01$ | $0.07 \pm 0.002$ | $0.40 \pm 0.4$ |
| $SiO_2$ | $45.29 \pm 0.1$ | $33.05 \pm 0.06$ | $45.29 \pm 0.06$ | $42.12 \pm 0.06$ | $29.59 \pm 0.06$ |
| $P_2O_5$ | $0.01 \pm 0.01$ | $0.39 \pm 0.01$ | $0.01 \pm 0.01$ | $0.01 \pm 0.01$ | $0.06 \pm 0.01$ |
| $V_2O_5$ | $0.18 \pm 0.01$ | $0.02 \pm 0.01$ | $0.18 \pm 0.01$ | $0.16 \pm 0.001$ | $0.32 \pm 0.01$ |
| $TiO_2$ | $0.01 \pm 0.01$ | $0.82 \pm 0.01$ | $0.01 \pm 0.01$ | $0.65 \pm 0.001$ | $1.07 \pm 0.05$ |
| CuO | $0.01 \pm 0.01$ | $0.01 \pm 0.01$ | $0.01 \pm 0.01$ | $0.0 \pm 0.01$ | $<0.01 \pm 0.01$ |
| $SO_2$ | $0.14 \pm 0.01$ | $1.38 \pm 0.01$ | $0.14 \pm 0.01$ | $0.52 \pm 0.01$ | $<0.01 \pm 0.01$ |
| $Cr_2O_3$ | $0.01 \pm 0.01$ | $0.01 \pm 0.01$ | $0.01 \pm 0.01$ | $0.01 \pm 0.01$ | $0.03 \pm 0.01$ |

The elemental composition for probable catalytic materials collected from all the sites show that silicon dioxide was the highest in the composition. This was followed by aluminium oxide, then iron (II) oxide, magnesium dioxide, calcium oxide and traces of another mineral's element. The compounds of aluminium oxide and silicon dioxide are vital in catalytic activity. This is result are in agreement with the report by Yakovlev comparison among the different catalyst. (Yakovlev *et al.,* 2009)

**Table 4. 5: Computed values of $SiO_2/Al_2O_3$ ratio**

| Catalyst | $Al_2O_3$ % ±0.05 | $SiO_2$% ±0.05 | $SiO_2/Al_2O_3$ ratio |
|---|---|---|---|
| Kilembe | 6.76 | 30.42 | 7.65 |
| Tiira | 14.47 | 29.59 | 3.48 |
| Usuuku | 10.57 | 42.12 | 6.78 |
| Manafwa | 6.46 | 32.54 | 8.56 |
| Katwe Rock salt | 9.45 | 45.29 | 8.15 |

The acidity of the catalyst expressed as $SiO_2/Al_2O_3$-ratio (SAR) is based on the product selectivity (Engtrakul *et al.*, 2016). The more aluminium (III) oxide incorporated in the catalyst, the lower the ratio of Brønsted/Lewis acid sites. A higher SAR means a decrease in number of acid sites and apparently a lower total acidity. (Engtrakul*et al*., 2016).
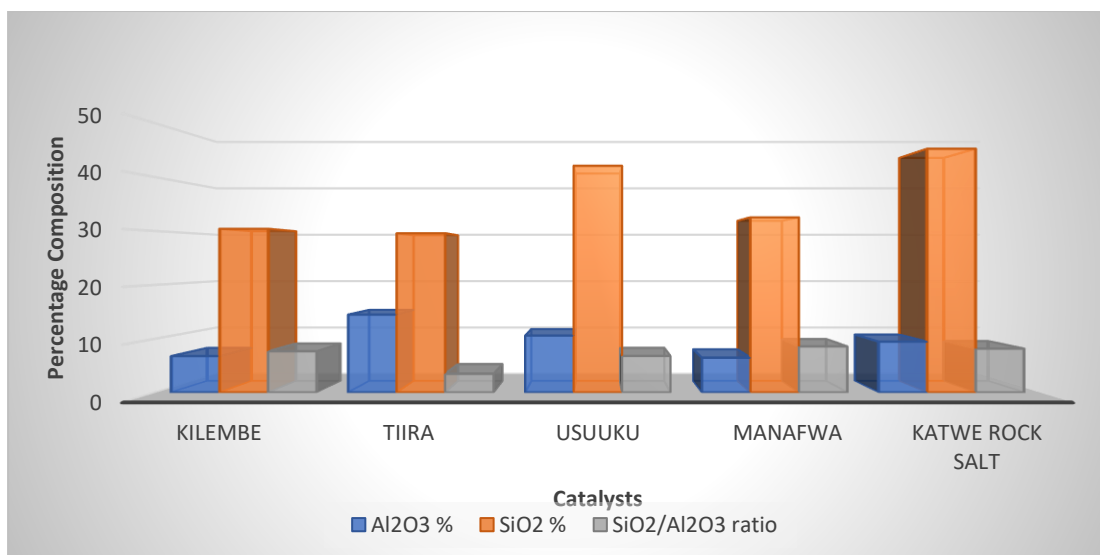
**Figure 4.1: Catalyst with the corresponding silica to alumina (SiO₂/Al₂O₃) ratio**

The rock salt had the highest percentage of silicon dioxide followed by Usuuku, then Kilembe and lastly Tiira. For the case of alumina, Tiira had the highest alumina, followed by Usuuku, then Katwe rock salt and lastly Kilembe. The$SiO_2/Al_2O_3$ ratio of the Five-Catalyst had adifferent trend. Manafwa river zeolite had the highest ratio, followed by Katwe Rock salt, then Kilembe, Usuuku and lastly Tiira. The acidity of the Catalyst is expressed as $SiO_2/Al_2O_3$ ratio. The high $SiO_2/Al_2O_3$ ratio means a decrease in the number of acid sites and apparently lower total acidity(Engtrakul et al., 2016)

**4.3 Pyrolysis yields using the different catalysts**

The mass balance obtained for the pyrolysis experiment is shown in the Table 4.6 below. The solid char and liquid bio-oil were obtained by weighing the components before and after the experiments. The gases are obtained by the difference, a bio-oil liquid yield of up to 42%(by weight) was recorded for the catalytic experiments, which is marginally higher than the yield from non-catalytic runs that had 31.76% (by weight). The pyrolysis conditions were classified as fast pyrolysis due to the yield according to Yildiz work (Yildiz *et al.,* 2017). The synthetic catalyst HZSM-5 produced the highest

amount of bio-oil of 41.36 ± 4.59, followed by Manafwa zeolite a local catalyst 39.39 ± 1.57 then Katwe 37.14 ± 0.01, Kilembe 32.65 ± 0.02 and Usuuku 31.67 ± 0.01

**Table 4. 6: Summary of pyrolysis precursor yield results at 500ºC for selected catalyst**

| Catalyst | Char (% weight) | Liquid (% weight) | Gas (% weight) |
|---|---|---|---|
| No Catalyst | 39.36±0.01 | 31.76±0.08 | 28.88±0.03 |
| HZSM-5 | 35.92±0.008 | 41.36±4.59 | 21.72 ±0.01 |
| Manafwa | 37.95±0.035 | 39.39±1.57 | 22.66±4.04 |
| Katwe | 38.32±0.01 | 37.14±0.01 | 24.54±0.02 |
| Kilembe | 38.97±0.01 | 32.65±0.02 | 27.38±0.02 |
| Usuuku | 39.67±0.02 | 31.67±0.01 | 28.66±0.02 |
| Tiira | 39.68±0.02 | 30.41±0.02 | 29.91±4.30 |
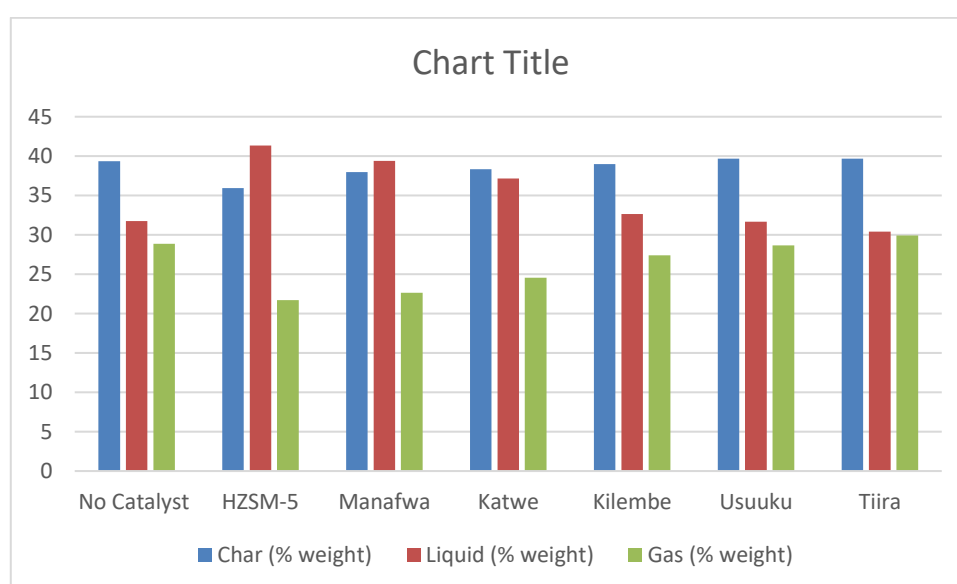


**Figure 4.2: Shows pyrolysis precursor yield for the five catalysts**

The results for pyrolysis in Table 4.6 show that the synthetic HZSM-5 had the highest yield of liquid 42% (by weight), lowest gas $21.72 \pm 0.01\%$ and the lowest char.$35.92 \pm 0.008\%$. The locally identified catalytic materials also impacted yield, Manafwa had the highest bio-oil yield of $39.36 \pm 1.57\%$ followed by the Katwe $37.14 \pm 0.01\%$, then Kilembe $32.65 \pm 0.02\%$, Usuuku $31.67 \pm 0.01\%$ and lastly Tiira$30.41 \pm 0.02\%$. The trend for gas was increasing as $21.72 \pm 0.01\%$ HZSM, $22.66 \pm 4.04\%$ Manafwa, $24.54 \pm 0.02\%$ Katwe, $27.3 \pm 0.02$ % Kilembe, $28.66 \pm 0.02\%$ Usuuku, $29.91 \pm 4.30\%$Tiira respectively. The presence of the catalyst had negligible variation on the yield of char but great impact on bio-oil liquid and gas yield as elaborated in the work of Oasmaa (Oasmaa & Peacocke, 2001).This means that catalytic pyrolysis generally resulted in increase in the yield of bio-oil. The increase in liquid products could be attributed to the secondary cracking of the pyrolysis vapor products by the catalyst.

**4.4.0 Bio-oil Properties**

**Table 4. 7: Results for characterization of bio-oil produced by different Catalyst**

| Component | Non | HZSM-5 | Manafwa | Katwe | Kilembe | Usuuku | Tiira |
|---|---|---|---|---|---|---|---|
| Carbon | 41.7 | 47.89 | 44.94 | 45.17 | 44.5 | 44.2 | 44.4 |
| Hydrogen | 8.20 | 11.29 | 9.46 | 9.34 | 8.5 | 8.4 | 7.10 |
| Nitrogen | 0.40 | 0.11 | 0.84 | 0.30 | 0.35 | 0.86 | 0.80 |
| Sulfur | 0.2 | 0.05 | 0.01 | 0.07 | 0.01 | 0.03 | 0.01 |
| Oxygen | 48.4 | 40.66 | 44.75 | 45.12 | 45.23 | 46.51 | 47.69 |
| H/C | 2.36 | 2.83 | 2.64 | 2.48 | 2.35 | 2.28 | 1.92 |
| S/C | 0.002 | 0.0004 | 0.0001 | 0.0006 | 0.00008 | 0.00003 | 0.00008 |

| | Non-Catalyzed | HZSM-5 | Manafwa | Katwe | Kilembe | Usuuku | Tiira |
|---|---|---|---|---|---|---|---|
| N/C | 0.01 | 0.002 | 0.016 | 0.0057 | 0.0067 | 0.016 | 0.0154 |
| O/C | 0.87 | 0.64 | 0.74 | 0.75 | 0.76 | 0.79 | 0.81 |
| Molecular formula | $CH_{2.36}O_{0.87}N_{0.008}$ | $CH_{2.83}O_{0.64}N_{0.002}$ | $CH_{2.64}O_{0.74}N_{0.016}$ | $CH_{2.48}O_{0.75}N_{0.006}$ | $CH_{2.29}O_{0.76}N_{0.007}$ | $CH_{2.28}O_{0.79}N_{0.016}$ | $CH_{1.92}O_{0.81}N_{0.0154}$ |
| Density(g/cm$^3$) at 25$^o$C | 1.08 | 1.04 | 1.05 | 1.06 | 1.08 | 1.08 | 1.09 |
| pH value | 2.8 | 4.2 | 3.8 | 3.5 | 3.2 | 3.0 | 2.8 |

The atomic ratios (H/C, O/C, N/C and S/C) for bio-oils were calculated to elucidate their empirical formulae. The empirical formula for non-catalyzed oil, HZSM, Manafwa, Katwe, Kilembe, Usuuku and Tiira were $CH_{2.4}N_{0.08}O_{0.9}$, $CH_{2.8}N_{0.002}O_{0.6}$, $CH_{2.6}N_{0.016}O_{0.7}$, $CH_{2.5}N_{0.01}O_{0.8}$, $CH_{2.29}N_{0.07}O_{0.76}$ $CH_{2.28}N_{0.016}O_{0.79}$ and $CH_{1.93}N_{0.02}O_{0.81}$, respectively.

**Table 4. 8: Results for detailed carbon yieldfor different Catalysts using Eraspec**

| Compound | Non-Catalyzed Vol% | HZSM-5 Vol% | Manafwa Vol% | Katwe Vol% | Kilembe Vol% | Usuuku Vol% | Tiira Vol% |
|---|---|---|---|---|---|---|---|
| Toluene | 0.29 | 0.86. | 0.51 | 0.46 | 0.47 | 0.33 | 0.29 |
| o-xylene | 0.70 | 1.05 | 0.79 | 0.70 | 0.69 | 0.63 | 0.73 |
| Ethylbenzene | 0.26 | 1.84 | 1.05 | 1.14 | 1.11 | 0.71 | 0.25 |
| 2-Ethylbenzene | 1.01 | 2.31 | 1.38 | 1.02 | 0.00 | 0.88 | 1.01 |
| 3-Ethylbenzene | 1.24 | 0.22 | 0.38 | 1.05 | 1.22 | 0.99 | 1.24 |
| 4-Ethylbenzene | 0 | 1.02 | 0.80 | 0.77 | 0.65 | 0 | 0 |
| Pseudocumene | 1.20 | 1.32 | 1.48 | 1.51 | 1.51 | 1.43 | 1.22 |
| Hemellitol | 1.54 | 2.22 | 1.80 | 1.76 | 1.73 | 1.56 | 1.55 |
| Naphthalene | 0.12 | 0.14 | 0.21 | 0.23 | 0.23 | 0.24 | 0 |

| Olefiin | 0 | 0.3 | 0.1 | 0 | 0 | 0 | 0 |
|---|---|---|---|---|---|---|---|
| Aromatics | 4.4 | 5.8 | 4.7 | 4.7 | 4.5 | 4.4 | 4.5 |
| Saturates | 95.3 | 90.6 | 95.2 | 95.3 | 95.5 | 95.6 | 95.5 |
| Isodurene | 0,50 | 0.64 | 0.88 | 0.81 | 1.27 | 0 | 0.52 |
| C9+Aromatics | 2.22 | 3.22 | 2.33 | 2.40 | 2.28 | 2.72 | 2.22 |

Table 4.8 showssome of the compound found in the bio-oils produced by the different catalyst. The catalysts were able to influence the formation of both cyclic ring and saturated compounds. Katwe and Manafwa produced the highest aromatics and this is in agreement with the findings of Aho influence of the acidity of zeolite where low acidity favoured formation of aromatics (Aho *et al.,* 2007). From Table 4.5, Manafwa and Katwe catalyst altered the quality of pyrolysis bio-oil where the highest C9 + Aromatic compounds was produced and this is in agreement with Stocker's study where porous natural materials were used as catalyst (Stöcker, 2008).

**Fourier Transform Infrared Spectroscopy (FTIR)**
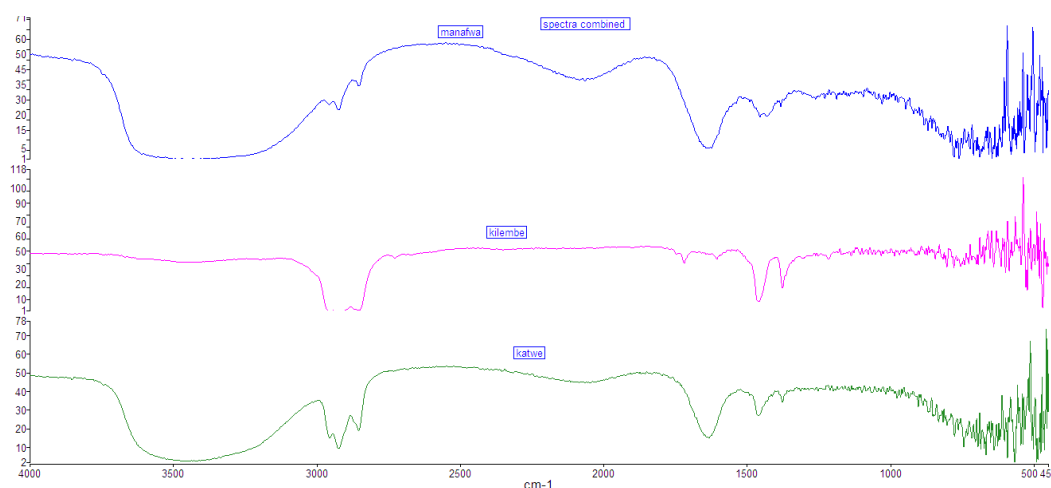


**Figure 4. 3: Spectra of bio-oils using different catalyst**

The FT-IR spectra of bio-oil fractions from Manafwa pyrolysis of groundnut shell presented in Figure 4.3. Various peaks with strong, medium, broad and weak intensities

were found indicating different bond types such as C–H, C–O, O–H, N–H and C–N in the bio-oil fractions. The C–O stretching vibrations between 1680 and 1780 cm$^{-1}$ was because of ketones and aldehydes(Schnitzer et al., 2007). Similarly, the bands between 1575 and 1675 cm$^{-1}$ represented C–C stretching vibrations due to the presence of alkenes and aromatics. The C–H stretching vibrations between 1300 and 1400 cm$^{-1}$ and deformation vibrations between 1350 and 1475 cm$^{-1}$ indicated the presence of alkanes. Presence of both O–H and C–O stretching vibrations indicated the presence of carboxylic acids and their derivatives in the bio-oils with the exception for Kilembe Catalyst. The main absorption bands corresponded to 2963 and 2852 cm$^{-1}$ region is assigned as stretching of C–H saturated bonds, 1741 cm$^{-1}$ as C=O stretching of the carbonyl functionalities, 1585 cm$^{-1}$ as C=C stretching of the C–C double bonds (Siengchum et al., 2013)). n particular, the C=O carbonyl components (1733 cm$^{-1}$), as well as C–C alkenes and aromatics (1677 cm-$^{1}$), were found to be predominant in Manafwa zeolite and Katwe catalysed bio-oils. On the other hand, C–H alkanes (2963 and 2852 cm$^{-1}$) along with C≡C alkynes (2370 cm$^{-1}$) were distinctively found in prominent amounts in bio-oils.
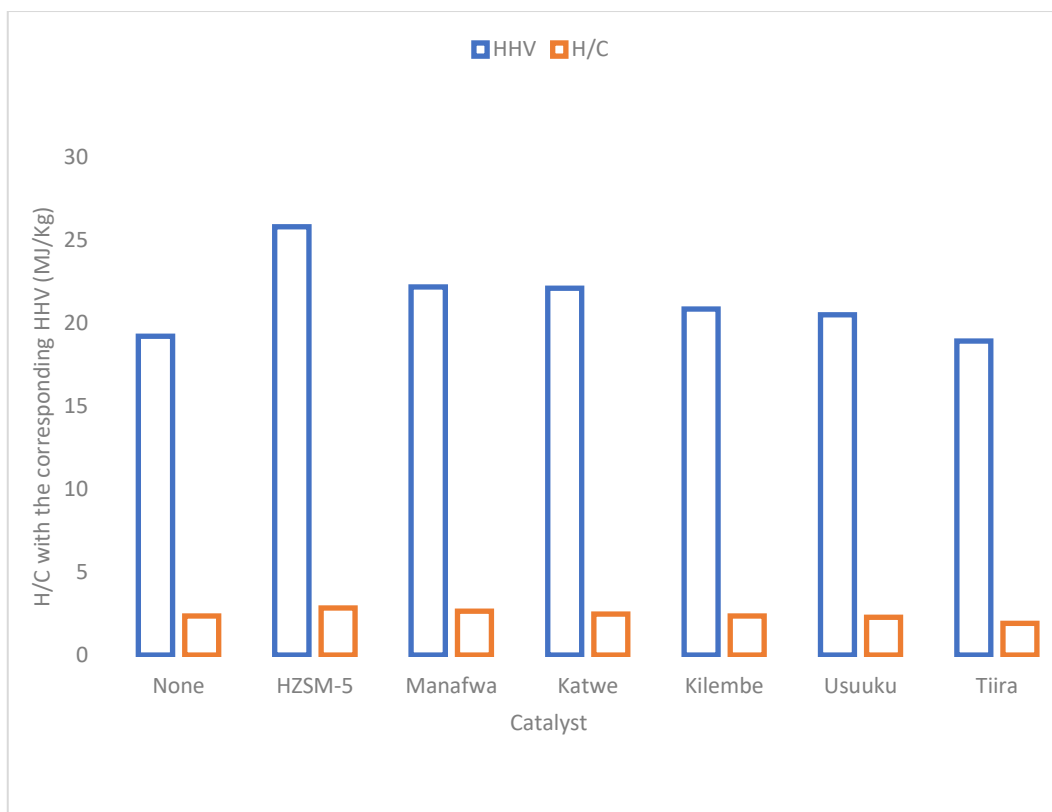
**Figure 4. 4: Effect of Hydrogen /Carbon (H/C) ratio to High heating value(HHV) yield**

The high H/C means high hydrogen molecules in the fuel. Hydrogen has the highest heating value and the heating value generally increases with increase in hydrogen to carbon ratio. The presence of the catalyst improved on the H/C value, the HSM-5 had the highest ratio of 2.83, Manafwa2.63, Katwe2.48, Kilembe2.35, Usuuku2.28 and Tiira had the least of 1.9.
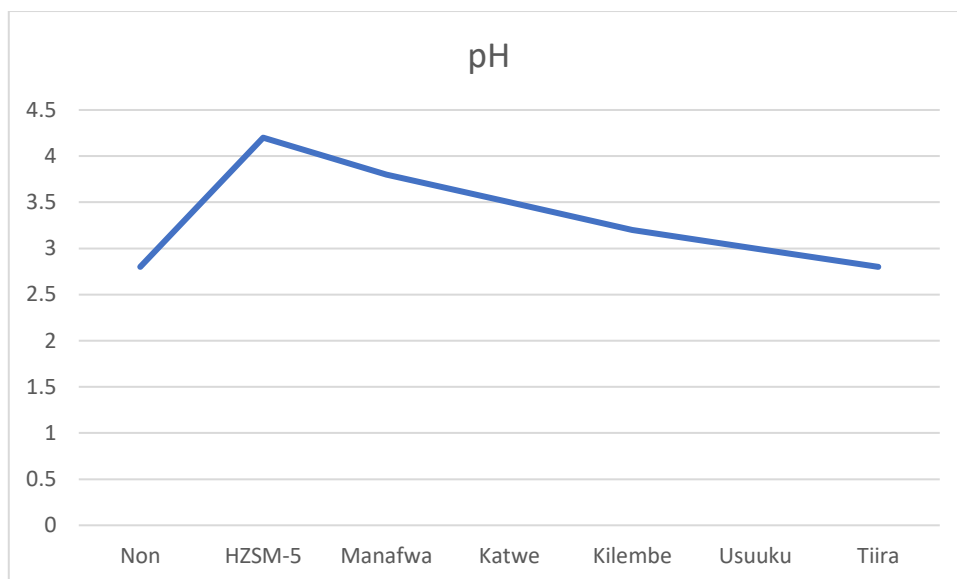
**Figure 4. 5: Graph of pH vs bio-oil using catalysts**

The acidity of bio-oil is due to volatile acid, mainly carboxylic that is formic acid and acetic acid. Phenolic compounds also contribute to the acidity of bio-oil. The use of Catalyst tends to reduce organic acid thereby facilitating the utilization of bio-oil in fuel application. From Figure 4.3, the use of the catalyst enhanced on the acidity of the bio-oil from pH 2.8 to pH 4.2, that is Tiira2.8, Usuuku3.0, Kilembe3.2, Katwe3.5, Manafwa3.8 and HSM-5 catalyst 4.2.

**Table 4. 9: Show relationship between $SiO_2/Al_2O_3$ ratio and H/C ratio**

| Catalyst | $SiO_2/Al_2O_3$ ratio | Hydrogen /Carbon ratio |
|----------|----------------------|------------------------|
| Kilembe | 7.65 | 2.35 |
| Tiira | 3.48 | 1.92 |
| Usuuku | 6.78 | 2.28 |
| Manafwa | 8.56 | 2.64 |
| Katwe Rock salt | 8.15 | 2.48 |
| HZSM-5 | 30 | 2.83 |

The lower density (High $SiO_2/Al_2O_3$) tends to deactivate faster and generates more hydrocarbons such as paraffin and aromatics (Yakovlev *et al.,* 2009). This is shown by the results in the table 4.9 Among the locally identified catalytic materials, Manafwa with the highest SAR had the highest H/C ratio and more hydrogen, therefore, a high heat value.

The different catalysts were found to have an impact on product composition, with catalysts with highest $SiO_2/Al_2O_3$ producing more light gases. The results are in agreement with Zhao (Zhao et al., 2011) who studied furan conversion to aromatics and olefins using HZSM-5. Products included CO, $CO_2$, allene, $C_2$-$C_6$ olefins, benzene, toluene, styrene, benzofuran, indene, and naphthalene. The different catalyst favoured different final products, i.e. Kilembe ore for benzofuran; Katwe salt catalyst for aromatics formed. Manafwa catalyst for olefins along with CO and aromatics.

# CHAPTER FIVE

# 5. CONCLUSION, RECOMMENDATIONS AND CHALLENGES

## 5.1 Conclusion

From the results we confirm that, the selected materials had an impact on bio-oil quantity and quality. The new catalysts were successfully selected and activated from natural zeolites and selected metallic ores. The liquid yield reached a maximum of 39.39 ± 1.57 % with Manafwa catalyst, 37.14 ± 0.01% with Katwe Catalyst, 32.65 ± 0.02% with Kilembe Catalyst, 31.67 ± 0.01% with Usuuku and lastly 30.41 ± with Tiira catalyst as compared with the pyrolysis without the catalyst under the same conditions.

Moreover, by catalytic pyrolysis bio-oil quality was better as reflected in the high ratio of H/C and the lower ratio of O/C. This clearly indicated high application potential of these catalysts in production of bio-oil with low oxygenated compounds.

## 5.2 Recommendations

Basing on the conclusions, it was recommended that the natural catalytic materials should be used in pyrolysis reactions to produce petroleum like compounds. These materials are Kilembe ore for production of benzofuran; Katwe salt for production of aromatics; and Manafwa catalyst for production of olefins, CO and aromatics.

The non-catalyzed pyrolysis had H/C ratio of 2.36 while Usuuku and Tiira had 2.28 and 1.92 respectively which meant that the catalysts had a negative impact on the ratio It is therefore recommend  of Usuuku and Tiira catalys, this because the higher the H/C in the bio-oil, the higher the quality.

Further studies should be conducted where Usuuku and Tiira clays should be modified, enhanced or developed. The clays could be mixed to get a hybrid material. Studies on the effect of catalyst dosage, the effect of biomass amount, the effect of catalyst hybrids, the effect of temperature, the effect of pre-treatment

## 5.3 Challenges

One of the major challenges was outsourcing equipment to perform the different test, and the scent that was not decent.

## REFERENCES

Adhikari, A., Reponen, T., Grinshpun, S. A., Martuzevicius, D., & LeMasters, G. (2006). Correlation of ambient inhalable bioaerosols with particulate matter and ozone: a two-year study. *Environmental Pollution, 140*(1), 16-28.

Adjaye, J. D., & Bakhshi, N. (1994). Upgrading of a wood-derived oil over various catalysts. *Biomass and bioenergy, 7*(1-6), 201-211.

Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., & Murzin, D. Y. (2007). Catalytic pyrolysis of biomass in a fluidized bed reactor: influence of the acidity of H-beta zeolite. *Process Safety and Environmental Protection, 85*(5), 473-480.

Akia, M., Yazdani, F., Motaee, E., Han, D., & Arandiyan, H. (2014). A review on conversion of biomass to biofuel by nanocatalysts. *Biofuel Research Journal, 1*(1), 16-25.

Amadi, B., Agomuo, E., & Ibegbulem, C. (2004). Phytochemical tests: Research methods in Biochemistry: Supreme publishers Owerri.

ASTM, D. 3177. *Standard Test Method for Total Sulfur in the Analysis Sample of Coal and Coke.(Reaprovada) 2007b*, 1-4.

ASTM, D. (1989). 3176-89. Standard Practice for Ultimate Analysis of Coal and Coke. *ASTM: Philadelphia, PA, USA*.

ASTM, D. (1996). 5291 standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants. *ASTM, West Conshohocken*.

ASTM, D. (2010). 4294. *Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry, ASTM International, West Conshohocken, PA*.

ASTM, E. (1755). 95, Standard Test Method for Ash in Biomass. *Annual Book of ASTM Standards1995, 11*(1243), 14.

Balat, M., Balat, M., Kırtay, E., & Balat, H. (2009). Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. *Energy conversion and management, 50*(12), 3147-3157.

Bartholomew, C. H., & Farrauto, R. J. (2011). *Fundamentals of industrial catalytic processes*: John Wiley & Sons.

Bridgwater. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and bioenergy, 38*, 68-94.

Bridgwater, A. (1996). Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. *Catalysis Today, 29*(1-4), 285-295.

Brown, R. C., & Holmgren, J. (2009). Fast pyrolysis and bio-oil upgrading. *Gas, 13*, 25.

Carlson, T. R., Vispute, T. P., & Huber, G. W. (2008). Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds. *ChemSusChem, 1*(5), 397-400.

Channiwala, S., & Parikh, P. (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel, 81*(8), 1051-1063.

Conti, J., Holtberg, P., Beamon, J., Schaal, A., Ayoub, J., & Turnure, J. (2011). Annual energy outlook 2011 with projections to 2035: US Energy Information Administration. *Washington DC*.

Conti, J. J., Holtberg, P. D., Beamon, J. A., Schaal, A. M., Ayoub, J., & Turnure, J. T. (2014). Annual energy outlook 2014. *US Energy Information Administration*.

DeSisto, W. J., Hill, N., Beis, S. H., Mukkamala, S., Joseph, J., Baker, C., . . . Frederick, B. G. (2010). Fast pyrolysis of pine sawdust in a fluidized-bed reactor. *Energy & fuels, 24*(4), 2642-2651.

Dickerson, T., & Soria, J. (2013). Catalytic fast pyrolysis: a review. *Energies, 6*(1), 514-538.

Diebold, J. P. (1999). *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils*. Retrieved from

E872-82, A. (2013). Standard test method for volatile matter in the analysis of particulate wood fuels: ASTM International West Conshohocken, PA.

Elliott, D., & Water, A. (1994). Char in Flash Pyrolysis Oils. *Biomass Bioenergy, 7*, 179-185.

Engtrakul, C., Mukarakate, C., Starace, A. K., Magrini, K. A., Rogers, A. K., & Yung, M. M. (2016). Effect of ZSM-5 acidity on aromatic product selectivity during upgrading of pine pyrolysis vapors. *Catalysis Today, 269*, 175-181.

Fahmi, R., Bridgwater, A., Darvell, L., Jones, J., Yates, N., Thain, S., & Donnison, I. (2007). The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow. *Fuel, 86*(10-11), 1560-1569.

Gayubo, A. G., Aguayo, A. T., Atutxa, A., Aguado, R., & Bilbao, J. (2004). Transformation of oxygenate components of biomass pyrolysis oil on a HZSM-5 zeolite. I. Alcohols and phenols. *Industrial & Engineering Chemistry Research, 43*(11), 2610-2618.

Gollakota, A. R., Reddy, M., Subramanyam, M. D., & Kishore, N. (2016). A review on the upgradation techniques of pyrolysis oil. *Renewable and Sustainable Energy Reviews, 58*, 1543-1568.

Goyal, H. B., Saxena, R. C., & Seal, D. (2008). *Thermochemical conversion of biomass to liquids and gaseous fuels*: CRC Press, Taylor & Francis Group.

Hartmann, M., Machoke, A. G., & Schwieger, W. (2016). Catalytic test reactions for the evaluation of hierarchical zeolites. *Chemical Society Reviews, 45*(12), 3313-3330.

Hayes, D. J. (2013). Biomass composition and its relevance to biorefining *The role of catalysis for the sustainable production of bio-fuels and bio-chemicals* (pp. 27-65): Elsevier.

Huber, G. W., & Dumesic, J. A. (2006). An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. *Catalysis Today, 111*(1-2), 119-132.

Jacobson, K., Maheria, K. C., & Dalai, A. K. (2013). Bio-oil valorization: a review. *Renewable and Sustainable Energy Reviews, 23*, 91-106.

Jakab, E., Mészáros, E., & Borsa, J. (2010). Effect of slight chemical modification on the pyrolysis behavior of cellulose fibers. *Journal of Analytical and Applied Pyrolysis, 87*(1), 117-123.

Junming, X., Jianchun, J., Yunjuan, S., & Yanju, L. (2008). Bio-oil upgrading by means of ethyl ester production in reactive distillation to remove water and to improve storage and fuel characteristics. *Biomass and bioenergy, 32*(11), 1056-1061.

Lin, Y.-C., & Huber, G. W. (2009). The critical role of heterogeneous catalysis in lignocellulosic biomass conversion. *Energy & Environmental Science, 2*(1), 68-80.

Linck, M., Felix, L., Marker, T., & Roberts, M. (2014). Integrated biomass hydropyrolysis and hydrotreating: a brief review. *Wiley Interdisciplinary Reviews: Energy and Environment, 3*(6), 575-581.

Mante, O. D., Agblevor, F., & McClung, R. (2013). A study on catalytic pyrolysis of biomass with Y-zeolite based FCC catalyst using response surface methodology. *Fuel, 108*, 451-464.

Mohan, D., Pittman, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & fuels, 20*(3), 848-889.

Morris, M. (2011). Production of bio-oils via catalytic pyrolysis *Handbook of biofuels production* (pp. 349-389): Elsevier.

Mortensen, P. M., Grunwaldt, J.-D., Jensen, P. A., Knudsen, K., & Jensen, A. D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General, 407*(1-2), 1-19.

Narayanan, S., Sultana, A., Krishna, K., Mériaudeau, P., & Naccache, C. (1995). Synthesis of ZSM-5 type zeolites with and without template and evaluation of physicochemical properties and aniline alkylation activity. *Catalysis letters, 34*(1-2), 129-138.

Oasmaa, A., & Peacocke, C. (2001). *A guide to physical property characterisation of biomass-derived fast pyrolysis liquids*: Technical Research Centre of Finland Espoo.

Oasmaa, A., Solantausta, Y., Arpiainen, V., Kuoppala, E., & Sipilä, K. (2009). Fast pyrolysis bio-oils from wood and agricultural residues. *Energy & fuels, 24*(2), 1380-1388.

Owczuk, M., & Kołodziejczyk, K. (2015). Liquid Fuel Ageing Processes in Long-term Storage Conditions. *Storage Stability of Fuels*, 101.

Özçimen, D., & Karaosmanoğlu, F. (2004). Production and characterization of bio-oil and biochar from rapeseed cake. *Renewable energy, 29*(5), 779-787.

Petrov, L. (1998). Present State and Prospects for Development of Industrial Catalysis, Bulg. *Chem. Ind, 69*, 65-72.

Schnitzer, M. I., Monreal, C. M., Facey, G. A., & Fransham, P. B. (2007). The conversion of chicken manure to biooil by fast pyrolysis I. Analyses of chicken manure, biooils and char by 13C and 1H NMR and FTIR spectrophotometry. *Journal of Environmental Science and Health Part B, 42*(1), 71-77.

Siengchum, T., Isenberg, M., & Chuang, S. S. (2013). Fast pyrolysis of coconut biomass–An FTIR study. *Fuel, 105*, 559-565.

Soltes, J., & Lin, S.-C. K. (1984). Hydroprocessing of biomass tars for liquid engine fuels *Progress in biomass conversion* (Vol. 5, pp. 1-68): Elsevier.

Stefanidis, S., Karakoulia, S., Kalogiannis, K., Iliopoulou, E., Delimitis, A., Yiannoulakis, H., . . . Triantafyllidis, K. (2016). Natural magnesium oxide (MgO) catalysts: A cost-effective sustainable alternative to acid zeolites for the in situ upgrading of biomass fast pyrolysis oil. *Applied Catalysis B: Environmental, 196*, 155-173.

Stöcker, M. (2008). Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. *Angewandte Chemie International Edition, 47*(48), 9200-9211.

Venderbosch, R. (2015). A critical view on catalytic pyrolysis of biomass. *ChemSusChem, 8*(8), 1306-1316.

Venderbosch, R., & Prins, W. (2010). Fast pyrolysis technology development. *Biofuels, bioproducts and biorefining, 4*(2), 178-208.

Vichaphund, S., Aht-ong, D., Sricharoenchaikul, V., & Atong, D. (2015). Production of aromatic compounds from catalytic fast pyrolysis of Jatropha residues using metal/HZSM-5 prepared by ion-exchange and impregnation methods. *Renewable energy, 79*, 28-37.

Wang, K., Kim, K. H., & Brown, R. C. (2014). Catalytic pyrolysis of individual components of lignocellulosic biomass. *Green Chemistry, 16*(2), 727-735.

Westerhof, R. J. M., Brilman, D. W. F., Kersten, S. R., & van Swaaij, W. P. M. (2008). *Effect of condenser operation on the biomass fast pyrolysis oil.* Paper presented at the Proceedings of the 16th European Biomass Conference from research to industry and markets.

Yakovlev, V., Khromova, S., Sherstyuk, O., Dundich, V., Ermakov, D. Y., Novopashina, V., . . . Parmon, V. (2009). Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel. *Catalysis Today, 144*(3), 362-366.

Yaman, S. (2004). Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy conversion and management, 45*(5), 651-671.

Yildiz, G., Pronk, M., Djokic, M., van Geem, K. M., Ronsse, F., van Duren, R., & Prins, W. (2013). Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading. *Journal of Analytical and Applied Pyrolysis, 103*, 343-351.

Yildiz, G., Ronsse, F., & Prins, W. (2017). Catalytic Fast Pyrolysis Over Zeolites *Fast Pyrolysis of Biomass* (pp. 200-230).

Zhang, Q., Chang, J., Wang, T., & Xu, Y. (2007). Review of biomass pyrolysis oil properties and upgrading research. *Energy conversion and management, 48*(1), 87-92.

Zhao, L., Gao, J., Xu, C., & Shen, B. (2011). Alkali-treatment of ZSM-5 zeolites with different SiO2/Al2O3 ratios and light olefin production by heavy oil cracking. *Fuel processing technology, 92*(3), 414-420.

APPENDIX 1; Physical propertiesof bio-oil in compulsion with crude and light oils

| Composition | Bio-oil | Crude oil | Light fuel oils |
|---|---|---|---|
| Water (wt. %) | 15-30 | 0.1 | 0.03 |
| pH | 2.8-3.8 | - | Neutral |
| Density(kg/L) | 1.05-1.25 | 0.86 | 0.96 |
| Viscosity 50oC (cP) | 40-100 | 180 | <24 |
| HHV(MJ/kg) | 16-19 | 44 | 42-44 |
| C (wt. %) | 55-65 | 83-86 | 85-86 |
| O (wt. %) | 28-40 | <1 | |
| H (wt. %) | 5-7 | 11-14 | 10-14 |
| S (wt. %) | <0.05 | <4 | <4 |
| N (wt. %) | <0.4 | <1 | |
| Ash (wt. %) | <0.2 | <0.1 | |
| H/C | 0.9-1.5 | 1.5-20 | |
| O/C | 0.3-0.5 | 0 | |
| Stability | Not stable | Stable | Stable |
| Flash Point | 40-110 | | 6 |
| Pour Point | -36 to -9 | | 15 |
| Distillation | Not Distillable | 160-400 | 160-300 |

Retrieved from Bridgewater 2012

## APPENDIX 2; Catalytic pyrolysis product yield

| Catalyst | Char | Liquid | Gas |
|---|---|---|---|
| | 39.36 | 31.74 | 28.90 |
| **No catalyst** | 39.34 | 31.76 | 28.90 |
| | 39.36 | 31.82 | 28.82 |
| | 39.38 | 31.74 | 28.70 |
| Average | **39.36±0.0346** | **31.76±0.0802** | **28.88±0.2** |
| Variance | **0.00019999** | **0.001075** | **0.0066999** |
| Standards deviation | **0.01414213** | **0.032787192** | **0.08185353** |
| | 35.92 | 42.36 | 21.72 |
| | 35.90 | 42.38 | 21.72 |
| **ZSM-5** | 35.92 | 42.36 | 21.74 |
| | 35.92 | 31.76 | 21.70 |
| Average | **35.92±0.0212** | **42.36±11.234** | **21.72±0.0346** |
| Variance | **7.50E-5** | **21.094075** | **0.0001999999999** |
| Standards deviation | **0.008660** | **4.59282865** | **0.014142135623731** |
| | 37.95 | 39.39 | 22.66 |
| **Manafwa Catalyst** | 37.90 | 39.44 | 22.66 |
| | 38.00 | 35.78 | 32.00 |

|  | | | |
|---|---|---|---|
|  | 37.95 | 39.36 | 22.66 |
| Average | **37.95±0.0865** | **39.39±3.831** | **22.66±9.892** |
| Variance | **0.00125** | **2.45336875** | **16.356675** |
| Standards deviation | **0.03535533905933** | **1.5663233223061** | **4.0443386356733** |
|  | 38.32 | 37.14 | 24.54 |
| **Katwe Catalyst** | 38.33 | 37.12 | 24.55 |
|  | 38.31 | 37.13 | 24.56 |
|  | 38.34 | 37.15 | 24.51 |
| Average | **38.32±0.0273** | **37.14±0.0273** | **24.54±0.0458** |
| Variance | **0.000125** | **0.000125** | **0.00034999999999** |
| Standards deviation | **0.011180339887499** | **0.0111803398875** | **0.018708286933869** |
|  | 39.97 | 32.65 | 27.38 |
| **Kilembe Catalyst** | 39.95 | 32.62 | 27.35 |
|  | 39.98 | 32.66 | 27.39 |
|  | 39.98 | 32.67 | 27.40 |
| Average | **38.97±0.03** | **32.65±0.0458** | **27.38±0.0458** |
| Variance | **0.00014999999999** | **0.00035000000000** | **0.000349999999999** |
| Standards deviation | **0.012247448713913** | **0.018708286933871** | **0.018708286933869** |

|  |  |  |  |
|---|---|---|---|
|  | 39.69 | 31.66 | 28.69 |
| **Usuuku Catalyst** | 39.65 | 31.66 | 28.64 |
|  | 39.66 | 31.67 | 28.67 |
|  | 39.68 | 31.69 | 28.64 |
| Average | **39.67±0.0387** | **31.67±0.03** | **28.66±0.0519** |
| Variance | **0.00025000000000001** | **0.00015000000000001** | **0.00045000000000002** |
| Standards deviation | **0.015811388300842** | **0.012247448713916** | **0.021213203435597** |
| **Tiira Catalyst** | 39.70 | 30.44 | 20.00 |
|  | 39.66 | 30.39 | 29.95 |
|  | 39.67 | 30.42 | 29.91 |
|  | 39.69 | 30.40 | 29.91 |
| Average | **39.68±0.0387** | **30.41±0.047** | **29.91±10.51** |
| Variance | **0.00025000000000004** | **0.00036875000000003** | **18.46386875** |
| Standards deviation | **0.015811388300843** | **0.019202864369672** | **4.2969604082421** |

# APPENDIX 3 Equipment used



**Figure 3.2; Rollar mill**

# APPENDIX 4.  Some of the photos taken during the research



Material Preparation and Collected bio-oil

Setting of the equipment for pyrolysis



The figure shows a complete set up of the pyrolysis unit and the extreme show burning of pyrolysis

gas



Nut fastening of the reactor containing the biomass.

# APPENDIX 5 FTIR SPECIFICATIONS

ERASPEC Instrument Specifications

**Detection method:** mid-FTIR interferometer (patented rugged design)

**Optics:** permanently aligned retro-reflector design, no realignment necessary

**Wavenumber range:** 630 – 4000 cm-1

**Calibration:** factory calibrated, comes with a data base of several hundred fuels from international sources.) Additional calibration samples can easily be added without the use of an external PC within a few seconds. Users can also easily develop new calibrations for existing parameters as well as create up to 10 new user defined parameters directly on the ERASPEC.

**Warm-up time:** approx. 1 minute

**Measurement time:** approx. 1 minute (standard measurement)

**Reference measurement:** Fully automatic, no reference substance necessary. Unusual samples are identified based on the Mahalanobis distance from the calibration set and are indicated by an alarm message.

**Sample introduction:** Integrated pump

**Sample volume:** approx. 12 ml

**Display:** 8.4'' colour touch screen (resistive

**Languages:** English (other languages available upon request)

**Communication:** 6 x USB (front: 2x USB | back: 3x USB, 1x USB-B)

Ethernet

RS-232

**Power requirements:** auto switching 85-264 V AC, 47-63 Hz, 70 W

**Field application:** 12 V/8A DC (vehicle battery, adapter available upon request)

| | |
|---|---|
| **Cabinet/Chassis** | fully portable, rugged aluminium; includes carrying; handle |
| **Operating temperature:** | 5°C to 45°C |
| **Humidity:** | up to 90% RH, non-condensing |
| **Storage temperature:** | 0°C to 50°C |
| **Size** | W x H x D: 29 x 35 x 34 cm |
| **Weight:** | 9.7 kg |