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Hydrothermal conversion of agricultural and food waste

By

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KEYWORDS

Hydrothermal liquefaction, biofuels, bio-crude oil, co-liquefaction, fossil fuels, non-renewable energy, bio-crude oil, hydrolysis, decarboxylation

ABSTRACT

The global dependence on non-renewable fossil fuels to meet energy needs cannot be sustained for a long time and it is already evident in the escalation of fuel prices over the past decade. This research was performed towards renewable energy production from agricultural and food waste. The use of agricultural and food waste has benefits such as being grown in a land that is not in competition with food crops protein, all year round availability, and having high lipid content. The produced bio-crude oil can be upgraded to remove moisture and acidity level, and can be used as a substitute for heavy oils such as diesel to power static appliances or can be used as petrol distillate fuel alternative.

Hydrothermal liquefaction (HTL) process is one of the commonly used technologies for converting agricultural and food waste into liquid biofuels. This process was carried out in water under various reaction conditions with the aim to improve the yield and quality of the bio-crude oil. The co-processing of agricultural waste with food waste was performed in the catalytic and non-catalytic HTL process and this work demonstrated the interaction between agricultural waste and food waste with water and catalyst as well as impact on product distribution.

Different compositions of agricultural waste and food waste ranging from 0:100-100:0 by mass were processed at a reaction temperatures ranging from 260-340°C at 30-150 minutes reaction times. The feedstocks were analysed using scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS) and fourier transform infrared spectrometry (FTIR) to determine the morphology, elemental composition and the functional groups which were present in the feedstock, the differences in functional groups and elemental composition demonstrate considerable gaps in understanding the expected characteristics of the liquid bio-crude oil as a result of reaction parameters. The produced liquid bio-crude oil was analysed using the GC-MS in order to elucidate the process by which different compounds are distributed in products at different operational parameters.

The groups which were present in all the feedstocks were the alcohols, amines, carbonyl compounds as well as alkyl halides. The elements which were present in the prepared feedstock include oxygen, magnesium, potassium; the amount of oxygen increased as the amount of agricultural waste was increased with a corresponding decrease in the amount of food waste. Scanning electron microscopy images exhibited nano particles with the uniform monodisperse particles with the diameter of the pores that ranging from 155-221 nm.

Hydrothermal liquefaction at 340°C and 60 minutes reaction time is best suitable for the production of a high yield of liquid bio-crude oil for feedstock comprising of agricultural waste and food waste at a 100:0 ratio. Liquid bio-crude oil was formed by hydrolysis or depolymerization reaction of agricultural waste and food waste into smaller compounds that form liquid bio-crude oil. Bio-crude oil produced contained very high concentration of organic acids as well as hydrocarbons. The use of H-ZSM-5 as a catalyst did not play any noticeable role during the formation of the compounds as there was no trend observed.

In the catalytic and non-catalytic HTL, as the temperature and reaction times were increased, there was an increase in the liquid bio-crude oil which was accompanied by a decrease in solid biochar and gases. A sudden decrease in the yield of liquid bio-crude oils with accompanying increase in solid bio-char and gases was observed as the temperature went beyond 320°C and as the reaction time went beyond 120 minutes.

The gas chromatography-mass spectrometry (GC-MS) evidenced that the bio-crude oils obtained both in the catalytic and non-catalytic HTL contain various organic acids, nitrogenated compounds, hydrocarbons, oxygenated compounds as well as the aromatics. Lower concentrations of cyclic oxygenates, oxygenated compounds, and aromatics were detected meanwhile hydrocarbons and organic acids were detected at a higher concentration. Carbohydrates were hydrolysed to form glucose that was degraded to form cyclic oxygenates. Nitrogenated compounds and oxygenated compounds were formed from the Maillard reaction of amino acids from the hydrolysis of protein. Hydrocarbons and alcohols were formed from lipid that hydrolysed to form fatty acids that undergo decarboxylation to form hydrocarbons and alcohols

DECLARATION

I **MAKHADO TSHIMANGADZO** hereby declare that this work titled **''HYDROTHERMAL LIQUEFACTION OF AGRICULTURAL AND FOOD WASTE''** is the product of my research efforts; undertaken under the supervision of Professor Lindiwe Khotseng and Professor Yusuf Makarfi Isa. To the best of the researcher's knowledge, this work has not been presented or published elsewhere at other examination offices for the award of a degree or certificate. All sources have been duly distinguished and appropriately acknowledged by complete references.

Makhado T on the 15th day of February 2022

(Student)

__________________________ on the ____ day of __________________

(Supervisor)

__________________________ on the ____ day of __________________

(Co-supervisor)

DEDICATION

I would like to dedicate my master's degree to my lovely mother, Makhado Mushaisano Gladys.

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I thank the ALMIGHTY GOD for the invaluable guidance and protection over me during the period of my study. With HIM everything has been made possible. To HIM I give glory.

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LIST OF ACRONYMS

HTL	Hydrothermal liquefaction
FTIR	Fourier-transform infrared spectroscopy
SEM	Scanning Electron Microscope
GCMS	Gas chromatography-mass spectrometry
DCM	Dichloromethane
AW	Agricultural waste
FW	Food waste
EDS	Electron dispersive spectroscopy

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Chapter 1

1. INTRODUCTION

This chapter provides an overview of the depletion of non-renewable energy resources and a general introduction to the importance of developing suitable and renewable energy source such as biomass. Biomass-derived fuels can be produced through the hydrothermal liquefaction (HTL) process by valorising biomass for the production of bio-crude oil. Research aims and objectives, approaches, and methodology are also outlined in this chapter. The structure of the thesis outline concludes this chapter.

1.1 Background and motivation

In today's society energy is a basic need of people for livelihoods, lifestyles, traditional practices as well as a priority need both in developed and developing countries. Without energy; industries, commerce as well as a society cannot function hence it is important that the future generation has access to this energy. Throughout ages, human beings adapted to natural climate changes by arranging their local shelters, food production, energy provision, and lifestyle in consonance with long-term climate and environmental conditions [1].

In the 19th century or before the discovery of fossil fuels, human beings have been using bioenergy and biofuels for domestic purposes, such as cooking and heating. Wood has been burned for heat and to warm shelters, to be used in cooking and as well as treating clay artifacts. In the wonderwork cave of Kuruman hills in South Africa, archaeologists identified charred animal bones and stone tools in wood ash which provide evidence of controlled fire by human-kind creatures millions of years ago. Moreover, fire has also been used to clear land and also to attract enemies during war. Dry plant materials ignite in the air to cause a fire while releasing inherent bioenergy in heat and light. Currently, commercial production of electricity and transportation as liquid fuel is being practiced in most countries [1-4].

1.1.1 Non-renewable energy sources

Ever since the industrial era started, there has been an increase in the use of fossil fuels which is coal, oil, and gas and this has resulted in an increase in the atmospheric concentration of greenhouse gases (GHG) as well as affecting human health. Greenhouse gas has the potential to change space-time patterns of global climate with various impacts including the rise in sea levels, global warming, etc... The rate of consumption of fossil fuels is going to multiply with the growth of the population and their aspirations and the apocalyptic day is not too far when all fossil fuels will run out and there will be nothing left to burn [5-7].

An increase in urbanization and industrialization in developed countries has affected the environmental quality and the major concerns are the quality of air, traffic congestion, and temperature increase. Modern society depends on non-renewable energy. Non-renewable energy refers to natural resources that cannot be replaced quickly and the earth is endowed with these considerable energy-giving resources mainly in the form of fossil fuels, oil for transportation fuels and chemical manufacture; coal for power generation, and natural gas for power production [1, 7]. Fossil fuels are distributed globally unevenly and they are depleting, their uses raise questions regarding the security of supply and environmental sustainability. Fossil fuels are easy to store, transport, and use. However, in rural areas of developing countries, some people are living without access to energy. Sustainable energy in developing countries is needed for transport, water pumping, cooking, heating as well as lighting [5, 6]. Cooking and heating using biomass such as wood can lead to deforestation and also compete with the need to generate energy. Deforestation can also result in a high dependence on imports and it is not sustainable as it is important to bridge the gap between developed and developing countries by providing sustainable self-sufficiency by examining technologies that are available and making them economically feasible to create sustainable self-sufficiency. In addition, if these renewable energy facilities are located in rural areas, this will also contribute to employment [5, 8, 9].

Extraction of oil produces methane, carbon monoxide, and carbon dioxide while burning coal results in the emission of carbon dioxide. Furthermore, agricultural activities including the changes in the land use and the land cover promote the emission of methane and nitrous oxide. Gases that are released from industries and transport also contribute to atmospheric pollution, an increase in atmospheric concentration has led to the depletion of the ozone layer. The ozone layer protects life on earth from harmful ultra-violet radiation from the sun. Gases that are released from domestic and fire extinguishers also contribute to atmospheric pollution by releasing aerosols in the atmosphere which changes the cooling effect of the radioactive balance, however, these aerosols do not stay in the atmosphere for a long period. Climate change has an impact on the energy systems, for example, a rise in sea level affects offshore gas and oil exploitation, pipelines, and oil imports. In addition, climate changes such as global warming and acid rain can cause damages to agricultural crop resources. It is important to develop an efficient energy system that increases its reliance on clean and renewable energy sources while meeting growing energy demand [5, 8, 10-12]. Global warming is one of the greatest environmental challenges facing the world today and it is the key driver for the development of the renewable energy industry [11].

1.1.2 Renewable energy resources

Renewable energy refers to the wide range of naturally occurring; replenishable energy sources and these sources can be used to supply energy in industry, transport, and buildings. Renewable energy technologies convert renewable energy sources into solid and liquid fuels, heat, and electricity and they offer the best option for meeting local energy requirements, environmental, and economic needs. Since most of the renewable energy resources are climate-sensitive, there should be sustainable development of renewable resources for future generations. There should be a collaboration between scientists, engineers as well as private sectors both in developing and developed countries to provide education and awareness regarding renewable energy resources, energy conservation, and reduction of pollution of the environment. Furthermore, strategies for capacity-building, application, and transfer of clean energy technologies should be addressed so that there is an increase in the use of renewable energy resources and also improve the efficiency of production, distribution, and the use of fossil energy resources, especially in developing countries [8, 13, 14].

Even though renewable energy source competes with the non-renewable energy source, this competition should not be on a financial basis. Many barriers can inhibit the development of renewable energy especially in developing countries and this includes difficulty in obtaining, arranging, and finding financial support. Participation from private sectors including international participation could make a significant contribution to financing, risk sharing, and technical assistance to ensure access to the latest technology and operating practices and it is important to have adequate rates of return to attract investments [8, 13].

There's an exciting future of biomass for bioenergy. Biomass will transition from a handful of products to multi-products such as transportation fuels, biogas, chemicals, fertilizers, etc. Availability of biomass is dependent on human and animal wastes, industrial and agricultural wastes, and this is all determined by meteorological as well as hydrological factors. Sources of renewable energy sources are biomass by-products of crops excluding land agricultural purposes, biomass by-products of sustainably managed forestry operations, biomass by-products of food processing and production industries, sewage treatment as well as biomass components mixed municipal wastes [15, 16].

Agricultural and forest products as industrial raw materials have been used over the past years and their products include paper-pulp, building materials, liquid fuels, woven fibres, chemicals as well as pharmaceutical intermediates. Raw biomass materials which are not competing with food production provide environmental as well as economic benefits for the production of fuels on soil, water, food, and land. Biofuels refer to plant biomass and the refined products that can be combusted for energy, biofuels exist in solid, liquid, and gas. Biofuels can be categorized into first, second, and third-generation according to their sources of biomass. First-generation biofuel is obtained from food crops such as corn, soybean, sugarcane, etc., second-generation biofuel is produced from non-food crops such as rice husk, peels, and wheat straw. Third-generation biofuel is produced from microalgae biomass [15-17].

Renewable energy technologies should be affordable, appropriate as well as accessible to everyone, and only developed countries will benefit since most of the energy will be manufactured in industrialized countries and imported into developing countries and the greater reliance on such products is less in developing economies. It is important to increase interest in opportunities to reduce the dependence on imports of oil, improve the environment through reduction of local air pollution and greenhouse gas emissions and meet the increasing consumer demand for renewable and natural products therefore new technologies are required to adopt new energy challenges by providing cleaner, more efficient and environment-friendly energy systems [13, 16].

The growth of the human population will result in economic growth and results in the growth of food production. It seems unrealistic to expect food crops would free up large areas which are currently used croplands for planting energy crops. Food insecurity is a harsh reality to millions of people, however, overeating and food waste are also common too. Food insecurity is caused by extreme weather conditions, growth in biofuels competing for cropland, and high oil prices. When the supply of food increases, food is perceived cheaply and is easily accessible, and ends up wasted. Food is wasted through the supply chain, from agricultural production to final household consumption. Producing food that will not be consumed leads to food being disposed of in landfills and results in unnecessary carbon dioxide emissions and the economic value of the food produced and also represent a waste of resources used such as water, energy, land, and other inputs [8, 11].

Developing as well as developed countries have almost the same quantities of food losses. In developing countries, food is lost during harvest and processing levels, it can get lost in the land due to lack of storage, cooling systems, and poor transport mechanism while in developed countries food loss occurs at retail and consumer levels which are associated with lack of technical and managerial skills and this could be avoided if the all the food can be eaten, stored or managed better but it is difficult to eat all the food when there are things like bones, cores, and peelings. However, these things can be used as a resource for other manufactured products, used as animal feed, like fertilizers, and used in the petroleum industries [8, 11, 15].

Biomass is an attractive option because of its relatively low costs, storage ability and can be easily substituted for fossil fuels in heat, power as well as in fuels. Biomass should provide a large amount of clean energy at an acceptable environmental cost with little negative and large positive socioeconomic effect in the next decade [7, 8, 10, 18]. However, it is also possible that there would be low potentials and large adverse effects such as biodiversity loss, substantial greenhouse gas emissions as well as increased hunger. There should be efforts to increase annual yields in agriculture and forestry through fertilization, irrigation since freshwater availability has become a limit due to climate change and forest management. Humans harvest biomass for food, livestock feeding, fibre, and bioenergy and to produce that biomass, humans destroy plants that are not harvested or left in the field as well as biomass burned in anthropogenic vegetation fires [7, 18].

1.1.3 Hydrothermal liquefaction process

Hydrothermal liquefaction (HTL) is a thermochemical process where high water-content materials are liquefied hydrothermally and directly. This process normally operates at higher pressure and temperature. It involves the decomposition of organic materials by heat in the absence of oxygen. Water is used as a solvent mostly in subcritical or near-critical conditions and this makes HTL a promising conversion method for high-water-content biomass as it eliminates the need for the costly de-watering or drying processes. The main products of HTL are bio-crude oil, water-soluble products, char, and gas [7, 17, 19]. Liquid biofuels industries use sugarcane, molasses, and maize while fermentation of sugar syrups provides bulk chemicals, organic acids, antibiotics, fragrances, amino acids, and flavours. Animal and vegetable oils are used in the oleo chemical industry to produce substitute diesel fuels, soaps, cutting oils, hydraulic fluids, pharmaceutical products, etc. The methyl ester is normally produced from rapeseed as well as from sunflower, and all these species are produced for human consumption [20-22].

1.2 Problem statement

Chemistry over the past decade has been at the forefront when it comes to the production of valuable materials through chemical processes in laboratories and industries. On an industrial scale, these chemical processes involve a lot of reagents and solvents. Most of these chemical processes do not produce only the intended products but also huge quantities of hazardous and harmful processes in many forms such as gases. Harmful gases generated by chemical industries can be eradicated by the world switching over to renewable and sustainable energy alternatives that mimic the natural geological process thought to be involved in the production of fossil fuels.

An increase in the world’s population has increased energy consumption, the global dependence on non-renewable fossil fuels to meet energy’s needs cannot be sustained for a long time and it is already evident in the escalation of fuel prices over the past decade and the severe environmental impacts like climate change.

Food that is being produced for human consumption end up as waste and has become the largest component of landfills. Greenhouse gases are then released into the atmosphere after the decomposition of food waste through anaerobic digestion. Agricultural wastes and food wastes are rich in energy carriers that can be converted to fuels for transportation through the hydrothermal liquefaction process and it is the suitable alternative of repurposing food waste as feedstock for bioenergy.

1.2.1 Aim and objectives

Aim: to hydrothermally valorise agricultural and food waste

Objectives:

- Investigate the effect of temperature on hydrothermal liquefaction process
- Effect of time on the conversion
- Effect of feedstock composition on the quantity and quality
- Effect of catalyst on product distribution

1.3 Research approach

It is essential to find alternative and renewable resources to replace petroleum for the production of energy, fuels, and chemicals. The research project involves the production of bio-crude oil products and is divided into two parts:

- The first part involves hydrothermal valorisation of agricultural and food waste in the absence of a catalyst. Effects of various operating parameters such as reaction temperature, feedstock composition, and residence time on product distribution and bio-crude properties were examined. Characterization techniques such as scanning electron microscopy (SEM-EDS), fourier transform infrared spectrometry (FTIR), and gas chromatography-mass spectrometry (GCMS) were used to study the physical properties of prepared feedstock and catalysts to understand the morphological structures of the materials and their crystallinity properties.

- The second part involves the application of H-ZSM5 on the investigation of catalyst effect on product distribution under various operating parameters. Various characterization techniques such as scanning electron microscopy (SEM-EDS), fourier transform infrared spectrometry (FTIR), and gas chromatography-mass spectrometry (GCMS) were used to study the properties of the liquefaction yields to confirm the success of the bio-crude.

Thesis outline

CHAPTER ONE is an introduction to the research project titled hydrothermal liquefaction of agricultural and food waste as well as the research approach to this study.

CHAPTER TWO is a detailed review of the available literature on the production of bio-crude oil and biogas through different conversion technologies on various biomass in the production of biofuels. Factors affecting the production of biomass-derived biofuels such as temperature, residence time, feedstock composition, and presence of catalyst are also underlined together with the types of biomass that can be used in the production of biofuels.

CHAPTER THREE outlines the sampling methods used, experimental approach as well as analytical techniques used in this research work. It focuses on finding the optimum operating conditions for the production of bio-crude oil from the HTL process using a mixture of potato peels and grape plant which presents feedstock composition.

CHAPTER FOUR reports the results obtained from hydrothermal liquefaction of agricultural and food waste (grape plant leaves and potato peels) in the absence and presence of H-ZSM5 under various reaction conditions to obtain a higher quantity of bio-crude oil products. The results obtained from characterization techniques are also included in this chapter.

CHAPTER FIVE presents the conclusion from this present work and recommendations for future research directions.

Chapter 2

2 LITERATURE REVIEW

This chapter reviews the methods which are available for energy recovery from biomass in the forms of bio-oil and biogas. Overview of different types of biomass for bio-oil production is also discussed. Hydrothermal liquefaction reaction pathways together with the effect of various parameters such as residence time, reaction temperature, feedstock composition, presence of catalyst together with the role of water at sub-critical and super-critical conditions.

2.1 Development and utilization of liquid fuels

2.1.1 Biofuels

Biofuels are biomass-derived liquid hydrocarbons that meet the existing petrol distillate fuel specifications and are ready to drop in into the existing fuel supply and use infrastructure. Drop-in biofuels are formed from production pathways such as fermentation of lignocelluloses sugars, catalysis of lignocelluloses sugars, pyrolysis of biomass, hydrothermal biomass liquefaction as well as syngas upgrading. Butanol, liquefied biomass, sugar hydrocarbon as well as syngas complexes are amongst the candidates for drop-in fuels [17].

Lignocelluloses sugars can be transformed into petrol fuel-like hydrocarbon fuels through catalysts assisted dehydrogenation, deoxygenation, hydrogenolysis, and cyclization reactions. Pyrolysis of algal biomass at 300-400°C in the presence of hydrogen gas results pyrolysis oil that can be refined to quality biofuels. Hydrothermally treating water-based slurry containing oil-rich biomass at 300-350°C results in an organic liquid that can be further upgraded to drop-in biofuels. Butanol can be produced by an acetone-Butanol-ethanol fermentation process using solventogenic clostridia bacteria strain. Ethanol can be upgraded into n-Butanol using catalysts such as ruthenium. Biomass-derived syngas can be transformed into gasoline through a series of catalyst-assisted reactions. Production and utilization of drop-in biofuels is a future renewable fuel development direction [10], [12].

2.1.1.1 Bioethanol

Gasoline has been produced from crude oil or petroleum and has been used to power petrol engine automobiles. It is a volatile liquid that contains a mixture of C_4-C_{12} hydrocarbon. Gasoline is being used highly daily since there are millions of cars that are traveling the streets and roads, and, renewable sources of gasoline substitutes should be developed to work together with the existing liquid fuel. Biomass is a renewable feedstock material that is being used to produce liquid fuel, ethanol is being produced by fermenting plant biomass-derived simple sugars such as monosaccharide, glucose, and fructose and this ethanol can be used as a gasoline substitute to power petrol engines [23].

In 1913 ethanol was tested as an engine fuel before the commercial production of gasoline. In 4000 BC, human beings used to make alcohol as a drink from berries, grapes, and cereals. Plant materials that are composed of cellulose, hemicelluloses, and lignin can be used to generate bioethanol since these construction compounds form a cell wall of a plant. Starch/sugar-based crops including sugar beet, sweet sorghum, corn, barley, cassava as well as sugarcane are recently being used to produce bioethanol. Bioethanol that is produced from food crops competes with animal feed and human food for the source material and it is viewed as the first generation. It becomes important to manufacture second-generation bio-ethanol from non-food lignocelluloses plant material to minimize the effects. Materials such as forest slashes, crop residues, yard trimmings, food processing waste as well as municipal waste are widely available and can be used to generate bioethanol. Many costs are involved in bioethanol production including the cost of the feedstock, cost of the feedstock preparation as well as the cost of ethanol production [10, 12, 23].

2.1.1.2 Biodiesel

Fractional distillation of petroleum at 200-350℃ has been used to produce diesel, a C_8-C_{25} hydrocarbon liquid fuel. Diesel is been used as a fuel for diesel engines and is also an important fuel for home heating. Tractors, trucks, mining equipment, military carriers as well as other heavy-duty vehicles and machines are powered by diesel engines. Because of the difference in ignition mechanisms, diesel engines cannot use gasoline as fuel. Petroleum reserves are depleting, renewable fuel source alternatives to petrol diesel are needed. Biodiesel is composed of mono-alkyl esters of fatty acids and it is a yellowish liquid derived from vegetable oil, animal fats, algal lipids, or waste through transesterification in the presence of alcohol and alkaline catalyst. This biodiesel can be used as a petrol diesel substitute [2, 10, 23].

In the 18th century before the invention of gas lights and electric light, vegetable oil, and animal fats were widely used in oil lamps for lighting. In 1893, Rudolf diesel envisioned that pure vegetable oil could power the machine for agriculture and also carried out extensive tests on various vegetable oil fuels, and in this way, farmers can benefit from producing their fuels [10].

Animal fats such as beef tallow and chicken fat, vegetable oils, algal lipids, and used vegetable oils can be used as a feedstock to produce biodiesel. Common oilseed plants such as canola, castor bean, coconut, soybean, rapeseed, sunflower, etc. can also be used to produce biodiesel [23].

Cleaner emission profile, production simplicity, ease of use, and cost competitiveness are amongst the benefits of using biodiesel. With the growing demand for biofuels, global production and consumption of biodiesel will maintain a consistent increase. The future of biodiesel lies in the world’s ability to economically produce renewable feedstock such as vegetable oils and algal lipids sustainably without supplanting land for food production [10, 23].

2.1.2 Bio-oil

Fossil fuels are formed under the work of geothermal heat and pressure, from the remains of plants and animals that died millions of years ago. There has been an attempt to produce similar fuels which involve treating vegetative biomass in a high temperature, pressure as well as oxygen environment, and this process is called pyrolysis. This technique was used in ancient china to prepare charcoal to generate bio-char. Pyrolysis of plant material results in three products namely; bio-char, bio-oil, and syngas [15, 20].

Crude pyrolysis bio-oil contains significant contents of char particles and water and differs from petrol distillate fuels in physical, chemical and energy properties. Compounds that have been identified in the pyrolysis oil include acids, alcohol, aldehydes, esters, ketones, sugars, furans, alkenes, aromatics, esters, etc... Because of high moisture and acid content, crude oil becomes unstable corrosive, viscous, and low in energy density as well as being immiscible with hydrocarbon, it becomes difficult to ignite. Significant upgrading is needed before the oil is used as petrol distillate fuel alternate [23].

Several upgrading techniques are available, and these are hydrogenation, hydro-deoxygenation, esterification, catalytic cracking, molecular distillation, supercritical fluidization, emulsification, steam reforming, and blending. The process of upgrading is to reduce the moisture content and acidity levels, improve its heating value as well as improve storage ability. Upgraded bio-oil can be applied to substitute heavy fuel oils such as diesel to power static appliances including boilers, furnaces, engines, and electric generators. This bio-oil can also serve as a potential feedstock for valuable chemicals, preservatives, lubricants, binders, paints, thickeners, and stabilizers [10, 17].

2.2 Process for converting biomass into biofuels

Disposing a huge amount of waste generated daily and continuously has become a huge problem and it is increasing gradually and there should be a safest and cost-effective management of disposal. Wastes are categorized into four types:

- Organic biodegradable wet waste: Residues of plants, food, agriculture, garden waste, etc.
- Inorganic and recyclable: ceramics
- Dry incinerable waste: paper, wood,
- Recyclable and non-biodegradable waste: glass, metals, plastics, etc.

The treatment methods for this waste include composting, burning, and dumping in landfalls and these methods are associated with environmental pollution [24, 25]. There’s a global problem of sustainable management of food waste as food generated for human consumption and is no longer suitable for human consumption and the one wasted after eating is deposited in landfills [25].

If waste is untreated or is not treated properly, it will be hazardous to the environment and can cause problems in landfills and wastewater treatment. Conversion of plant material into a suitable form of energy such as electricity or fuel for internal combustion engine can be achieved through several energy conversion techniques such as biological conversion, thermochemical conversion, and chemical conversion and it is shown in **figure 2.1** [21, 25, 26]. These are attractive processes especially for farmers because of the possibility of treating farm waste properly, in this case, farmers will be able to benefit from bio-crude oil production as well as using char as organic fertilizer in their agricultural activities [27].

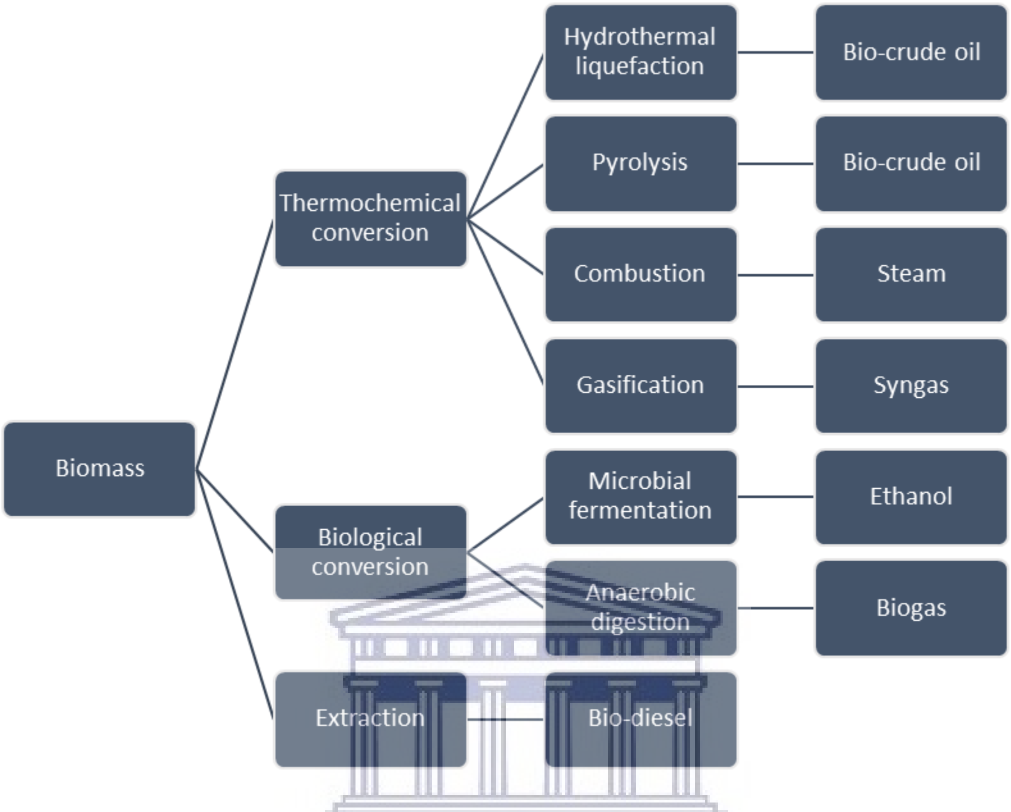


Figure 2.1: Technologies and processes for converting biomass into useful products [27].

2.2.1 Thermochemical conversion processes

The thermochemical process applies heat and chemical processes to produce energy and chemicals from biomass and this include:

2.2.1.1 Combustion

The most commonly used biomass feedstock for combustion is wood and lignocellulose material including residuals and by-products that have high total solid content such as bark residuals, straw, sawdust, etc. because of their combustion properties. Biomass is burnt in the presence of atmospheric air or oxygen. The temperature of the combustion chamber, residence time, amount of air, and the turbulence of the burning gases are the most important parameters for obtaining an efficient and environmentally satisfactory combustion process. Stoves, boilers, furnaces, and steam turbines can be used to convert chemical energy in biomass into heat or power [27].

2.2.1.2 Gasification

Biomass suitable for this process is comprised of a wide range of materials such as energy crops, agricultural residues, wood pellets, etc. The effectiveness of this process is highly dependent on characteristics of biomass such as moisture content, dust content, and energy content. It is important to dry biomass to reduce the moisture content before being fed into the gasifier as the temperature inside the gasifier depends on moisture content. In this process, biomass is heated to about 100℃ to convert moisture into steam and then undergoes pyrolysis stage whereby biomass burns completely without supplying oxygen which results in decomposition of biomass into solid, liquid, and gaseous parts are charcoal, tar, etc. Air is then introduced into the gasifier and oxidation takes place. Carbon dioxide and heat are produced through the reaction of charcoal with oxygen in the air. Hydrogen is produced as the secondary fuel and synthesis gas is comprised of hydrogen and carbon monoxide and leaves the gasifier with products of pyrolysis [27].

2.2.1.3 Pyrolysis

Variety of biomass can be converted such as forestry by-products, timbering waste, agricultural residues, and burned trees. Materials with high lignin content are appropriate for pyrolysis as they contribute to different products of the process since cellulose and hemicellulose decompose to condensable vapours, gas, and solid char [25]. Particle size and moisture content are the most important parameters which affect the product yield as higher moisture content leads to a high level of water in the process while lower moisture content results in undesired dust formation instead of oil. Pyrolysis occurs at 400-800℃, at this temperature lignin is decomposed along with cellulose and hemicellulose contents in the biomass. Liquid bio-oil is obtained from the condensation of vapours as the gas cool and the remaining parts of biomass remain in the solid in the form of bio-char. Reaction temperature, biomass composition, heating rate, residence time, and catalyst effect are amongst the factors that affect product yield [25, 27].

2.2.1.4 Hydrothermal liquefaction

Feedstock appropriate for HTL includes agricultural residues, forestry, waste from the food processing industry, grass, sewage sludge, aquatic energy crops, algae, and domestic waste with high moisture content. Criteria for feedstock properties include the number of contaminants such as rocks, sand, metals, water, and organic and mineral content. Wet residues streams such as garden, fruit, and vegetable residues contain significant amounts of contaminants. Conditions such as temperature, pressure, and reaction time influence the conversion of biomass into bio-oil [25, 27].

2.2.2 _Biological_process

This process conducts the breaking down of biomass into gaseous or liquid fuels through the use of microorganisms, bacteria, and enzymes. Most common types of biological processes:

2.2.2.1 Anaerobic digestion

This process is suited for wet biomass and feedstocks that don't have to be wasted but any feedstocks with biodegradable organic content. Non-woody plants, animal matter, crop residue, and municipal solid waste can be used for anaerobic digestion. The lignin content of biomass cannot be broken down by anaerobic microorganisms. Retention time, process temperature, selection of process temperature, feeding rate, and content of the biomass mixture are amongst the factor that affects conversion efficiency in the digester. This process starts with bacteria breaking down the carbohydrates in the biomass mixture to make them digestible for the second bacteria which convert the formed amino acids and sugars into hydrogen, carbon dioxide, organic acids, and ammonia. The third bacteria comes along and produces methane and carbon monoxide. After the desired time, a gaseous fuel namely biogas occurs in the digester. Heat and power units can be used to convert biogas into electrical and thermal energy [27].

2.2.2.2 Fermentation

Crops that contain a high amount of sugars such as corn, sweet potatoes, and sugarcane can be used for the production of bioethanol. pH, temperature, and sugar concentration of fermentation are the important parameters that should be met to facilitate the bacteria. Bacteria, fungi, and yeast can be used to produce enzymes that catalyze chemical reactions for breaking down sugars into lower molecule sugars which can be converted into chemicals and by-products. Fermentable simple sugars are broken down and released by pre-treatment and decomposition of biomass material. Simple sugars are fermented by a living organism to produce organic acids or alcohol in temperature-controlled tanks [27, 28].

2.2.3 Biomass_extraction

This is a process that is used to extract oil from the seeds of various oleaginous plants such as soybean, sunflower, corn, and grape seed. Apart from crops, waste vegetable oil and animal can also be used as raw materials for biodiesel production. In this process, the biomass is placed and compressed in a container that is surrounded by small perforations from where the oil leaves the system the seeds are exposed to mechanical pressure by a permeable barrier to squeeze the oil from plants or oil. Solvent extraction takes place in the case where mechanical pressing is insufficient to squeeze all types of oil from biomass materials [27].

Selecting appropriate process to depend on:

- Quantity of waste
- Energy demand for the process
- Physical and chemical properties of waste e.g. moisture content
- Desired form of energy product
- Efficiency of energy conversion method
- Economic feasibility of the product

2.3 Hydrothermal liquefaction process

Hydrothermal biomass processing at temperature and pressure near and below the critical point provides an excellent opportunity for processing food waste streams that contain high water content by producing valuable energy products. The conditions in HTL lead to the fast conversion of biomass feedstock into bio-crude that is suitable for upgrading to conventional liquid fuels and also allow direct conversion of wet biomass into liquid precursors without the need for drying [25, 26, 29-31].

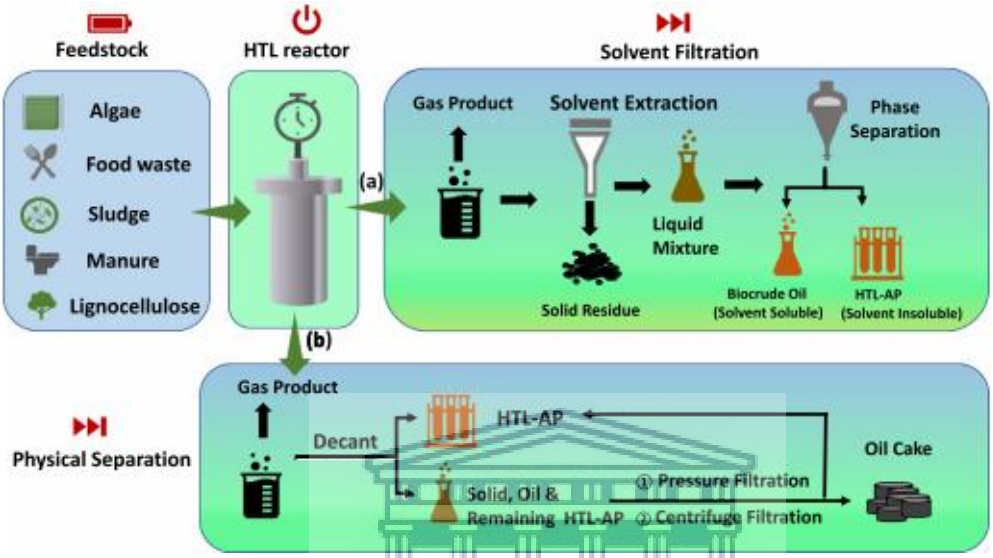


Figure 2.2: Schematic representation of HTL process [31].

Hydrothermal liquefaction (HTL) process begins by hydrolysis of biomass in micellar forms and is followed by depolymerization of biomass fractions (cellulose, hemicellulose, and lignin) to form monomers and unit structure. The produced monomers (thermally and chemically) are then decomposed or degraded to form intermediates through reactions of dehydration, dehydrogenation, cleavage, deamination, decarboxylation and cracking/fragmentation. The macromolecules of biomass are hydrolysed into small fragments that can be converted to smaller compounds, for example, amino acids transform into hydrocarbons, amines, aldehydes, and acids [25, 26].

In hot compressed water, triacylglycerides are hydrolyzed into glycerol and fatty acids. Supercritical upgrading converts heavy oil into lighter oil at a higher temperature. Under these conditions, reaction rates are appropriate for the large-volume product (upgraded crude oil) while minimizing gas and solid by-products. Conversion of glycerol is inclined to produce water-soluble compounds such as methanol, acetaldehyde, allyl alcohol, and formaldehyde with gas products mainly CO, CO_2, and H_2, however carbohydrates content of the biomass varies depending on biomass type. This is then followed by the removal of oxygen-containing functional groups in the presence of hydrogen [32-34]. Rearrangement of reactive fragments/intermediates through depolymerization, condensation, and cyclization to form products. HTL products consist of four phases:

- gas-phase mainly carbon dioxide
- top phase of bio-oil
- An aqueous by-product
- Bottom phase mainly solid residue

HTL is a significant energy technique as compared to the pyrolysis process as shown in Table 2.1 since there is high energy demand in the drying process and high-temperature operation in pyrolysis [25, 27, 28].

Table 2.1: Comparison between pyrolysis and hydrothermal liquefaction process [28].

Treatment conditions	Pyrolysis	Hydrothermal liquefaction
Temperature (℃)	350-500	250-350
Pressure (Mpa)	Atmosphere	5-20
Pre-treatment	Drying is necessary	Drying is necessary
High Heating Value (MJ/kg)	35	22

Pyrolysis requires dried feedstock before being subjected to pyrolysis is carried at a temperature range of 350-500℃ and this leads to the production of bio-fuel with high oxygen content and low oxygen content. The presence of oxygen in high quantities leads to inferior thermal stability for bio-fuel as well as increased cost for upgrading. However, in HTL there’s no excess energy required for drying the feedstock and is operated at a temperature range of 250-350℃. Bio-fuel produced in this process has lower oxygen content and higher energy content [4, 26].

2.4 Water content and its importance

2.4.1 Role of water

2.4.1.1 Freshwater

Water is environmentally non-toxic, inexpensive, easily recoverable, low cost, and most abundant solvent as well as the acid-base catalyst. Water is benign and won't react with organic molecules under standard environmental conditions (20°C and 101.325 kph). Water that is heated below its critical point under a pressurized condition to maintain a liquid state is known as subcritical water. Increasing temperature and pressure near its critical point causes the properties of water to change and differ from those of ambient water and this causes the liquid phase to become less dense because of thermal expansion, the gas phase becomes denser with rising pressure. Densities of the liquid and gas phase become identical and the distinction between the liquid and gas disappears. Supercritical water state shares the physical properties with the liquid and gas phase. Above the critical water point, the interface line separating the two phases disappear, and this is shown in **Figure 2.**. Properties of water such as dielectric constant, ion product, density, thermal conductivity, and viscosity are influenced by subcritical and supercritical conditions [35-39]. **Table 2.2** summarises the different properties of water at different conditions.

Table 2.2: Properties of water at different conditions [39].

Properties	Water under ambient conditions	Subcritical water region	Supercritical water region
Temperature, T (°C)	25	250	400
Pressure, P (MPa)	0.1	5	50
KW	14	11.2	11.9
Heat capacity, cp (kJ kg^{-1} °C^{-1})	4.22	4.86	6.8
Dielectric constant, ε	78.5	27.1	10.5
Density, ρ (kg m^{-3})	1000	800	580
Viscosity, μ (m Pa s)	0.89	0.11	0.07

Heat conductivity, λ (mW $m^{-1}C^{-1}$)	608	620	438

In the subcritical water region, it is possible to make water not only a polar solvent but also an acid-base catalyst to decompose organic compounds through catalyst reaction and hydrolysis. The reaction of organic compounds under subcritical conditions is influenced and controlled by the ionic product and dielectric constant. When increasing temperature, the dielectric constant decreases, and the number of hydrogen bonds decrease leading to a decrease in their strength. Subcritical water behaves like a polar solvent for polar organic compounds. Densities, dielectric constant, and ionic product further decrease in supercritical water with increasing temperature so supercritical water is an efficient solvent for non-polar organic compounds which have very low solubility at subcritical water conditions. Subcritical and supercritical water conditions dissolve many types of biomass and their waste [40, 41].

HTL takes advantage of the properties of water at high pressure and temperature, being a liquid or relatively dense supercritical near the critical point. Supercritical water can donate hydrogen to stabilize intermedia radicals thus inhibiting coke formation [17, 40].

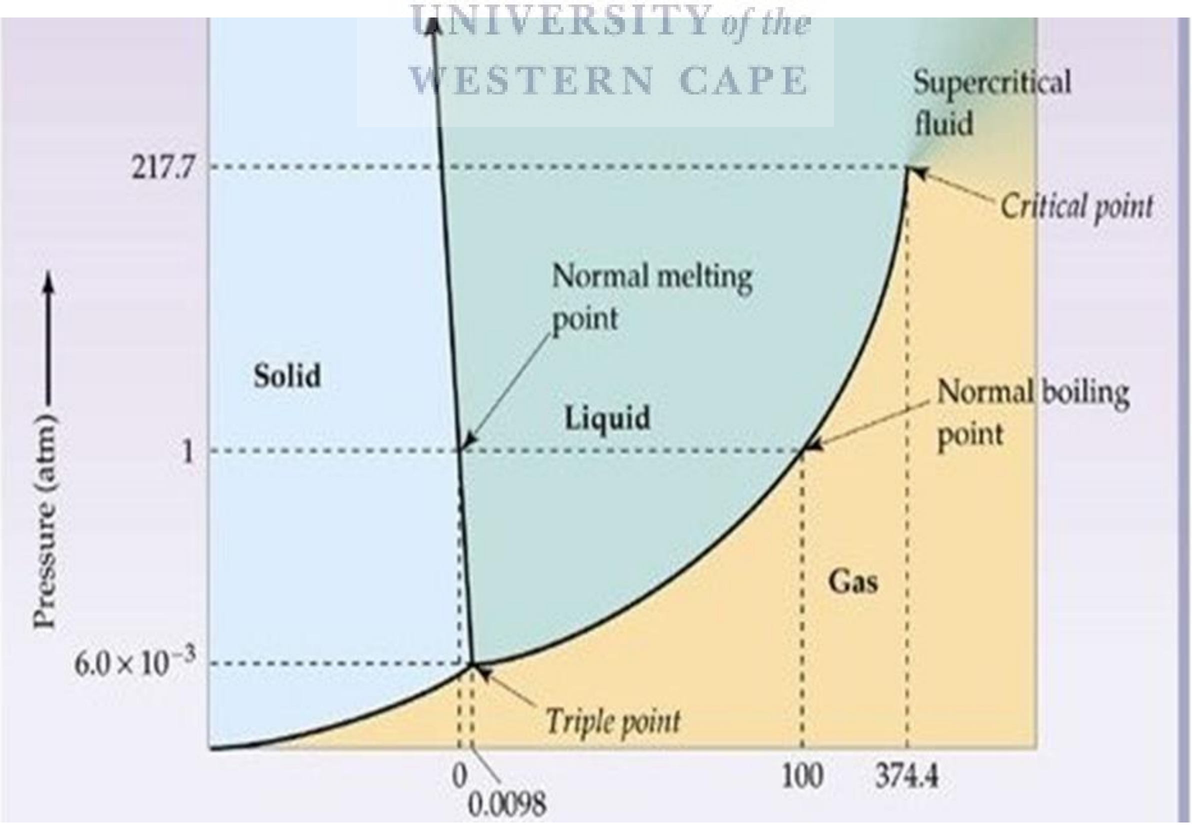


Figure 2.3: Phase diagram of water [40]

Water can carry out condensation, cleavage, and hydrolysis reactions to affect selective ionic chemistry which is not accessible thermally, largely due to changes in its chemical and physical properties. Moreover, hot water as a reactant and catalyst likely creates a second pathway for the cascade of molecular transformation that leads to oil. Water first acts as a base, which nibbles away certain linkages in the organic material, as new molecular fragments build up and modify the reaction environment and can then change its catalytic nature and can then act as an acid by accelerating different reactions [20, 42].

2.4.1.2 Seawater

The rapid growth in population and industrialization is resulting in scarcity or shortage of freshwater. More than 70% of the earth's surface is covered by the ocean and 97% of the earth's water is seawater. Since seawater is inexpensive and is widely available it is good to explore its use in bio-based chemicals or fuel production. Seawater can be used instead of freshwater for the fermentative and chemo-enzymatic synthesis of biochemical. However, the presence of minerals in seawater can avoid the addition of nutrients in fuel production [24, 43].

2.5 Factors affecting HTL process

The hydrothermal liquefaction process depends on various physical and operating parameters such as:

2.5.1 Temperature

Temperature affects bio-crude oil yield and its properties. Temperature ranges between 200-400℃, however, there's no optimum temperature for biomass liquefaction since the choice depends on the biomass feedstock, solvent, catalyst, and other operating parameters. Bio-fuel yield increases with an increase in temperature because when the reaction temperature is sufficiently above the activation energy of bonds cessation, biomass depolymerizes to its unit structures such as glucose and phenolic compounds which transform into bio-crude oil, and however, there is a temperature limit after which further increase reduces the bio-oil yield [44].

The decrease in bio-crude oil yield at higher temperatures is caused by the competition of hydrolysis and depolymerisation reactions which produces more gaseous products and char. Solid residues increase with an increase in temperature due to condensation or polymerization reactions of oil intermediates to form heavier higher molecules that remain in the solid. On the other hand, lower temperatures lead to incomplete conversion of biomass which results in the lower yield of bio-crude oil. Therefore, the selection of an optimum temperature is very important for the hydrothermal liquefaction of biomass for bio-crude oil [42, 44, 45].

2.5.2 Residence time

Residence time is the duration of the reaction, the period during which the temperature for HTL does not account for heating or cooling periods. Optimization of residence time is necessary for the effective conversion of organic compounds in biomass. From the previous studies, residence time depends on biomass type, catalyst type, and operating conditions. Increasing this time increases bio-crude yield due to restriction of secondary or tertiary reactions that will convert the produced heavy oils into the water, solid residue, or gaseous products, however beyond a certain threshold further in residence time, the yield of bio-crude oil decreases [44].

2.5.3 Feedstock composition

Feedstock type and composition such as lignin, carbohydrates, and lipid content have a large effect on the characteristics of the produced bio-crude oil. Under hydrothermal liquefaction conditions, conversion rates for different biomass constituents are in the order: lipids>protein>hemicellulose>cellulose>lignin. Lignin and cellulose hydrolise to oxygen-containing compounds such as phenolic compounds, sugars (carbohydrates), pyran derivatives, aldehydes, acetic acids as well as ketones, and these organic compounds contain high oxygen content of the bio-crude oil. However, higher temperatures are needed in cases where biomass contains a high amount of lignin. Protein, lignin, and carbohydrates form phenolic compounds while lipids produce fatty acids/esters and cholesterol [26, 30, 40].

2.5.4 Catalyst

Using catalyst when converting biomass into bio-fuels reduces the required reaction temperature by enhancing reaction kinetics and thus improve the yield of desired products and also improve process efficiency by reducing tar and char formation and by removing heteroatoms such as Oxygen, Nitrogen, and Sulphur [17]. Catalyst can either be homogenous or heterogeneous. Homogeneous catalysts include alkali hydroxides, carbonates, and alkali formats while heterogeneous catalysts include Pd/C, Pt/C, Ru/C, and zeolites. Homogeneous catalyst decreases solids production, increases bio-oil yield, and improves bio-crude properties [27, 34]. Catalyst can also reduce the condensation or repolymerization reaction of the intermediate products. Zeolite can also improve the properties of crude bio-oil. Choice of catalyst depends on the feedstock and its selection is critical as it can have either positive or negative effects on the desired decomposition and decomposition reactions [26]. A homogeneous catalyst such as formic acid can add extra cost to the HTL process due to its corrosive nature and separation/recovery issues. Heterogeneous catalysts are not reactive to the reactor walls and can be easily separated from HTL products and can be recycled for reuse [17].

2.4.5.1 Zeolites

Zeolites are porous crystalline alumina silicates that are built from SiO_4 and AlO_4 tetrahedra which are linked to each other through oxygen ions. Recently, the majority of the solid acid catalysts used in the petrochemical industries are the zeolite-based catalyst and they have shown a relevant growth in the area of oil refining and bulk chemical production. The use of zeolites in the petrochemical process occurs in the production of olefins and derived products as well as in the production of aromatics [34, 46, 47]. Advantages of using zeolites and zeolite-like catalysts as compared to conventional catalysts include:

- Environmental tolerance;
- Ability to adsorb and transform molecules in the inner volume;
- High surface area;
- Inorganic crystalline structures provide a variety of structures differing in channel diameters, geometry, and dimensionality.
- Possibility for isomorphous substitution of some trivalent cations into the silicate framework which enables tuning of the strength and concentration of the acid sites
- Shape selectivity which is given by the ratio of the kinetic diameters of the reactants, intermediates, and products to the dimensions of the channels and cavities [46, 48].

The number of tetrahedral in the ring around the pores have a huge impact on the pore diameters, and zeolites are grouped according to their pore dimensions as follows:

- Small-pore zeolites
- Medium-pore zeolites
- Large-pore zeolites
- Extra-pore zeolites

Moreover, the orientation of the plane of the ring also affects pore diameters. Shape selectivity is an important property of zeolite catalysts as it differentiates between reactants, products, and reaction intermediates according to their shape and size. The advantage of shape-selective catalyst is that it can favour the formation of desirable isomers over less desirable ones, avoid undesirable competing reactions such as coking or polymerization as well as crack undesirable molecules into smaller fragments that can be easily removed by distillation [46, 48, 49].

Molecules whose dimensions are less than critical size can enter the pores and have access to internal catalytic sites and react there while molecules appear in the final product. However, some of the molecules in a reactant mixture are too large to diffuse through catalyst pores while some of the products formed within the pores are too bulky to diffuse out as observed products. Moreover, certain reactions are prevented because of the corresponding transition state that would require more space than the one available in the cavities or pores [49].

From the wide variety of catalysts, it is important to select the most appropriate zeolite depending on the acid strength, pore size, shape, dimensionality, and pore shape from a variety of zeolites to catalyse reactions [47, 50]. **Table 2.3** lists the most utilized structure types of zeolites for the synthesis and transformation of alkylbenzene.

Table 2.3: Different types of zeolites and their characteristics for synthesis and transformation of hydrocarbon [50].

Zeolite	IZA code	Channel dimensionality	Channel type	Pore dimensions (nm)
Beta	*BEA	3D	12	0.66×0.67
			12	0.56×0.56
ITQ-7	ISV	3D	12	0.61×0.65
			12	0.59×0.66
$AlPO_4$-5,	AFI	1D	12	0.73×0.73
SAPO-5				
NU-87	NES	2D	10	0.48×0.57
SSZ-33	CON	3D	12	0.59×0.70

			10	0.45×0.51
			12	0.64×0.70
CIT-5	CFI	1D	14	0.72×0.75
L	LTL	1D	12	0.71×0.71
Mordenite	MOR	1D	12	0.70×0.65
MCM-22,	MWW	2D	10	0.40×0.55
ERB-1,			10	0.41×0.51
MCM-56				
NCL-1	–	1D	12	0.57×0.86
Y	FAU	3D	12	0.74×0.74
Omega	MAZ	1D	12	0.74×0.74
ZSM-5	MFI	3D	10	0.53×0.56
			10	0.51×0.55
ZSM-11	MEL	3D	10	0.53×0.54
ZSM-12	MTW	1D	10	0.56×0.60
ZSM-22	TON	1D	10	0.46×0.57
ZSM-23	MTT	1D	10	0.45×0.52
ZSM-48	–	1D	10	0.53×0.56
ZSM-21	FER	1D	10	0.42×0.54
EU-1	EUO	1D	10	0.41×0.54

2.5.5 Effects of biomass to water ratio

Along with temperature, residence time, the composition of feedstock and catalyst, the mass ratio of biomass to water is also a key parameter in the HTL of biomass. More concentrated solutions are desirable for bio-crude oil production during HTL since low water concentration restrict hydrolysis of biomass which leads to a smaller yield of bio-crude and a higher yield of the solid residue or char [4, 21, 51, 52].

2.5.6 Effect of particle size

Particle size poses no significant impact on the yield of bio-crude oil however particle size is very critical when drying is required since the exposed surface area can determine the drying time, methods, and conditions that are needed to remove moisture. Particle size should meet the requirements of supplying feedstock to the reactor and the conversion process. The preferred particle size in the hydrothermal liquefaction process is 4-10 mm. Particle size increases the utility of biomass by which a higher degree of fragmentation and hydrolysis takes place. This leads to more bio-crude oil yield to be obtained with more degree of hydrolysis and fragmentation. The cost of the process increases with a reduction in particle size, grinding cost with pestle and mortar became double for wheat straw, barley straw, and switchgrass as more energy is utilized to convert coarse particles to fine particles. Pestle and mortar, blenders, dry shredders, metal hammers on rotating shafts or drums, hammermills, and agricultural choppers are amongst the techniques that can be used for size reduction [53, 54].

2.5.7 Organic solvents

The solvent should either be cheap and easily recoverable, be produced within the process, or be co-processed with the bio-oil to the end product. Solvent selection is important to obtain high liquefaction bio-crude oil yields and improve bio-crude oil properties. Organic solvents such as ethanol, methanol, ethanol, dichloromethane, and ethanol are the alternative reaction solvents to replace water [54, 55].

2.6 Converting biomass into bio-crude oil

Motor vehicles and power plants consume large amounts of fossil fuels and this results in greater levels of air pollution as well as depletion of fossil fuel reserves. In the past or in preindustrial times, human’s basic survival depended on the availability of biomass for energy which was used for heating and cooking, animal consumption, and also building materials. However, in this industrial society biomass has a wide range of uses. It has been used as the raw material for the production of energy. Developing areas of the world consume more biomass energy than developed or industrial regions [56-58].

Carbon-containing materials that are renewable over a short period and available in large quantities are needed to maintain and supplement energy supplies, and biomass is a major source that can meet these requirements. Biomass captures solar energy during photosynthesis and in this process, carbon monoxide is converted into organic compounds during their growth. Biomass is harvested for food, fiber, feed and has also been used as a material for construction and can be left in the growth areas where decomposition can occur, and they can be recovered after a long period as fossil fuels [59].

Bio-crude oil refers to liquid fuel that is produced from biomass and can be used as a transport fuel. The criteria used in categorizing bio-crude oil is relevant for the feasibility of meeting bio-crude oil target sets and categorizing bio-crude oil is based on the type of feedstock that has been used when it's been produced, climate mitigation potential, and ecological impact from the land in which the feedstock is obtained [60, 61]. Biofuels can be categorized as:

- FIRST-GENERATION FUEL: this refers to biofuels produced from feedstock that can also be used as food crops, such as sugar, starch, and vegetable oils.
- SECOND AND THIRD-GENERATION BIOFUELS: refers to biofuels that are produced from feedstock that do not compete directly with food crops and these are the waste and agricultural residues, for example, municipal waste, wheat straw, and non-food crops such as algae.

Conventional biofuel is ethanol derived from corn starch while advanced biofuels are cellulosic biofuel, biomass-based diesel, and other advanced biofuels [57, 60].

It is important to select suitable biomass for the production of energy products and synfuels. Many parameters must be studied before selection, and these include soil type, quality, and topography, propagation and planting procedure, growth cycle, fertilizer, herbicide, and pesticide, disease resistance of monoculture, precipitation, and irrigation. Moreover, biomass selected should have a high yield, have a low-cash value that has short growth cycles [58, 59, 62].

Temperature, precipitation as well as insolation are amongst the factors that affect the production and yield of biomass species, and these factors are beyond human control. Amongst these factors, insolation and temperature do not affect the growth of biomass especially during their normal growing seasons; however, precipitation has the greatest impact since drought can cause stunted growth on biomass [58, 59, 63].

2.6.1 Factors affecting production and yield of biomass

2.6.1.1 Isolation

For photosynthesis to occur, there must be incident solar radiation from the earth's surface, and this process is ideal for the growth of biomass, without this solar radiation there won't be growth. Isolation depends on the geographical location, time of the day, the season of the year, and it is mostly done in the tropics or areas close to the equator [62, 63].

2.6.1.2 Precipitation

Aquatic biomass grows very well in water meanwhile the growth of terrestrial biomass is water-limited. Crops such as wheat grow very well with less water. During the growth season, water is supplied from the soil after rainfall, snow, sleet, or hail depending on the atmospheric temperature and other conditions which are governed by the movement of the air. In areas where there is low precipitation, water can be supplied through irrigation. However, the productivity of biomass is not determined by rainfall alone because of the differences in soil characteristics, water evaporation rates as well as infiltration [63, 64, 65].

2.6.1.3 Temperature

Biomass species such as corn, kenaf, and grass grows very well in temperature between 15℃ and 32℃ [59].

2.6.1.4 Nutrients

For living biomass to synthesize cellular materials they need macronutrients such as carbon, hydrogen, oxygen, phosphorus, potassium and these nutrients are supplied by the soil and they can deplete over some time and hence they have to be supplied by fertilizers to maintain soil fertility of the soil and most of these fertilizers are produced by fossil fuels mainly natural gas [66, 67].

2.6.2 Composition of biomass

Biomass is composed of carbohydrates, proteins, and amino acids, as well as lipids and these, are shown in **Figure 2.3.**

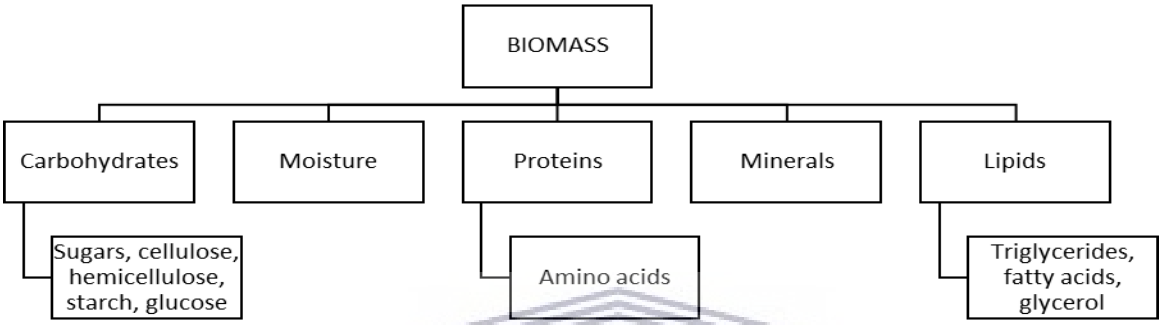


Figure 2.3: Composition of biomass [53].

2.6.2.1 Carbohydrates

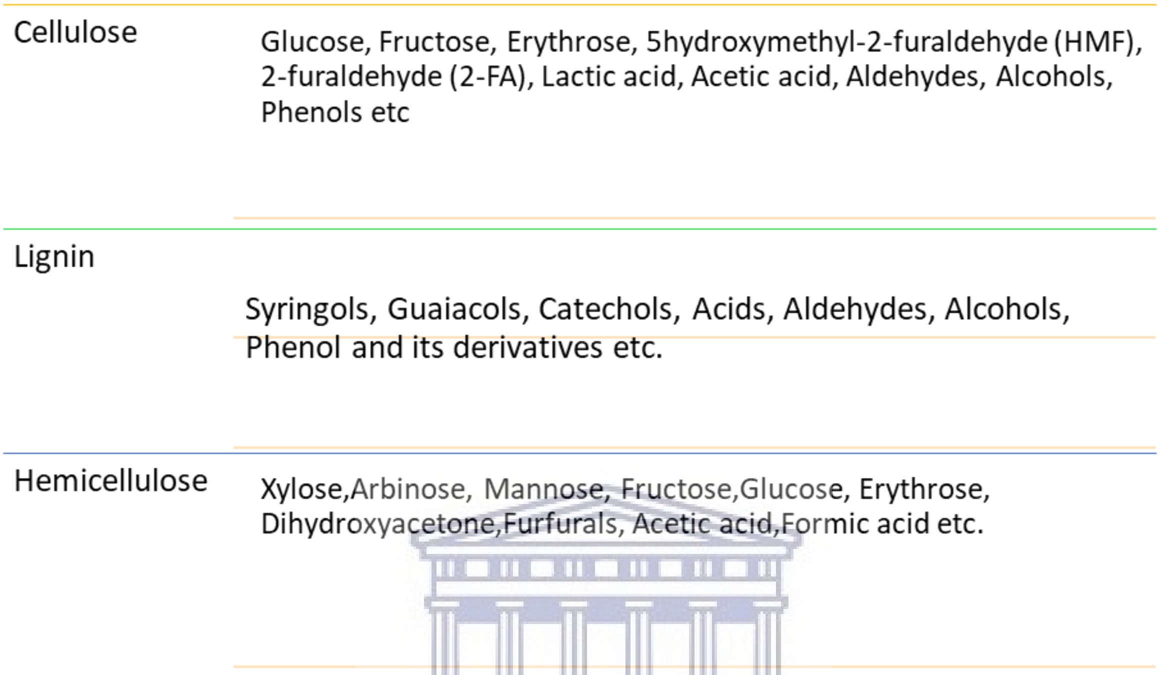
Lignocelluloses

This compound is the principal substance that composes plants and they belong to the carbohydrates group of organic compounds, their products are listed in **Figure 2.3**. Lignocellulose is the hydroxyl aldehydes, hydroxyl ketones, etc. is are classified as:

- Cellulose: it has a crystalline structure and this makes it water-insoluble. However, subcritical water with a high ionic product can break its crystallinity. This polysaccharide only yield D-glucose upon hydrolysis

- Hemicellulose: it is a non-crystalline and random structure that is easy to hydrolyze even at a lower temperature. Hydrolysis of hemicellulose produces a mixture of polysaccharides composed mainly of five-carbon and six-carbon sugars

- Lignin: resembles a network of aromatic compounds linked together in a more random fashion [20, 42, 53].



Cellulose	Glucose, Fructose, Erythrose, 5hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA), Lactic acid, Acetic acid, Aldehydes, Alcohols, Phenols etc
Lignin	Syringols, Guaiacols, Catechols, Acids, Aldehydes, Alcohols, Phenol and its derivatives etc.
Hemicellulose	Xylose,Arbinose, Mannose, Fructose,Glucose, Erythrose, Dihydroxyacetone,Furfurals, Acetic acid,Formic acid etc.

Figure 2.4: Products of cellulose, hemicellulose and lignin [53].

2.6.2.2 Proteins and amino acids

These are the polymers of amino acids which are mostly found in animal or microbial types of biomass, they contain a large fraction of nitrogen which can affect the properties of bio-oil [42, 53].

2.6.2.3 Lipids

These substances can be dissolved away from biological material by solvents that are nonpolar or slightly polar. Fatty acids are long straight-chain carboxylic acids that are saturated and contain one or more bonds [20, 42].

2.6.3 Types of biomass

High-yield biomass species selected must be characterized for their physical and chemical properties to define their growth requirements and rate their energy use potential. Several species have been proposed for energy use.

2.6.3.1 Trees and grasses

The world's land area is forest land and trees are dominant species in areas near the equator. Trees are grown through:

- Naturalistic: growing of selected species that can match the ecology of the area
- Short rotation: growing of trees that can grow quickly and can be harvested in a short period.
- Exploitative: harvesting the trees without regard to regeneration
- Conventional extensive: harvesting of mature trees about regeneration
- Conventional intensive: growing and harvesting of commercial tree species

Most of these trees are being produced to produce fiber for the manufacture of paper products, and the wood wastes have been used to produce heat, steam, and electricity [58, 68].

The grass is an abundant form of biomass that grows in all land habitats which is capable of supporting a higher form of life. They are grown for decorative purposes, as farm crops, preserving the balance of productive capacity of lands by crop rotation, stabilizing arid areas, protecting watersheds as well as controlling erosion on sloping lands. Grasses that have been given serious consideration as raw material for the production of energy and synfuels include Bermuda grass and its hybrids etc. [59, 68].

2.6.3.2 Other cultivated crops

Terrestrial biomass species have been proposed as a renewable energy resource for their high-energy components that can be used as fuels. Several biomass species have been selected for conversion to biofuels and chemicals and among them is Kenaf. Kenaf is a brown plant fiber used to make ropes, in paper products, in building materials, and as animal feeds. This plant exhibit rapid growth, has a high yield and has high cellulose content, and produces seed only. Sunflower is an oilseed plant that is grown annually. Amongst others are buffalo gourd;

rapeseed; alfalfa; as well as other oilseed crops that produce high-quality oil and protein [58, 68, 69].

2.6.3.3 Aquatic biomass

Aquatic biomass such as unicellular and multicellular algae, freshwater plants, and marine species have been considered as the most suitable biomass for energy production since they exhibit higher organic yield than terrestrial biomass. These types of biomass have rapid growth rates, renewable, strong ability to survive in a variety of environments, have no competition with agricultural land and high quality and versatility of the by-products, and also reduce the net greenhouse emission by using the atmosphere [55, 56].

2.6.3.4 Algae

Microalgae have been used as renewable energy resources and other useful products. Unicellular algae such as *Chlorella* and *Scenedesmus.* They are produced as slurries in lakes and in ponds, the nutrients for their production are supplied by municipal biosolids and other wastewater streams [31, 56]. However, most of the unicellular algae are grown in fresh water and this limits their energy application [29, 31].

2.6.3.5 Freshwater swamps

They offer a good opportunity for energy production. Cattail grows naturally in monocultures, is highly productive, and is found in wetlands and marginal lands. Hyacinth is another biomass species that is highly productive especially in warm climates and could be suitable biomass for non-fossil sources for synfuels manufacture and also in the manufacturing of paper [42, 58].

2.6.3.6 Municipal solid waste

Because of an increase in population in the urban areas, the production of municipal solids increases inappropriately and there are difficulties which are associated with their disposal. Collection and disposal costs increase and proper disposal becomes more difficult to achieve. However, there is a loss of natural resources in the municipal solid waste if they are not recovered. In the early years, the municipal solids waste generated would be disposed of by burning and there was no effort made in recovering the heat evolved. The most common disposal method for municipal solid is landfilling. Municipal solid waste is available in abundance and is collected for disposal in all industrialized countries. A land-filled municipal solid waste provides energy as fuel gas for heat, steam, and electric power production [35, 51, 70].

2.6.3.7 Waste water biosolids

Industrialized countries receive wastewaters from groundwater infiltration, residential sources, industries as well as storm water runoff. Pollutants that are associated with these sources include suspended and dissolved compounds and oxygen-demanding materials which are toxic. Heavy metals, inorganic nutrients, viruses, organic compounds, and bacteria are amongst pathogenic components which can be found in municipal wastewater treatment plants. In the wastewater treatment process, these pollutants are reduced. Biosolids are collected in municipal wastewater systems and are therefore available in abundance. Although there are processes that can be used to treat and stabilize the waste at the same time recovering energy, it is essential to treat the biosolids for health reasons [35, 51].

2.6.3.8 Agricultural biosolids

Animal wastes have been transformed from a definite asset to a liability, and disposal of the waste has become a serious problem. Animal waste can be disposed of on land and this can provide fertilizing benefits. The utilization of livestock and poultry manure as waste biomass resources for energy application can help to mitigate the pollution. The high population of certain animals can offer the greatest opportunity to serve as sources of waste biomass because they generate waste in high amounts. Domestic farm animals such as cattle, pigs, sheep, and lambs and those confined to feedlots such as poultry are the appropriate choices and can produce large, localized quantities of excreta. Animal excreta as waste biomass are not available in abundance as most of the waste is dropped in the field by animals is used in the soil as fertilizers [30, 58].

2.6.3.9 Agricultural crop residues

Agricultural waste has high levels of organic matter and nutrient content, spreading of these wastes on agricultural land as natural fertilizers can result in excess nutrient supply in soil and can lead to potential contamination of water bodies and groundwater if they are not managed properly. Current agricultural and forestry practices do not harvest all the material [16, 17].

Agricultural crop residues are those which are left in the field or accumulated during harvesting (sorting and cleaning of produced crops) and their disposition is a difficult task and these crops include sugarcane, hay, forage crops, corn, soybean, sorghum, rice, oats as well as bagasse. Most of these crops can be returned to soil; for soil conditioning, erosion control, and nutrient values, used to feed animals, and can be used as a fuel. As much as these crop residues are needed to be utilized for energy, it is also important that these crop residues are used to cover erodible lands especially during winter months to reduce erosion, but some crops residues have energy content and cannot be used for such purposes [20, 71-73].

2.6.3.10 Industrial waste

Many industries generate waste biomass and these include food processing industries and the pulp and paper industries. The pulp and paper industry is one of the largest energy-consuming industries which relies on its captive sources of waste biomass such as bark, black liquor, and wood residues. In the pulp and paper industry, black liquor is the major waste biomass resource and a by-product and it is formed when cellulosic fibers are separated from the debarked, chipped wood and most of the lignin is dissolved in the process, and the pulp is then washed to remove chemicals before further processing of the pulp into a paper. The mixture of dissolved wood components and used pulping chemicals in the extract(black liquor) is burned in recovery boilers to recover the pulping chemicals and to generate steam, wood residues serve as boiler fuel and the chemicals are processed for reuse in the pulping step [71-73].

2.6.3.11 Food waste

Food waste is organic and contains a significant amount of nutrients such as Nitrogen, Potassium, Magnesium, and Potassium. Developing countries suffer from food loss in the early stages of the supply chain while developed countries contribute more to food loss at the retail and consumption phase [53, 74]. Food waste can also be generated from animal processing, fruits, vegetables, dairy products, and grain production. During industrial food processing, large quantities of food processing waste are produced from food to drinks. Sectors of food processing are namely as:

- Meat and fish processing
- Milk processing
- Fruits and vegetable processing
- Wine processing

Waste that is produced within the food and drinks processing industry is seemed to be a large and ever-increasing problem [75, 76].

Food waste is made up of 30% solid residue and 70% water and it consists of abundant quantities of organic materials that are classified into three main biological groups, namely: carbohydrates, proteins, and lipids. Food waste is easier to process as they contain carbohydrates group such as cellulose, starch, and sugars, a protein that can be hydrolyzed to amino acids, minerals as well as lipids that are hydrolyzed to fatty acids [20, 53, 75].

2.7 Feedstock preparation for HTL process.

Adsorption and exposure to precipitation are the mechanisms of water uptake by biomass. In the adsorption process, moisture is transferred from air to the surface of biomass from the attraction between polar water molecules and the negatively charged surfaces of the wood meanwhile absorption process involves water molecules being drawn into permeable pores of the biomass due to diffusion and osmotic forces followed by capillary condensation and the moisture absorbed depends upon the pore diameter and distribution of capillaries. Moreover, the transpiration of soil moisture, temperature, and humidity of the surrounding air can also affect the moisture content [26, 51].

2.7.1 Drying

It is important to dry the raw biomass before conversion failure to do so will result in more energy consumed by the conversion process than will be produced in the form of energy or fuel. Solar drying in open-air is the cheapest method however materials that are not suitable for this type can be dried more rapidly using industrial dryers, convection ovens, and forced air furnaces. The moisture content is the property of biomass that should be examined. High water content biomass includes microalgae biomass, water hyacinth, giant brown kelp, and chlorella as they contain a large amount of intracellular moisture. Moreover, industrial, municipal as well as farm and animal wastes are also produced in association with water and they need to be dried before they can be used. Agricultural crop residues such as corn cobs, rice hull, and orchard crops contain less moisture since they are exposed to open-air solar drying and depend on the season of the year and the geographic location [54, 75].

2.7.2 Drying methods

The moisture of feedstocks needs to be reduced before conversion. There is various equipment that can be used for dewatering and this includes centrifuges, extrusion as well as water extractors. Aquatic species can be dewatered by direct physical separation to remove moisture but this can disrupt the cell walls. Solar drying in the open air is the cheapest method but most of the biomass species which contain a high amount of moisture can result in the loss of energy content and carbon and can also decompose since solar drying depends on the climate. It is important to arrange biomass that has a high moisture content in piles to facilitate exposure to air circulation and sunlight, and the biomass piles should be turned periodically to prevent a fungal infection of wet biomass [28, 56].

Chapter 3

3 METHODS AND MATERIALS

This chapter includes a detailed presentation of the experimental methods and chemicals used during the research project. Characterization of materials and products is essential for understanding their properties and application. Instruments and instrumental setup used for characterization are also described in this chapter.

3.1 Materials and chemicals

Analytical grade Dichloromethane (DCM) was purchased from KIMIX and was used for the reaction without further purification.

The model feedstocks used here is potato peels, potato peels were chosen to be food waste as it represents the dominant polysaccharides available in food. Grape leaves were obtained as a waste material after grape harvesting and were selected as agricultural waste.

3.1.1 Preparation of feedstock

Fresh potatoes were purchased from a fruit and vegetable market in Cape Town, South Africa. After domestic use, potato peels were collected and sundried for 7 days. The wastes were collected and homogenized using pestle and mortar. A sieve was used to obtain the same particle size.

Grape leaves were picked from the grape plant in the vineyard and sundried for 7 days. Pestle and mortar were used to grind the leaves and a sieve was used to obtain the same particle size and also consistency.

The composition of the prepared feedstock comprised of food waste and agricultural waste were in a 100:0, 75:25, 50:50, 25:75, and 0:100 ratio.

3.1.2 Feedstock characterization

Dried samples were kept in a container at room temperature to maintain minimum moisture. Elemental analysis was done using energy dispersive X-ray Spectroscopy (EDS) while the surface morphology was done using a scanning electron microscope (SEM). Fourier transform infrared spectroscopy (FTIR) was used to quantitatively determine the functional groups which are present in the feedstock.

3.1.3 Catalyst preparation

NH4-ZSM-5 was converted to H-ZSM-5 through Calcination at 500℃ for 5 hours.

3.2 Method for production of bio-crude oil

This section focuses on the methodology used to synthesize the bio-crude oil.

3.2.1 Experimental conditions

Temperature, reaction time, feedstock composition, presence of catalyst along feedstock/water ratio are the parameters that influence the quality and yield of HTL products. The effect of temperature on product distribution was studied at the temperature ranging from 260-340℃. The duration of the reactor in a furnace at the desired temperature was from 30-150 minutes. The composition of the feedstock was comprised of food waste and agricultural were in a 100:0, 75:25, 50:50, 25:75, and 0:100 ratio and the feedstock/water ratio was 1:14. No inert gas or reducing gas was pressurised into the system.

3.2.2 Hydrothermal liquefaction process

The reaction was performed for each feedstock composition at 260℃, 280℃, 300℃, 320℃, and 340℃ in a 250 ml stainless steel reactor, heated using an electric furnace. Feedstocks were taken for HTL after size reduction. 2g of prepared feedstock and 28 ml of distilled water were loaded into the reactor and the contents of the reactor were stirred. The reactor was sealed and loaded into a furnace. Process variables were controlled through a temperature controller and the furnace was heated to the desired temperature, and the reactor was inserted for attained optimal reaction temperature and maintained for the desired reaction time. The experiments were conducted for each condition with each feedstock composition. After completion of the reaction, the reactor was removed from the furnace and cooled by running tap water for 3 minutes to stop the reaction immediately.

Once the reactor was cooled, it was opened and the mixture was transferred into a beaker. Vacuum filtration was used to separate the unreacted and inert materials, firstly solids were isolated and quantified using filter papers (Whatman no 4). An aqueous solution that passed through the filter was transferred to a separatory funnel. The resulting filtrate was then extracted with 25ml of DCM and evaporated using rotary evaporation at 39℃ for 10 minutes to get bio-crude oil and was taken for further analysis. The residues obtained after filtration were dried in a vacuum oven and weighed.

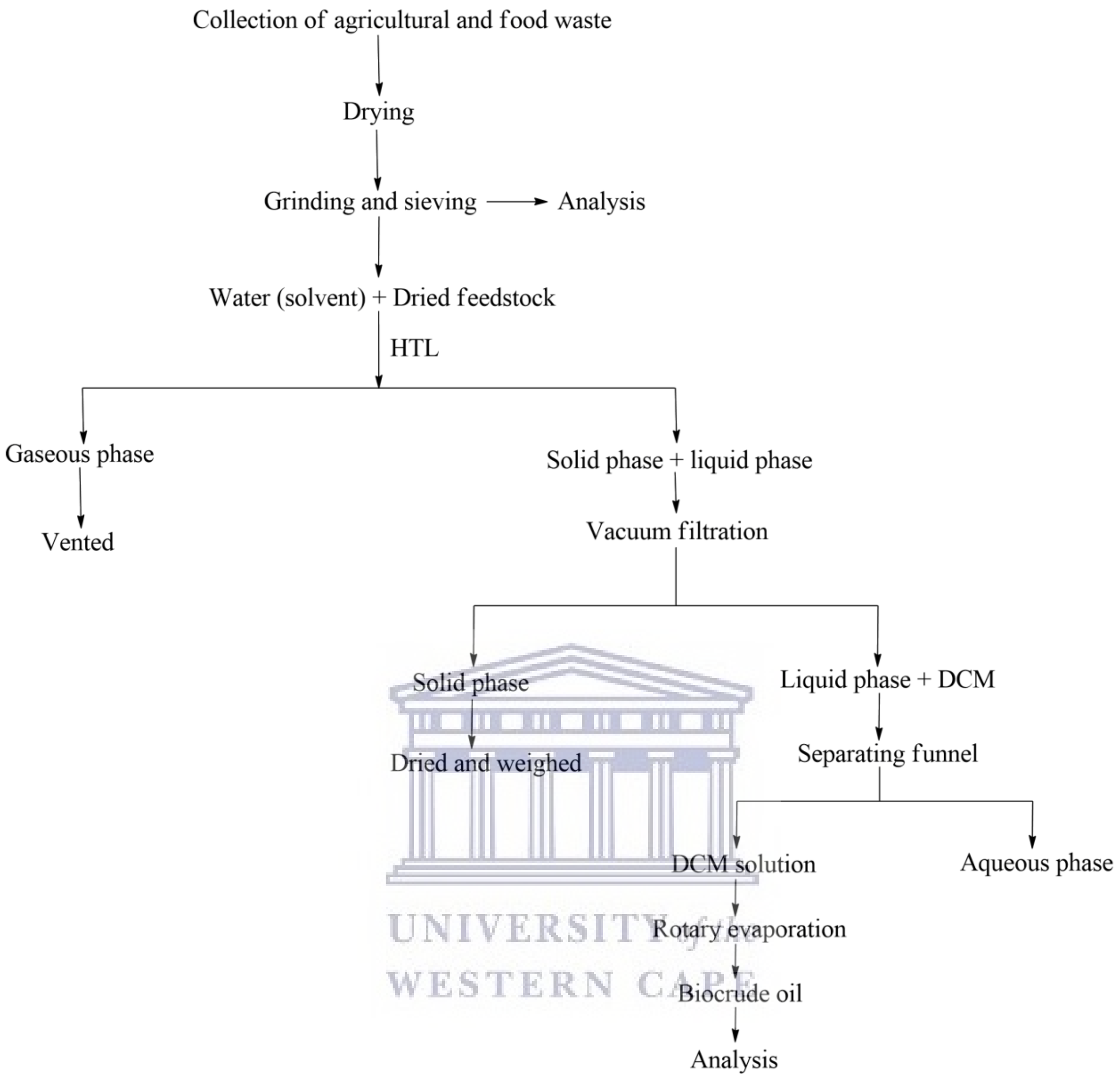


Figure 3.1: Production of hydrothermal liquefaction bio-crude oil

3.2.3 Catalytic hydrothermal liquefaction process

For catalytic hydrothermal liquefaction process, the same procedure described for non-catalytic hydrothermal process was followed. However, 1g of H-ZSM-5 was added before the reactor was inserted into the furnace.

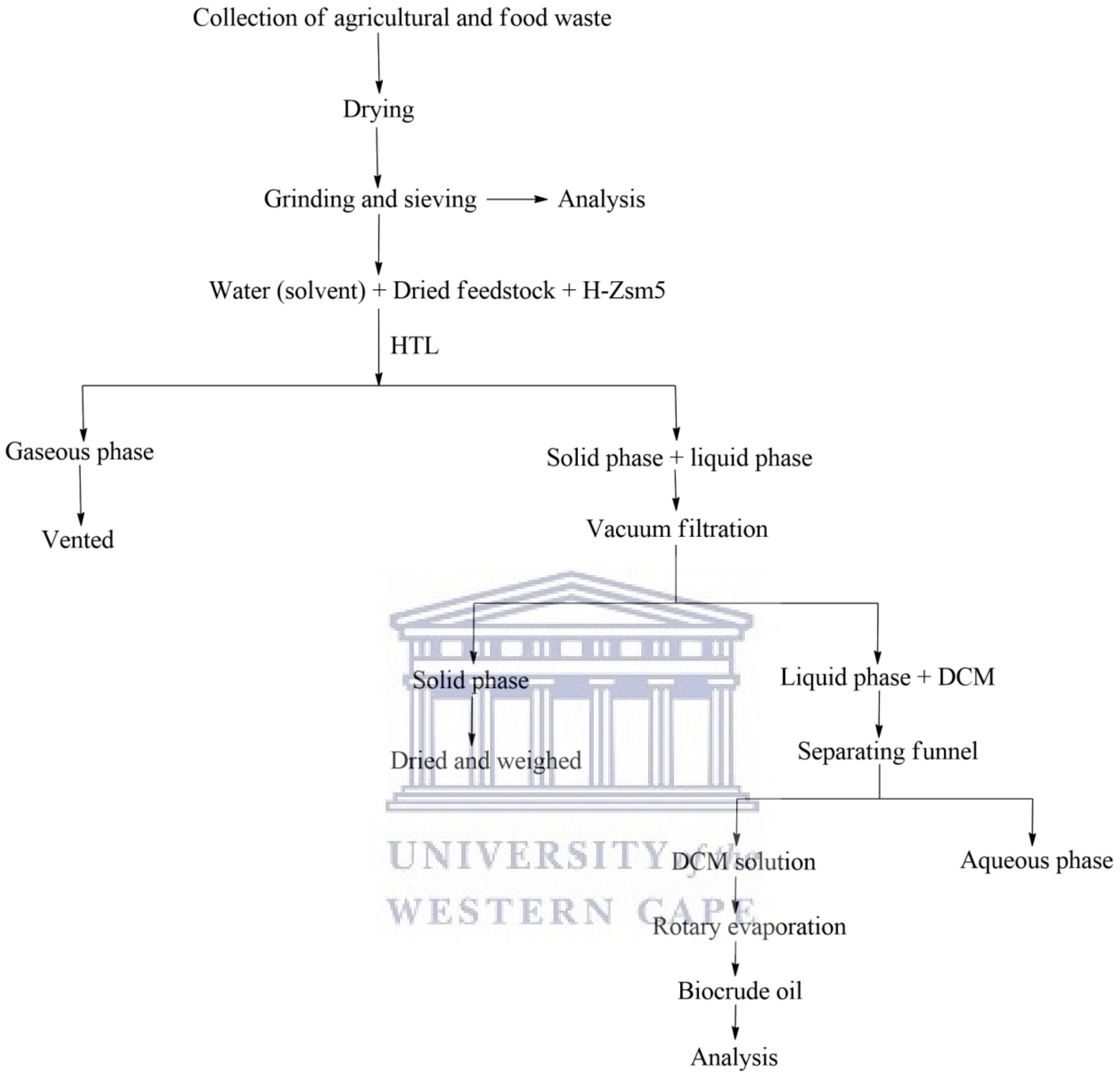


Figure 3.2: Production of catalytic hydrothermal bio-crude oil

3.3 Volume of bio-crude oil per grams of biomass feedstock

After rotary evaporation, the remaining product in the evaporating flask was transferred into a measuring cylinder. The cylinder was then placed on a flat surface and the height of the liquid in the cylinder was recorded.

3.4 Bio-crude oil yields

Yield of each product was calculated as mass percentage on dry basis. Bio-crude oil yield was calculated from mass left after the removal of residual solvent through rotary evaporator. Because the density of the produced bio-crude oil was unknown, the measuring cylinder with bio-crude oil was weighed to determine mass. The yield of HTL bio-crude oils was determined using equation 1:

Bio-crude oil yield (wt.%)= $\frac{Mbio-crude\ oil}{Mfeedstock}$ x 100………………………………….(1)

With $M_{\text{bio-crude oil}}$ being the mass of the bio-crude oil and $M_{\text{feedstock}}$ being the mass (g) of the feedstock. Bio-char yield was calculated from the collected char mass on filter paper after letting it dry in the oven at 50°C for 24 hours. Bio-char yield was calculated using equation 2:

Bio-char yield (wt.%)= $\frac{Msolid\ residue}{Mfeeedstock}$ X 100………………………………………….(2)

The yield of gaseous products and losses was determined by the difference using equation 3:

Gases and loses (wt.%)= 100-solid yield-bio-crude oil yield………………………….(3)

3.5 Characterisation techniques

Different characteristics have been used to characterize the feedstock and as well as the produced bio-crude oil. The objectives were to study their properties such as chemical composition as well as their surface morphology. The techniques used for analysis were: scanning electron microscopy (SEM-EDS), fourier transform infrared microscopy (FTIR), and gas chromatography-mass spectrometry (GCMS).

3.5.1 Scanning Electron Microscopy

3.4.1.1 Principle

Scanning electron microscope (SEM) is a very useful imaging that uses a beam of electrons to acquire high magnification images of specimens. SEM was used to analyse nanoparticle imaging characterisation of agricultural and food waste feedstock. The objectives of using this technique was to determine the surface morphology and elemental composition of the agricultural and food waste feedstock. SEM images are formed scanning a beam across the sample and form the image point-by-point [77].

3.4.1.2 Instrumentation

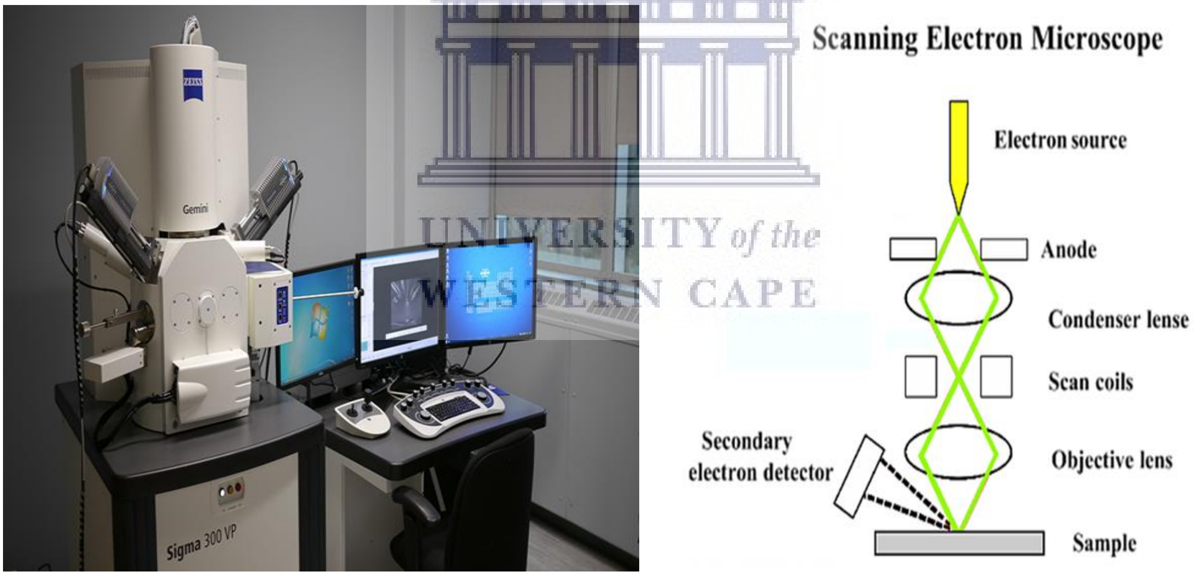


Figure 3.3: SEM instrument [77]

In this instrument, largely magnified images are formed by using electrons instead of light. The beam of electrons is produced at the top of the microscope by an electron gun, electron beam follows a vertical path through the microscope which is held inside the vacuum. The beam travels through an electromagnetic field and lenses, which focus on the beam toward the sample. Electrons and X-rays are ejected from the sample once the beam hits the sample. The X-rays, backscattered electrons, and secondary electrons are collected by detectors and they get converted into a signal that is sent to a screen that is similar to a television screen, and this produces the final image [77].

This technique was used to study the surface morphology and the elemental composition of the materials by using a beam of electrons that interact on the surface of the samples. Images of the samples are created by scanning the materials. Samples were coated with carbon to make the surface electrically conductive. SEM images were analysed at an accelerating voltage of 2 Kv by using a TESCAN Vega TC instrument, equipped with an X-ray detector for energy dispersive X-ray analysis (EDS) operated at 5 Kv.

3.4.1.3 Sample preparation

SEM samples were prepared by placing double-sided conductive carbon tape on an aluminium specimen stub. A small amount of the sample was deposited on the specimen tub and flattened with a spatula, then gently tapped to remove the excess and loose sample. Energy dispersive spectroscopy (EDS) detector connected to the HRSEM was used to investigate the elemental composition of the feedstock experimental parameters used for SEM Auriga for this study are as follows:

- Working distance: 10 nm
- Accelerating voltage: 5 KeV
- Tilt angle: 0 degrees

3.4.2 Fourier Transform Infrared Spectroscopy

Infrared spectrometry (IR) has been used for the identification of compounds by matching the spectrum of an unknown compound with the reference spectrum into the identification of functional groups in the unknown substances. The electromagnetic spectrum of the IR region covers the range from 50-12 500 cm^{-1}. Functional groups present in the feedstock were analysed using FTIR spectroscopy [78].

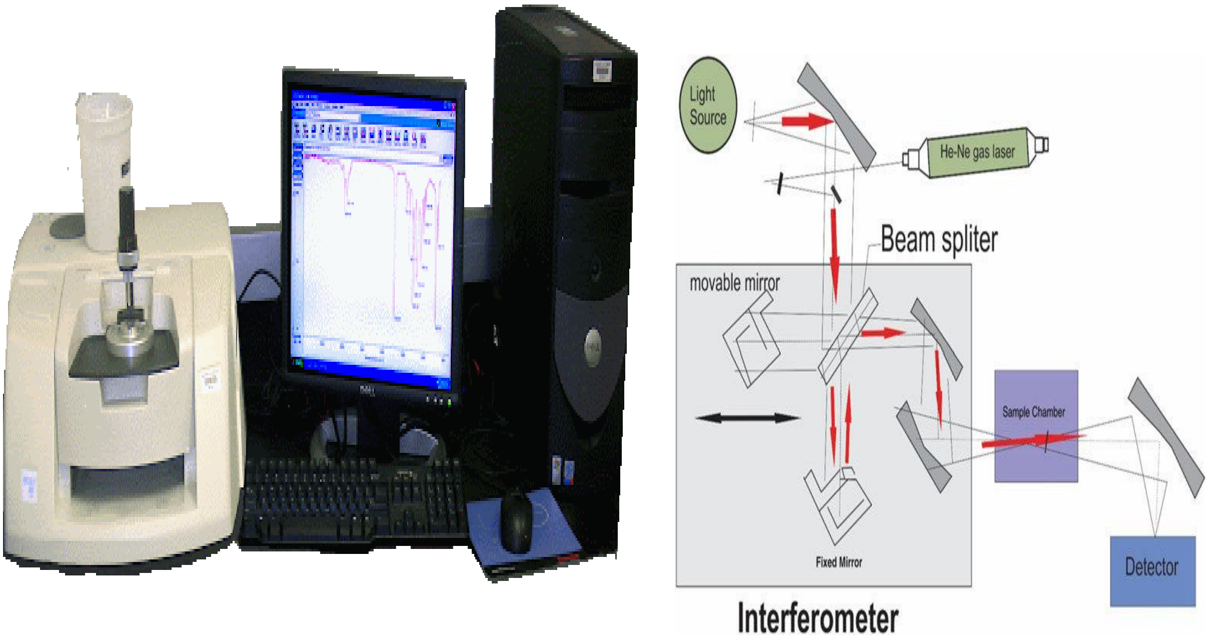


Figure 3.4: FTIR instrument [78]

3.4.2.1 Principle

In this technique, infrared light is passed through an organic compound sample, some frequencies are absorbed, while others are transmitted without being absorbed. Transitions involved in infrared absorption are associated with vibrational changes in the molecules. Different functional groups have different vibrational frequencies, the presence of these bonds in a molecule is detected by identifying the characteristic frequency as an absorption in the infrared spectrum. The infrared spectrum is the plot between transmittance against frequency [78].

3.4.2.2 Instrumentation

In an FTIR system, there are three basic spectrometer components namely: radiation source, interferometer, and detector. IR radiation from a broadband source is directed into an interferometer first, where it is divided and later recombined after the split, beams travel different optical paths to generate constructive and destructive interference. The resulting beam passes through the sample compartment and then reaches the detector [78]. In the case of solid samples to be analysed, it is important to make sure that the sample is ground and pressed. FTIR was performed using a Perkin Elmer FTIR spectrophotometer.

3.4.2.3 Sample preparation

A small amount of the sample was placed on the ATR sampling accessory and pressed. The samples were analysed at a wavelength range of 400-4000 cm^{-1}.

3.4.3 Gas Chromatography-Mass Spectrometry

GCMS is an analytical method that combines the features of gas chromatography-mass spectrometry to identify different substances within test samples. It can be used for environmental analysis, identification of unknown samples, etc. It allows analysis and detection even of tiny amounts of a substance

3.4.3.1 Principle

The GC-MS is composed of two major building blocks namely: the gas chromatogram and mass chromatogram. The gas chromatograph utilizes a capillary column whose properties regarding molecule separation depend on the column's dimensions (length, diameter, film thickness) as well as the phase properties. The difference in the chemical properties between different molecules in a mixture and their relative affinity for the stationary phase of the column promotes the separation of the molecules as the sample travels the length of the column. The molecules are retained by the column and then elute (come off) from the column at different times, and this allows the mass spectrometer downstream to capture, ionize, accelerate, deflect, and detect the ionized molecules separately. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass-to-charge ratio [79, 80].

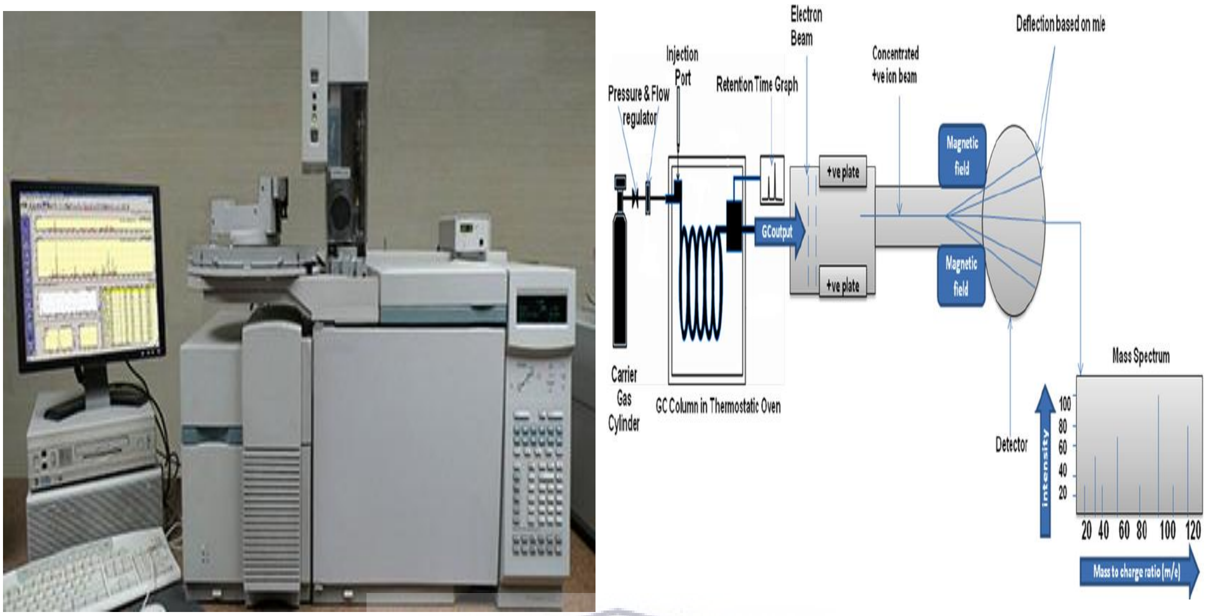


Figure 3.5: GCMS instrument [80]

3.4.3.2 Instrumentation

In this technique, the sample mixture is injected, vaporized, and flows into the thermally controlled column by an inert gas. Sample compounds can interact with the stationary phase through various intermolecular forces such as Van der Waals forces and dipole-dipole interactions. Some compounds tend to interact more strongly due to their polarity, which results in a higher concentration in the stationary phase compared to the mobile phase. As a result, these compounds are strongly retained in the column and have a longer retention time as compared to the compounds of weaker interactions with the stationary phase. As time passes with a continual flow of inert gas and a thermally controlled column, the variations in the partition coefficients of the compounds result in the separation of the compounds in the mixture. The separated compounds subsequently elute from the column and get detected [79, 80].

The separation of compounds in the GC mainly depends on two factors namely: the polarity as well as the boiling point of the compound. The lower the boiling point, the higher the tendency of the compound being in the gaseous phase and thus travels faster in the gaseous form through the column. Compounds with similar boiling points elute concerning their polarity, where compounds of weaker interaction with stationary phase elute first. Compounds with similar polarity elute in order of increasing boiling points, where compounds of lower boiling points have a shorter retention time. The time taken for the compound to travel from the injection port to the detector is termed retention time. Retention time depends on various factors such as column type and dimensions, carrier gas and flow, temperature [79, 80].

3.4.3.3 Sample preparation

This analysis was carried out to identify different compounds which were present in the samples. 1 µl sample from a 2 ml vial loaded on the auto sampler was injected (split injection) into the GC coupled to an MS.

For the auto sampler, there were three rinses with the solvent, followed by one rinse with the solvent and also rinsed twice with the sample.

The source temperature was set at 220℃, Helium gas was used as carrier gas with purity at a flow rate of 3.0 ml/min. The total flow was 50 ml/min. The flow control mode was the pressure of 100 kPa at a linear velocity of 46.3 cm/sec. The oven temperature was initially set to 60.0℃ with a holding time of 2 minutes, then increased at 20℃ min^{-1} until reaching 280.0℃, samples were injected and held constant for 25.00 minutes. The source temperature was 200℃, while the interface temperature was 250℃. The solvent cut time was 2 minutes.

Chapter 4

4 RESULTS AND DISCUSSION

Characterization of materials is very important for understanding their properties as well as their applications. This chapter discusses the results which were obtained from instrumental analysis of the bio-crude oil produced from the HTL of agricultural and food waste. Techniques that have been used for characterization include Gas Chromatography-Mass Spectrometry, Fourier Transform Infrared Spectroscopy, X-ray diffraction as well as Scanning Electron Microscopy.

4.1 Characterisation of feedstock

The prepared feedstock was composed of agricultural and food waste. These feedstocks were characterized using FTIR, SEM, and EDS.

4.1.1 FTIR analysis

This technique is used for the identification of compounds by matching the spectrum of the unknown compound with the reference spectrum. Five samples that differ in their composition were prepared and analysed by the technique to determine the functional groups and structures present in agricultural waste and food waste. The FTIR spectra are presented in a waterfall configuration to visualize differences in chemical structure. This technique gives information about the presence of functional groups which are in the sample.

4.1.1.1 Feedstock composed of agricultural waste and food waste in 0:100 ratio

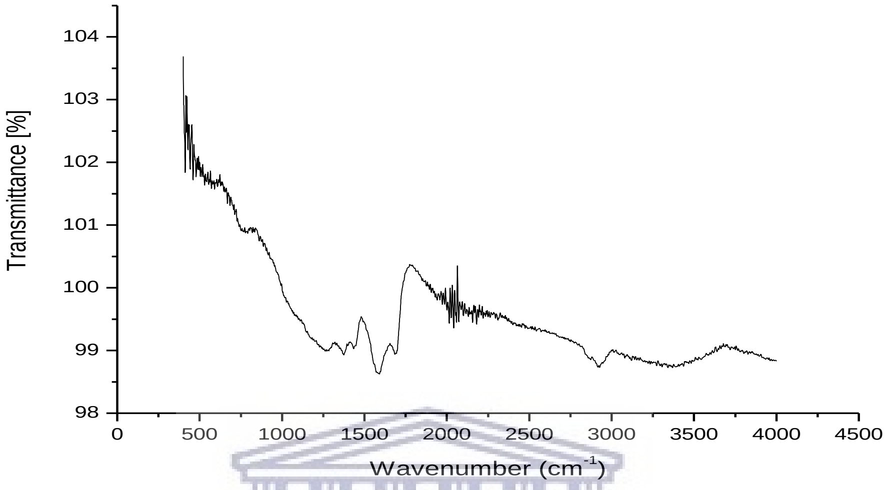


Figure 4.1: FTIR spectrum of agricultural waste and food waste in 0:100 ratio

This feedstock is composed of agricultural waste and food waste food waste in a 0:100 ratio. The spectrum above shows a sharp absorbance at 1000 cm^{-1} which account for C-O in alcohol and C-N in amines. The sharp absorbance at 1700 cm^{-1} is assigned to C=O which entails the presence of carbonyl compounds such as carbonyl carboxylic acid, ketone, esters, etc. The absorption band at about 500 cm^{-1} is attributed to the C-Br which entails alkyl halides. The broad absorbance at 3000-3700 cm^{-1}is attributed to the stretching vibrations mode of O-H in alcohol.

4.1.1.2 Feedstock composed of agricultural waste and food waste in 25:75 ratio

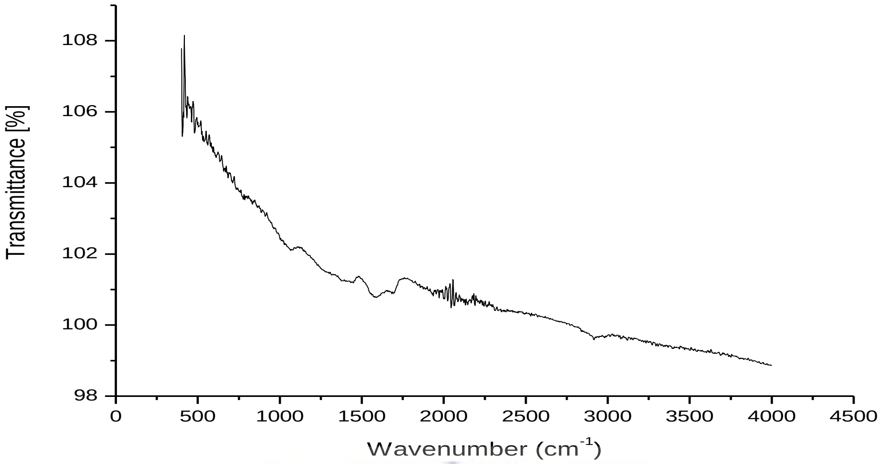


Figure 4.2: FTIR spectrum of agricultural waste and food waste in 25:75 ratio

This feedstock is composed of agricultural waste and food waste in the ratio of 25: 75. The FTIR spectra contained a sharp absorption band at 1500 cm^{-1} which is attributed to aromatics as well as stretching vibrations from nitro compounds.

4.1.1.3 Feedstock composed of agricultural waste and food waste in 50:50 ratio

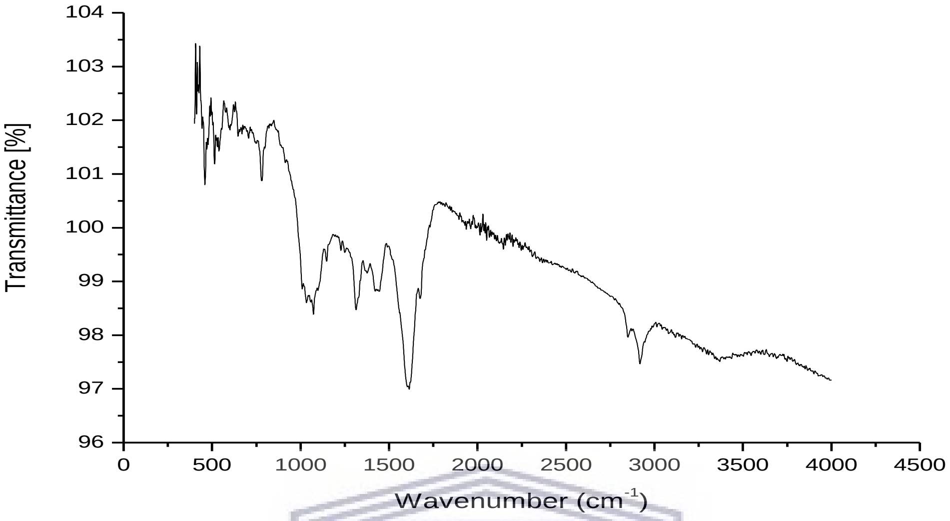


Figure 4.3: FTIR spectrum of agricultural waste and food waste in 50:50 ratio

This feedstock has been prepared from agricultural and food waste in 50: 50 ratio. The presence of nitrogen has been attributed by broad N-H and C-N absorbance bands at 3100-3500 cm^{-1}, in addition, this absorbance is also attributed to O-H as well as the carboxylic acid, which shows the presence of alcohols. Strong absorbance at 2900 cm^{-1} entails the presence of the C-H group. The sharp absorption at 1600 cm^{-1} is attributed to C=O which shows the stretching vibrations from carbonyl compounds. The sharp absorbance at 1200 cm^{-1} is attributed to C-N and this shows the presence of amines. Absorption around 1000 cm^{-1} shows the presence of C-O group. The presence of alkyl halides has been shown by the absorption at 500 cm^{-1}.

4.1.1.4 Feedstock composed of agricultural waste and food waste in 75:25 ratio

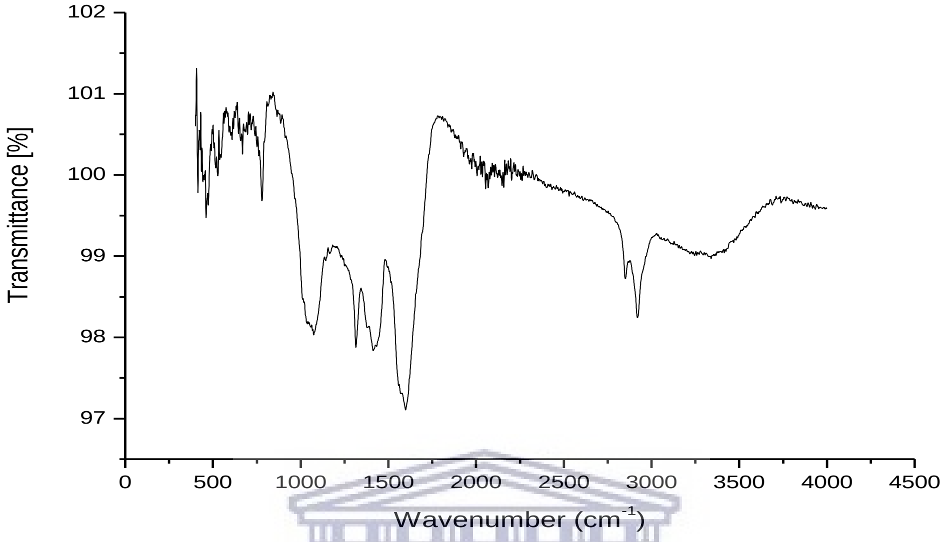


Figure 4.4: FTIR spectrum of agricultural waste and food waste in 75:25 ratio

The feedstock is composed of agricultural and food waste in 75: 25 ratio. The presence of aromatics in the spectra is shown by strong C-H and C=C absorbance at 1600 and 2900 cm^{-1}. The strong absorbance at 1000 cm^{-1} is attributed to stretching vibration modes of C-O. Strong absorption at 1500 cm^{-1} shows the presence of aromatics. The presence of amines in this sample is being shown by the medium absorption at around 1200 cm^{-1} and 1000 cm^{-1} moreover this absorption band also shows the presence of C-O group. The absorption band at around 400-900 cm^{-1} shows is attributed to the alkyl halides, which are C-Cl, C-Br as well as C-I.

4.1.1.5 Feedstock composed of agricultural waste and food waste in 100:0 ratio

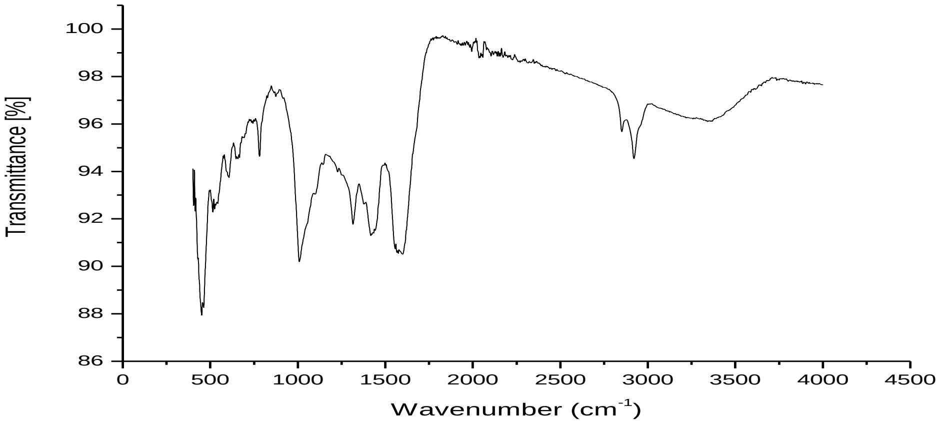


Figure 4.5: FTIR spectrum of agricultural waste and food waste in 100:0 ratio

This feedstock is composed of agricultural waste and food waste in a 100:0 ratio. The medium absorption at around 3000 cm^{-1} being attributed to =C-H group. The sharp absorbance at 1600 cm^{-1} being assigned to C=C which entails the presence of alkanes or aromatics. The absorption band at about 500 cm^{-1} is attributed to the C-Br which entails alkyl halides. The broad absorbance at 3250-3500 cm^{-1} is attributed to the stretching vibrations mode of O-H in alcohol. The strong absorption band at 1000 cm^{-1} shows the presence of C-O group.

The functional groups which were present in all the feedstocks were the alcohols, amines, carbonyl compounds as well as alkyl halides. There was no observed trend on the intensity of the absorption band which is associated with the presence of functional group as the composition of agricultural and food wastes feedstock were changed in different ratios. Few functional groups were detected, and weak absorbance bands were observed when the amount of agricultural waste was increased from 0 wt.% to 25 wt.%. However, a further increase in the amount of agricultural and food wastes in a 50:50 ratio played no role in the intensity of the absorbance band and in the presence of functional groups as compared to the case where the composition of the feedstock was 0wt% agricultural waste and 100wt% food waste. A further increase in the amount of agricultural waste to 100wt% and a decrease in the amount of food waste to 0wt% played no role in the presence of functional groups as well as the intensity of their absorption band. Therefore, feedstock composition in different ratio played no role in the presence of functional groups and on the intensity of the absorption peaks.

4.1.2 Scanning Electron Microscope

Morphological analysis is a useful characterisation techniques that is used to determine the elemental composition and morphologies of the feedstock and this was done using scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) analysis. SEM-EDS analysis was done for the prepared feedstocks.

4.1.2.1 Feedstock composed of agricultural waste and food waste in a 0:100 ratio

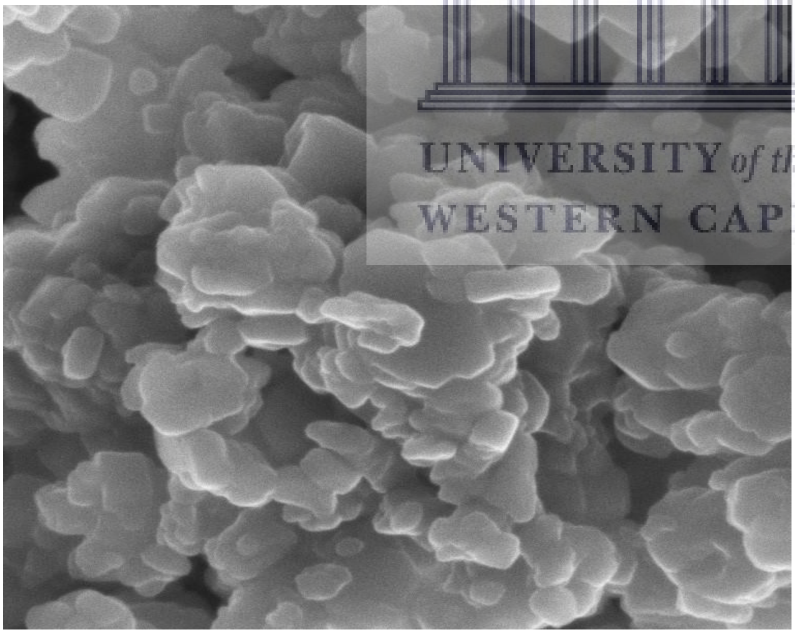


Figure 4.6: SEM image of a feedstock composed of agricultural waste and food waste in 0:100 ratio

Figure 4.6 shows the surface of the feedstock composed of agricultural and food waste in a 0:100 ratio. The image exhibit nanosized particle. Close observation of the nanostructure revealed the hollow-porous structure with the uniform monodisperse particles having pores diameter ranging from 191-221 nm.

Dry matter content reflect the origin of the sample. Elemental composition of the raw material reveal distinct differences of elements which are present in the feedstock. From Table 4.1, high quantity of Oxygen was detected and the presence of Oxygen is also supported by the FTIR which showed the strong absorbance which is attributed to C-O. Moreover, Silicon was also detected at a high quantity meanwhile the detection for Aluminium and Sulphur was minimal.

Table 4.1: Elemental composition of a feedstock composed of agricultural waste and food waste in 0:100 ratio

Elements	**Quantity**
Oxygen (O)	51.44
Aluminium (Al)	0.84
Silicon (Si)	25.44
Sulphur (S)	0.27

4.1.2.2 Feedstock composed of agricultural waste and food waste in a 25:75 ratio

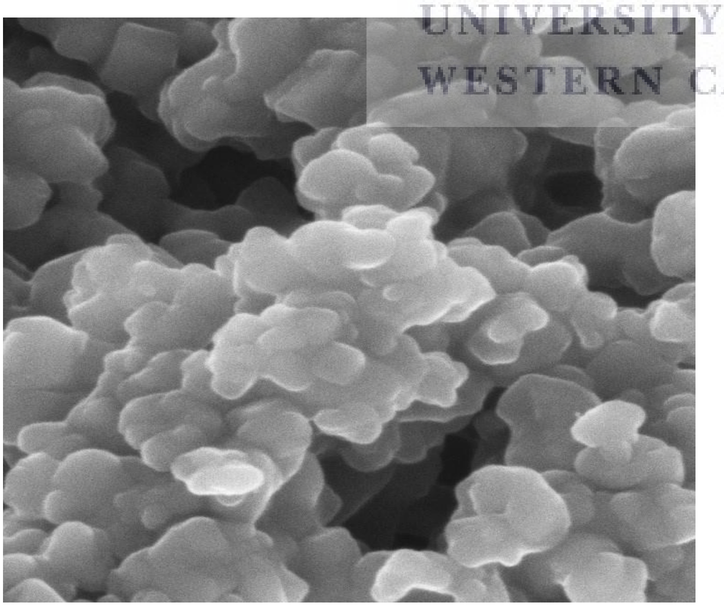


Figure 4.7: SEM image of a feedstock composed of agricultural waste and food waste in 25:75 ratio

The feedstock composed of agricultural waste and food waste in a 25:75 ratio demonstrated a small nanoparticle fibres. The morphology is hollow-porous composed of uniform monodisperse particles, with the pores diameters ranging from 165-189 nm.

The content of oxygen is very high due to photosynthesis. The inorganic matter in this feedstock could be present in the form of minerals and their presence can results in operational and environmental problems during the HTL process, and could results in the decreased yield of hydrocarbon. From the elemental analysis, small quantity of Silicon, Sulphur and Potassium were detected and this could be seen in Table 4.2.

Table 4.2: Elemental composition of a feedstock composed of agricultural waste and food waste in 25:75 ratio

Elements	**Quantity**
Oxygen (O)	40.39
Silicon (Si)	10.68
Sulphur (S)	0.34
Potassium (K)	0.2

4.1.2.3 Feedstock composed of agricultural waste and food waste in a 50:50 ratio

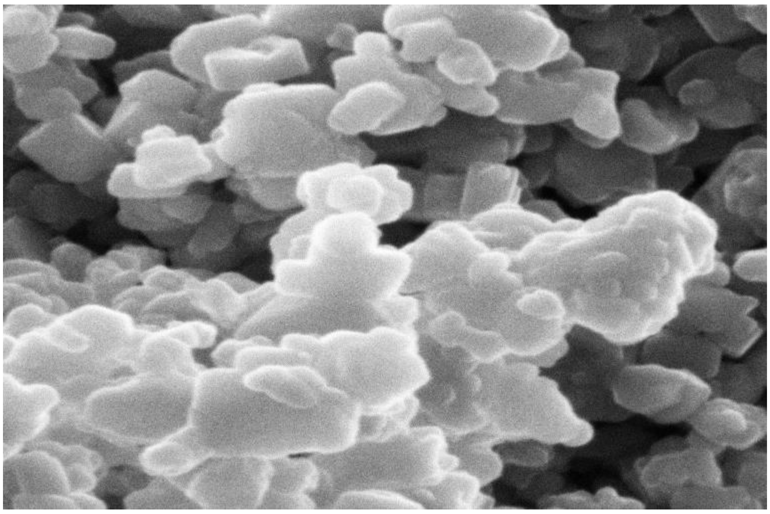


Figure 4.8: SEM image of a feedstock composed of agricultural waste and food waste in a 50:50 ratio

SEM image for the feedstock composed of agricultural waste and food waste in a 50:50 ratio demonstrated a hollow-porous morphology. The particles are nanosized and are uniformly dispersed. Pores in the nanofiber surface had a diameter ranging from 165-185 nm.

The composition majorly depend on the living habitat of the people, season and time of collection as well as source of collection. From the elemental composition in table 4.3, this feedstock composed of Oxygen (O), Silicon (Si), and Chlorine (Cl) as well as Potassium (K). The other minerals that have been obtained comes from the soil as well as from fertilisers and have been dissolved in water and get absorbed by plants. The presence of Chlorine has been supported by the strong absorption band at 400-900 cm^{-1} from the FTIR spectra in **Figure 4.3** above.

Table 4.3: Elemental composition of a feedstock composed of agricultural waste and food waste in a 50:50 ratio

Elements	**Quantity**
Oxygen (O)	39.03
Silicon (Si)	2.18
Chlorine (Cl)	2.11
Potassium (K)	4.87

4.1.2.4 Feedstock composed of agricultural waste and food waste in a 75:25 ratio

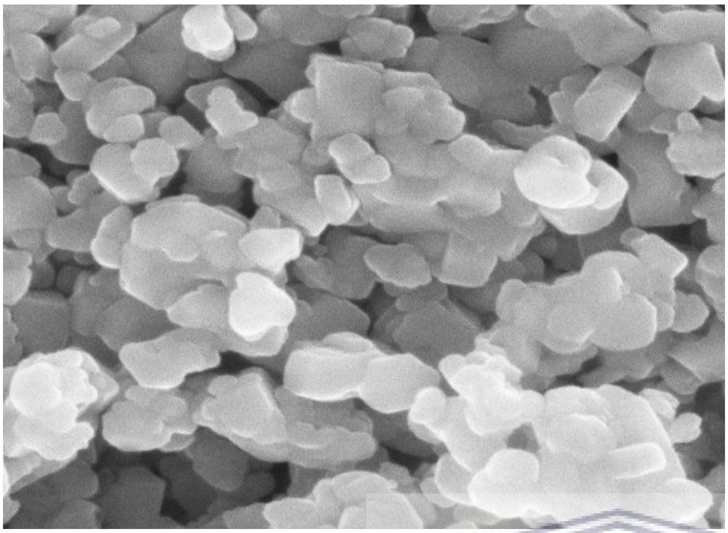


Figure 4.9: SEM image of a feedstock composed of agricultural waste and food waste in a 75:25 ratio

The image in Figure 4.9 shows nanosized particles consist of uniform monodisperse particles with a hollow-porous morphology. The pore sizes are ranging from 150-160 nm.

Many elements such as magnesium, aluminium, silicon, chlorine as well as potassium have been detected in this feedstock and this is shown in Table 4.4, and their presence is not fully supported by the FTIR spectra expect for chlorine. The content of Oxygen is much higher and is supported by the strong absorption band at 1000-1200 cm^{-1} in the FTIR spectra in Figure 4.4

Table 4.4: Elemental composition of a feedstock composed of agricultural waste and food waste in a 75:25 ratio

Elements	**Quantity**
Oxygen (O)	44.53
Magnesium (Mg)	0.11
Aluminium (Al)	0.14
Silicon (Si)	4.24
Chlorine (Cl)	0.2
Potassium (K)	2.09

4.1.2.5 Feedstock composed of agricultural waste and food waste in a 100:0 ratio

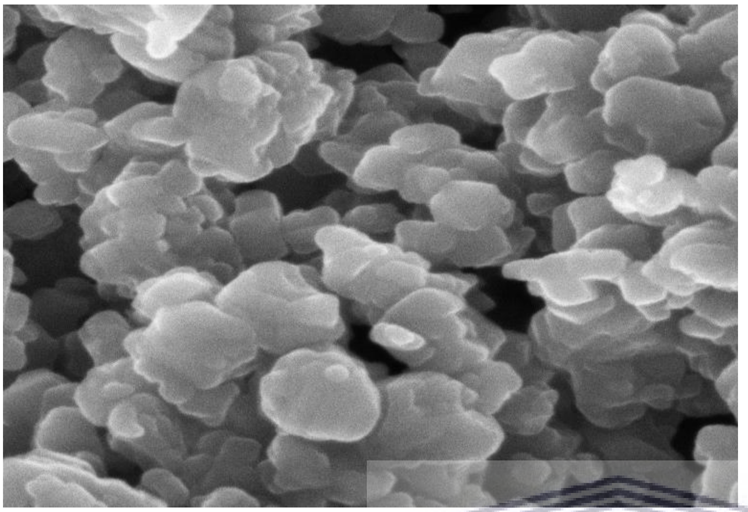


Figure 4.10: SEM image of a feedstock composed of agricultural waste and food waste in a 100:0 ratio

Close observation of the nanostructure in Figure 4.10 shows that the particle has hollow-porous morphology. The pore sizes are ranging from 147-151 nm.

It can be seen from Table 4.5 that the feedstock is rich in oxygen as compared to the other elements. There was a minimal detection of minerals in this feedstock, and this has a less effect during HTL. The presence of these minerals is highly dependent on cultivating environment and this make the vineyard to be the ideal location for collection of feedstock for HTL process to produce bio-crude oil based on their elemental composition.

Table 4.5: Elemental composition of a feedstock composed of agricultural waste and food waste in a 100:0 ratio

Element	**Quantity**
Oxygen (O)	39.72
Aluminium (Al)	0.47
Silicon (Si)	5.94
Potassium (K)	0.26
Calcium (Ca)	1.58

The observed trend on the pore sizes from the SEM images, showed a decrease in the diameter of the pores as the amount of food waste was decreased with an increase in the amount of agricultural waste in 0:100 ratio to 100:0 ratio.

The observed trend in the elemental analysis was the decrease in the content of oxygen as the amount of agricultural waste was increased with a decrease in the amount of food waste. However, this was observed for the feedstocks composed of agricultural waste and food waste in 0:100 ratio, 25:75 ratio and 50:50 ratio. A further increase in the amount of agricultural waste with a decrease in the amount of food waste in a 75:25 ratio, has resulted in the drastic increase in the content of oxygen moreover a sudden decrease in the content of oxygen when the amount was further increased in a 100:0 ratio of agricultural waste and food waste was observed. Similar trend was observed in the other inorganic elements such as silicon, potassium and aluminium. An increase in the amount of agricultural waste resulted in the increase in the content of calcium.

4.2 Effect of process parameters on product distribution

Hydrothermal liquefaction of biomass comprises of three reaction mechanisms, namely decomposition, recombination, and depolymerization. Because of the highly reactive nature of biomass constituents, the macromolecules decompose into smaller compounds, polymerize, and subsequently form liquid biofuels, gases as well as a solid product. When water was added into the biomass, the constituents of biomass disintegrates into small molecules fragments and form a solid residue or a char, water phase having high organic carbon content as well as gas.

4.2.1 Effect of temperature

The effect of temperature on the hydrothermal liquefaction of food waste was studied at 260℃ 280℃, 300℃, 320℃ and 340℃ in different reaction times; 30, 60, 90, 120, and 150 minutes using 2g of food waste.

4.2.1.1 Effect of temperature on hydrothermal liquefaction process at 30 minutes reaction time.

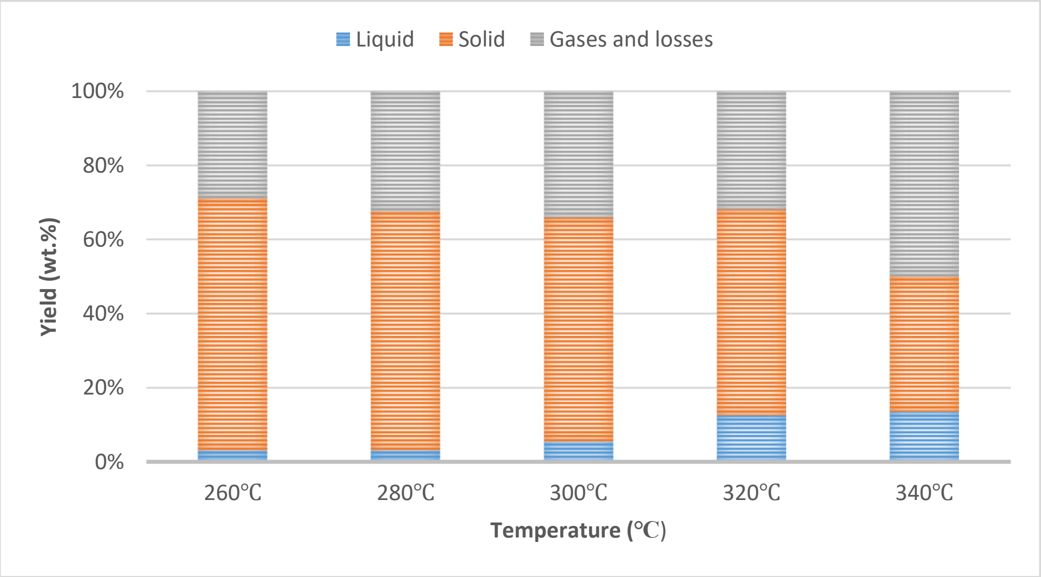


Figure 4.11: Product distribution at 30 minutes reaction time

As the temperature was increased from 260℃ to 280℃ there were no significant changes which were observed on the liquid bio-crude oil as the yield remained constant at 3.13 wt.%, liquefaction of biomass at a low temperature produces an insignificant amount of liquid oils especially at a shorter time, and promotes the formation of biochar [81]. However, when the temperature was increased to 300℃, the yield of the liquid bio-crude oil increased to 5.47 wt.% and the yield of solid bio-char decreased from 64.54 wt.% to 60.51 wt.%. It is evident from Figure 4.11 that lower temperature can lead to incomplete conversion thereby promoting the formation of solid biochar as well as gaseous products and losses. Higher temperature promotes enforced bond cessation and also promotes hydrolysis of biomass macromolecules and this has resulted in the yield of biomass to increase from 11.36 wt.% to 12.5 wt.% as the temperature was increased to 320℃. The highest liquid biofuel of 18.75 wt% was obtained at 340℃, it can also be seen that the yield of the liquid bio-crude oil increased with an increase in temperature whereas the yield of the solid biochar decreased from 68.08 wt.% to 50.61 wt.% as the temperature was increased from 260℃ to 340℃. A further increase in temperature has resulted in the solid biochar yield to decrease from 55.56 wt.% to 50.61 wt.%. Moreover, as the temperature was increased from 260℃ to 340℃, the yield of the gaseous products and losses increased from 28.79 wt.% to 69.36 wt.%.

4.2.1.2 Effect of temperature on hydrothermal liquefaction process at 60 minutes reaction time.

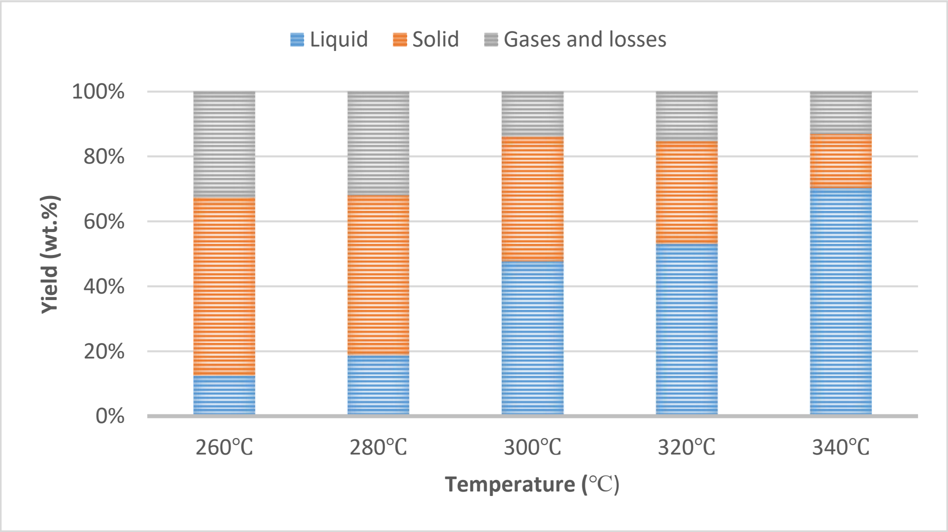


Figure 4.12: Product distribution at 60 minutes reaction time

The effect of temperature on product distribution was also studied at 60 minutes. At 260℃ the obtained yield of liquid bio-crude oil was 12.50 wt.%, when the temperature was increased from 260℃ to 280℃ the yield increased to 18.75 wt.%. Increasing the temperature also resulted in an increase in the yield of liquid bio-crude oil while the yield of solid biochar and gaseous products and losses decreased. A further increase in temperature to 320℃ promoted the high yield of liquid bio-crude oil of 53.13 wt.% and at 340℃, the highest yield of liquid bio-crude oil peaked at 70.31 wt.% with 16.61 wt.% of solid biochar and 13.08 wt.% of gaseous products and losses. The observed trend was the increase in the yield of liquid bio-crude oil as the temperature was increased from 260℃ to 340℃. Moreover, the yield of the solid biochar together with the yield of gaseous products and losses decreased as the temperature was increased from 260℃ to 340℃. An increase in the yield of liquid biofuel with an increase in temperature is caused by hydrolysis or depolymerization reaction of biomass into smaller compounds that form liquid biofuel. The energy to overcome activation energy increases with an increase in temperature and extensive biomass depolymerization occurs which results in higher oil yield. Such variation of an increase in liquid biofuel yield with HTL reaction temperature is in good agreement with studies which were done previously by Jindal et al, who studied the catalytic hydrothermal liquefaction of waste furniture sawdust to bio-oil [81].

4.2.1.3 Effect of temperature on hydrothermal liquefaction process at 90 minutes reaction time

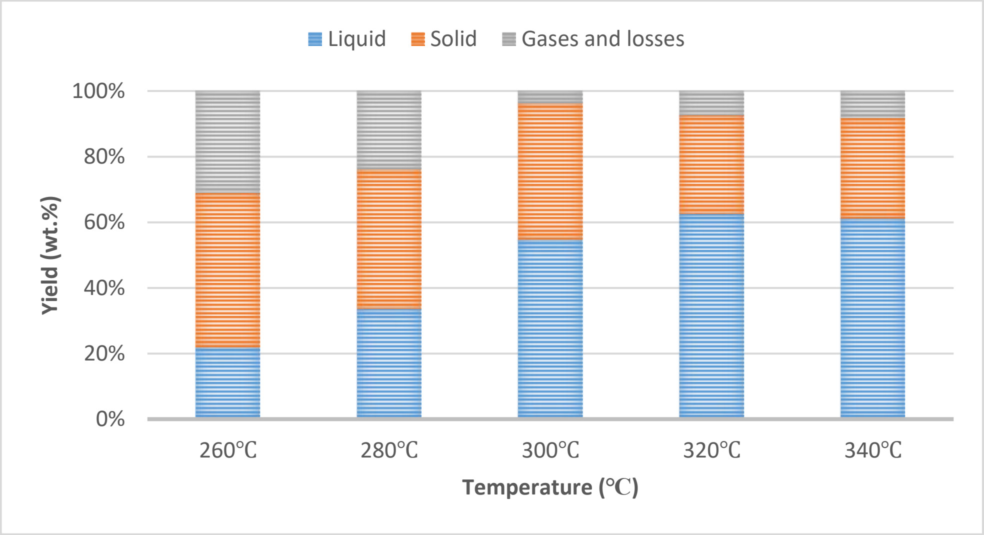


Figure 4.13: Product distribution at 90 minutes reaction time

At 90 minutes reaction time, with the same feedstock composition and the same temperature values, a study for the effect of temperature on product distribution was also conducted. It was found that as the temperature was increased from 260°C to 280°C, the yield of liquid bio-crude oil increased from 21.88 wt% to 33. 58 wt.%. A further increase in temperature to 300°C gave a yield of 54.69 wt.%. Moreover, the highest liquid bio-crude oil yield of 62.50 wt.% was obtained at 320°C, a further increase in temperature to 340°C resulted in a small decrease in the yield of liquid bio-crude oil to 61.72 wt%. It is evident from Figure 4.13 that as the temperature was increased from 260°C to 340°C, the yield of solid bio-char decreased from 47.1 wt.% to 30.9 wt%. In addition, the yield of gaseous products together with the losses decreased from 30.9 wt.% to 8.28 wt.% as the temperature was increased from 260°C to 340°C. When the operating temperature is around the sub-critical region, the dielectric constant; density, and polarity of water decrease, and this accelerates hydrolysis reaction which improves the solubility of hydrophobic organic compounds [82].

4.2.1.4 Effect of temperature on hydrothermal liquefaction process at 120 minutes

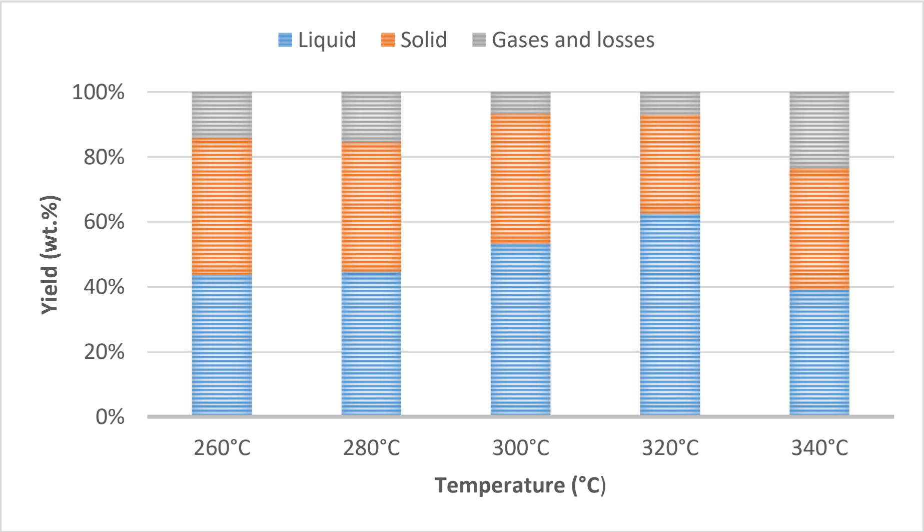


Figure 4.14: Product distribution at 120 minutes reaction time

At 120 minutes reaction time, as the temperature was increased from 260℃ to 280℃, the yield of the liquid bio-crude oil increased from 43.75 wt.% to 44.53 wt%. And a further increase in temperature to 300℃ resulted in the yield of liquid bio-crude oil to increase to 53.13 wt.%. The highest yield of liquid bio-crude oil of 62.50 wt.% was obtained at 320℃ and drastically decreased to 39.06 wt.% with the further increase in temperature to 340℃. The decrease in the yield of liquid bio-crude oil at a temperature above 320℃ is likely to be caused by the thermal cracking of oil compounds into gaseous or water-soluble products into producing 37.66 wt.% of solid biochar and 23.28 wt.% of gaseous products and losses. Moreover, at a higher temperature, thermal cracking could also form lighter and more volatile oil compounds that were not able to be recovered as they were lost during the solvent evaporation stage for liquid biofuel recovery. The yield of the solid biochar drastically decreased from 42. 19 wt.% at 260℃ to 30.61 wt.% at 320℃, and thereafter increased to 37.66 wt.% at 340℃. This could be due to the endothermic nature of biomass macromolecules degradation, when increasing the reaction temperature more fractions of the biomass macromolecules were liquefied and then converted into liquid bio-crude oil, solid biochar, and gaseous products together with the losses. Moreover, a further increase in temperature above the critical point favor carboxylation and steam reforming of the biofuel product and lead to the formation of biochar, gases, and aqueous phase as shown in the figure above [81]. The obtained results are in agreement with the study done by Jindal et al, According to Jindal et al, product distribution mainly depends on temperature and bio-crude oil yield increased with the rise in temperature from 180℃ to 280℃ meanwhile the yield decreased with a temperature of above 300℃.

4.2.1.5 Effect of temperature on hydrothermal liquefaction process at 150 minutes

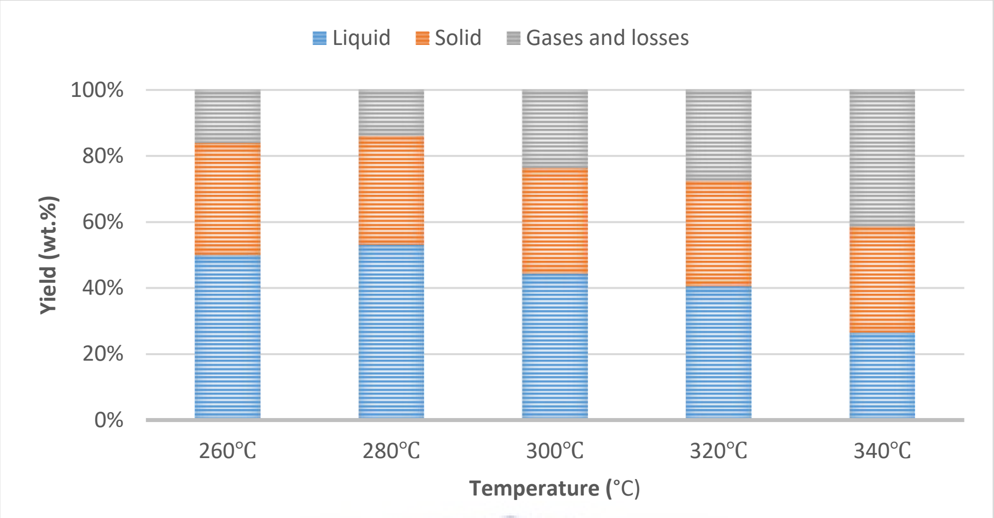


Figure 4.15: Product distribution at 150 minutes reaction time

At 150 minutes reaction time, the yield of liquid bio-crude oil increased from 50 wt.% to 53.13 wt.% when the temperature was increased from 260°C to 280°C. When the process temperature was further increased to 300°C, the yield decreased to 44.53 wt.%. A further increase in temperature to 320°C resulted in the yield of liquid bio-crude to decreased to 40.63 wt.%. A much lower yield of liquid bio-crude oil of 26.56 wt.% was achieved when the temperature was further increased to 340°C. When the reaction temperature was increased from 280°C to 340°C the liquid bio-crude oil yield decreased from 53.13 wt.% to 26.26 wt.% and was accompanied by an increase in the yield of gaseous products together with the losses from 13.91 wt.% to 41.30 wt.%. The observed trend was a resultant of the thermal conversion of liquid bio-crude oil into a gaseous product which indicate that polymerization reaction is not favored at higher temperatures [1]. Moreover, liquid biofuel can be destructed at higher temperatures and can rearrange through intermolecular or intramolecular cyclization, condensation, and polymerization reactions to form new set compounds which can either be favored in the aqueous phase or escape as gases or can result in char. Such a strong dependency of biofuels on temperature has been reported in previous studies [81], [83], [84]. The results obtained are in agreement with Tekin et al, on the study of hydrothermal liquefaction of beech wood and obtained the highest bio-oil yield of 24 wt.% at 250°C and lowest bio-oil yield of 9 wt.% at 350°C [83] the results obtained are similar to the ones of Wang et al, who concluded that temperature range of 300-315°C is suitable for high production of liquid oils, in the findings highest bio oil was obtained at 300℃ and lowest bio oil yield was obtained at 350℃ [84] .

4.2.2 Effect of reaction time

The effect of time on product distribution was also studied in different times; 30 minutes, 60 minutes, 90 minutes, 120 minutes, and as well as 150 at 260℃-340℃.

4.2.2.1 Effect of residence time on hydrothermal liquefaction process at temperature of 260℃

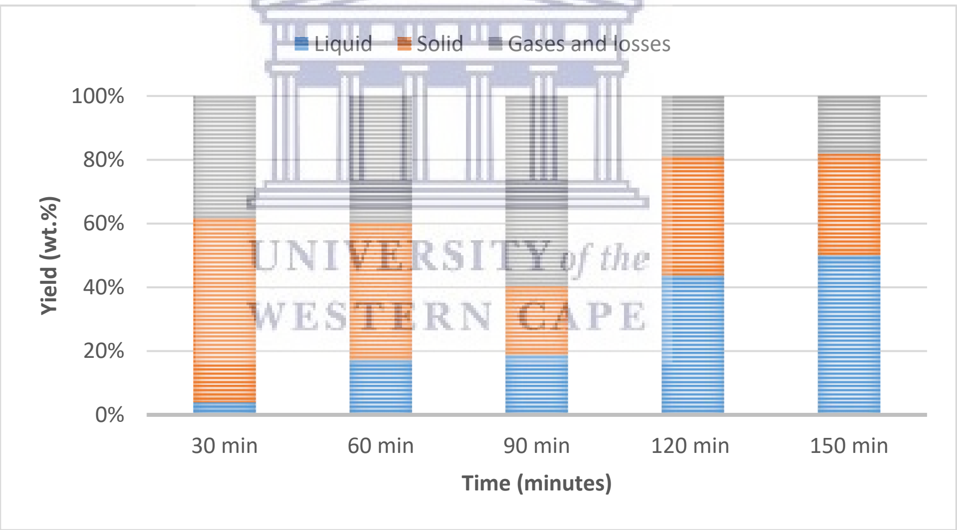


Figure 4.16: Product distribution at reaction temperature of 260℃

As the reaction time was increased from 30 minutes to 90 minutes, the yield of the liquid bio-crude oil increased from 3. 91 wt.% to 17.19 wt.%, the yield of solid biochar decreased from 57.9 wt.% to 43.11 wt.%. Obtaining a lower amount of liquid biofuels and higher amount of solid and gaseous products together with the losses can be a result of insufficient residence time which lead to an incomplete conversion process [70]. When the reaction time was prolonged to 90 minutes, the yield of the liquid bio-crude oil increased to 21.88 wt.%, with a sudden increase in the yield of gases together with the losses from 38.19 wt.% to 59.63 wt.% Moreover, when the reaction time was further increased to 120 minutes the yield of the liquid bio-crude oil increased to 43.75 wt.%. The highest yield of liquid bio-crude oil of 50 wt.% was obtained at the residence time of 150 minutes. The yield of the liquid bio-crude oil increased from 3.19 wt.% to 50 wt.% as the reaction time was increased from 30 minutes to 150 minutes meanwhile the yield of solid biochar decreased from 57.9 wt.% to 31.88 wt.%. Moreover, the yield of gaseous products together with the losses decreased from 38.19 wt.% to 18.12 wt.% as the reaction time was increased from 30 minutes to 150 minutes. These findings are similar to the study done by Sreenivasan et al, on Bails mediated catalytic thermos liquefaction to convert municipal solid waste into carbon densified liquid and obtained that residence time has significant impact on process commercialization and enhancement, in the findings, an increase in residence time results in the increase in liquid biofuels.

4.2.2.2 Effect of residence time on hydrothermal liquefaction process at temperature of 280℃

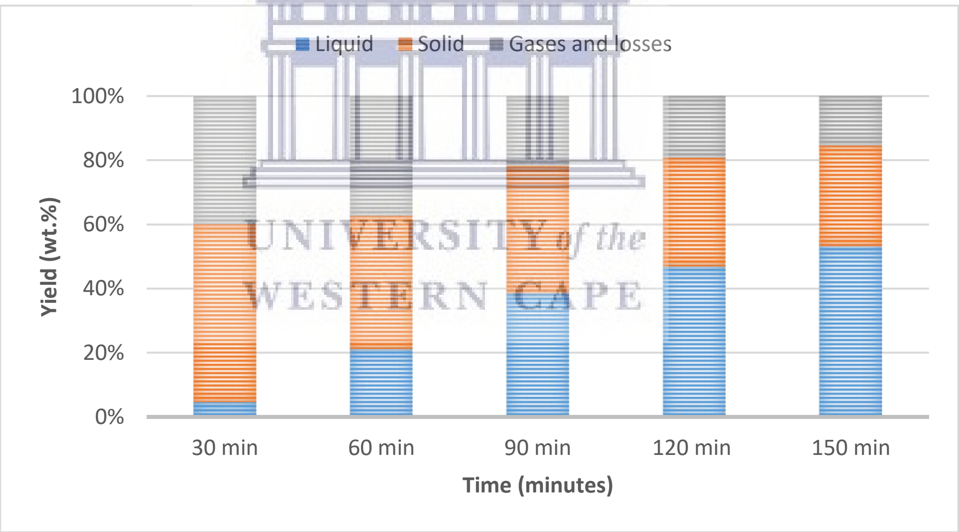


Figure 4.17: Product distribution at reaction temperature of 280℃

At 280℃ reaction temperature, with the same feedstock composition, it is evident from Figure 4.17 that longer residence time promoted higher yield of liquid bio-crude oil and smaller yield of solid biochar and gases together with the losses. When the residence time was increased from 30 minutes to 60 minutes, the yield of liquid bio-crude oil increased from 4.69 wt.% to 21.09 wt% meanwhile the yield of solid biochar decreased from 55.39 wt.% to 41.64 wt.%. A further increase in residence time from 90 minutes to 120 resulted in an increase in the yield of liquid bio-crude oil from 38.59 wt.% to 46.88 wt.%, at these reaction times the yield of gases together with the losses decreased from 21.77 wt.% to 19.13 wt.%. A further increase in residence time to 150 minutes resulted in the highest yield of liquid bio-crude oil to be 53.13

wt.%, meanwhile the yield of gases and losses was 15.36 wt.%. The observed trend was the increase in the yield of liquid bio-crude oil as the reaction time was prolonged, however prolonging the reaction time did not favour solid biochar yield as the yield decreased at longer reaction time. In addition, the yield of gases together with the losses decreased as the reaction time was prolonged.

4.2.2.3 Effect of residence time on hydrothermal liquefaction process at temperature of 300°C

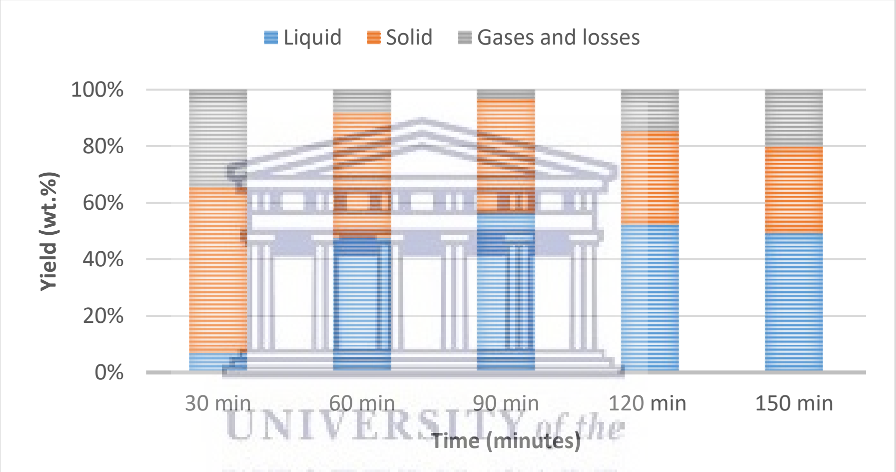


Figure 4.18: Product distribution at reaction temperature of 300°C

The yield of the liquid bio-crude oil increased as the reaction time was increased. The yield of the liquid bio-crude oil increased as the reaction time was increased but when the reaction time was further increased, the yield of the liquid bio-crude oil decreased. At 30 minutes, the yield of liquid bio-crude oil was 7.03 wt.%, meanwhile the yield of solid biochar was 58.61 wt.% and the yield of gases together with the losses was 34.31 wt.%. When the reaction time was increased from 60 minutes to 90 minutes, the yield of the liquid bio-crude oil increased from 47.66 wt.% to 56.25 wt.%, the yield of solid bio-char decreased from 44.41 wt.% to 40.51 wt.% and the yield of gases together with the loses decreased from 7.93 wt.% to 3.24 wt.%. However, a further increase in residence time to 120 minutes resulted in the yield of liquid bio-crude to decrease to 52.34 wt.%, the yield of gases together with loses increased to 14.67 wt.% and the yield of solid biochar decreased to 32.99 wt.%. Moreover, as the reaction time was further increased to 150 minutes, the yield of the liquid bio-crude oil further decreased to 49.22 wt.%.

Extending the duration of the reaction can accelerate the gas and char formation and this can be caused by the occurrence of secondary and tertiary reactions [19].

4.2.2.4 Effect of residence time on hydrothermal liquefaction process at temperature of 320°C

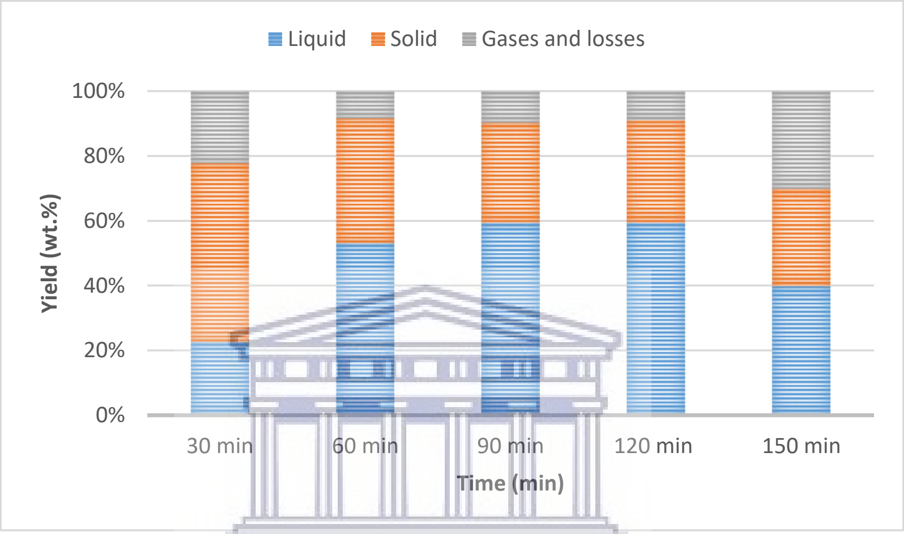


Figure 4.19: Product distribution at reaction temperature of 320°C

At 30 minutes reaction time, the yield of liquid bio-crude oil was 22.66 wt.%, the yield of solid biochar was 55.11 wt.% and the yield of gases together with the loses was 22.23 wt.%. When the reaction time was increased to 90 minutes the yield of the liquid bio-crude oil also increased to 53.13 wt.% meanwhile the yield of solid biochar decreased to 38.45 wt.%. With the further increase in reaction time to 120 minutes the yield of liquid biofuel remained constant at the value of 59.38 wt.%. A further increase in the reaction time to 150 minutes resulted in the decrease in the yield of liquid bio-crude oil to 39.48 wt.%, the yield of solid bio-char decreased to 30.11 wt.% and the yield of gases together with the losses increased to 30.05 wt.%. From Figure 4.19, it can be seen that excessive reaction time caused the liquid bio-crude oil to undergo secondary reactions such as decomposition, polymerization, etc. Secondary reactions resulted in a lower amount of liquid bio-crude oil, and promoted higher formation of gases together with the losses as well as solid biochar. The obtained results are in agreement with Yin et al., who found that irrespective of the process, longer reaction time resulted in the decreased the bio-oil yield [38].

4.2.2.5 Effect of residence time on hydrothermal liquefaction process at temperature of 340°C

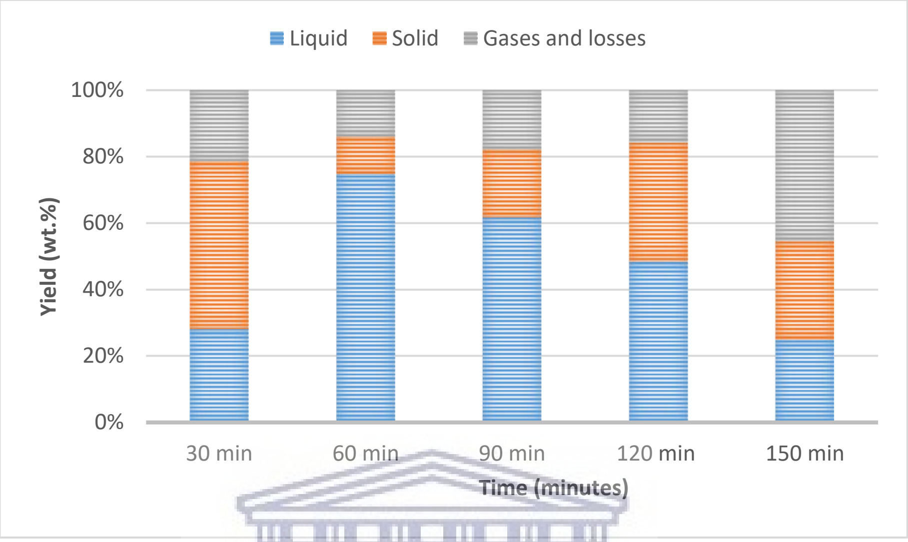


Figure 4.20: Product distribution at reaction temperature of 340°C

The same trend of the decrease in the yield of the liquid bio-crude oil with the increase in the yield of solid biochar, gases as well as losses at longer reaction was also observed at 340℃ reaction temperature. 28.13 wt.% yield of liquid bio-crude oil was achieved at 30 minutes reaction time, and 21.36 wt.% yield of gases and loses was achieved. Shorter reaction time at higher temperatures gave the highest yield of liquid bio-crude oil and this was observed when the residence time was increased to 60 minutes. At 60 minutes reaction time, the highest yield that amounted to 70.31 wt.% was achieved. But a further increase in residence time to 90 minutes resulted in the decrease in the yield of liquid bio-crude oil to 61.72 wt.%, and the yield of gases and loses decreased to 17.67 wt.%. When the reaction time was further increased from 120 minutes to 150 minutes, the yield of liquid bio-crude oil decreased to 25 wt%. A decrease in the yield of liquid bio-crude oil at longer residence time resulted from subsequent cracking which can either form gaseous or light products or can undergo repolymerization to form solid residues of liquid bio-crude oil yield. This tendency is consistent with the results obtained in the previous studies [38], [70].

4.2.3 Effect of composition

In order to investigate the effect of composition on product distribution, hydrothermal liquefaction experiments with various compositions of agricultural waste and food waste feedstock in a; 100:0, 75:25, 50:50, 25:75, and 0:100 ratio were performed at five different times: 30-150 minutes. 320℃ was selected as the reaction temperature to investigate the effect of composition on product distribution.

4.2.3.1 Effect of composition on hydrothermal liquefaction process at 30 minutes reaction time

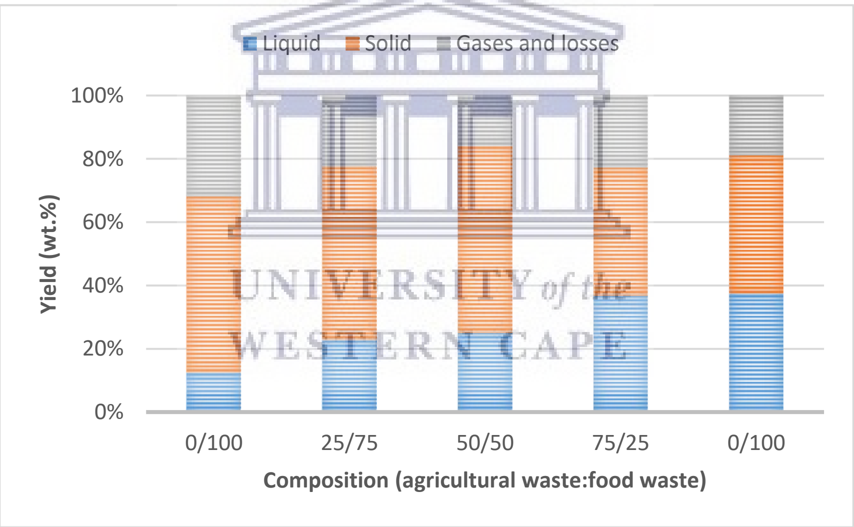


Figure 4.21: Product distribution at 30 minutes reaction time

As the amount of agricultural waste was increased with the decrease in the amount of food waste from a 0:100 ratio to 25:75 ratio, the yield of the liquid bio-crude oil increased from 12.5 wt.% to 22.66 wt.%, the yield of gases and losses decreased from 31.84 wt.% to 22.23 wt.%. When the amount of agricultural waste was further increased with a further decrease in the amount of food waste to a 50:50 ratio, the yield of liquid bio-crude oil increased to 25 wt.% , the yield of solid biochar drastically increased to 59.1 wt.% and the yield of gases and loses decreased to 15.9 wt.%. Moreover, when the amount of agricultural waste was further increased with the further decrease in the amount of food waste to 75:25 ratio, the yield of the liquid bio-crude oil increased to 36.72 wt. %, the yield of solid biochar decreased to 40.61 wt.% and the yield of gases and loses suddenly increased to 22.67 wt.%. The highest yield of liquid bio-crude oil of 37.5 wt.% was obtained when the amount of agricultural waste was increased with the decrease in the amount of food waste to a 100:0 ratio. The observed trend was the increase in the yield of liquid bio-char with the decrease in the yield of solid biochar as well as gases and losses as the amount of agricultural waste in the feedstock was increased with the decrease in the amount of food waste from 0:100 ratio to 100:0 ratio. The observed trend was possibly due to the water readily dissolving relatively light molecules from the intermediates of agricultural waste than high molecular intermediates from food waste.

4.2.3.2 Effect of composition on hydrothermal liquefaction process at 60 minutes reaction time

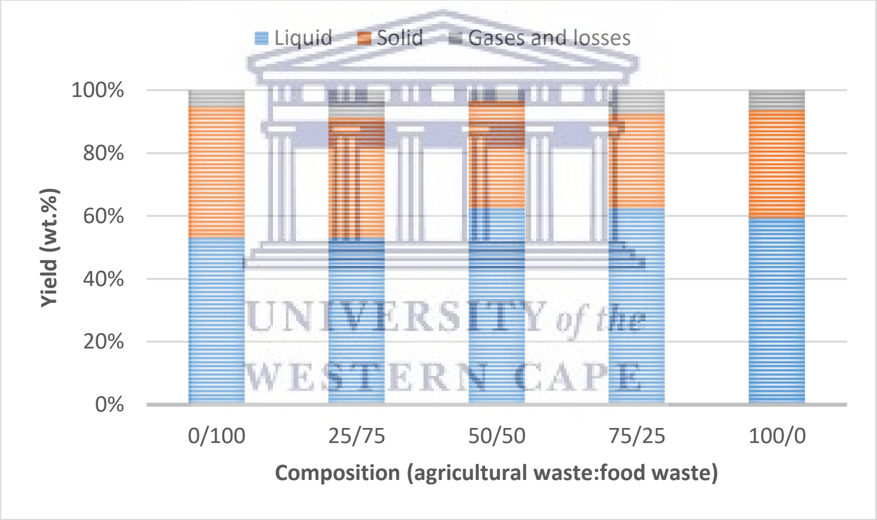


Figure 4.22: Product distribution at 60 minutes reaction time

The effect of composition on product distribution was also studied at 60 minutes. At 0:100 ratio of agricultural waste and food waste, the obtained yield of liquid bio-crude oil was 53.13 wt.%, solid biochar yield was 41.66 wt.% and the yield of gases and loses was 5.21 wt.%. When the amount of agricultural waste was increased with the decrease in the amount of food waste to a 50:50 ratio, the yield of liquid bio-crude oil increased to 62.5 wt.%, the yield of solid biochar decreased to 34.12 wt.% and the yield of gases and losses also decreased to 7.39 wt.%. A further increase in the amount of agricultural waste with the decrease in the amount of food waste to a 100:0 ratio also resulted in a decrease in the yield of liquid bio-crude oil to 59.38 wt.% while the yield of solid biochar and gaseous products and losses decreased. The observed trend was the increase in the yield of liquid bio-crude oil with the decrease in the yield of solid biochar and gases and losses as the amount of agricultural waste in the feedstock was increased with the decrease in the amount of food waste from 0:100 ratio to 100:0 ratio.

4.2.3.3 Effect of composition on hydrothermal liquefaction process at 90 minutes reaction time

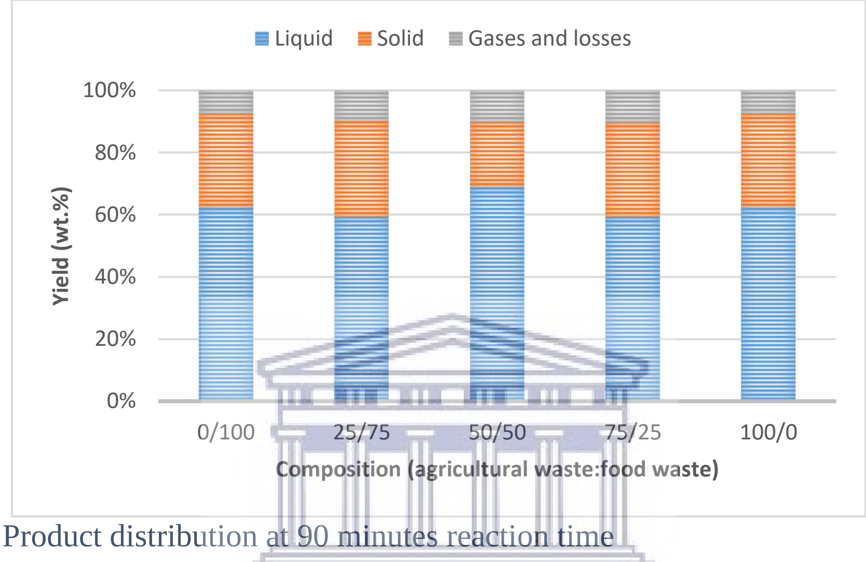


Figure 4.23: Product distribution at 90 minutes reaction time

The yield of the liquid bio-crude oil increased as the amount of agricultural waste was increased with the decrease in the amount of food waste but when the amount of agricultural waste was further increased with the further decrease in the amount of food waste, the yield of the liquid bio-crude oil decreased. At 0:100 ratio of agricultural waste and food waste, the yield of liquid bio-crude oil was 62.5 wt.%, meanwhile the yield of solid biochar was 30.16 wt.% and the yield of gases together with the losses was 7.35 wt.%. When the amount of agricultural waste was increased with the decrease in the amount of food waste from 25:75 ratio to 50:50 ratio, the yield of the liquid bio-crude oil increased from 59.38 wt.% to 68.75 wt.%, the yield of solid bio-char decreased from 30.99 wt.% to 20.93 wt.% and the yield of gases together with the loses increased from 9.63 wt.% to 10 wt.%. However, a further increase in the amount of agricultural waste with the decrease in the amount of food waste to 75:25 ratio resulted in the yield of liquid bio-crude to decrease to 59.38 wt.%, and the yield of solid biochar increased to 30.15 wt.%. Moreover, as the amount of agricultural waste was further increased with the further decrease in the amount of food waste to 100:0 ratio, the yield of the liquid bio-crude oil further increased to 62.5 wt.%.

4.2.3.4 Effect of composition on hydrothermal liquefaction process at 120 minutes reaction time

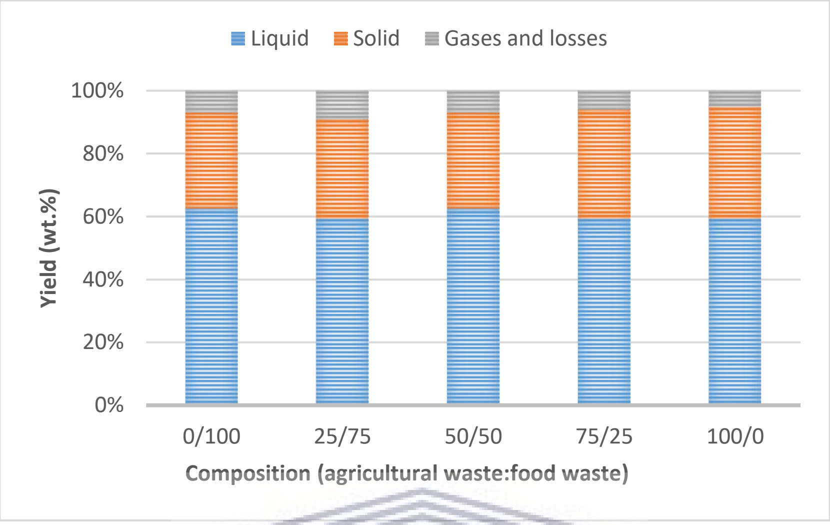


Figure 4.24: Product distribution at 120 minutes reaction time

At 120 minutes reaction time, as the amount of agricultural waste was increased with the decrease in the amount of food waste from 0:100 ratio to 25:75 ratio, the yield of the liquid bio-crude oil decreased from 62.5 wt.% to 59.38 wt.%. A further increase in the amount of agricultural waste with the decrease in the amount of food waste to 50:50 ratio resulted in the yield of liquid bio-crude oil to increase to 62.5 wt.%, increase in the yield of solid biochar to 30.61 and decrease in the yield of gases and losses to 6.89 wt.%. The highest yield of liquid bio-crude oil of 59.38 wt.% was obtained at 75:25 ratio and 100:0 ratio of agricultural waste and food waste. The solid biochar yield increased with the further increase in the amount of agricultural waste with the decrease in the amount of food waste from 6.89 wt.% at 0:100 ratio to 35.57 wt.% at 100:0 ratio of agricultural waste and food waste. At all the compositions, yield of solid biochar is obtained from metals and other inorganic materials which were present in the feedstock, while the gases and loses were more dependent on water and solvent extraction reaction.

4.2.3.5 Effect of composition on hydrothermal liquefaction process at 150 minutes reaction time

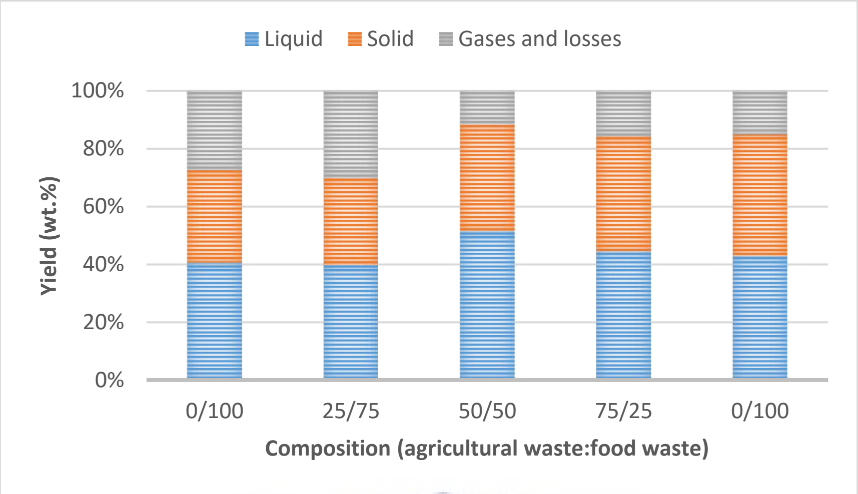


Figure 4.25: Product distribution at 150 minutes reaction time

The effect of the composition of the feedstock on product distribution was also studied at 150 minutes reaction time, the yield of liquid bio-crude oil increased from 40.63 wt.% to 51.56 wt.% when the amount of agricultural waste was increased with the decrease in the amount of food waste from 0:100 ratio to 50:50 ratio. When the amount of agricultural waste was further increased with the decrease in the amount of food waste, the liquid bio-crude oil yield decreased to 44.53 wt.%. A further increase in the amount of agricultural waste with the further decrease in the amount of food waste to 100:0 ratio resulted in the yield of liquid bio-crude to decrease to 42.97 wt.%. The solid biochar yield increased with the increase in the amount of agricultural waste with a decrease in the amount of food waste from 0:100 ratio to 100:0 ratio. Moreover, the yield of gases and loses decreased from 27.46 wt.% to 15.03 wt.% as the ratio of agricultural waste and food waste was changed from 0:100 to 100:0.

4.3 Effect of process parameters on chemical composition of bio-crude oil products

There is no available literature on the characterisation of bio-crude oil obtained from agricultural waste such as grape leaves and food waste such as potato peels. The major chemical compounds present in the bio-crude oil were analysed using GC-MS. The effect of temperature on the product distribution has been studied at temperatures in the range of 260-340°C for different reaction times, 30 minutes, 60 minutes, 90 minutes, 120 minutes, and 150 minutes. Many volatile chemical compounds were detected by the GC-MS, and they were grouped into classes:

- Oxygenated compounds including ketones, alcohol, ethers, esters, and aldehydes,
- Organic acids including fatty acids, carboxylic acids, and fatty acids methyl esters
- Cyclic oxygenate including furans and pyrans
- Aromatics including phenols, phenyls, and arenes,
- Nitrogenated compounds including azides, amines, amides, nitriles, imines, and azoles
- Hydrocarbons including straight chains of alkanes, alkenes and alkynes

4.3.1 Effect of temperature

4.3.1.1 Effect of temperature on the chemical composition of bio-crude oil produced at 30 minutes reaction time

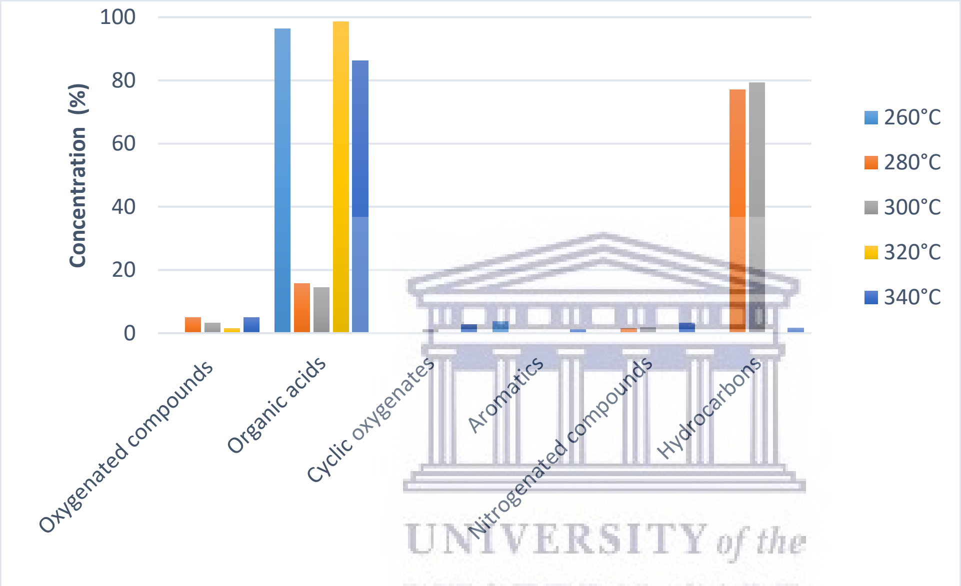


Figure 4.26: Major compounds detected using GC-MS in the bio-crude oil obtained from the hydrothermal liquefaction process at 260-340°C at a reaction time of 30 minutes.

From Figure 4.26, small amounts of oxygenated compounds, cyclic oxygenates, aromatics as well as nitrogenated compounds were detected by the GC-MS at all the temperatures. There was no observed trend on the concentration of the volatile compounds as the temperature was increased. Temperature played no effect in the formation of those compounds. For oxygenated compounds, the concentration slightly increased from 4.98% to 5.01% as the reaction temperature was increased from 280°C to 340°C. At 260°C reaction temperature, 3.64% of aromatics were detected. As the reaction temperature was increased from 260°C to 340°C, aromatics were not detected. Moreover, 96.35% of the organic acids were detected at 260°C reaction time, and drastically decreased to 15.78% as the reaction temperature was increased to 280%. A further increase in the reaction temperature to 340°C, resulted in the sudden increase in the concentration of organic acids as 86.27% was detected. At 260°C, no hydrocarbons were detected. There was a decrease in the concentration of the hydrocarbons from 77.05% to 1.63% as the reaction temperature was increased from 280°C to 340°C. Temperature played no role in the formation of cyclic oxygenates as well as nitrogenated compounds as their detection was minimal at all temperatures.

4.3.1.2 Effect of temperature on the chemical composition of the bio-crude oil produced at 60 minutes reaction time

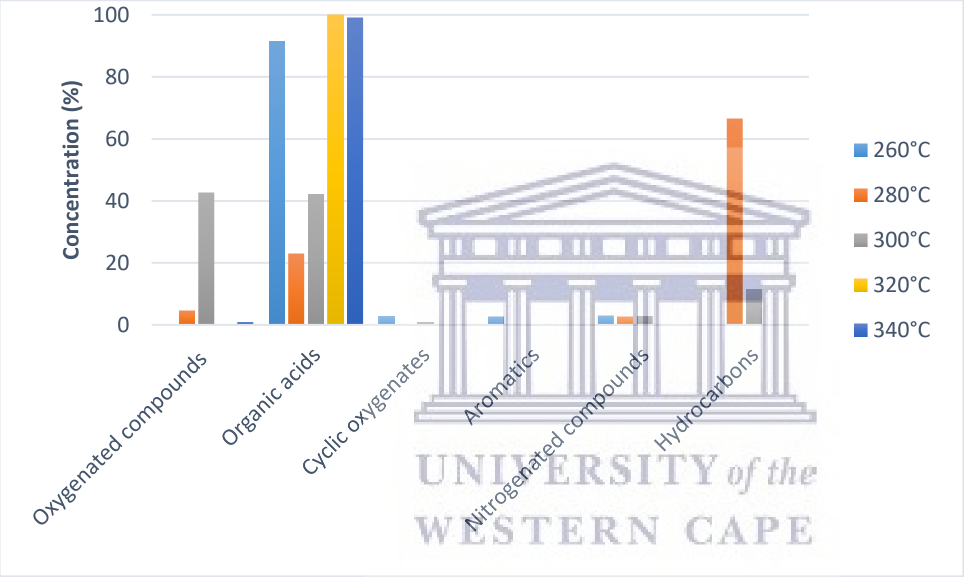


Figure 4.27: Major compounds detected using GC-MS in the bio-crude oil obtained from the hydrothermal liquefaction process at 260-340°C at a reaction time of 60 minutes.

Higher concentrations of organic acids, oxygenated compounds and hydrocarbons were detected. At 260°C, 91.57% of organic acids were detected. However, there was a drastic decrease in the concentration when the temperature was raised to 280°C, at this temperature, 22.94% was detected. A further increase in the temperature to 300°C resulted in the concentration of organic acids to increase to 42.22%, and a further increase in temperature to 340°C resulted in the increase in concentration to 99.08%. The observed trend was quite different for the hydrocarbons, at 260°C hydrocarbons were not detected. As the temperature was raised to 280°C, there was a drastic increase in the concentration to 66.49%. However, when the temperature was further raised to 340°C, no hydrocarbons were detected. The concentration of oxygenated compounds increased from 4.62% to 42.64% as the reaction temperature was increased from 280°C to 300°C, however when the reaction temperature was further increased to 340°C, no oxygenated compounds were detected. Cyclic oxygenates, aromatics and nitrogenated compounds were detected at a lower concentration, and there was no observed trend in their concentration with the change in reaction temperature.

4.3.1.3 Effect of temperature on the chemical composition of bio-crude oil produced at 90 minutes reaction time

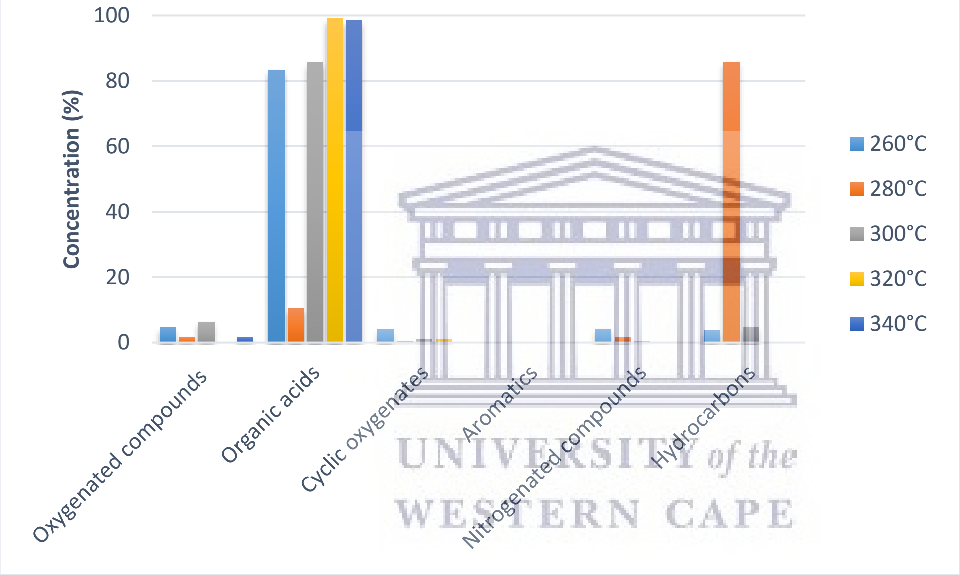


Figure 4.28: Major compounds detected using GC-MS in the bio-crude oil obtained from the hydrothermal liquefaction process at 260-340°C at the reaction time of 30 minutes.

83.4% of organic acids were detected at 260°C, however, when the reaction temperature was raised to 280°C, the concentration drastically decreased 10.4% and suddenly increased to 85.85% when the reaction temperature was increased to 300°C. Moreover, when the temperature was further increased to 340°C, 98.42% of organic acids were detected. The detected concentrations of nitrogenated compounds, oxygenated compounds and cyclic oxygenates were very minimal at all reaction temperatures.. The nitrogenated compounds which were detected include 9-octadecenamide(CAS), octadecenamide(CAS) and N-(n-heptyl)trifluoroacetamide. At all reaction temperatures, aromatics were not detected. The concentration of the hydrocarbons increased from 3.7% to 85.74% as the reaction temperature was increased from 260°C to 280°C. The concentration of the hydrocarbons drastically decreased to 4.63% as the reaction temperature was further raised to 300℃. Hydrocarbons were not detected at 320℃ and 340℃ reaction temperatures.

4.3.1.4 Effect of temperature on the chemical composition of bio-crude oil produced at 120 minutes reaction time

Figure 4.29: Major compounds detected using GC-MS in the bio-crude oil obtained from the hydrothermal liquefaction process at 260-340℃ at a reaction time of 120 minutes.

A high concentrations of organic acids such as isopropyl palmitate were detected in abundance at all temperatures, reaction temperature played no role for their formation during the hydrothermal liquefaction process. At 260℃ reaction temperature, 82.24% of organic acids were detected. When the reaction temperature was raised to 280℃, 56.09% of organic acids were detected and rapidly increased to 92.47% when the reaction temperature was 320℃. However, a further increase in temperature to 340℃ resulted in the rapid decrease in the concentration to 41.31%. An increase in reaction temperature resulted in an increase in the concentration of oxygenated compounds from 12.74% at 260℃ to 24.88% at 280℃ and peaked 30.91% when the temperature was further raised to 300℃. When the reaction temperature was further raised to 340℃, the concentration decreased to 3.07%. Oxygenated compounds detected include 2-furancarboxaldehyde,5-(hydroxymethyl), (7s)trans-syn-cis-Tricyclo[7.3.0.0(2,6)]dodecan-7-oldimethylpentafluorophenylsilyl ester and diazepin-1-one.

Cyclic oxygenates, nitrogenated compounds, aromatics and hydrocarbons were detected at lower concentrations.

4.3.1.5 Effect of temperature on the chemical composition of bio-crude oil produced at 150 minutes reaction time.

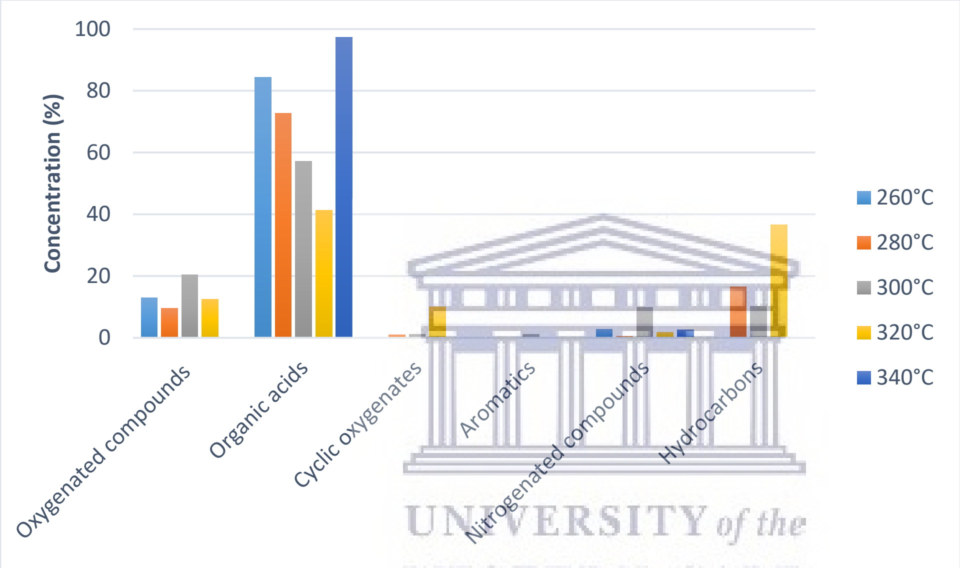


Figure 4.30: Major compounds detected using GC-MS in the bio-crude oil obtained from the hydrothermal liquid process at 260-340°C at a reaction time of 150 minutes.

At 150 minutes reaction time, hydrothermal liquefaction process promoted the formation of organic acids, oxygenated compounds and hydrocarbons than the formation of aromatis, cyclic oxygenates and nitrogenated compounds. High concentrations of organic acids were at all the temperatures, the observed trend was the decrease in the concentration from 84.32% to 41.31% as the reaction temperature was increased from 260°C to 320°C and drastically increased to 97.37% as the reaction temperature was further raised to 340°C. There was no observed trend in the concentrations of oxygenated compounds, cyclic oxygenates, aromatics and nitrogenated compounds as the reaction temperature was raised from 260°C to 340°C. At 260°C, no hydrocarbons were detected. As the reaction temperature was raised to 300°C, the concentration increased to 36.61% and a further increase in temperature to 340°C, no hydrocarbons were detected.

4.3.2 Effect of reaction time

4.3.2.1 Effect of temperature on the chemical composition of bio-crude oil produced at 260℃ reaction temperature.

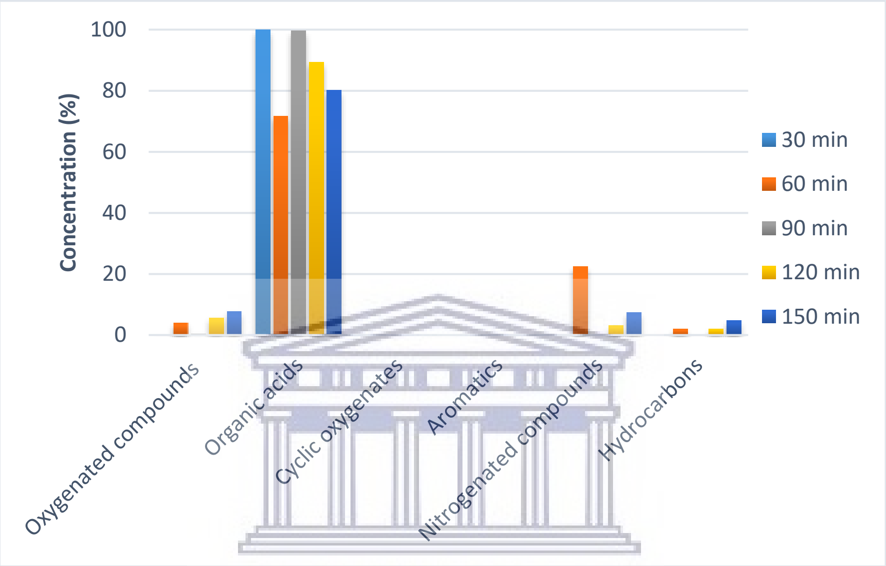


Figure 4.31: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 30-150 minutes at reaction temperature of 260℃

The bio-crude oils produced had high concentration of organic acids, during their production, residence time played no role. At 30 minutes reaction time, 100% of the organic acids were detected, but when the reaction time was increased to 60 minutes the concentration decreased to 71.64% and rapidly increased to 99.6% as the reaction time was increased to 90 minutes. A further increase in the reaction time resulted in the decrease in the concentration to 89.29% and further decreased to 80.16% as the reaction time was further prolonged to 150 minutes. Increasing the reation time to 90 minutes resulted in an increase in the content of the organic acids. At 30 minutes reaction time, nitrogenated compounds were not detected, an increase in the reaction time to 60 minutes resulted in the concentration of nitrogenated compounds to increase to 22.48%. Concentration of nitrogenated compounds suddenly decreased, at 90 reaction time, nitrogenated compounds were not detected and at 150 minutes reaction time, 7.41% was detected. Oxygenated compounds, nitrogenated compounds and hydrocarbons were detected at lower concentrations while cyclic oxygenates and aromatics were not detected. There has been an oxygenated compound content detected in all residence times.

4.3.2.2 Effect of temperature on the chemical composition of bio-crude oil produced at 280°C reaction temperature

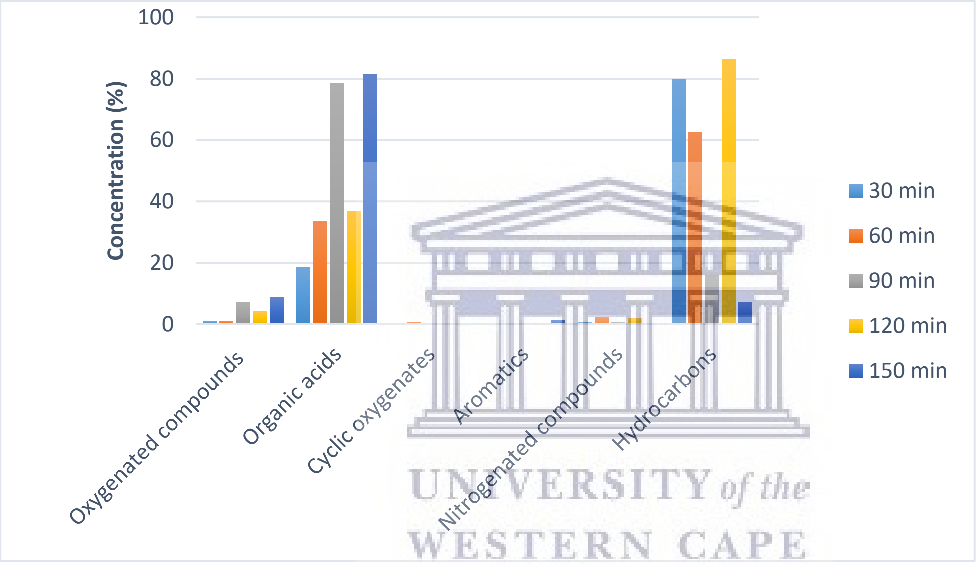


Figure 4.32: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 30-150 minutes at reaction temperature of 280°C

At all reaction times, cyclic oxygenates were not detected meanwhile aromatics and nitrogenated compounds were detected at lower concentration. There is no observed trend on detected concentrations of oxygenated compounds, organic acids as well as hydrocarbons with the change in time. 79.95% of hydrocarbons were detected at 30 minutes reaction time. An increase in the reaction temperature to 60 minutes resulted in the decrease in concentration to 62.43% and further decreased to 16.05% as the reaction time was increased to 90 minutes. A further increase in the reaction time to 120 minutes resulted in the rapid increase in the concentration to 86.21% and drastically decreased to 7.27% as the reaction time was further increased to 150 minutes. 18.44% of organic acids were detected at 30 minutes reaction time. An increase in the reaction time from 60 minutes to 90 minutes resulted in an increase in the concentration of organic acids from 33.63% to 78.53%. However, as the reaction time was further increased to 120 minutes, the concentration decreased to 36.9%. As the reaction time was further increased, the highest concentration peaked at 81.41% when the reaction time was further increased to 150 minutes.

4.3.2.3 Effect of temperature on the chemical composition of bio-crude oil produced at 300℃ reaction temperature

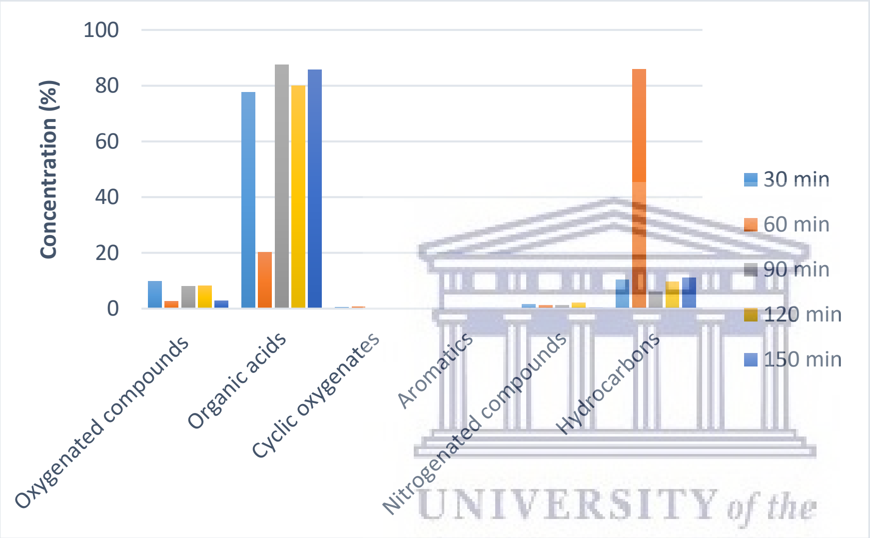


Figure 4.33: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 30-150 minutes at reaction temperature 300℃

Aromatics were not detected at all reaction times, while nitrogenated compounds and cyclic oxygenates were detected at lower concentrations. Reaction time played no role during their formation as there was no trend observed with the increase in reaction time. The concentration of the organic acids was 77.61% at 30 minutes. When the reaction time was increased to 60 minutes, the concentration decreased to 20.25% but suddenly increased to 87.45% at 90 minutes reaction time. A further increase in the reaction time to 150 minutes resulted in the decrease in the concentration to 79.95% and suddenly increased to 85.74% as the reaction time was increased to 150 minutes. 10.34% of hydrocarbons was detected at 30 minutes, and increased to 85.83% when the reaction time was increased to 60 minutes. There was a drastic decrease in the concentration to 9.56% as the reaction time was increased to 90 minutes. A further increase in the reaction time from 120 minutes to 150 minutes resulted in the concentration of the hydrocarbons to slightly increase from 9.56% to 11.1%.

4.3.2.4 Effect of temperature on the chemical composition of bio-crude oil produced at 320°C reaction temperature

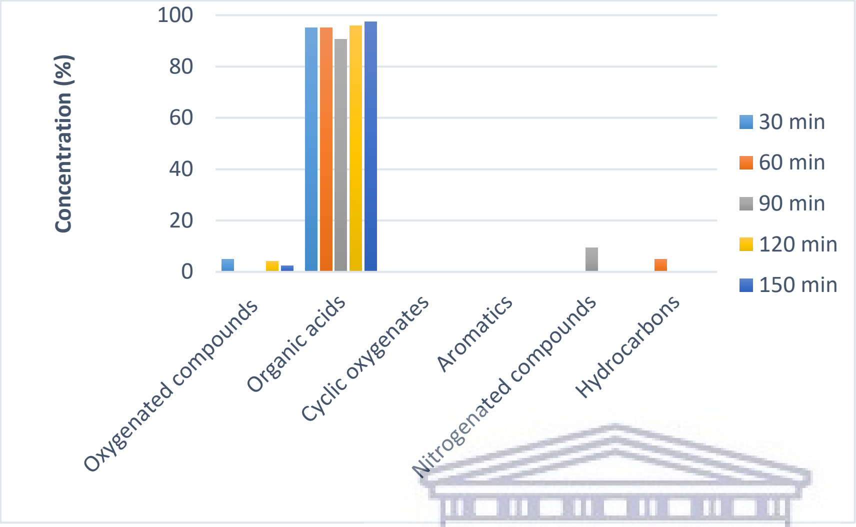


Figure 4.34: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 30-150 minutes at reaction temperature of 320°C.

Mostly organic acids were detected, and a small concentrations of nitrogenated compounds, oxygenated compounds and hydrocarbons were detected. Organic acids which were formed include isopropyl palmitate. Cyclic oxygenates and aromatics were not detected. Organic acids were detected in abundance at all the reaction times. The highest concentration of 97.52% of organic acids was detected in the bio-crude oil produced at 150 reaction minutes, however there was no trend observed in the detected concentrations of organic acids with the increase in the reaction time.

4.3.2.5 Effect of temperature on the chemical composition of bio-crude oil produced at 340°C reaction temperature

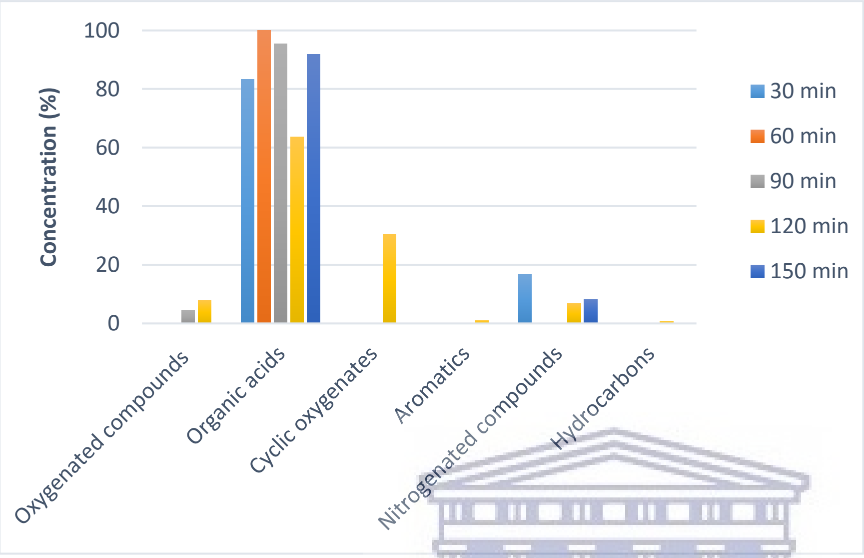


Figure 4.35: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 30-150 minutes at reaction temperature of 340°C

The GC-MS profile depicted the existence of several families of organic compounds such as oxygenated compounds, organic acids, cyclic oxygenates aromatics as well as nitrogenated compounds, and their detected concentrations depend on feedstock composition and have been obtained because of bond cleavage, and bond formation during condensation, dehydration, polymerization as well as elimination reactions. Hydrocarbons were not detected from the bio-crude oil detected at all reaction times. 16.64% of nitrogenated compounds was detected from the bio-crude oil produced at 30 minutes. As the reaction time was increased to 60 minutes, nitrogenated compounds were not detected in the bio-crude oil. As the reaction time was further increased from 120 minutes to 150 minutes, the concentration increased from 6.84% to 8.21%. For the bio-crude oil produced at all reaction times, there was no aromatics which were detected. The same trend was observed for cyclic oxygenates as well as oxygenated compounds, reaction time had no effect on the formation of these volatile compounds. High concentration of 30.45% of cyclic oxygenates was detected for the bio-crude oil obtained at 120 minutes. Oxygenated compounds which were detected include cyclononasiloxane-octadecamethyl, cyclooctasiloxane-hexadecamethyl as well as eicosamethylcyclodecasioxane.

4.3.3 Effect of composition

4.3.3.1 Effect of composition on the chemical composition of bio-crude oil produced at 30 minutes reaction time

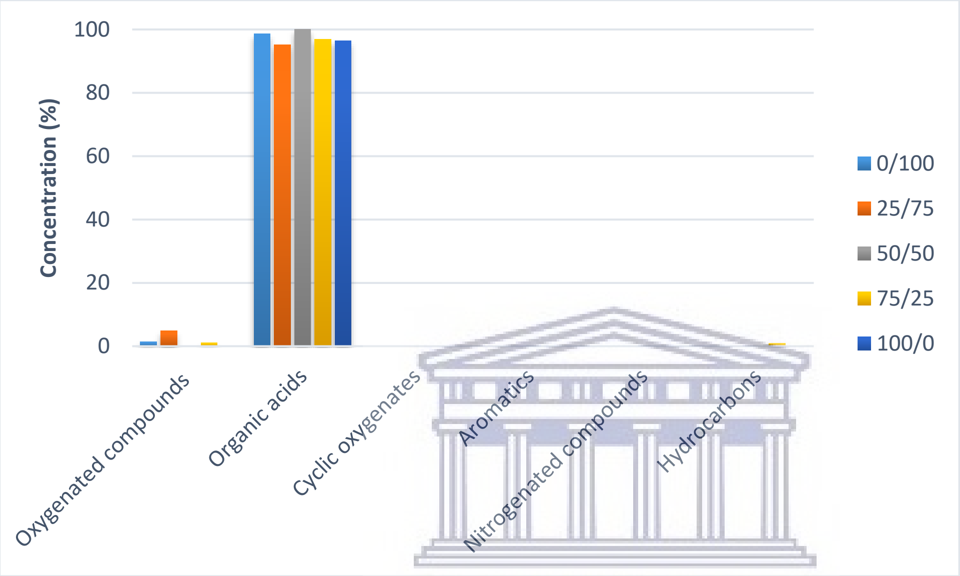


Figure 4.36: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 30 minutes reaction time

No concentrations of aromatics, cyclic oxygenates and nitrogenated compounds were detected from the bio-crude oil obtained at all compositions, meanwhile oxygenated compounds and hydrocarbons were detected in minimal concentrations. 98.59% of organic acids were detected from the bio-crude oil produced using 0:100 ratio of agricultural waste and food waste. When the amount of agricultural waste was increased with the decrease in the amount of agricultural waste to 25:75 ratio, the concentration decreased to 95.17% and suddenly increased to 100% for the bio-crude oil produced when the amount of agricultural waste was increased with the decrease in the amount of food waste to 50:50 ratio. However, when the amount of agricultural waste was further increased with the further decrease in the amount of food waste from 75:25 ratio to 100:0 ratio, the concentration detected in the bio-crude oil slightly decreased from 96.85% to 96.42%. It is evident from the graph in figure 4.36 above that composition played no role on the concentration of various volatile compounds.

4.3.3.2 Effect of composition on the chemical composition of bio-crude oil produced at 60 minutes reaction time

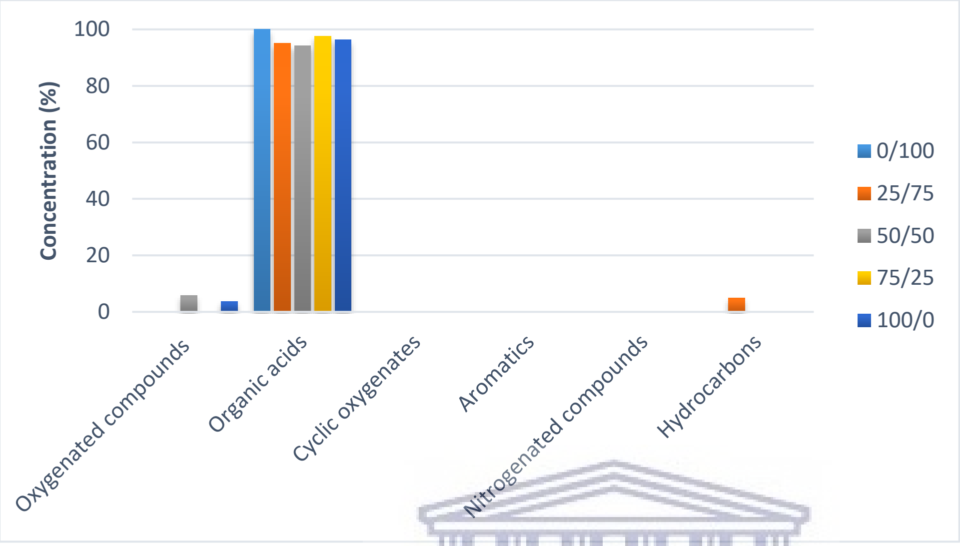


Figure 4.37: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 60 minutes reaction time

Cyclic oxygenates, aromatics and nitrogenated compounds were not detected from the bio-crude oil produced at all the compositions, while oxygenated compounds and hydrocarbons were detected a minimal concentrations. It is evident from figure 4.37 above that hydrothermal liquefaction favoured and promoted the formation of organic acids as these acids were detected a higher concentration while lowering the concentration or production of other volatile compounds such as aromatics, nitrogenated compounds as well as cyclic oxygenates. High concentration of organic acids was detected at all compositions, the highest concentration detected peaked to 100% and this was from the bio-crude oil obtained when food waste was only used as the feedstock in a 0:100 ratio.

4.3.3.3 Effect of composition on the chemical composition of bio-crude oil produced at 90 minutes reaction time

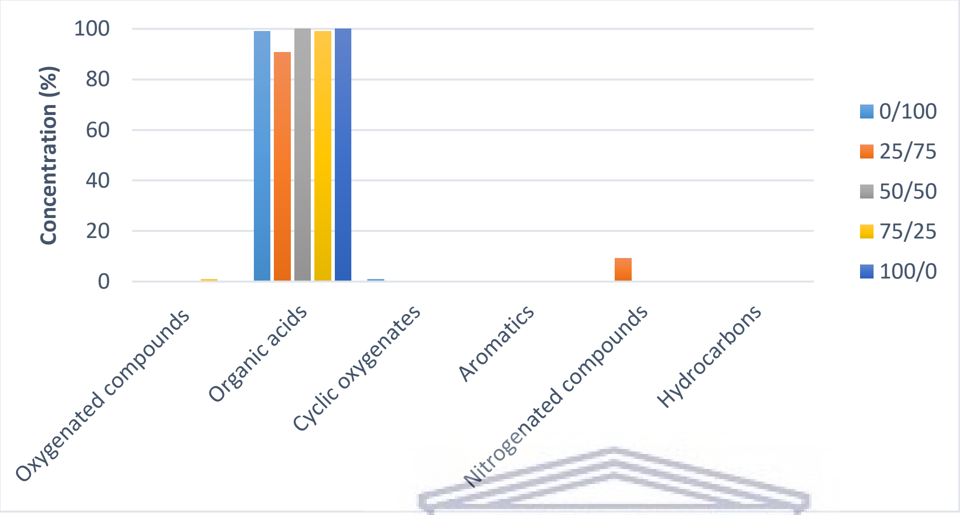


Figure 4.38: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 90 minutes reaction time.

The concentrations for aromatics and hydrocarbons were not detected from the bio-crude oil produced at all composition. Lower concentration of oxygenated compounds of 0.99% was detected from the bio-crude oil produced when the composition of the feedstock was agricultural waste and food waste in a 75:25 ratio. The highest concentration of nitrogenated compounds from bio-crude oil produced from agricultural waste and food waste in a 25:75 ratio peaked 9.31%. The highest concentration of organic acids that was detected peaked at 100%, and this was from the bio-crude oil produced when the composition of the feedstock was in 50:50 ratio as well as 100:0 ratio of agricultural waste and food waste. Because of the higher concentrations of organic acids and nitrogenated compounds and lower concentrations of oxygenated compounds, cyclic oxygenates, aromatics and hydrocarbons were detected, this showed that there was no breakdown of lignin and cellulose to form hydrocarbons, aromatics and acids but rather they were distributed into organic acids and nitrogenated compounds.

4.3.3.4 Effect of composition on the chemical composition of bio-crude oil produced at 120 minutes reaction time

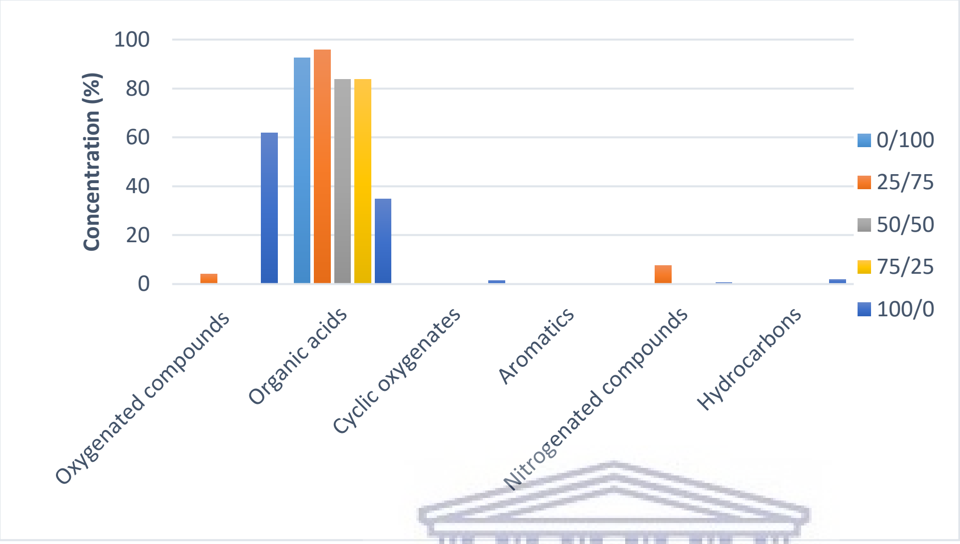


Figure 4.39: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 120 minutes reaction time.

The difference in the structures of the feedstocks has led to different components and volatile compounds to be present in the bio-crude oil. It is evident from Figure 4.39 above that composition played no role in the formation of the volatile compounds during hydrothermal liquefaction process. Highest detected concentration of oxygenated compounds peaked at 61.75%, this concentration was from the bio-crude oil obtained from agricultural waste and food waste in a 100:0 ratio. Isopropyl palmitate was amongst the organic acids that was detected at higher concentrations from the bio-crude oil obtained in all the compositions, and the highest concentration detected from the bio-crude oil obtained from the feedstock composed of agricultural waste and food waste in a 25:75 ratio peaked 95.85%.

4.3.3.5 Effect of composition on the chemical composition of bio-crude oil produced at 150 minutes reaction time

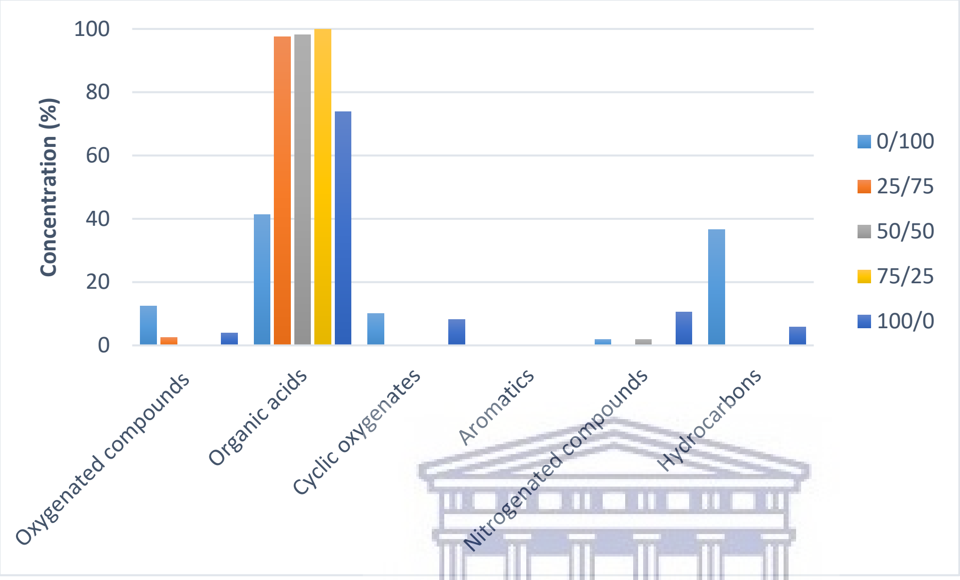


Figure 4.40: Major compounds detected using GC-MS in the bio-crude oil obtained from hydrothermal liquefaction process at 150 minutes reaction time

The concentrations of volatile compounds detected for the bio-crude oil produced at 150 minutes reaction were much higher for organic acids and nitrogenated compounds. Hydrocarbons, oxygenated compounds and cyclic oxygenates were detected in minimal concentrations. There is no trend observed with the change in composition therefore composition of the feedstock played no role during hydrothermal liquefaction process. The organic acids detected include long chain organic acids which include saturated fatty acid, monounsaturated fats and polyunsaturated fats. Moreover, oxygenated compounds detected include amides, alcohols as well as esters were detected at lower concentrations. The highest detected concentration of the organic acid peaked at 99.88% for the bio-crude oil obtained from agricultural waste and food waste in a 75:25 ratio.

There was no observed trend in the detection of the concentration of the volatile compounds from the bio-crude oil produced during the hydrothermal liquefaction process as the reaction time and reaction temperature was increased as well as the change in composition. The presence of oxygenated compounds, organic acids, and hydrocarbons in the bio-crude oil showed that they were possibly formed from polysaccharides that were hydrolysed to produce oligosaccharides and monosaccharides such as fructose, maltose as well as glucose. At a longer reaction time, glucose was converted into short-chain carboxylic acids, hydrocarbons, phenolic compounds, aldehydes, amines as well as ketones, and this is supported by the high concentration of organic acids and hydrocarbons. In addition, organic acids, hydrocarbons, and nitrogenated compounds were formed through the degradation reaction pathways known as the decarboxylation reaction of amino acids to produce carbonic acids and amines which was followed by a deamination reaction to produce ammonia, amines, aldehydes, hydrocarbons, and organic acids.

Moreover, lower concentrations of cyclic oxygenates, oxygenated compounds, and aromatics implied that there was no breakdown of lignin and cellulose but rather they were distributed into organic acids and nitrogenated compounds. Carbohydrates are hydrolysed to form glucose that is degraded to form cyclic oxygenates. Nitrogenated compounds and oxygenated compounds were formed from the Maillard reaction of amino acids from the hydrolysis of protein. Hydrocarbons and alcohols were formed from lipid that hydrolysed to form fatty acids that undergo decarboxylation to form hydrocarbons and alcohols.

4.4 Effect of catalyst on product distribution

Catalytic hydrothermal liquefaction involves incorporating catalyst during the conversion of biomass to liquid bio-crude oil which improves the properties and the yields. The liquid bio-crude oil property includes reduction of the heteroatom and also improving high heating values. This enhances the quality of the liquid bio-crude oil and its capability for combustion as well as upgrading to transportation fuel. Catalytic hydrothermal liquefaction lowers the activation energy which leads to an increase in the product; liquid bio-crude oil, solid, aqueous phase, and gas. The effect of catalyst on product distribution was studied at 260℃, 280℃, 300℃, 320℃, and 340℃ reaction temperatures. Reaction times that were selected for this study ranged from 30-150 minutes using different compositions of agricultural waste and food waste.

4.4.1 Effect of H-ZSM-5 at 260-340℃ reaction temperatures

4.4.1.1 Effect of H-ZSM-5 during hydrothermal liquefaction process at 30 minutes reaction time

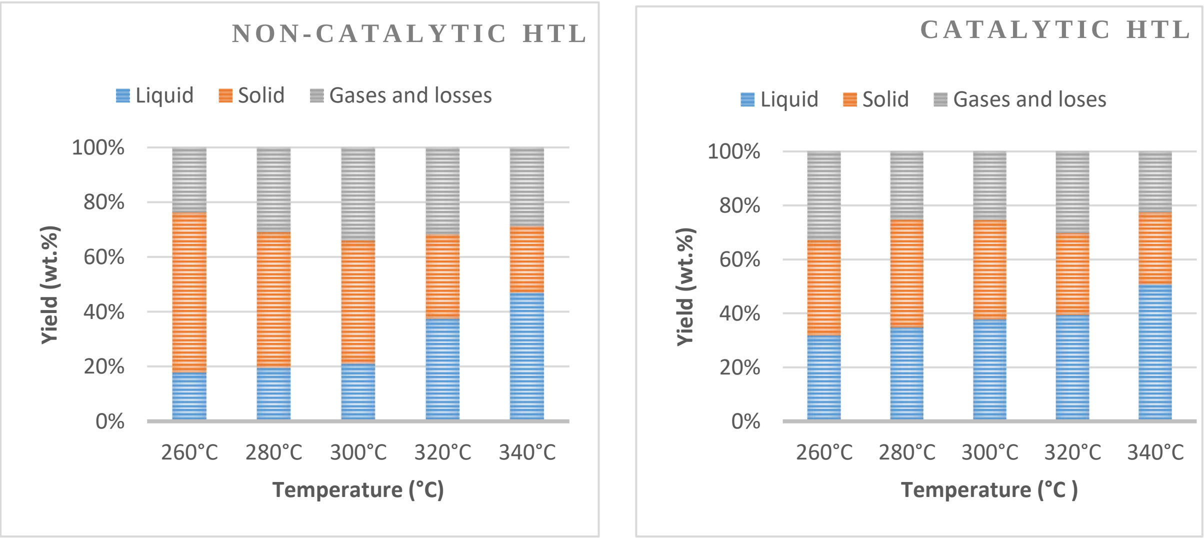


Figure 4.41: Product distribution at 30 minutes reaction time

Liquid bio-crude oils yields obtained from the catalytic HTL were much higher as compared to the yield obtained during the non-catalytic hydrothermal liquefaction. In contrast, there was a decrease in the solid biochar at 260℃ reaction temperature markedly from 58.43 wt.% to 35.38 wt.%. The observed trend was the increase in the liquid bio-crude oil as H-ZSM-5 was added. At 340℃ reaction temperature, liquid bio-crude oil yield was 46.88 wt.% and when the catalyst was added, the yield increased to 50.76 wt.%. At 300℃, the solid biochar yield decreased to 36.97 wt.% from 44.99 wt.% upon the addition H-ZSM-5. H-ZSM-5 favored the formation of liquid bio-crude oil than for the formation of gases and losses, and this can be seen by an increase in the gases and losses from 23.79 wt.% to 32.84 wt.% upon the addition of H-ZSM-5.

4.4.1.2 Effect of H-ZSM-5 during hydrothermal liquefaction process at 60 minutes reaction time

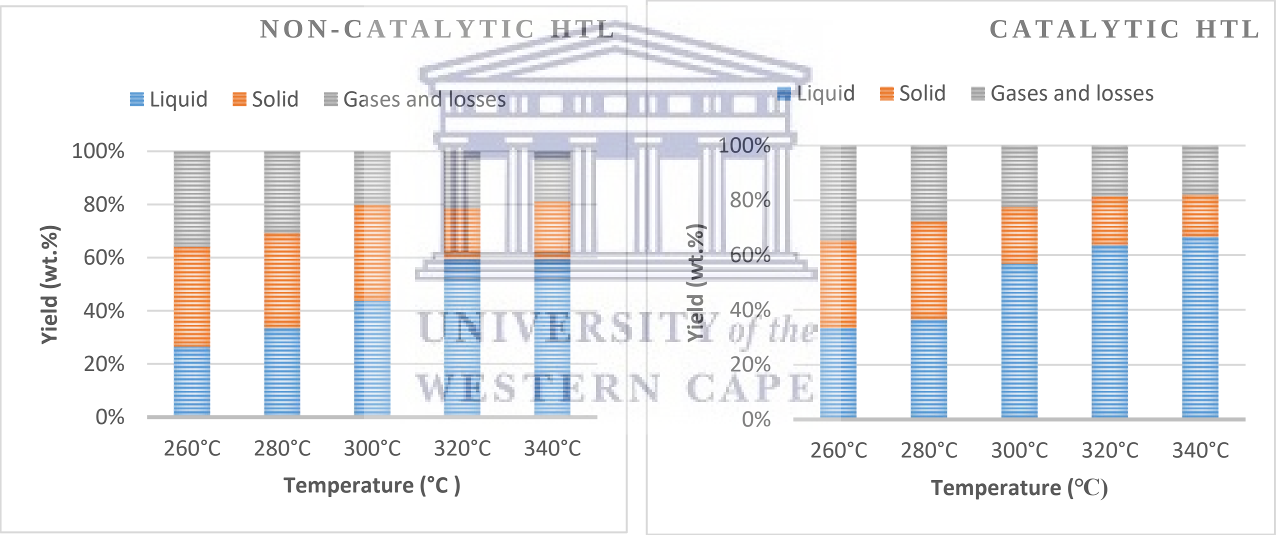


Figure 4.42: Product distribution at 60 minutes reaction time

With the use of H-ZSM-5, the highest yield of liquid bio-crude oil peaked to 66.67 wt.% from 59.38 wt.% at 340℃ reaction temperature. It is evident from figure 4.42 above that the yield of the liquid bio fuel increased with a decrease in the yield of solid biochar and gases and loses. At 280℃ reaction temperature, the yield of gases and loses decreased from 30.54 wt.% to 22.38 wt.% in the presence of H-ZSM-5. In addition, the solid biochar yield decreased from 36.21 wt.% to 20.8 wt.%.

4.4.1.3 Effect of H-ZSM-5 during hydrothermal liquefaction process at 90 minutes reaction time

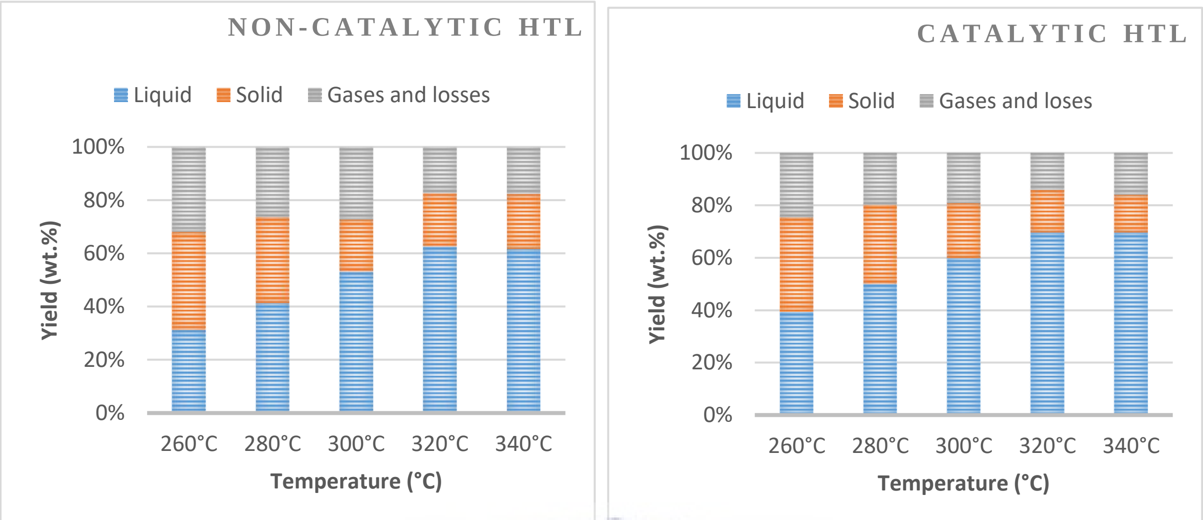


Figure 4.43: Product distribution at 90 minutes reaction time

Solid biochar yields obtained from the non-catalytic HTL were much higher, addition of the H-ZSM-5 upon to the HTL system resulted in the decrease in the yield of solid biochar. At 280℃ in the non-catalytic process the yield of solid biochar was 33.33 wt.%, and when the H-ZSM-5 was added, the yield of solid biochar slightly decreased to 30.31 wt.%. In contrast, there was an increase in liquid bio-crude oil yield at 320°C reaction temperature markedly from 62.5 wt.% to 69.7 wt.% upon the addition of H-ZSM-5. The observed trend was the increase in the liquid bio-crude oil as H-ZSM-5 was added, with the decrease in solid biochar together with the gases and losses. At 280℃ reaction temperature, the yield for gases and losses was 26.26 wt.% and when the H-ZSM-5 was added, the yield decreased to 19.69 wt.%.

4.4.1.4 Effect of H-ZSM-5 during hydrothermal liquefaction process at 120 minutes reaction time

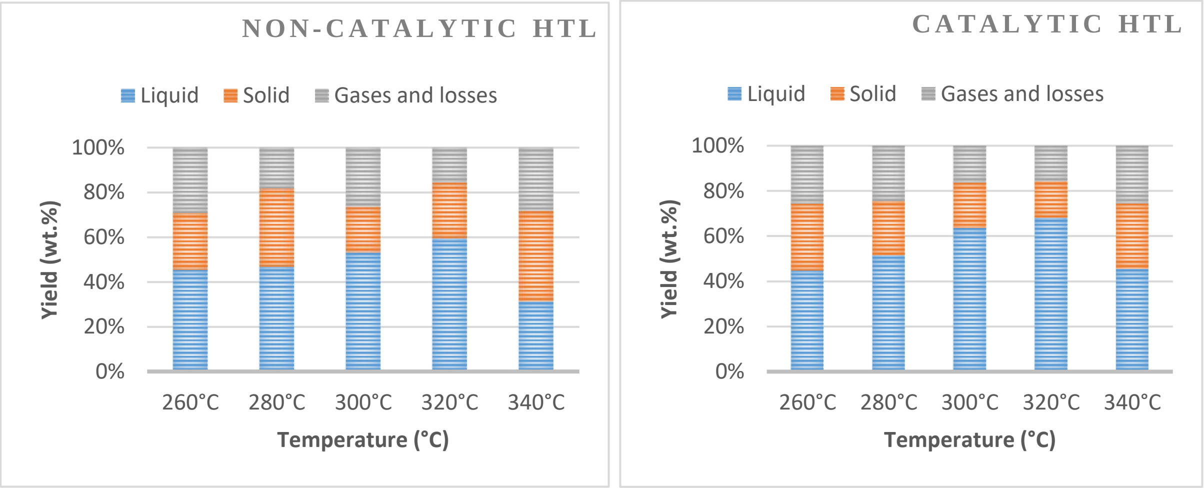


Figure 4.44: Product distribution at 120 minutes reaction time

At 260℃ reaction temperature in the non-catalytic HTL, the solid biochar yield was 25.5 wt.% and when H-ZSM-5 was added in the catalytic HTL, the solid biochar yield increased to 29.69 wt.%. At the same temperature, gases and losses yield decreased from 29.19 wt.% in the absence of H-ZSM-5 to 25.61 wt.% upon the addition of H-ZSM-5. Liquid bio-crude oil yield slightly decreased from 45.31 wt.% in the non-catalytic HTL to 44.7 wt.% in the catalytic HTL. The trend that was observed at 320℃ was an increase in the yield of liquid bio-crude oil with the decrease in the yield of solid bio-char and gases and losses. Liquid bio-crude oil yield peaked to 68.18 wt.% from 59.38 wt.% after the addition of H-ZSM-5 meanwhile solid biochar yield decreased from 25 wt.% to 16.13 wt.%. Moreover, there was no observed changes to the gases and losses yield.

4.4.1.5 Effect of H-ZSM-5 during hydrothermal liquefaction process at 150 minutes reaction time

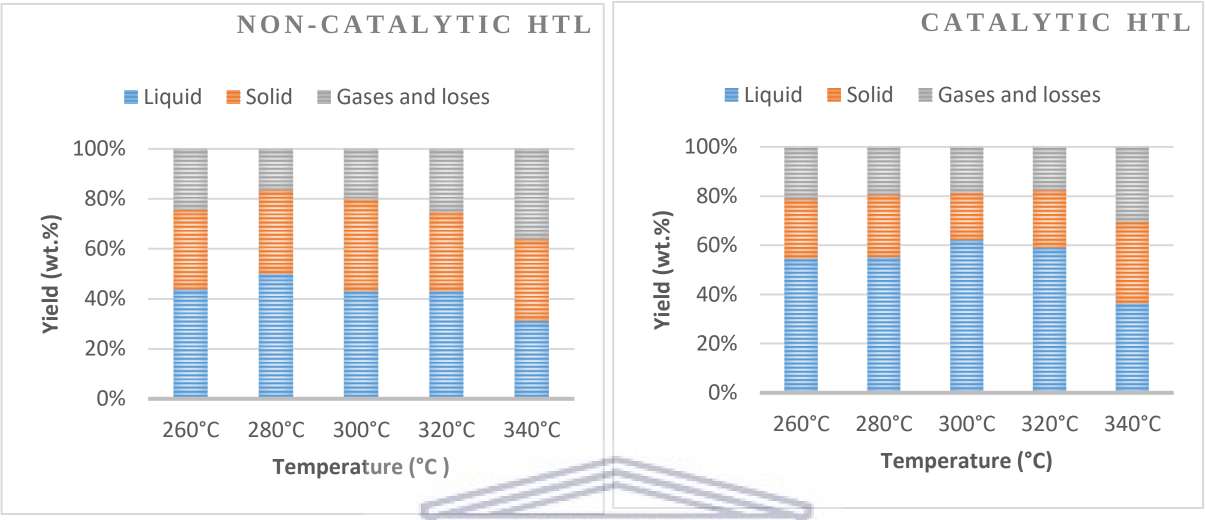


Figure 4.45: Product distribution at 150 minutes reaction time

The observed trend at 340°C was an increase in liquid bio-crude yield and solid biochar yield with the decrease in the yield for gases and losses upon the addition of H-ZSM-5. Liquid bio-crude oil yield increased to 36.36 wt.% from 31.25 wt.% meanwhile the solid biochar yield increased from 32.63 wt.% to 33.32 wt.%. In addition, the yield for gases and losses decreased to 30.32 wt.% from 36.12 wt.% while H-ZSM-5 was added upon to the HTL system. At 320°C, the observed trend was the increased in the liquid bio-crude yield with the decrease in the yield for solid biochar as well as gases and losses. The liquid bio-crude oil yield peaked to 59.09 wt.% after the addition of H-ZSM-5 from 42,97 wt.%, solid biochar yield decreased to 23.43 wt.% and gases and losses yield decreased to 25.03 wt.% from 17.58 wt.%.

The observed trend in the catalytic and non-catalytic HTL was an increase in the liquid bio-crude oil, with the decrease in solid biochar and gases and losses as the temperature was increased and a sudden decrease in the yield of liquid bio-crude oil with the increase in solid bio-char and gases and losses as the temperature went beyond 320°C and this was a resultant of the thermal conversion of liquid bio-crude oil into gaseous product which indicate that polymerisation reaction is not favoured at higher temperature and the catalyst did not play any role at this temperature to inhibit the rearrangement of liquid bio-crude oil into formation of new set of compounds.

4.4.2 Effect of H-ZSM-5 at 30-150 reaction time

4.4.2.1 Effect of H-ZSM-5 during hydrothermal liquefaction process at 260°C reaction temperature

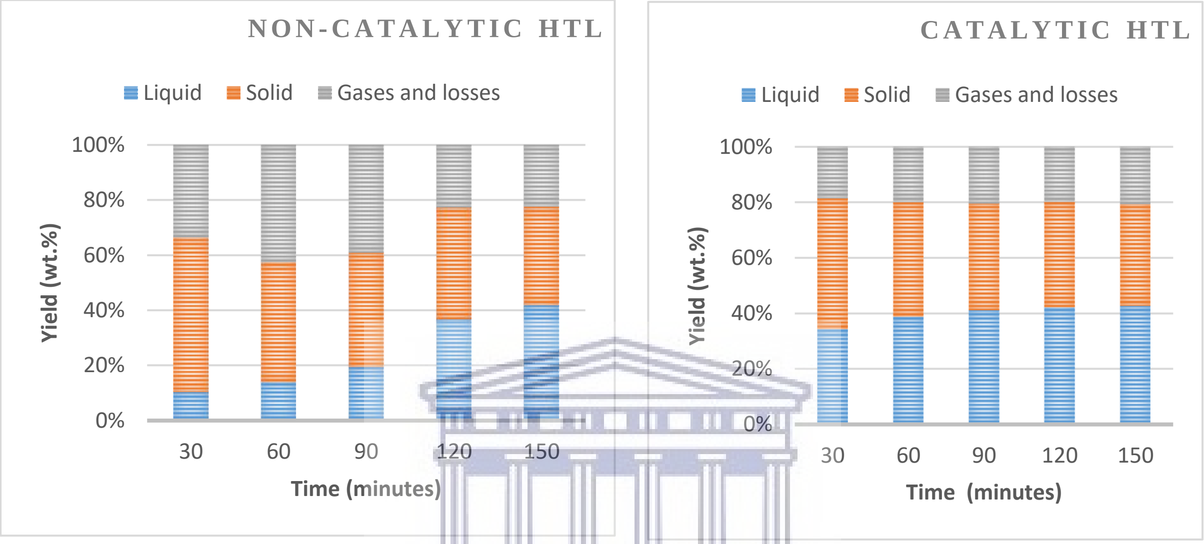


Figure 4.46: Product distribution at 260°C reaction temperature

Solid biochar yields obtained from the non-catalytic HTL were much higher, addition of the H-ZSM-5 upon to the HTL system resulted in the decrease in the yield of solid biochar to 46.93 wt.% from 50.39 wt.% at 30 minutes reaction time, liquid bio-crude oil yield increased from 9.38 wt.% to 34.24 wt.% and gases and losses decreased to 18.53 wt.% from 30.23 wt.%. At 150 minutes reaction time in the non-catalytic process, the yield of solid biochar was 21.76 wt.%, and when the H-ZSM-5 was added, the yield of solid biochar slightly decreased to 20.9 wt.%. In contrast, there was an increase in liquid bio-crude oil yield at 150 minutes reaction time markedly from 40.63 wt.% to 43.1 wt.% upon the addition of H-ZSM-5. The observed trend was the increase in the liquid bio-crude oil as H-ZSM-5 was added, with the decrease in solid biochar together with the gases and losses.

4.4.2.2 Effect of H-ZSM-5 during hydrothermal liquefaction process at 280°C reaction temperature

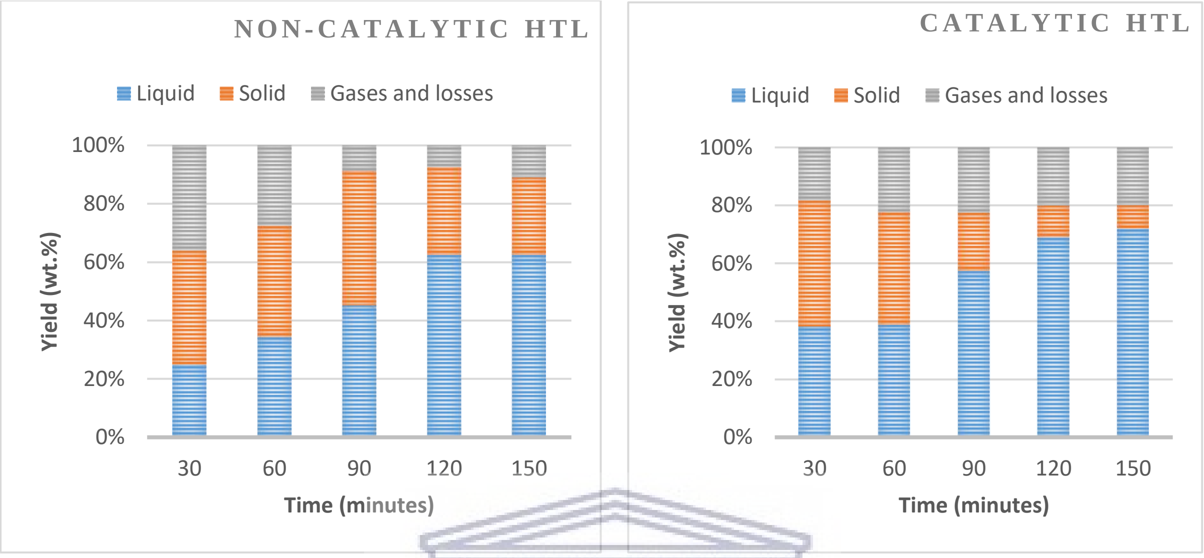


Figure 4.47: Product distribution at 280°C reaction temperature

Liquid bio-crude oils yields obtained from the catalytic HTL were much higher as compared to the yield obtained during the non-catalytic hydrothermal liquefaction. In contrast, there was a decrease in the gases and losses yield at 60 minutes reaction time markedly from 27.46 wt.% to 22.22 wt.%. The observed trend at 60 minutes reaction time was the increase in the liquid bio-crude oil and solid biochar with the decrease in gases and losses yield as H-ZSM-5 was added. At 120 reaction time, liquid bio-crude oil yield was 62.5 wt.% and when the catalyst was added, the yield increased to 68.94 wt.%, the solid biochar yield decreased to 11.06 wt.% from 30.11 wt.% and the yield for gases and losses decreased to 20 wt.% from 7.39 upon the addition H-ZSM-5.

4.4.2.3 Effect of H-ZSM-5 during hydrothermal liquefaction process at 300°C reaction temperature

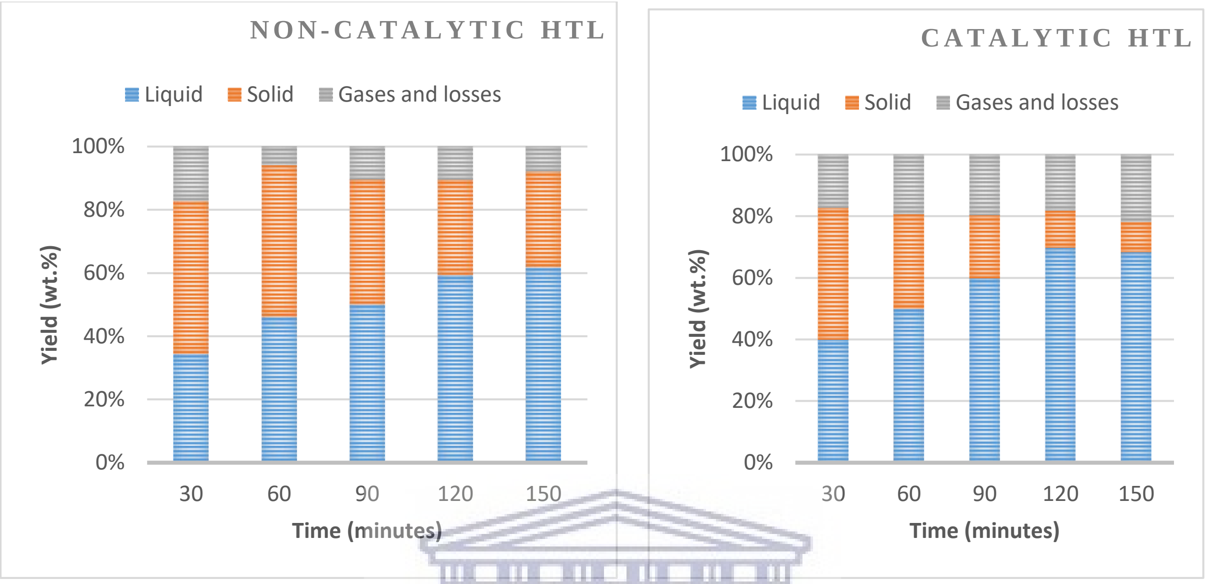


Figure 4.48: Product distribution at 300°C reaction temperature

The observed trend at 90 minutes was an increase in liquid bio-crude yield and gases and losses yield with the decrease in the yield for solid biochar upon the addition of H-ZSM-5. Liquid bio-crude oil yield increased to 59.85 wt.% from 50 wt.% meanwhile the solid biochar yield decreased from 39.66 wt.% to 20.5 wt.%. In addition, the yield for gases and losses increased to 19.64 wt.% from 10.34 wt.% when H-ZSM-5 was added upon to the HTL system. At 150 reaction time, the observed trend was the increase in the liquid bio-crude yield and gases and losses yield with the decrease in the yield for solid biochar. The liquid bio-crude oil yield peaked to 69.7 wt.% after the addition of H-ZSM-5 from 61.72 wt.%, solid biochar yield decreased to 10.06 wt.% from 30.45 wt.% and gases and losses yield increased to 22.24 wt.% from 7.83 wt.%.

4.4.2.4 Effect of H-ZSM-5 during hydrothermal liquefaction process at 320°C reaction temperature

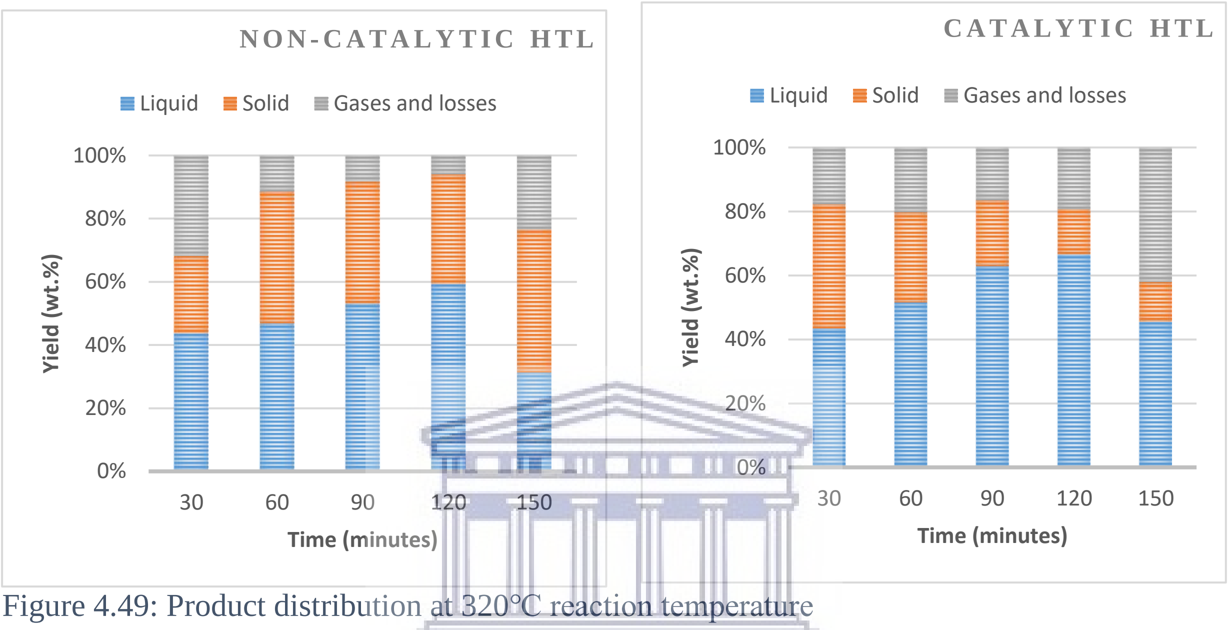


Figure 4.49: Product distribution at 320°C reaction temperature

At 30 minutes reaction time in the non-catalytic HTL, the solid biochar yield was 24.41 wt.% and when H-ZSM-5 was added in the catalytic HTL, the solid biochar yield increased to 38.9 wt.%. At the same reaction time, gases and losses yield decreased from 31.84 wt.% in the absence of H-ZSM-5 to 17.67 wt.% upon the addition of H-ZSM-5. Liquid bio-crude oil yield slightly decreased from 43.75 wt% to 43.43 wt.% in the catalytic HTL. The trend that was observed at 90 minutes reaction time was the increase in the yield of liquid bio-crude oil and gases and losses with the decrease in the yield of solid bio-char. Liquid bio-crude oil yield peaked to 51.52 wt.% from 46.88 wt.% after the addition of H-ZSM-5 meanwhile solid biochar yield decreased from 41.75 wt.% to 28.3 wt.%. Moreover, gases and losses yield increased from 20.18 wt.% to 11.37 wt.%

4.4.2.5 Effect of H-ZSM-5 during hydrothermal liquefaction process at 340°C reaction temperature

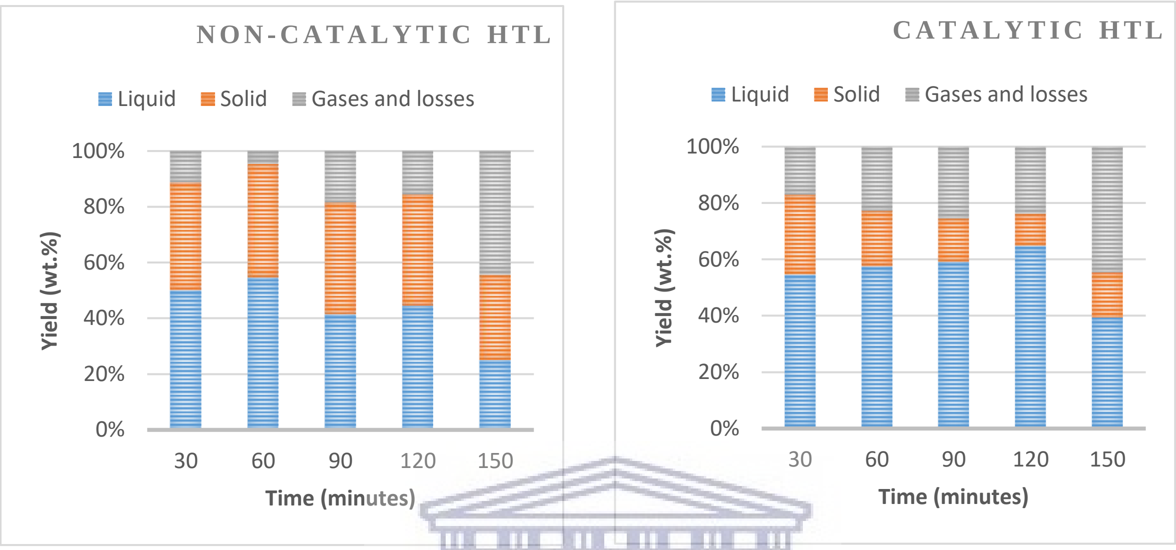


Figure 4.50: Product distribution at 340°C reaction temperature

With the use of H-ZSM-5, the highest yield of liquid bio-crude oil peaked to 59.09 wt.% from 44.53 wt.% at 120 minutes reaction time. It is evident from figure 4.50 above that the yield of the liquid bio-crude oil and gases together with the losses increased with a decrease in the yield of solid biochar. At 90 minutes reaction time, the yield of gases and loses increased from 18.43 wt.% to 25.47 wt.% in the presence of H-ZSM-5 while the solid biochar yield decreased from 39.9 wt.% to 10.39 wt.%.

The observed trend in the catalytic and non-catalytic HTL was an increase in the liquid bio-crude oil, with the decrease in solid biochar and gases and losses as the reaction time was increased and a sudden decrease in the yield of liquid bio-crude oil with the increase in solid bio-char and gases and losses as the reaction time went beyond 150 minutes and this was a resultant of the thermal conversion of liquid bio-crude oil into gaseous product which indicate that polymerisation reaction is not favoured at longer reaction time and the catalyst did not play any role at this temperature to inhibit the rearrangement of liquid biofuel into formation of new set of compounds.

4.4.3 Effect of H-ZSM-5 with different feedstock compositions

4.4.3.1 Effect of H-ZSM-5 during hydrothermal liquefaction process at 30 minutes reaction time

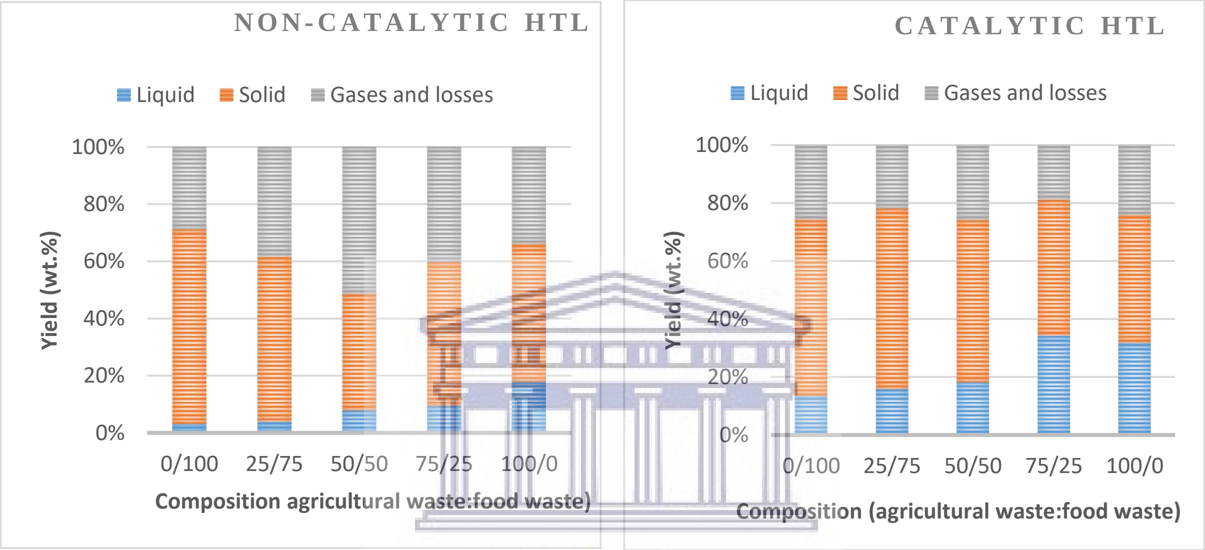


Figure 4.51: Product distribution at 30 minutes reaction time

Liquid bio-crude oils yields obtained from the catalytic HTL were much higher as compared to the yield obtained during the non-catalytic hydrothermal liquefaction. There was a decrease in the solid biochar at 0:100 ratio of agricultural waste and food waste markedly from 68.08 wt.% to 60.86 wt.%, increase in the liquid bio-crude oil from 3.13 wt.% to 13.58 wt.% and a decrease in the gases and losses yield from 28.79 wt.% to 25.56 wt.%. At 25:75 ratio of food waste and agricultural waste, liquid bio-crude oil yield was 3.91 wt.% and when the H-ZSM-5 was added, the yield increased to 15.85 wt.%, the solid biochar yield increased to 62.33 wt.% from 57.9 wt.% and gases and losses decreased to 21.82 wt.% from 38.19 wt.%.

4.4.3.2 Effect of H-ZSM-5 during hydrothermal liquefaction process at 60 minutes reaction time

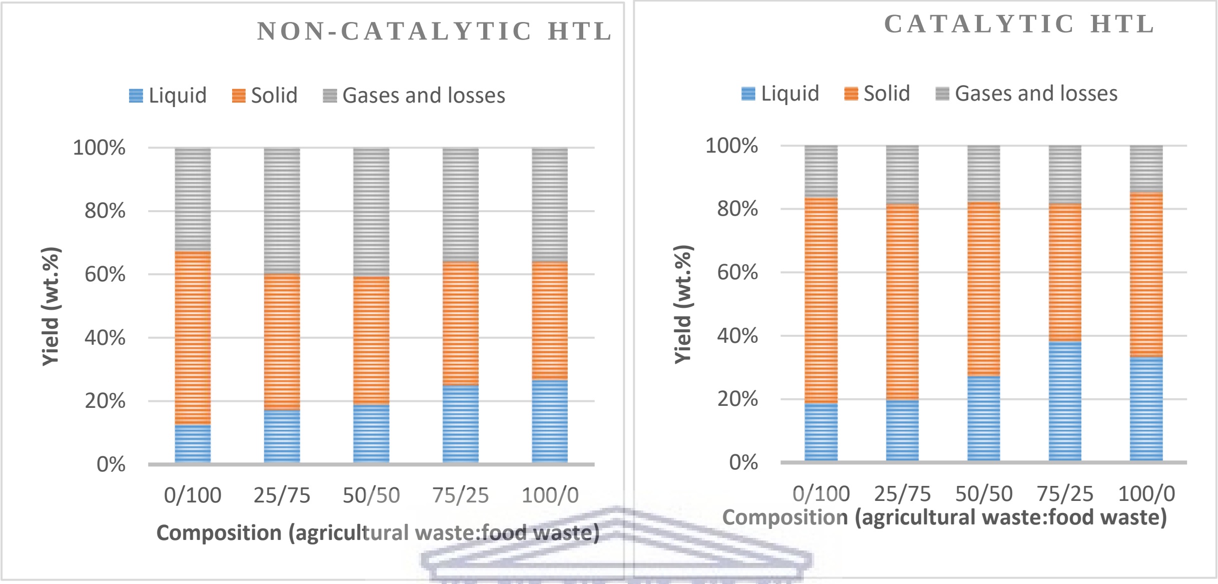


Figure 4.52: Product distribution in 60 minutes

At 50:50 ratio of agricultural waste and food waste in the non-catalytic HTL, the solid biochar yield was 40.66 wt.% and when H-ZSM-5 was added in the catalytic HTL, the solid biochar yield increased to 55.14 wt.%, gases and losses yield decreased from 40.59 wt to 17.59 wt.% and liquid bio-crude oil yield increased from 18.75 wt.% to 27.27 wt.%. The trend that was observed at 75:25 ratio of agricultural waste and food waste was the increase in the yield of liquid bio-crude oil and solid biochar with the decrease in the yield for gases and losses. Liquid bio-crude oil yield increased to 38.27 wt.% from 25 wt.% after the addition of H-ZSM-5 meanwhile solid biochar yield increased from 39.08 wt.% to 43.54 wt.% and gases and losses yield decreased to 18.19 wt.% from 35.86 wt.%.

4.4.3.3 Effect of H-ZSM-5 during hydrothermal liquefaction process at 90 minutes reaction time

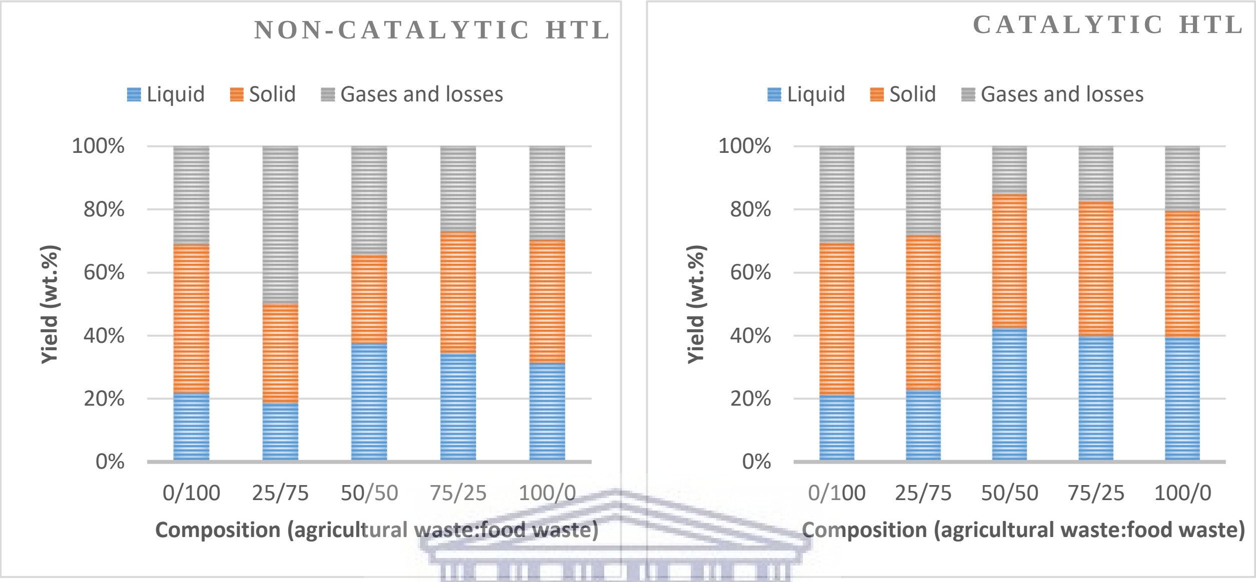


Figure 4.53: Product distribution at 90 minutes reaction time

Highest yield of liquid bio-crude oil obtained was 39.39 wt.% and there was an increase from 31.25 wt.% with the use of H-ZSM-5 . It is evident from figure 4.53 above at 100:0 ratio of agricultural waste and food waste that the yield of the liquid bio-crude oil and solid biochar increased with a decrease in the yield of gases and losses. At 0:100 ratio of agricultural waste and food waste, the yield of gases and loses decreased 31.02 wt.% to 30.49 wt.%, solid biochar yield increased to 48.3 wt.% from 47.1 wt.% and liquid bio-crude oil increased to 39.39 wt.% from 31.25 wt.% in the presence of H-ZSM-5.

4.4.3.4 Effect of H-ZSM-5 during hydrothermal liquefaction process at 120 minutes reaction time

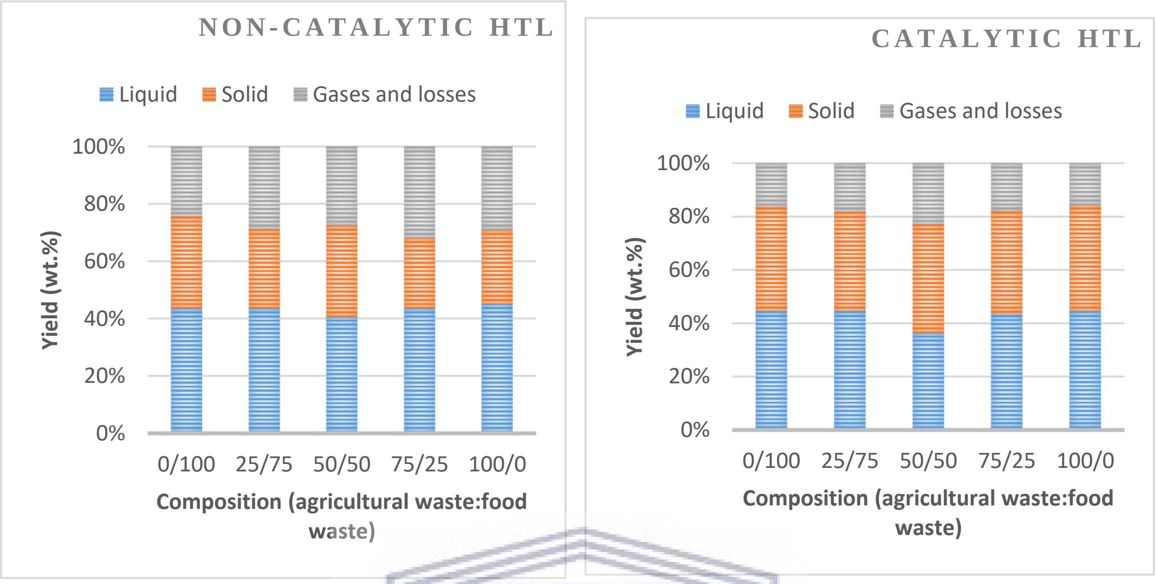


Figure 4.54: Effect of H-ZSM-5 on product distribution in 120 minutes

Solid biochar yields obtained from the catalytic HTL were much higher as compared to the yield obtained during the non-catalytic hydrothermal liquefaction. In contrast, there was a very small increase in the liquid bio-crude oil yield when H-ZSM-5 from 43.75 wt.% to 44.7 wt.% at 25:75 ratio of agricultural waste and food waste, solid biochar yield markedly increased to 37.48 wt.% from 27.47 wt.% and the yield for gases and losses decreased to 17.82 wt.% from 28.78 wt.%. At 75:25 ratio of agricultural waste and food waste, there was no observed changes on the yield for liquid bio-crude oil, 43.75 wt.% was obtained in the non-catalytic HTL and upon the use of H-ZSM-5, the yield was 43.43 wt.%, the solid biochar yield increased to 38.1 wt.% from 24.41 wt.%.

4.4.3.5 Effect of H-ZSM-5 during hydrothermal liquefaction process at 150 minutes reaction time

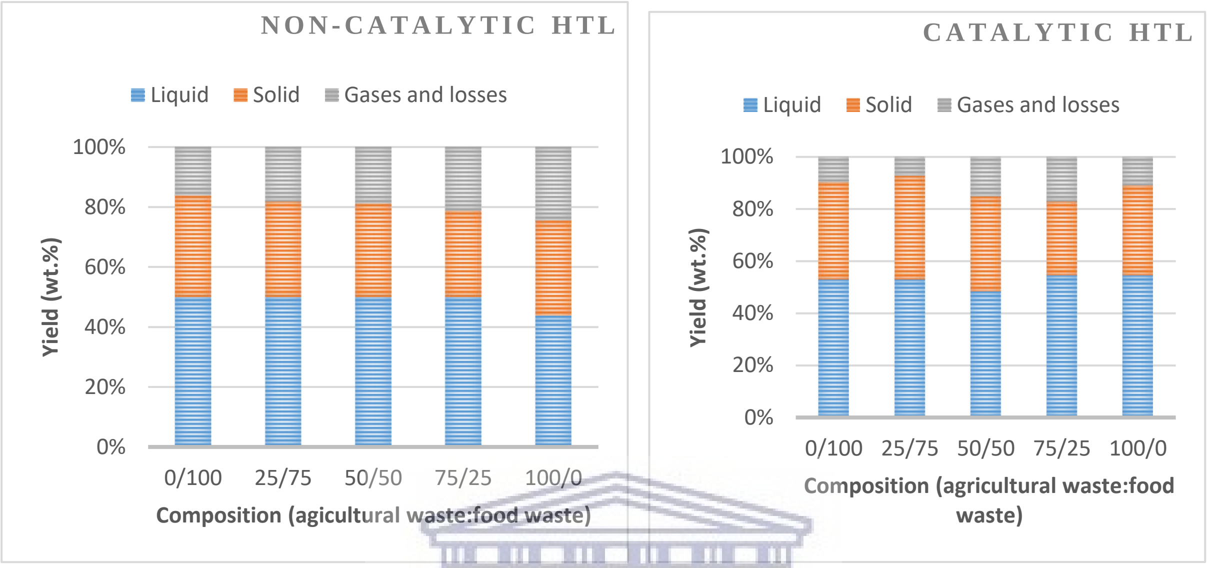


Figure 4.55: Product distribution at 150 minutes reaction time

The observed trend at 50:50 ratio of agricultural waste and food waste was the decrease in liquid bio-crude oil yield and gases and losses yield with an increase in the solid biochar yield upon the addition of H-ZSM-5. Liquid bio-crude oil yield decreased to 48.48 wt.% from 50 wt.% meanwhile the solid biochar yield increased from 31.28 wt.% to 36.45 wt.%. In addition, the yield for gases and losses decreased to 15.07 wt.% from 18.72 wt.% when H-ZSM-5 was added upon to the HTL system. At 100:0 ratio of agricultural waste and food waste, the observed trend was the increase in the liquid bio-crude yield and solid biochar yield and a decrease in the yield for gases and losses. The liquid bio-crude oil yield increased to 54.55 wt.% after the addition of H-ZSM-5 from 43.75 wt.%, solid biochar yield increased to 34.5 wt.% from 31.88 wt.% and gases and losses yield decreased to 10.95 wt.% from 24.37 wt.%.

The observed trend was an increase in the liquid bio-crude with the decrease in solid biochar and gases and losses as H-ZSM-5 to the HTL process. When the catalyst is introduced the activation energy is lowered and more macromolecules of the feedstocks can reach it, resulting in the high yield of the liquid bio-crude oil, with low yield of solid biochar and gases and losses.

4.5 Effect of H-ZSM-5 on chemical composition of bio-crude oil products.

4.5.1 Effect of H-ZSM-5 at 260-340°C reaction temperature

The effect of catalyst (H-ZSM-5) on HTL process was studied at 260-340°C. In this study agricultural waste was selected as the feedstock for the study.

4.5.1.1 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 30 minutes reaction time

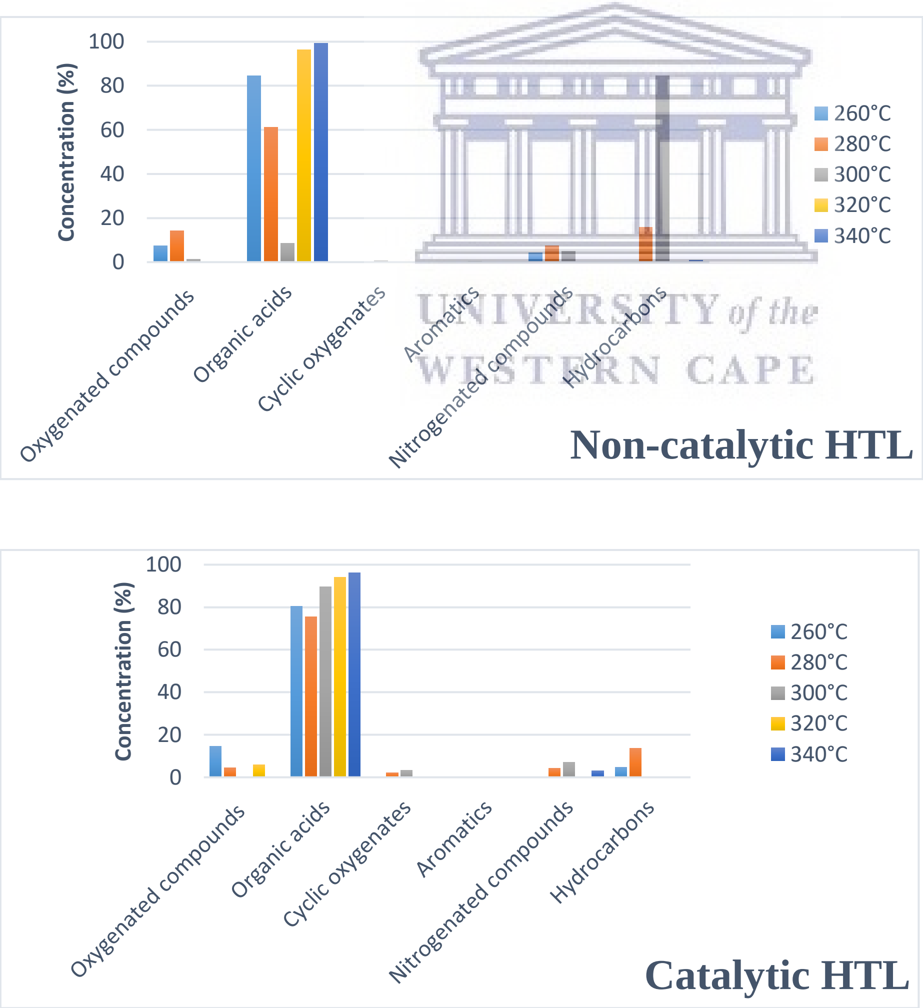


Figure 4.56: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 260-340°C at a reaction time of 30 minutes.

The liquid bio-crude oils obtained from non-catalytic HTL of agricultural waste contained high concentrations of organic acids and hydrocarbons and when H-ZSM-5 was added to the HTL system the concentrations detected in the liquid bio-crude oils were much higher while the detected concentrations for hydrocarbons decreased. Cyclic oxygenates and aromatics were not detected in the catalytic HTL, upon the use of HTL cyclic oxygenates were detected at a minimal concentration meanwhile aromatics were not detected. Oxygenated compounds, cyclic oxygenates and nitrogenated compounds from liquid bio-crude oil were detected at a lower concentrations, both in the catalytic and non-catalytic HTL.

4.5.1.2 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 60 minutes reaction time

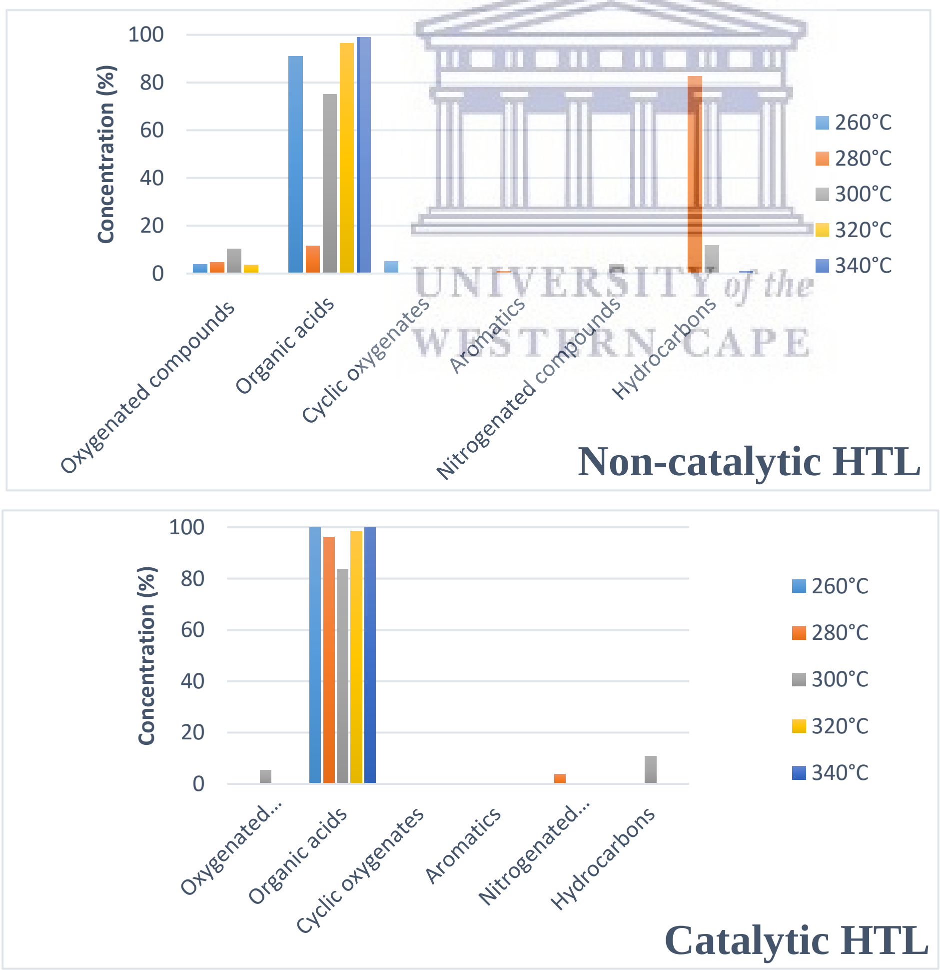


Figure 4.57: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 260-340°C at a reaction time of 60 minutes.

Cyclic oxygenates and aromatics were detected at a lower concentrations in the non-catalytic HTL, and upon the use of H-ZSM-5, there was no concentrations of cyclic oxygenates and aromatics was detected. Similar to what was observed in Figure 4.57, the detected concentrations for hydrocarbons from the non-catalytic HTL were much higher as compared to the concentrations detected in the catalytic HTL. In addition, the concentrations detected for the bio-crude oils produced both in the catalytic and non-catalytic HTL, contained lower concentrations of oxygenated compounds and nitrogenated compounds. Organic acids were detected in abundance both in the catalytic and non-catalytic HTL, but were detected at a higher concentration in the catalytic HTL.

4.5.1.3 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 90 minutes reaction time

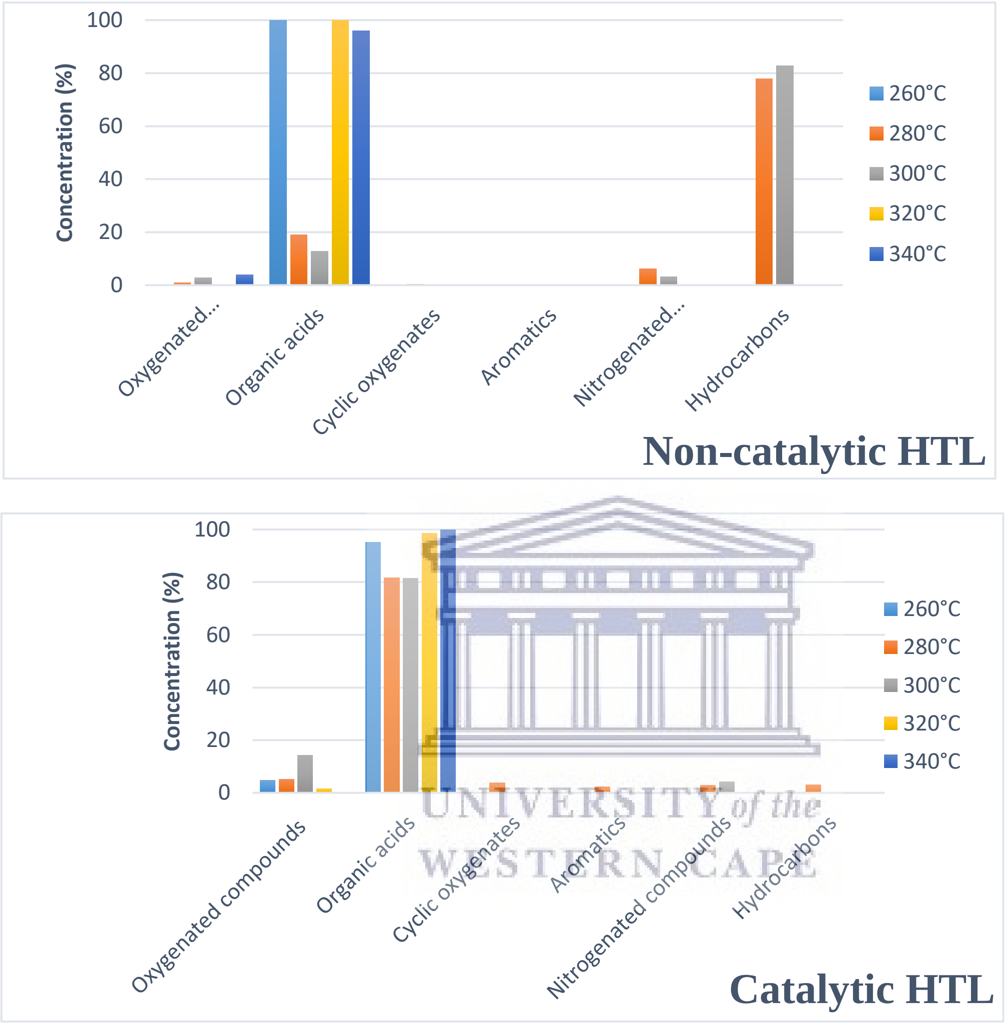


Figure 4.58: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 260-340℃ at a reaction time of 90 minutes.

The concentrations for cyclic oxygenates and aromatics in the liquid bio-crude oil produced at 90 minutes were not detected, but these volatile compounds were detected in the catalytic HTL but at a lower concentration. Oxygenated compounds in the catalytic HTL were detected at a higher concentration concentrations as compared to the non-catalytic HTL. Moreover, hydrocarbons detected in the non-catalytic HTL were lower as compared to the catalytic HTL. Organic acids were detected in the bio-crude oil from both catalytic and non-catalytic HTL but were detected in abundance in the bio-crude oil from catalytic HTL.

4.5.1.4 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 120 minutes reaction time

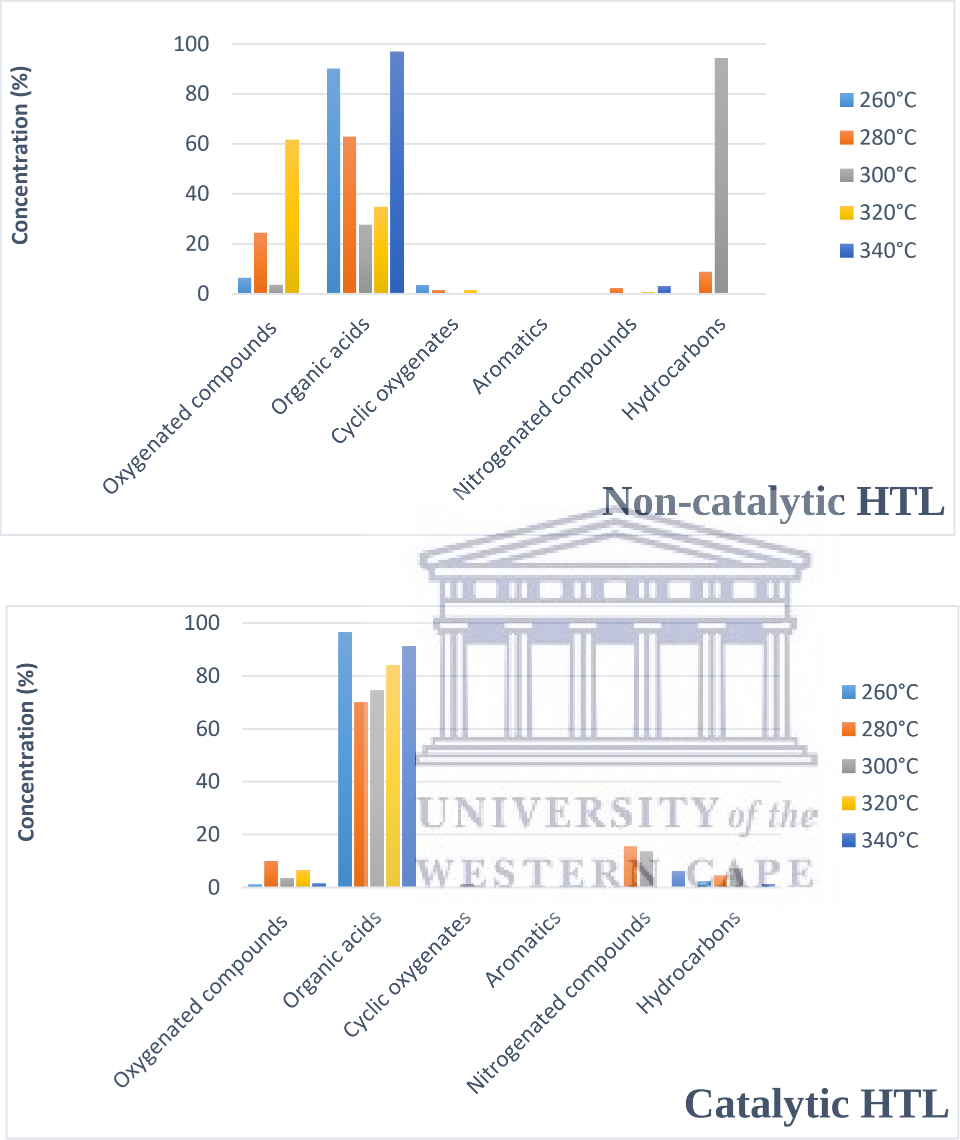


Figure 4.59: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 260-340°C at a reaction time of 120 minutes.

Oxygenated compounds and hydrocarbons were detected at a higher concentration in the liquid bio-crude oil from non-catalytic HTL as compared to the liquid bio-crude oil from catalytic HTL. Organic acids were detected at a higher concentration in the bio-crude oil from catalytic HTL as compared to the bio-crude oil from non-catalytic HTL. Bio-crude oil obtained from both catalytic and non-catalytic HTL contained lower concentrations nitrogenated compounds and cyclic oxygenates meanwhile aromatics were not detected in both cases.

4.5.1.5 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 150 minutes reaction time

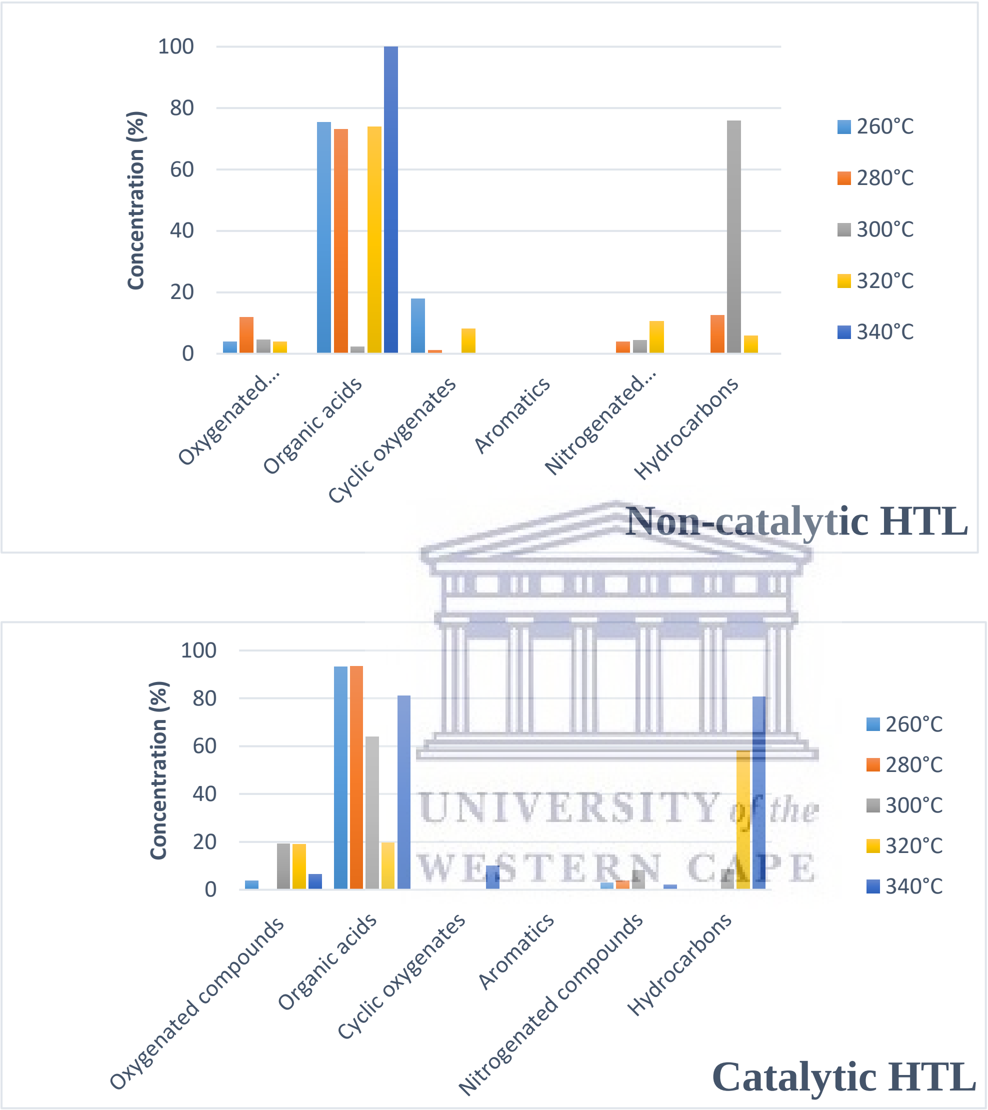


Figure 4.60: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction of at 260-340℃ at a reaction time of 150 minutes.

The detected concentrations for liquid bio-crude obtained from catalytic HTL, were much higher as compared to the concentrations for bio-crude oil from non-catalytic HTL meanwhile the concentration of organic acids were much higher in the non-catalytic HTL as compared to the bio-crude oil from catalytic HTL. The detected concentrations for nitrogenated compounds and cyclic oxygenates in the liquid bio-crude oil obtained from both catalytic and non-catalytic HTL were lower while the aromatics were not detected in both cases. In addition, the concentrations detected for oxygenated compounds were lower in the non-catalytic HTL and were higher in the catalytic HTL.

4.5.2 Effect of H-ZSM-5 at 30-150 minutes reaction time

4.5.2.1 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 260℃ reaction temperature

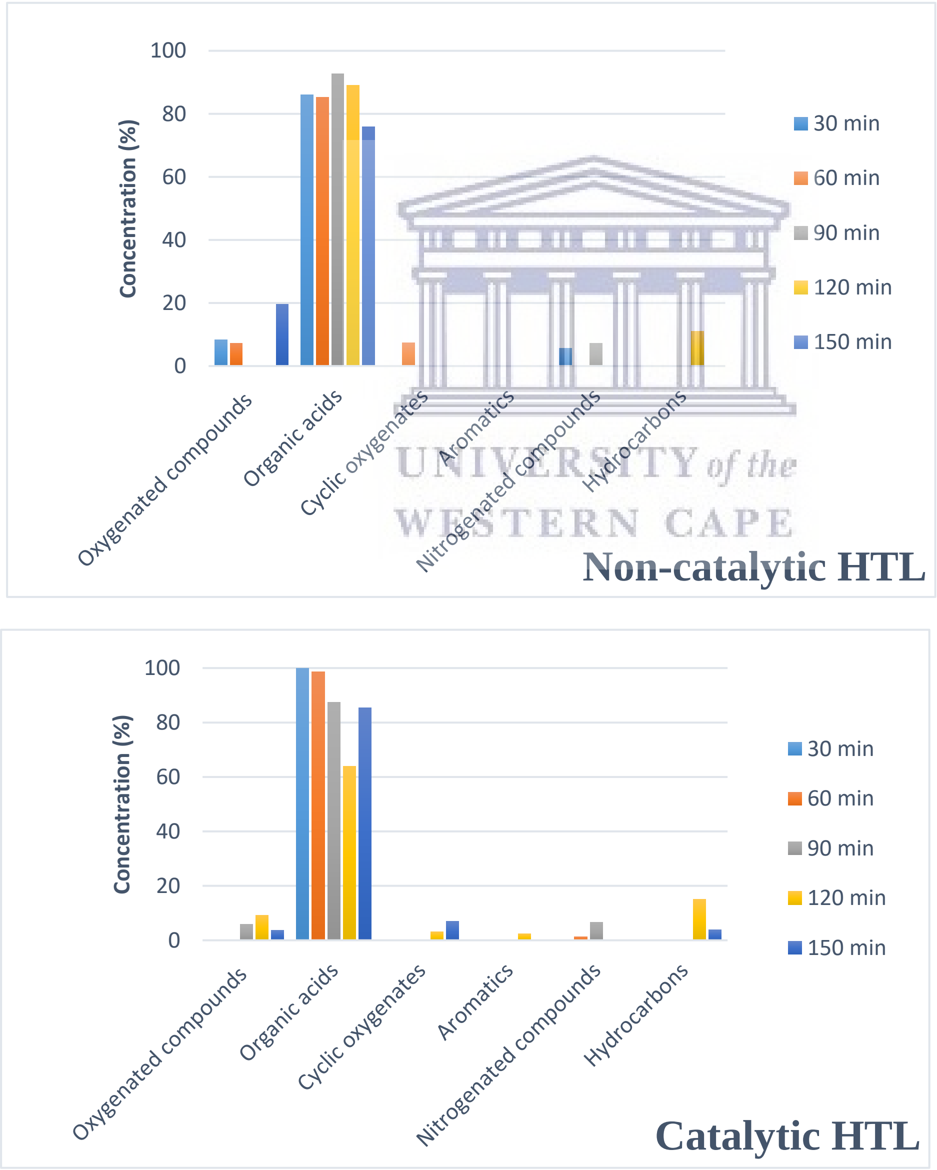


Figure 4.61: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process of agricultural at 30-150 minutes at a reaction temperature of 260℃.

The detected concentrations for hydrocarbons, nitrogenated compounds and cyclic oxygenated were detected at a very low in the liquid bio-crude produced both in the catalytic and non-catalytic HTL. Organic acids were detected at a higher concentration from the liquid bio-crude oil obtained from non-catalytic HTL as compared to the liquid bio-crude oil obtained from catalytic HTL meanwhile oxygenated compounds were detected at a higher concentration from the bio-crude oil from non-catalytic HTL as compared to the concentrations from catalytic HTL. In addition, aromatics were not detected in the bio-crude oil from non-catalytic HTL but were detected at a low concentration in the liquid bio-crude oil from catalytic HTL.

4.5.2.2 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 280℃ reaction temperature

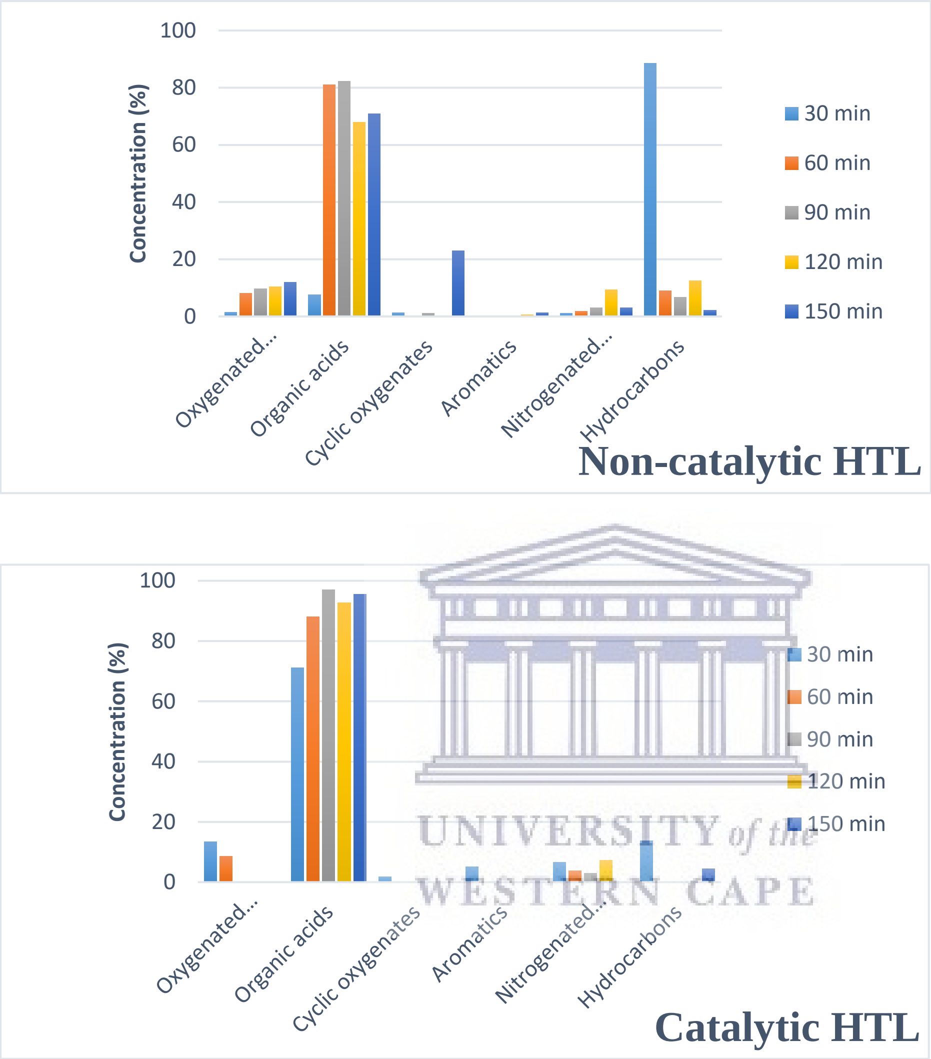


Figure 4.62: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 30-150 minutes at a reaction temperature of 280°C.

Cyclic oxygenates, hydrocarbons and oxygenated compounds were detected at a higher concentrations in the liquid bio-crude oil from non-catalytic HTL as compared to the bio-crude oil from catalytic HTL. Organic acids were detected at a higher concentration in the liquid bio-crude oil from catalytic HTL. In the liquid bio-crude oil obtained from both catalytic and non-catalytic HTL, the aromatics were detected at a lower concentration.

4.5.2.3 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 300°C reaction temperature

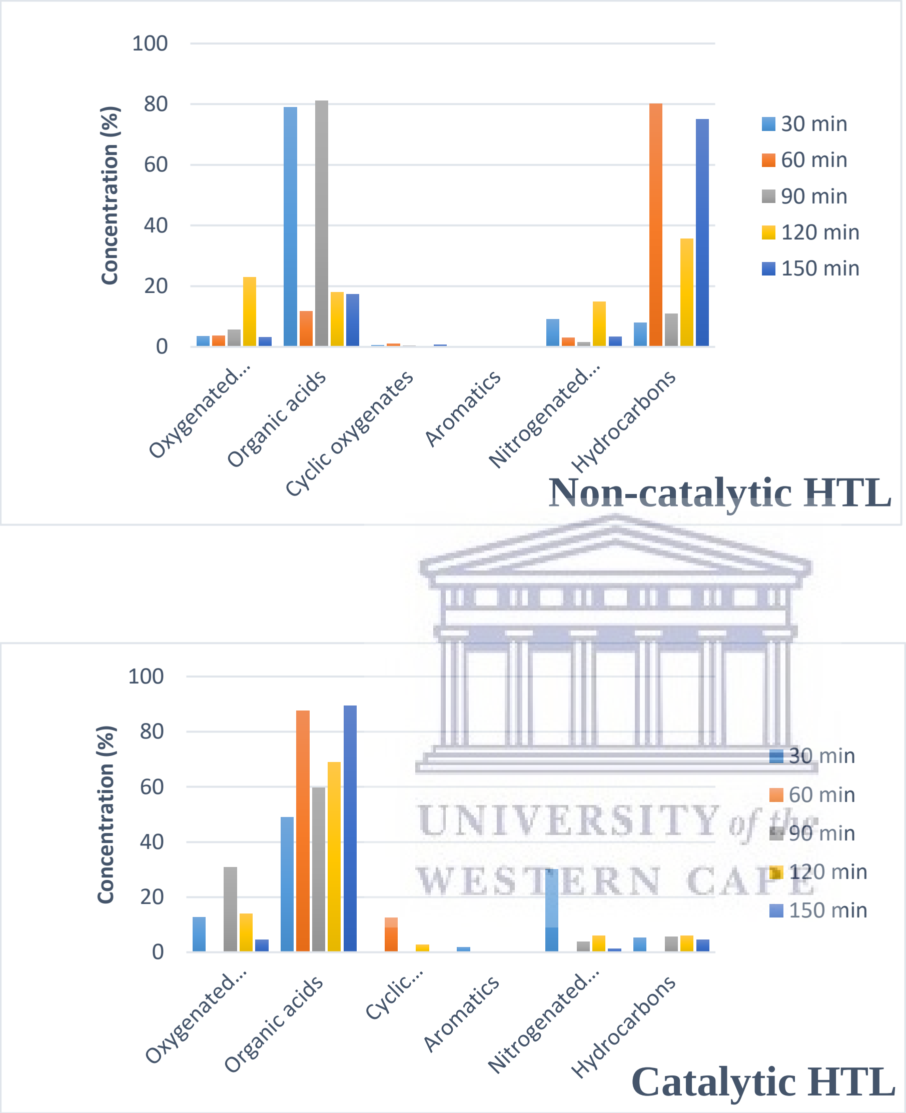


Figure 4.63: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction at 30-150 minutes at a reaction temperature of 300°C.

Organic acids were detected at a higher concentrations in the liquid bio-crude oil from both catalytic HTL and non-catalytic HTL but were the highest from catalytic HTL. Aromatics were not detected in the bio-crude oil from non-catalytic but were detected at a very low concentration from bio-crude oil in the catalytic HTL. Oxygenated compounds and nitrogenated compounds were detected at a higher concentration in the bio-crude oil from catalytic HTL as compared to bio-crude oil from non-catalytic HTL. Hydrocarbons were detected at a higher concentration in the liquid bio-crude oil from non-catalytic HTL as compared to the catalytic HTL. Moreover, cyclic oxygenates were detected at a lower concentration in the liquid bio-crude oil from non-catalytic HTL as compared to the catalytic HTL.

4.5.2.4 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 320°C reaction temperature

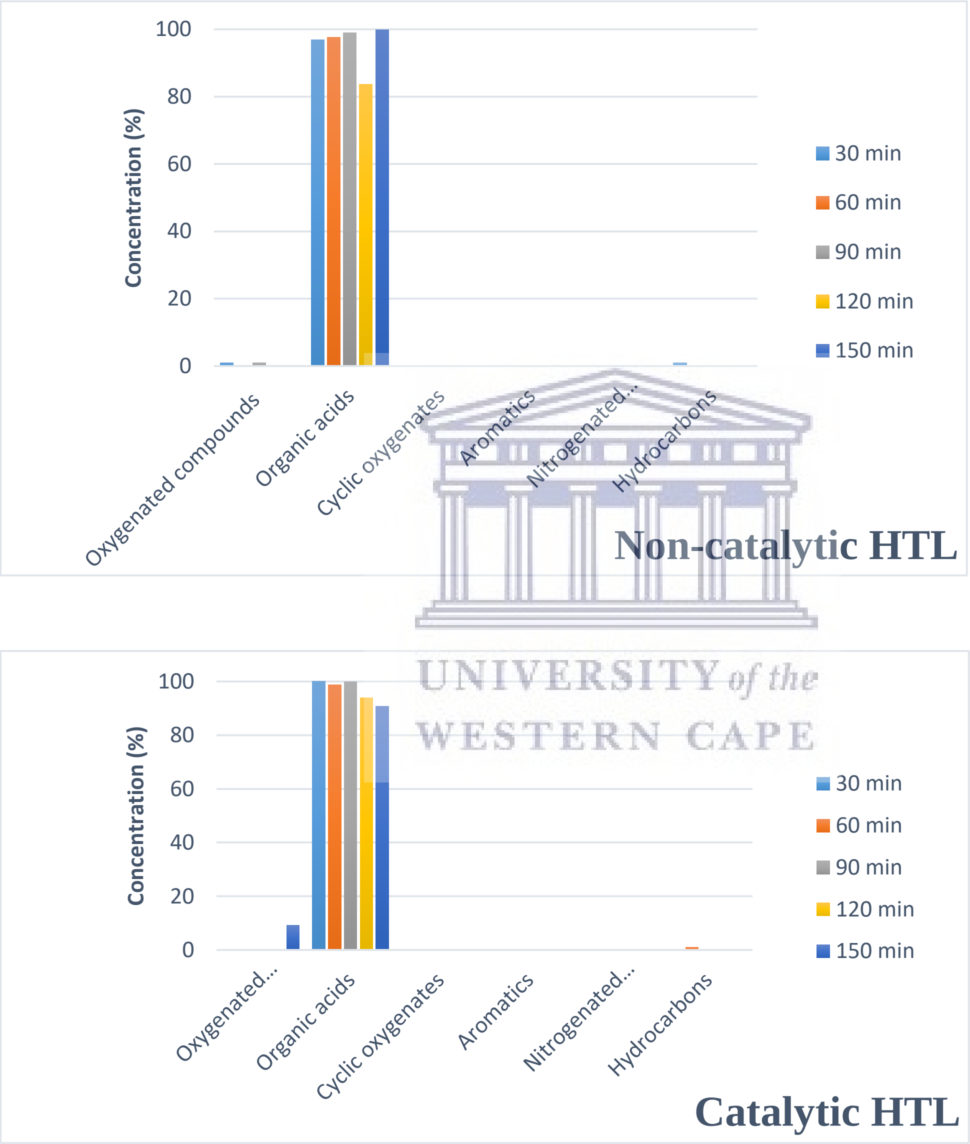


Figure 4.64: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 30-150 minutes at a reaction temperature of 320°C

Cyclic oxygenates, aromatics and nitrogenated compounds were not detected in the liquid bio-crude oil obtained from both catalytic and non-catalytic HTL meanwhile hydrocarbons and oxygenated compounds were detected at a very low concentration in both cases. However, organic acids were detected at higher concentrations in the liquid bio-crude oil from both catalytic and non-catalytic HTL.

4.5.2.5 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 340°C

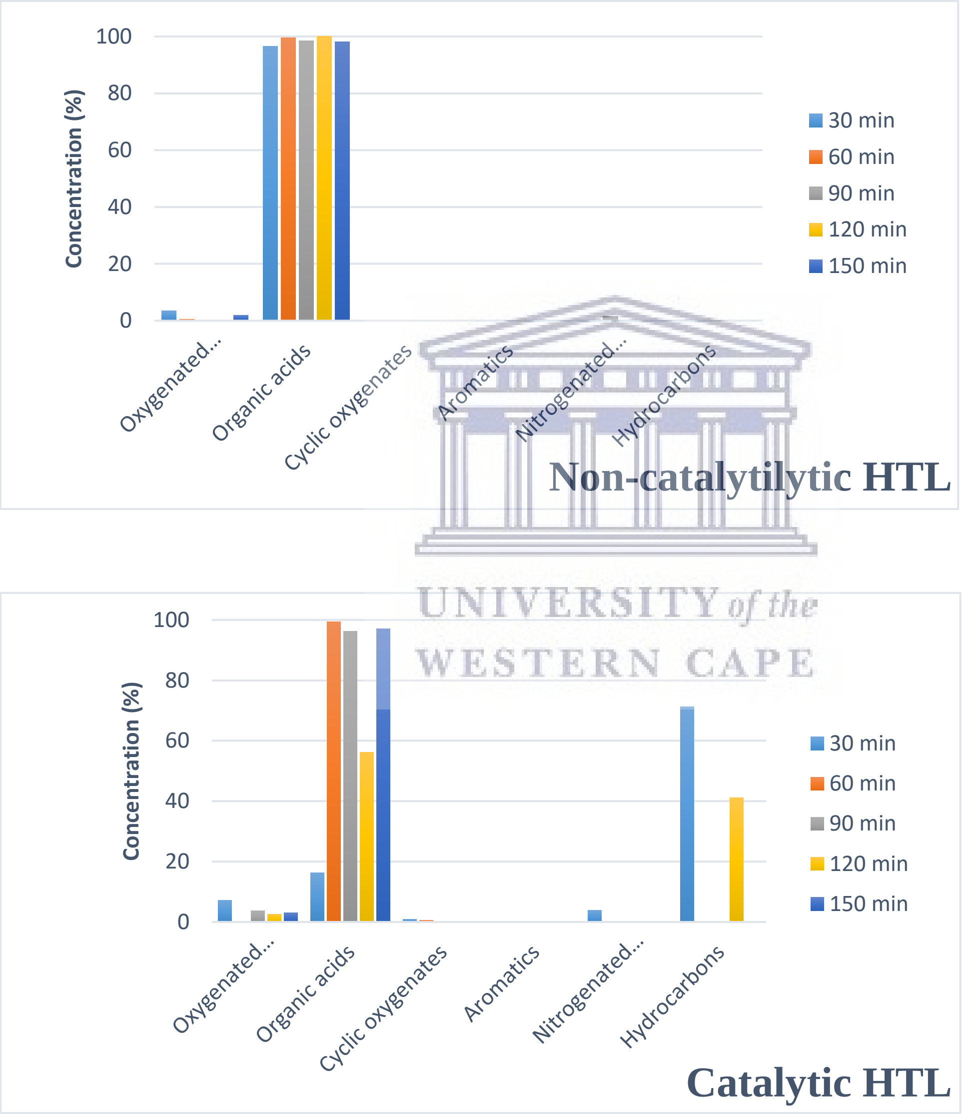


Figure 4.65: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 30-150 minutes at a reaction temperature of 260°C.

Hydrocarbons and cyclic oxygenates were not detected in the liquid bio-crude oil from non-catalytic HTL but were detected at a high concentration in the liquid bio-crude oil from catalytic HTL. Oxygenated compounds were detected at a very low concentration in the liquid bio-crude oil from non-catalytic HTL as compared to the catalytic HTL. The concentration for nitrogenated compounds were very low for liquid bio-crude oil obtained both in the catalytic and non-catalytic HTL, while the aromatics were not detected in both cases. Organic acids were detected at a high concentrations in the liquid bio-crude oil from both catalytic and non-catalytic HTL but the concentration was the highest in the bio-crude oil obtained from non-catalytic HTL.

4.5.3 Effect of H-ZSM-5 with different feedstock composition

4.5.3.1 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 30 minutes reaction time

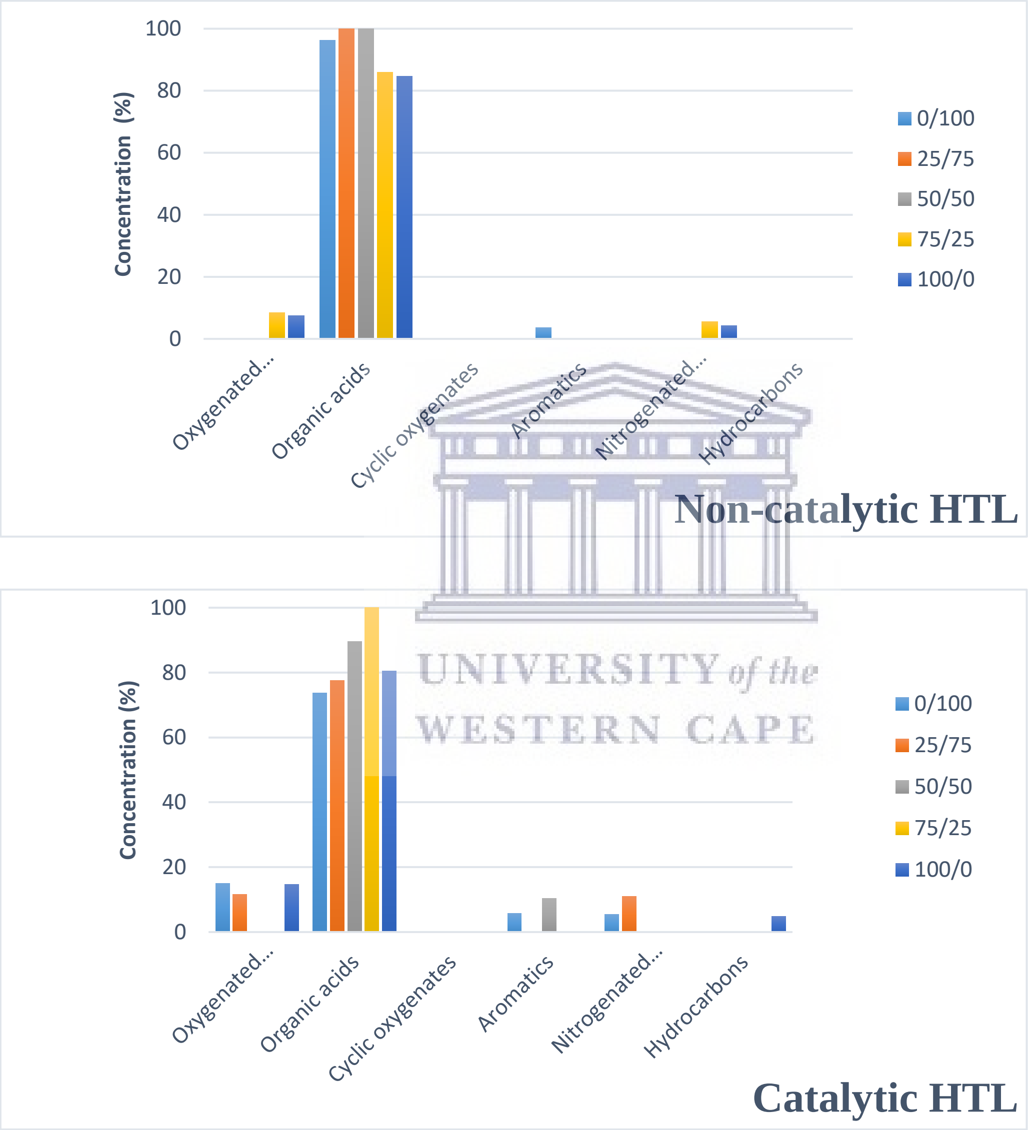
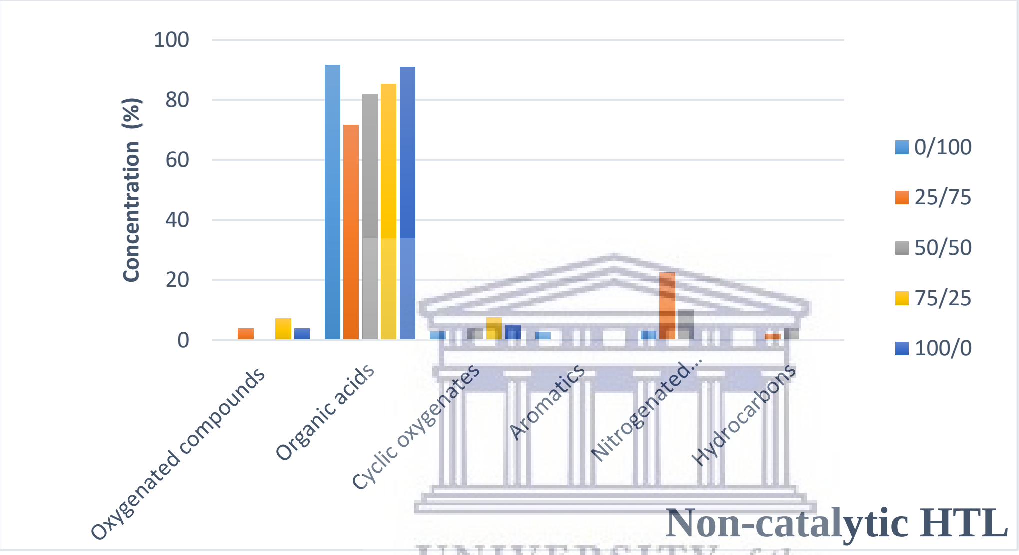


Figure 4.66: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 30 minutes at 0:100-100:0 ratio of the feedstock

Hydrocarbons were not detected in the liquid bio-crude oil from non-catalytic HTL but were detected at a low concentration in the catalytic HTL. Aromatics and nitrogenated compounds were detected at a very low concentrations in the liquid bio-crude oil from catalytic and non-catalytic HTL while cyclic oxygenates compounds were not detected in both cases. Oxygenated compounds were detected at a higher concentration in the liquid bio-crude oil from catalytic

HTL as compared to the non-catalytic HTL. Organic acids were detected at a much higher concentration in the liquid bio-crude oil from non-catalytic HTL as compared to the catalytic HTL.

4.5.3.2 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 60 minutes reaction time



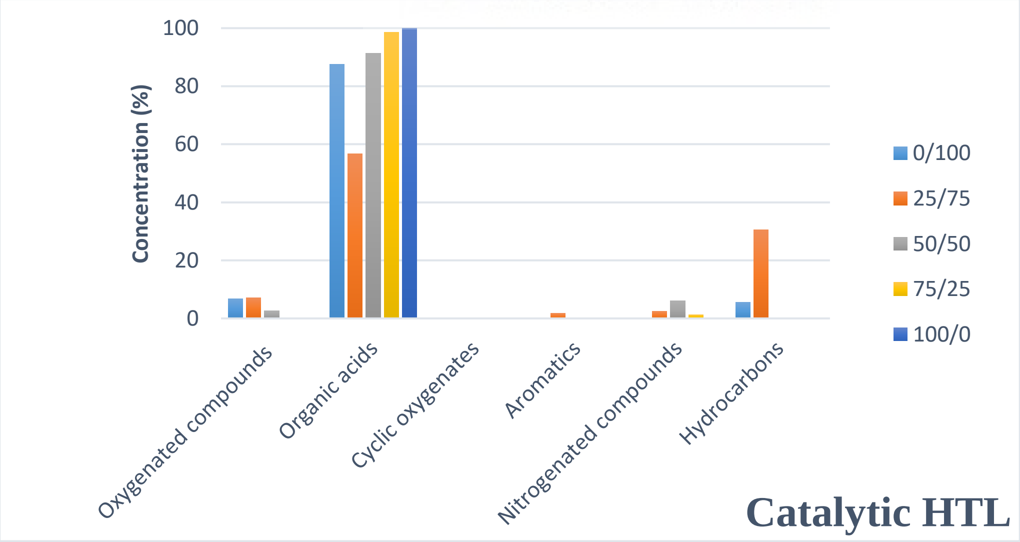


Figure 4.67: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 60 minutes at 0:100-100:0 ratio of the feedstock.

Cyclic oxygenates from the liquid bio-crude oil were detected at a lower concentration in the non-catalytic HTL but were not detected in liquid bio-crude oil from catalytic HTL. The concentration for hydrocarbons were higher in the catalytic HTL but were low in the non-catalytic HTL. Oxygenated compounds and aromatics were detected at a lower concentration both in the catalytic and non-catalytic HTL. Nitrogenated compounds were detected at a higher concentration in the liquid bio-crude oil from catalytic HTL and were low for catalytic HTL. In addition, organic acids were detected at a high concentration both in the liquid bio-crude oil from catalytic and non-catalytic HTL.

4.5.3.3 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 90 minutes reaction time

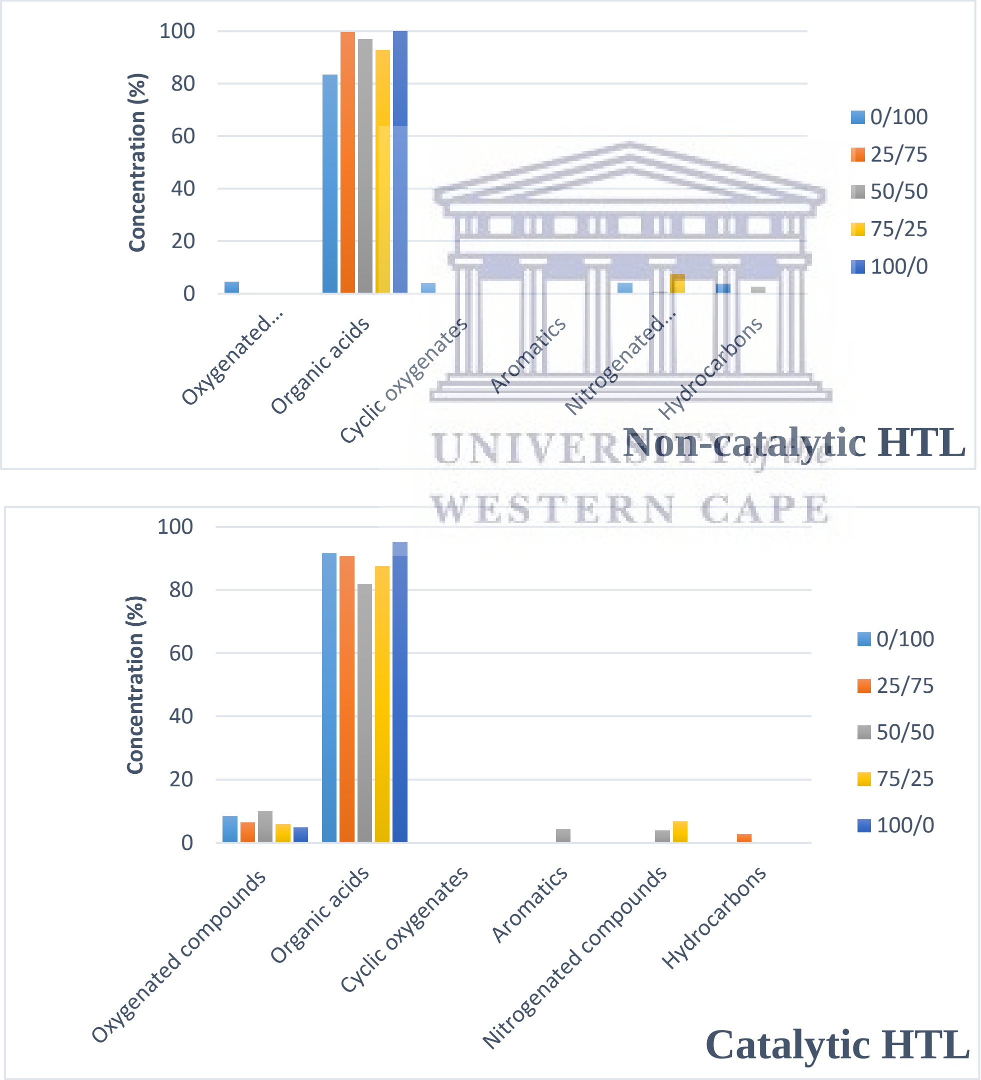
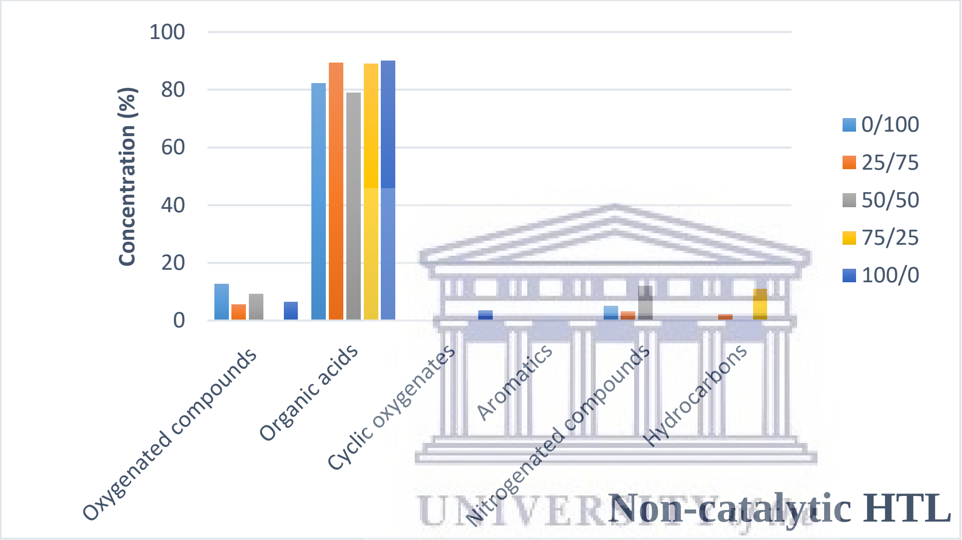


Figure 4.68: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 90 minutes at 0:100-100:0 ratio of the feedstock

Cyclic oxygenates were detected in the liquid bio-crude from non-catalytic HTL but were not detected in the catalytic HTL while aromatics were not detected in the bio-crude oil from non-catalytic HTL but were detected in the liquid bio-crude oil from catalytic HTL. Oxygenated compounds, nitrogenated compounds as well as hydrocarbons were detected at a low concentration in the liquid bio-crude oil from both catalytic and non-catalytic HTL meanwhile hydrocarbons were detected higher concentrations in both cases.

4.5.3.4 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 120 minutes reaction time.



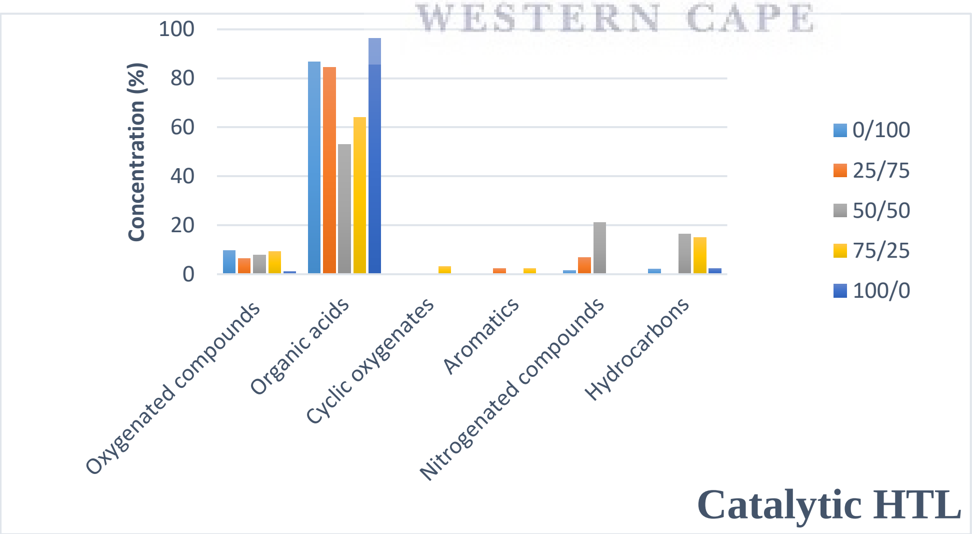
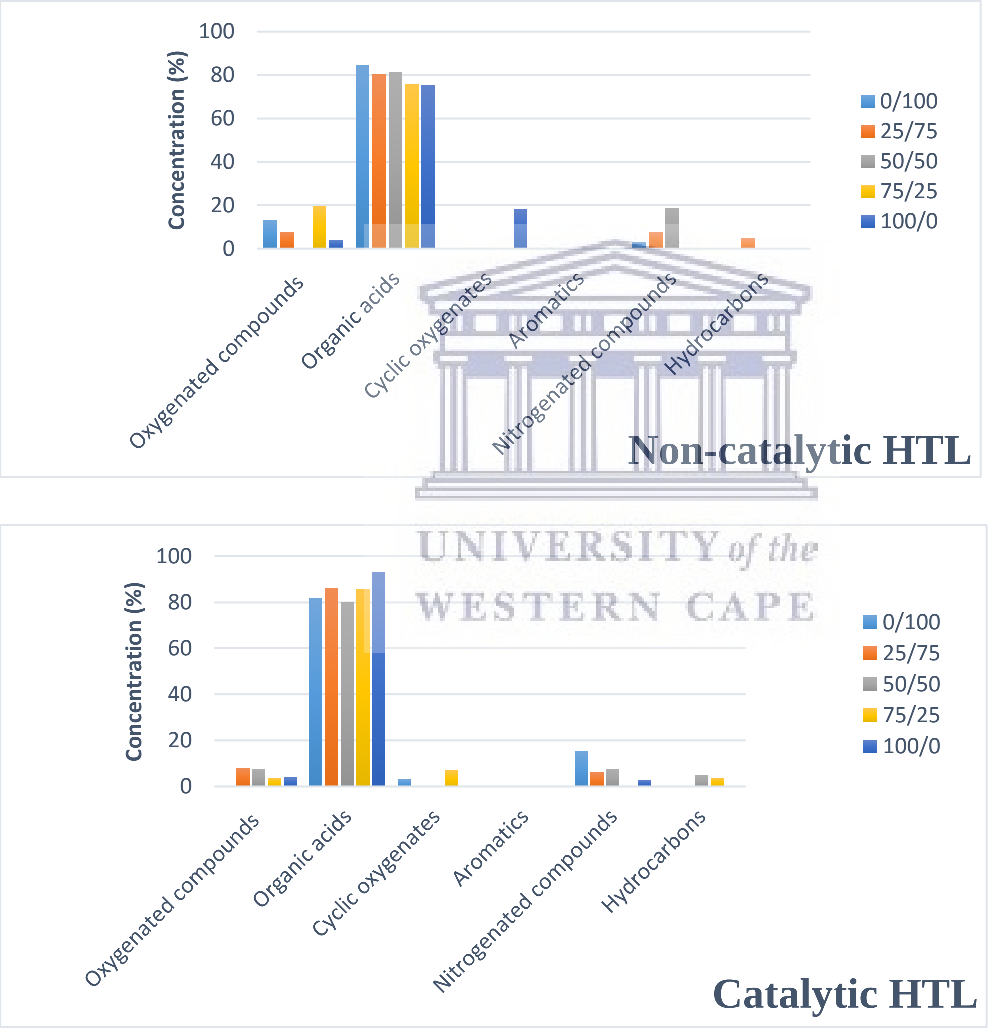


Figure 4.69: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction process at 120 minutes at 0:100-100:0 ratio of the feedstock

Organic acids were detected at a higher concentration in the liquid bio-crude oil from non-catalytic HTL as compared to the non-catalytic HTL. Oxygenated compounds, cyclic oxygenates, nitrogenated compounds and hydrocarbons were detected at a low concentration in the liquid bio-crude oil obtained from catalytic and non-catalytic HTL. Aromatics were detected at a very low concentration in the liquid bio-crude oil from catalytic HTL but were not detected in the non-catalytic HTL.

4.5.3.5 Effect of H-ZSM-5 on the chemical composition of bio-crude oil produced at 150 minutes reaction time



Non-catalytic HTL

Catalytic HTL

Figure 4.70: Major compounds detected using GC-MS in the bio-crude oil obtained from catalytic and non-catalytic hydrothermal liquefaction co-liquefaction at 150 minutes at 0:100-100:0 ratio of the feedstock

Organic acids were detected at higher concentration in the liquid bio-crude oil from both catalytic and non-catalytic HTL. Oxygenated compounds, cyclic oxygenates, nitrogenated compounds and hydrocarbons were detected at lower concentration in the liquid bio-crude oil from both catalytic and non-catalytic HTL meanwhile aromatics were not detected in both cases.

The non-catalytic bio-crude oil has the highest content of organic acids as compared to the H-ZSM-5, and this could be due to the inability of the H-ZSM-5 to extract lipids from the feedstock. H-ZSM-5 played no role in the chemical composition of the bio-crude oil since there was no trend in the concentration as the catalyst was added. High concentration of hydrocarbons, nitrogenated compound and organic acids shows that there was no breakdown of lignin and cellulose to form cyclic oxygenates, aromatics and oxygenated compounds but rather they were distributed into organic acids, hydrocarbons and nitrogenated compounds. The difference in the structures of the feedstocks has led to different components and volatile compounds to be present in the bio-crude oil.

Chapter 5

5 Conclusion and recommendations

This chapter summarises the findings of the research project by presenting an overview of the achievements of the research objectives, a discussion of the importance and contributions of the results is presented. Recommendations of the future work and research based on the concept of HTL of agricultural waste and food waste to produce bio-crude oil is highlighted.

5.1 Conclusion

Hydrothermal liquefaction is the promising technology for conversion of lignocellulosic biomass and it has been considered as a waste to energy technology by other` researchers, but it is still in the early stages of development. In this study, the effects of composition, residence time, temperature and catalyst on bio-crude oil yield and chemical composition were evaluated from hydrothermal liquefaction of grape plant and potato peels that are representative of agricultural waste and food waste, in order to determine the suitability of co-processing the waste feedstock together, the suitable residence time and temperature.

The observed trend on the pore sizes of the nano particles from the SEM images, showed a decrease in the diameter of the pores from 221 nm to 155 nm as the amount of food waste was decreased with an increase in the amount of agricultural waste in 0:100 ratio to 100:0 ratio.

The functional groups which were present in all the feedstocks were the alcohols, amines, carbonyl compounds as well as alkyl halides. There was no observed trend on the intensity of the absorption band which is associated with the presence of functional group as the composition of agricultural and food waste feedstock was changed in different ratios. Few functional groups were detected, and weak absorbance bands were observed when the amount of agricultural waste was increased from 0 wt.% to 25 wt.%. However, a further increase in the amount of agricultural and food waste in a 50:50 ratio played no role in the intensity of the absorbance band and in the presence of functional groups as compared to the case where the composition of the feedstock was 0wt% agricultural waste and 100wt% food waste. A further increase in the amount of agricultural waste to 100wt% and a decrease in the amount of food waste to 0wt% played no role in the presence of functional groups as well as the intensity of their absorption band. Therefore, feedstock composition in different ratio played no role in the presence of functional groups and on the intensity of the absorption peaks.

The observed trend in the elemental analysis was the decrease in the content of oxygen as the amount of agricultural waste was increased with a decrease in the amount of food waste. However, this was observed for the feedstocks composed of agricultural waste and food waste in 0:100 ratio, 25:75 ratio and 50:50 ratio. A further increase in the amount of agricultural waste with a decrease in the amount of food waste in a 75:25 ratio, has resulted in the drastic increase in the content of oxygen moreover a sudden decrease in the content of oxygen when the amount was further increased in a 100:0 ratio of agricultural waste and food waste was observed. Similar trend was observed in the other inorganic elements such as silicon, potassium and aluminium. An increase in the amount of agricultural waste resulted in the increase in the content of calcium.

Temperature effect is significant, bio-crude oil yields showed that the yields increased with an increase in temperature up until a certain temperature beyond which the bio-crude oil yield decreased due to further cracking of the liquid bio-crude oil to form gaseous products together with the losses. Residence time strongly affected the bio-crude oil yields, and the choice of selection depends on type of feedstock and temperature.

Hydrothermal liquefaction produced a bio-crude oil with a maximum or highest yield of 70.31 wt.% at 340℃ in 60 minutes with 0:100 ratio of agricultural waste food waste, in this bo-crude oil the volatile compounds which were detected in abundance (99.08%) were the organic acids in the form of hexadecanoic acid methy ester, isopropyl palmitate, 9-octadecanoic acid-methyl ester, and methyl stereate. Addition of H-ZSM-5 improved the yield to 75 wt.% and there was no significant changes in the composition of bio-crude oil.

The observed trend in the catalytic and non-catalytic HTL was an increase in the liquid bio-crude oil, with the decrease in solid biochar and gases and losses as the temperature and reaction time was increased and a sudden decrease in the yield of liquid biofuels with the increase in solid bio-char and gases and losses as the temperature went beyond 320°C and as the reaction time went beyond 120 minutes and this was a resultant of the thermal conversion of liquid bio fuels into gaseous product which indicate that polymerisation reaction is not favoured at higher temperature and the catalyst did not play any role at this temperature to inhibit the rearrangement of liquid biofuel into formation of new set of compounds.

Although the use of H-ZSM-5 did not exert positive effect on the chemical composition of bio-crude oil as there was no observed trend on the detected concentration of volatile compounds when H-ZSM-5 was added but it showed positive effect on the yield of the bio-crude oil by decreasing the activation energy of macromolecules and hence more macromolecules were hydrolised to form bio-crude oil at all the reactions. The non-catalytic bio-crude oil had the highest content of organic acids as compared to the H-ZSM-5, and this could be due to the inability of the H-ZSM-5 to extract lipids from the feedstock.

The GC-MS evidenced that the bio-crude oils obtained both in the catalytic and non-catalytic HTL contains various organic acids, nitrogenated compounds, hydrocarbons, oxygenated compounds as well as the aromatics. Lower concentrations of cyclic oxygenates, oxygenated compounds, and aromatics implied that there was no breakdown of lignin and cellulose but rather they were distributed into organic acids and nitrogenated compounds. Carbohydrates were hydrolysed to form glucose that was degraded to form cyclic oxygenates. Nitrogenated compounds and oxygenated compounds were formed from the Maillard reaction of amino acids from the hydrolysis of protein. Hydrocarbons and alcohols were formed from lipid that hydrolysed to form fatty acids that undergo decarboxylation to form hydrocarbons and alcohols.

High concentration of hydrocarbons, nitrogenated compound and organic acids shows that there was no breakdown of lignin and cellulose to form cyclic oxygenates, aromatics and oxygenated compounds but rather they were distributed into organic acids, hydrocarbons and nitrogenated compounds. The difference in the structures of the feedstocks has led to different components and volatile compounds to be present in the bio-crude oil

The oxygen in the bio-crude was mostly present in the form of carboxylic acids, esters, alcohols and ketones. The distinct amount of silicon transferred during HTL from the original sample can affect the bio-crude oil quality and this may cause limitations regarding its utilisation. Post hydrodeoxygenation, the bio-crude oil could either be used co-processing in refiniries alongside petroleum crude oil or used as a direct drop-in bio-diesel.

5.2 Recommendations

Although HTL has been demonstrated to be a promising and cost-effective route for biomass to energy conversions, no large scale production facility has been demonstrated and this brings difficulties in the usage of bio-crude oil due technical challenges of high content of heteroatom such as nitrogen and oxygen in the bio-crude oil and this will require additional upgrading treatment such as hydroprocessing before they can be issued as a liquid transportation fuel. Therefore, value added application of the bio-crude oil produced for bio-based chemicals and polymer materials need to be explored.

HTL is still at the early stage of development, this research on HTL of grape plant and potato peels has tried to fill the knowledge gap in the literature about how temperature, composition and residence time can influence bio-crude oil yield and properties and the role of H-ZSM-5 on bio-crude oil and its properties. With the knowledge gained from this research, the study on the intricacies of hydrothermal liquefaction can be expanded.

Although limited characterisation of the co-products was performed in this research, a more detailed study on the co-products analysis such as boiling points, thermal stability as well as metal analysis should be done in order to provide a clear understanding on how they can be used. A detailed study on the chemical constituents of the bio-char should be done to understand their formation and their use. The gas phase should also be studied to find out the gas composition of the grape plant and potato peels.

This research studied the effect of H-ZSM-5 only, but other heterogeneous and homogeneous catalyst should be taken under consideration for the study. The research was performed when using water as a reaction medium because of the ability of water to extract oil, other solvents should also be explored or both water and other solvents can also be used at variable ratios on the bio-crude oil yield and quality.

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