EFFECT OF OPERATING CONDITIONS ON THE HYDROTHERMAL VALORISATION OF SEWAGE SLUDGE

By

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DECLARATION

I, **Mbaliyezwe Precious Madikizela**, hereby declare that the work presented in this thesis is solely my own unaided work and that, to the best of my knowledge, the work is original, except where otherwise indicated by reference to other authors. Furthermore, no portion of this work has been submitted for any other degree or diploma.

_____	**05 January 2021**
Signature	**Date**

ABSTRACT

The accelerated population growth, in conjunction with the rapid urbanisation rate, are the principal driving forces behind the augmented volumes of municipal sewage sludge generated worldwide. The traditional approaches of sewage sludge treatment, which include landfilling and agricultural application, are no longer within the realms of possibility due to rigorous regulations, deficiency in the capacity of land available and the environmental and health adversities associated with detrimental constituents of sewage sludge. The population and urbanisation advancements do not only influence the emergent volumes of sewage sludge, but they also instigate fundamental provocations to the global energy demand. The reliance on fossil fuels poses a significant threat, not only to sustainable development, however they are also hugely responsible for the cumulative carbon dioxide and other greenhouse gas (GHG) emissions that deteriorate the environment, trigger global warming and deleteriously impact the livelihood of all life on earth. In line with the quest for sustainable and renewable alternative energy sources, the thermochemical treatment of municipal sewage sludge has a triple advantage of valorising the abundant volumes of the sludge, addressing the injurious nature of conventional fuels to the environment and seeking to bridge the gap as their supply diminishes.

This study followed a quantitative approach, with the purpose to convert municipal sewage to valuable bio-oils. The sewage sludge was subjected to hydrothermal liquefaction in 60 ml stainless steel batch reactors, where the effect of temperature, solvent composition, and solvent content were investigated, and all the other process parameters were maintained at a constant. The six temperatures that were explored were 220ºC, 250ºC, 280ºC, 310ºC, 340ºC, 370ºC. The two solvents investigated were de-ionised water (H_2O) and ethanol (E) which were applied in the following compositions: 1:0, 1:1 and 0:1 (H_2O:E). The five solvent contents investigated were 75%, 80%, 85%, 90% and 95%.

The process yielded bio-oils, solid phase and gaseous products and an aqueous phase. Dichloromethane was used as an extraction medium. The obtained results revealed that the temperature, solvent type and solvent content had a significant influence on the yield of bio-oil produced while temperature was the most influential out of the three parameters. When temperatures approached supercritical conditions of water, a notable decline in the bio-oil yields was observed. For each temperature, the bio-oil yields initially increased until about 85% solvent content, and then slightly decreased thereafter. The highest bio-oil yields were achieved at 310ºC and the best yields were obtained when the ratio of H_2O and E were 1:1. This study found that the optimum operating conditions were obtained at 310ºC, 85% solvent

content and a 1:1 composition of H_2O and ethanol; the bio-oil yields at those conditions was determined to be 40,6 wt%. The bio-oils were contained in the following order of prevalence, fatty acids, aliphatic hydrocarbons, N-containing compounds, O-containing compounds, aromatics and acid esters. Aliphatic hydrocarbons and fatty acids were the dominant functional groups. The following were the most abundant compounds in the 90 runs: heptadecane, pentadecane, eicosane, hexadecane 2,6,10,14-tetramethyl hexadecane and 9-octadecanoic acid.

Keywords: Municipal sewage sludge; hydrothermal liquefaction; bio-oil; ethanol

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DEDICATION

I wish to dedicate this thesis to my beloved mother, Sibongile Hellen Madlala. Ngiyibhalele wena Nqukhwe! Ingeyakho. Thank you for always being a strong pillar of support and love. I love you, Mommy.

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Abbreviations	Meaning
DCM	Dichloromethane
C	Carbon
CO_2	Carbon dioxide
E	Ethanol
H	Hydrogen
HTC	Hydrothermal carbonisation
HTG	Hydrothermal gasification
HTL	Hydrothermal liquefaction
MSW	Municipal solid waste
N	Nitrogen
O	Oxygen
SC	Solvent content
SCW	Supercritical water
subCW	Subcritical water
T	Temperature
W	Water

CHAPTER 1

1 Introduction

1.1 Background

The global energy crisis following the deficiencies of petroleum resources encountered in the 1970s has driven an advancement leaning towards diverse alternative fuels, in the interest of mitigating the immense reliance on conventional fuels (Xiu & Shahbazi, 2012). With the energy consumption escalating by 2% annually, owing to the rapid population growth that is expected to escalate to 9 billion by 2050 (Ghenai et al., 2020), coupled with the inadequate energy generation and supply, global efforts and policies have been strategically channelled in the direction of renewable and sustainable energy systems (Nam et al., 2020). Notwithstanding the realignment en route towards a 100% renewable energy system is an intricate process, encompassing various technical challenges (Stančin et al., 2020). There are, however, key benefits of employing alternative energy sources that confront environmental issues associated with the use of fossil fuels and bridges the gap of their diminution (Mayer et al., 2020).

Hydrothermal liquefaction is a thermochemical treatment process directly applied to wet biomass with the intention of converting it into liquid fuels (Elliott et al., 2015). This is achieved by conducting the process in a hot and pressurised water environment, for an appropriate duration, in the presence of a solvent and/or a catalyst in order to break down the solid biopolymeric structure into predominantly liquid components (Tzanetis et al., 2017). Amid other available routes of thermochemical conversion of sewage sludge, such as pyrolysis, gasification, direct combustion, supercritical fluid extraction, transesterification and steam reforming, hydrothermal liquefaction has been discovered to be an attractive technology owing to its capability of converting not only dry feedstock, also its also feasibility for wet feedstock conversion directly into fuel (Dimitriadis & Bezergianni, 2017; Gollakota et al., 2018).

From the available thermochemical treatment routes, hydrothermal liquefaction is comparable to pyrolysis in the sense that both the technologies yield oil-based intermediate products, in other words bio crude or bio-oil (Neveux et al., 2014; Kan et al., 2016; Tzanetis et al., 2017). Among other advantages of hydrothermal liquefaction, the process is appealing as it is conducted in the presence of water, thereby taking advantage of the biomass moisture, unlike pyrolysis, which consumes high energy and is capital-intensive due to the drying step that is imperative. In addition, the solvents used in hydrothermal liquefaction perform as catalysts that yield higher quality products as compared to those attained from pyrolysis (Tzanetis et al., 2017). Undoubtedly, hydrothermal liquefaction is more competitive for biomass and sewage

sludge conversion owing to the fact that the products obtained have a lower oxygen and moisture content and a greater heating value compared to those from pyrolysis, which significantly decreases both the fixed and operative costs of handling equipment and storage (Dimitriadis & Bezergianni, 2017).

Process parameters such as temperature, residence time, moisture content, addition of solvents or catalysts, particle size of the biomass sample charged in the reactor, pressure, feedstock type and heating rate have an effect on the hydrothermal liquefaction products. However, some parameters have a greater effect than others (Galadima & Muraza, 2018). Depending on the operating parameters, several compounds are produced as a result of the hydrothermal decomposition of biomass. A typical hydrothermal liquefaction process yields, bio-oil, an aqueous solution, solids and gases (Qian et al., 2017). Biomass-derived fuels serve as alternative, renewable and sustainable fuels. In its unprocessed state, the bio-oil derived from biomass is by nature, low in energy, high in moisture content and not free-flowing; therefore, upgrading the bio-oil is encouraged (Gollakota et al., 2018).

1.2 Problem statement

Wastewater sludge is an inevitable waste by-product obtained in the process of wastewater treatment. Its disposal through agricultural application together with landfilling, has in recent years become a great challenge due to stringent legislation for effluent and the environmental impacts associated with it (Chen et al., 2002). With the steady increase in urbanisation, industrialisation and population, there is a noticeable and direct impact on the amount of municipal wastewater sludge produced. The rising volume of municipal wastewater sludge produced in urban communities demands not only proper policy, but also developed technology for its treatment (Syed-Hassan et al., 2017). The thermochemical treatment of wastewater sludge, in particular hydrothermal liquefaction, has been discovered to be an attractive route to facilitate the transformation of this carbon-rich organic matter into valuable energy and fuel (Nazari et al., 2017). Being woke to the fact that the fuel demand in South Africa is continuously growing, the conventional fossil fuels are depleting at a rapid rate and the environmental pollution related to the use of these conventional fossil fuels triggers the desire to venture into alternative sources of fuel, and this has since become a major focus area in the country and the globe at large (Choudhury et al., 2017; Galadima & Muraza, 2018). Therefore, the study of valorising municipal wastewater sludge is necessitated as a path towards ensuring sustainability.

1.3 Research aim and objectives

The aim was to valorise wastewater sewage sludge using hydrothermal liquefaction technology.

The objectives were as follows:

- Investigate the effect of operating parameters on the yield of bio-oil.
- Investigate the effect of operating parameters on the conversion of municipal sewage sludge.
- Determine the effect of operating parameters on product distribution in the bio-oil produced.

1.4 Research questions

The research questions were as follows:

- Will the hydrothermal liquefaction process add value to sewage sludge?
- Will different parameters have a significant impact on the liquefaction of sewage sludge?
- What process conditions are likely to be optimal for sewage valorisation?

1.5 Hypothesis

The temperature will impart the greatest effect on the yield and conversion compared to solvent content and solvent type. Ethanol as a solvent will enhance the yield of bio-oil far more than water. The solvent content will have a great effect on the product distribution. Hydrocarbons similar to those of gasoline will be dominantly present in the bio-oils along with ester compounds.

1.6 Significance of the study

The fundamental significance of this study is to essentially valorise municipal sewage sludge, as its conventional disposal is no longer viable due to stringent regulations and diminishing landfill space in the province of Kwa-Zulu Natal and the country at large. Apart from addressing the issue of a large amount of sludge readily available that could potentially be valorised, the research confronts the ongoing problem of elevated demands of energy and fuels that are not met, the threat imposed by conventional fossil fuels and the environmental pollution associated with this source of energy. The research seeks to find alternative and amicable approaches of creating clean, renewable and sustainable energy, which remains a major focus globally.

1.7 Delineation of study

The scope of this research was limited to the investigation of the effect of temperature, solvent content and solvent type on the yield of bio-oil, the conversion of municipal sewage sludge and the product distribution of the bio-oil produced by the hydrothermal liquefaction process. The following were not considered:

- The effect of particle size
- The effect of catalyst
- The effect of biomass type
- The effect of residence time
- The effect of heating rate
- The effect of co-liquefaction

1.8 Thesis outline

The research presented in this thesis was conducted at the Durban University of Technology (DUT), Durban, South Africa. The thesis comprises of seven chapters, including this introductory chapter.

Chapter 1 presented the introduction which highlighted the background of the study, the problem statement, the research aim, objectives, and questions, the hypothesis, and the significance and delineation of the study.

Chapter 2 presents a comprehensive literature review which covers the history of conventional fuels and their challenges, then maps the direction towards renewable and sustainable resources. It further outlines the diverse biomasses available for alternative energy sources and focuses on wastewater sewage sludge and wastewater treatment from where it emanates. The literature also deliberates on the various thermochemical methods for the valorisation of biomass in particular sewage sludge, and the effect of various process parameters on the yield, conversion and product distribution.

Chapter 3 presents the materials and describes the methodology used in this work. A schematic diagram of the experimental procedure that was executed is also presented.

Chapter 4 presents the results and discussion of the effect of process parameters on the yield and conversion.

Chapter 5 presents the results and discussion of the effect of process parameters on product distribution.

Chapter 6 deliberates on the various conclusions that were drawn from the results presented in this thesis and recommends a perspective for future research work.

CHAPTER 2

2 Literature review

This chapter reviews the various literature which commences from the history of conventional fuels, and the challenges pertaining to their application and then maps the direction towards renewable and sustainable energy sources. Thereafter, it outlines the diverse biomasses that are potentials for alternative energy sources and focuses on wastewater sewage sludge and wastewater treatment from where it emanates. The literature also deliberates on the various thermochemical methods for valorisation of biomass, in particular sewage sludge, and the effect of various process parameters on yield, conversion, and product distribution.

2.1 Introduction

Energy plays an essential role in any form of development globally. It is a necessary and fundamental requirement in everyday life for the production of commodities and the operation of services (Mulaudzi & Bull, 2016). Energy demand in South Africa has been escalating consistently over the years; consequently, the country has been subjected to skyrocketing power prices due to very large load burdens especially in the peak seasons. The country has experienced numerous blackouts as a result of severe energy shortages, which does not only affect the general running of households, but also greatly disrupts the manufacturing and mining industries, hence stressing the country's economy (Pollet et al., 2015).

It is not only the continuous excessive demand of energy and the indisputable reality that fossil fuels will eventually diminish, but also the concern of environmental threats that have triggered the urgency to explore clean, sustainable, economical, effective and efficient energy technologies (Colpan & Kizilkan, 2016). The extravagant use of conventionally derived energy sources and an increase in carbon dioxide and other greenhouses gases, which result in detrimental environmental pollution, are inseparable (Xu et al., 2020). Clean energy includes wind, solar, geothermal, biomass and hydroelectric energy. Nuclear energy is also regarded as clean energy and is advantageous because it is inexpensive; however, it is threatening to both the environment and human life due to its radioactive waste (Chen et al., 2002).

Among other feedstock, biomass such as algae are reputable owing to their accelerated growth rates, exceptional lipid content, capability of being cultivated in non-arable land and because it does not use excessive water or compete with food or feed production (Sun et al., 2018). However, waste to energy has been found to be more attractive, having extended benefits such as being cost-effective and promoting recycling (Menyah & Wolde-Rufael, 2010). Furthermore, the exploitation of waste biomass such as sewage sludge is advantageous since

it is readily available and doesn't require cultivation. The conventional sewage sludge treatment methods, such as disposal, landfill, incineration, composting and anaerobic digestion, undermines the potential energy stored in the sludge and cannot produce value-added products, while lipids contained in the sludge have great value for bio-oils (Menyah & Wolde-Rufael, 2010).

There are various techniques to valorise biomass to bio-fuel, with the prominent ones including pyrolysis, transesterification, solvent extraction and hydrothermal liquefaction (Xu et al., 2020). Hydrothermal liquefaction, which is conducted at moderate temperatures less than 400ºC and high pressure 10-25 MPa compared to other thermochemical technologies, has the benefits that it can convert high moisture content biomass (Xu et al., 2018).

2.2 Energy fuels and sustainability

Fuel can be defined as any substance that has the potential to undergo an exothermic decomposition. Most conventional fuels are derived from oil and gas that were trapped in a sedimentary rock called reserves. The source of these hydrocarbons is understood to have emerged from plants and animals buried millions of years ago that gradually transformed into oils and gases of diverse qualities, owing to the extreme temperatures and pressures underground. These were recovered using special technology (Longwell, 1990).

Generally, fuels are organic, consisting of versatile carbon atoms (Karim, 2012). Fossil fuels have gained considerable popularity and favour in the past decades for their abundant reserves, the fact that they are inexpensive and comprise of high energy content. Engine technologies have been developed around gasoline and diesel fuels, but generally many products may be exploited as energy fuels (Hancsók & Srivastava, 2014), such as:

- alcohols,
- gasoline,
- diesel,
- gas oil,
- natural gas,
- liquefied petroleum gas,
- compressed natural gas,
- coal-derived liquid fuels,
- biofuels,
- hydrogen etc.

Environmental considerations, policies on emission, energy efficiency, and new engine technologies are the underlying motivations for the dramatic modifications in the fossil fuels and additive quality in the past few decades (Hancsók & Srivastava, 2014).

2.2.1 Classification of energy fuels

The knowledge of the type of fuel to be employed in energy applications is important due to the requirement of different chemical procedures for proper processing of material and to obtain optimal results (Elmaz et al., 2020). Fuel classification is thus imperative. Fuels may be classified based on their properties or application. The most typical classification depends on whether they are:

- Solid, liquid, or gas (at ambient conditions)
- Organic or nonorganic
- Raw or cooked
- Fossil or non-fossil
- Conventional or alternative
- Mineral fuels or biofuels
- Of low heating value, medium heating value, or high heating value
- Natural or manufactured (Karim, 2012; Gilchrist, 1977)

Hancsók et al. (2014), comprehensively classified conventional and alternative fuels in Figure 2.1 displayed below.

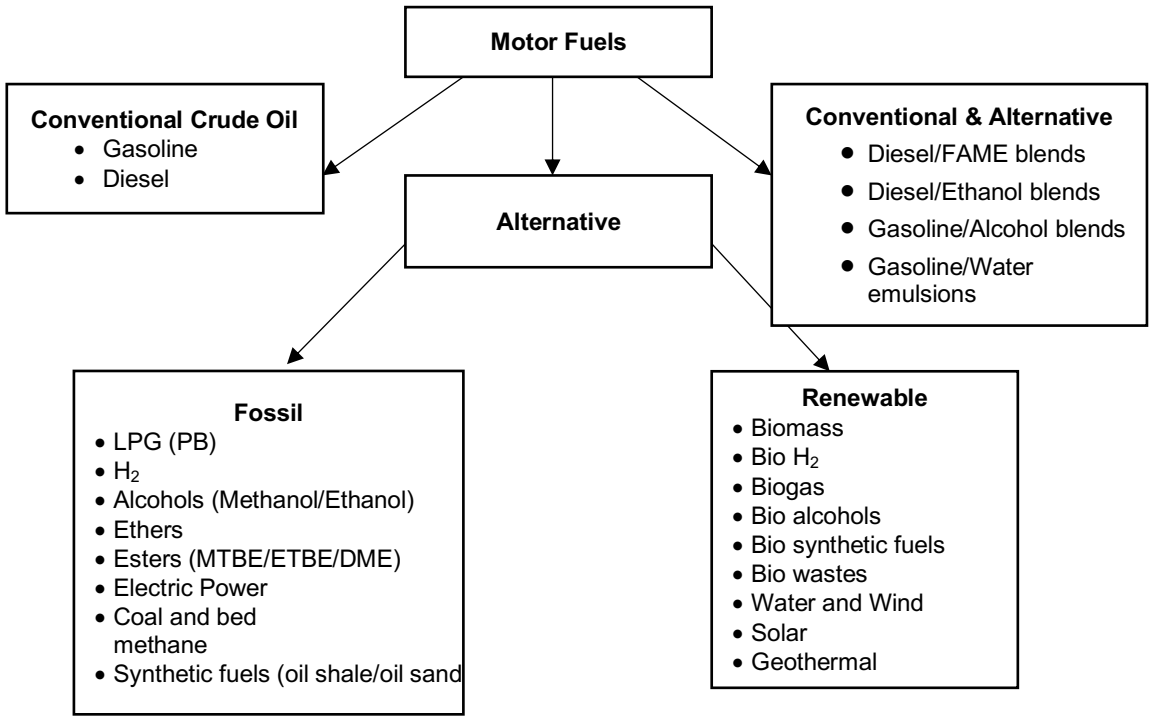

Figure 2.1 Classification of conventional and alternative fuels

Adapted from Hancsók et al. (2014)

2.3 Conventional fuels

Petroleum and coal are the most common fuels. They are regarded as conventional non-renewable fuels and include natural gas, shale gas, oil from shale, tar, and sand bitumen (Oakey, 2015). Petroleum alone covers approximately 40% of the globe's energy demand and produces 96% of transportation fuels (Hu & Gholizadeh, 2019). Oakey (2015) defines the following conventional energy sources:

- Petroleum – includes crude oil, natural gas, and heavy oil. Under typical conditions of standard temperature and pressure, hydrocarbons that are lighter in molecular weight remain at the surface and the heavier hydrocarbons in the liquid and semisolid or solid-state are positioned underneath.
- Natural gas – primarily methane. Other constituents are paraffinic hydrocarbons such as ethane propane and the butanes, nitrogen, carbon dioxide, and hydrogen sulphide. There are also some traces of argon, hydrogen, and helium.
- Coal – predominantly contains carbon, along with some hydrogen, nitrogen, oxygen, and sulphur. It is the most abundant and widely distributed fossil fuel. It exists in different forms and qualities.
- Shale gas – found in sedimentary basins and has been already identified in the most countries.
- Oil from shale – impermeable rock and nonporous sandstone or limestone formations that also contain natural gas and petroleum.

Conventional fuels generally have an advantage and are more superior to other fuels based on their very high energy source. Table 2.1 below displays the energies stored in the different fuels. From Table 2.1, it is evident that hydrogen has a higher energy storage capability than gasoline and diesel on a mass basis; however, on a volume basis, gasoline and diesel fuels are more superior to hydrogen in terms of energy storage capacity (Bolz, 1973).

Table 2.1 Energy stored in different fuels

Energy Fuel	Energy (MJ/kg)
Gasoline	42-44
Diesel	42,5
Methanol	19,7
Ethanol	26,8
Hydrogen	120
Methane	50
Lead-acid battery	50

Adapted from Bolz (1973)

2.4 Energy security

Energy is an essential requirement in the modern economy for the production of goods and services (Kosai & Unesaki, 2020). With the substantial escalation in the modernisation of life and massive industrial development, there has been a drastic increase in the urban population in the recent decades, emanating from rapid economic growth; hence, the energy consumption continues to rapidly rise in correlation with urbanisation (Sarıkoç et al., 2020; Barreto, 2018; Zhou et al., 2020). With this increase, energy security has emerged as an area of supreme focus and robust debate on a global scale (Cherp & Jewell, 2011; Martins et al., 2018)

It is worth noting that many authors point out that the definition of energy security and methods of its evaluation is somewhat ambiguous (Victor et al., 2014; Winzer, 2012; Löschel et al., 2010). For instance, there are disputes on whether economic, environmental, and social considerations are to be incorporated in its definition. Further deliberations argue the suitable scale at which the security may be measured, such as national, regional, or local scale (Jewell et al., 2014). Most studies that conceptualise energy security are biased towards oil supply; however, the conventional comprehension of energy security needs to be expanded and allow a broader comprehensive incorporation of other relevant factors and challenges (Stringer, 2008; Victor et al., 2014). Despite this ambiguity in the definition of energy security, there is a general agreement that energy security is closely associated with immense risk (Kosai & Unesaki, 2020). Jewell et al. (2014) defined energy security as “a low vulnerability of vital energy system”, while Stringer (2008b) defined it as “an umbrella term that covers many concerns linked to energy, economic growth, and political power”.

Vivoda (2010) identifies four key challenges that need to be included in the concept of energy security:

- Environment – If catastrophic issues such as global warming and climate change were to be resolved, then the energy security policies would have to be reformulated.
- Technology – Technology needs to be established that will incorporate specifically renewable energy sources.
- Demand-side management – Conventional energy security undermines demand-side risk and this risk needs to be categorically accounted for.
- Domestic socio-cultural and political factors – The importance of energy policy planning in the political arena.

Some additional challenges that need to be added into the concept, as pointed out by Vivoda (2010), include:

- Human security – Energy security needs to consider making electricity accessible to the entire population.
- International – Energy security policy needs to address the international implication of energy security challenges.
- Policy – Energy security policy must be clearly stated and address traditional and new energy security challenges.

2.5 Energy demand and supply in South Africa

Owing to the rapid population growth and steadfast urbanisation rate, there has been an inevitable increase on the reliance and consumption of energy (Syed-Hassan et al., 2017). Energy, which is also referred to as “the lifeblood of modern life”, is fundamental to any country’s economy (Ratshomo & Nembahe, 2018). It is also a paramount force that drives businesses, manufacturing, transportation, and service delivery. As the economy grows, a country relies heavily on imports of natural gas and coal to meet the energy demands (Kim et al., 2011).

South Africa’s economic growth, which includes industrialisation and a major electrification programme with the intention to introduce power into deep rural areas, has experienced a rapid climb in the demand for energy in recent years. This is illustrated in Figure 2.2 presented below, illustrating the shared percentage of energy demanded by diverse sectors, namely industrial, transport, agriculture, residential, commerce and public services (Ratshomo & Nembahe, 2019).

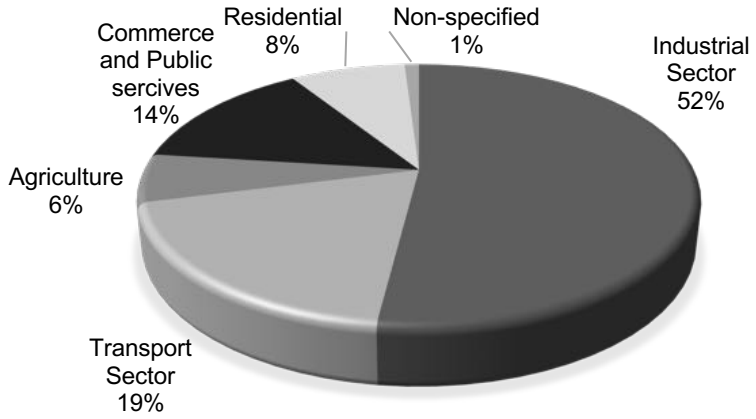

Figure 2.2 South African energy demand by sector

Adapted from Ratshomo & Nembahe (2019)

South Africa’s energy sector is dominated by coal, which is inexpensive and categorised among the cheapest goods in the world. South Africa also obtains energy locally from biomass,

namely wood, dung, natural gas, hydropower, nuclear power, solar power, and wind (Ratshomo & Nembahe, 2019).

The total South African energy supply is summarised in Figure 2.3 below, where coal is leading at 69% of the primary energy supply as per records of 2016, followed by crude oil at 14%, renewables and wastes at 11%, and finally, nuclear sitting at 3%.

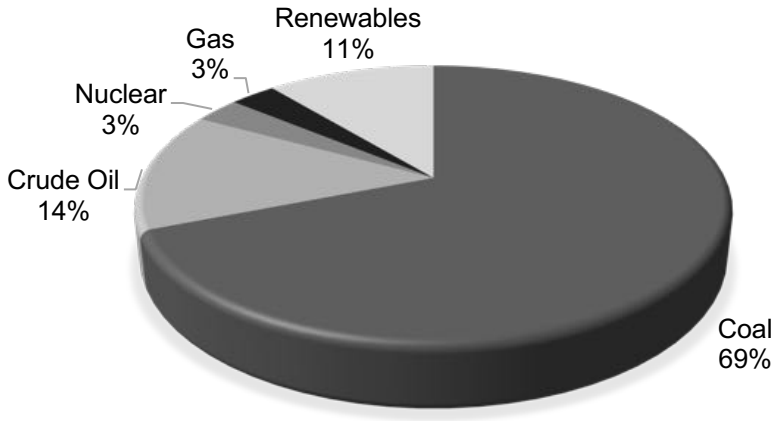

Figure 2.3 South African total primary energy supply

Adapted from Ratshomo & Nembahe (2019)

Due to a shortage of reserves, South Africa imports over 90% of its crude from Saudi Arabia, Nigeria and Angola. Most of the petroleum products are refined in the country (Ratshomo & Nembahe, 2019).

2.6 Fossil fuels and challenges

Fossil fuels are living matter that perished, descended to the floor of swamps, lakes, and seas, which then produced sponge-like matter. After a long period, with the combined action of temperature, pressure, catalysts, and bacteria, the matter converted into, coal, oil, and natural gas (Karim, 2012).

Since the commencement of the industrial era, fossil fuels have been employed as the primary source to attain energy for developed and underdeveloped countries. However, there are numerous negative impacts associated with them, such as global warming and air pollution (Martins et al., 2018). The hasty growth in industrialisation has resulted in a multiplied demand and elevated price drift for fossil fuels (Day & Day, 2017). It goes without saying that all fossil fuels are finite minerals and non-renewable in nature (Capellán-Pérez et al., 2014). There has

been a considerable increase in CO_2 in the atmosphere as a consequence of the emissions of anthropogenic greenhouse gas and other radiatively active gases (Chiari & Zecca, 2011; Höök & Tang, 2013). To be precise, Ahmed et al. (2020) reported a total amount of 1,83 trillion tons of carbon dioxide emissions caused by fossil fuels. Fossil fuel combustion accounts for the largest human sources of greenhouse gas emission on earth (Blockstein et al., 2015). According to Nam et al. (2020), greenhouse gases will increase by 30% in the next 20 years without any regulatory restriction on the use of fossil fuels. The climate policy is confronted with a fundamental challenge of discouraging fossil fuel-rich economies from disseminating emissions (Day & Day, 2017). However, global efforts have been employed to conquer the dependency on fossil fuels to mitigate global climate change and the adverse effect due to using these fuels (Nam et al., 2020).

Apart from the fact that fossil fuels remain to be the most economically viable fuel source, their undesirable contribution outweighs their favourable aspects associated with their use (Barreto, 2018). The instability and unreliability in the prices of fossil fuels is a major drawback from an economical perspective, the underlying fact that they are depleting and non-renewable in nature necessitates an inevitable quest for new and innovative solutions (Martins et al., 2018). Renewables are emerging, but unfortunately, the conversion towards these low-carbon fuel systems is rather retarded (Ridjan et al., 2016). This is owing to the fact that substituting conventional with alternative fuels is not a simple matter and certainly requires lengthy configurations. Apart from the pollution that is associated with fossil fuels, another concern is that their rapid depletion has resulted in stringent emission regulations, consequently channelling an appetite for additional research on cleaner energy sources and their implementation thereof (Ning et al., 2020). There is also a grave uncertainty associated with future price of fuel oils (Tan et al., 2020).

2.6.1 Global warming

Mankind's energy generation from fossil fuels is the major contributor to environmental problems such as air pollution and global warming (Martins et al., 2018; Blockstein et al., 2015). The rising global carbon dioxide emissions and their deposit in the atmosphere are the principal cause of global climate change and global warming that impact on the livelihood and activities of all life worldwide (Michaelides & Michaelides, 2020).

2.6.2 Pollution

Owing to the substantial growth in greenhouse emissions over the past few decades, environmental pollution has become a major setback (Wang & Zhan, 2019). The pollution from

utilisation of fossil fuels has not only inflicted detrimental pollution to the environment, but has affected local, regional, and global health (Blockstein et al., 2015).

2.6.3 Insecurity of supplies

The escalation in the demand of energy is consistent with the rapid expansion of the global population. This is why energy security is extremely vital for current and future generations (Kosai & Unesaki, 2020). Energy insecurities emerge from the physical unavailability of energy sources or processes that are either not competitive or overly volatile (Löschel et al., 2010). The dependence on fossil fuels also raises enormous threat to the energy supply, whereas, on the other hand, the development of other energy sources lessens this risk of scarcity to a great degree (Kosai & Unesaki, 2020).

2.7 Alternative and renewable fuels

Alternative fuels are favourable in many respects. They are produced through a sustainable and clean procedures. There are two core routes for the synthesis of alternative fuels: thermochemical conversion and direct utilisation of electricity surplus (Stančin et al., 2020). When referring to fuels, the terms “renewable” and “alternative” are often intertwined and it is critical to distinguish between the two and to not use them interchangeably. According to Ridjan et al. (2016), renewable fuels make use of renewable feedstock for their production. This includes a selection of fuels that use biomass and other renewable energy processes. Conversely, alternative fuels are any fuels other than gasoline that can be produced without taking into consideration the feedstock, denoting that they can be produced from either fossil or renewable fuels (Ridjan et al., 2016).

Apart from many favourable aspects of renewable energy sources, it is an unavoidable fact that some are more expensive than conventional fuels. The government needs to discourage the reliance on conventional fuels through policy, by either making fossil fuels more expensive due to the harm they pose or making regulations more stringent (Popp et al., 2011). This would alleviate the dependence on fossil fuels and help renewable energy become competitive (Aguirre & Ibikunle, 2014).

2.8 Biomass

The energy obtained from biomass is called bioenergy. Biomass is a biological material obtained from living or recently living plant-based substance that originates from nature and is synthesised from carbon dioxide and water through the photosynthesis process (Zhu & Xu, 2020). Unlike fossil fuels, biomass does not require a million years to develop (Basu, 2010). It

is versatile with a variety of uses and applications ranging from building products, furniture, clothing, plastic and paper production, food or feed, to fertiliser production and many more (Schmeichel, 2014). In 2000, Bhattacharya et al. (2000), reported that biomass was the fourth leading renewable energy source globally. Twenty years later, Kaczor et al. (2020) revealed in recent research that biomass is ranked the third-largest renewable energy source. Biomass production is anticipated to escalate further over the coming decades, as the notion to mitigate the use of fossil fuels is popular (Chen et al., 2020).

From biomass we get the following key categories of products (Basu, 2010):

- Chemicals such as methanol, fertilisers and synthetic fibre,
- Heat energy,
- Electricity and,
- Transportation fuels.

The three kinds of primary fuels produced from biomass (Basu, 2010):

- Liquid, for example ethanol, biodiesel, methanol, vegetable oil, and pyrolysis oil.
- Gaseous, for example biogas (CH_4CO_2), producer gas (CO H_2 CH_4 CO_2) syngas (CO H_2) and substitute natural gas (CH_4).
- Solid, for example torrefied biomass and bio char.

Ethanol and biodiesel as transport fuels have a duel benefit. They decrease the reliance on fossil fuels, and lower CO_2 emissions (Basu, 2010).

Biomass is used for diverse energy needs such as generating electricity, heating homes, fuelling vehicles and in industrial facilities (Amaro et al., 2012). It is generally considered to be the most attractive and promising renewable energy (Amaro et al., 2012). It is regarded as carbon neutral because the carbon released to the atmosphere during energy conversion was originally derived from the atmosphere during the process of photosynthesis (Pour et al., 2017; Jayarathna et al., 2020). In addition to that, biomass naturally has a lower nitrogen (N) and sulphur (S) content in comparison to coal and petroleum oil, which makes it an attractive alternative feedstock (Lo et al., 2021). The role of biomass in the future system is not questionable because it is already in use (Stančin et al., 2020). The utilization of biomass remains an attractive option for the production of fuels and chemicals as an alternative to fossil fuels because of its low cost, abundance, and topographical independence (Wang et al., 2019).

According to Ni et al. (2006), a range of biomass resources can be used to be transformed to energy. The available energy production processes are either thermochemical or biological. The two major biomass groups and the sub classifications are displayed in Table 2.2 below (Basu, 2010):

Table 2.2 Biomass Classification

Virgin	Terrestrial	Forest biomass Grasses Energy crops Cultivated crops
	Aquatic	Algae Water plants
Waste	Municipal	MSW Biosolids Sewage Landfills
	Agricultural	Livestock and manure Agricultural crop residue
	Forestry residues	Bark Leaves Floor residues
	Industrial wastes	Demolition wood Sawdust Waste oil or fat

Adapted from Basu (2010)

Biomass can differ considerably in its physical and chemical properties owing to its various origins and kinds. Structurally, biomass is composed of cellulose, hemicellulose, lignin, extractives and inert ash (Chen et al., 2003).

The fuels and residues derived from biomass can be transformed into valuable energy forms through a variety of processes, namely thermal, biological, mechanical and physical processes (Bridgwater, 2012; Wang et al., 2017; Ni et al., 2006). Biochemical processes typically produce methane and alcohols through fermentation and both anaerobic and aerobic digestions (Kwietniewska & Tys, 2014). The thermochemical processes convert biomass into suitable gaseous or liquid fuels through gasification, or pyrolysis or hydrothermal liquefaction (HTL) technologies (Hu & Gholizadeh, 2019). Among the favourable factors regarding the use of biomass for fuels, there are, however, some drawbacks to their application. Some bio-oil properties include low heating value, incomplete volatility, acidity, instability, and incompatibility with conventional petroleum fuels (French & Czernik, 2010). This is because in its regular form, biomass has an extensive amount of humidity and such humidity is

responsible for low calorific value (Tabakaev et al., 2019). The cost of bioenergy-based technology is yet another drawback. Their prices are generally significantly greater than those derived from fossil fuels (Gouws et al., 2021). This can explain why the price of fossil fuel to some extent remains superior to renewables, even with their popular negative connotations associated with the former.

2.8.1 Biomass types

There are serval types of biomass that can serve as alternatives to conventional fuel sources. It is also necessary to point out that as much as it is deemed necessary and beneficial to replace fossil fuels, their complete replacement is impeded by many factors such as climatic, seasonal and geographical dynamics that are present in specific areas (Amaro et al., 2012). Some regions have a high presence of wind while other places have restricted wind due to a presence of a large range of mountains and deep forests, while in other regions there are limited water resources (Izadyar et al., 2016; Patel, 2014). Another major factor to be mindful of when selecting biomass type is proximity. Production of bio-oil that occurs in close proximity to the biomass's original location tends to save significantly on transportation costs, consequently saving considerably on overall costs of production (Auersvald et al., 2020). These are all the factors that need to be considered when selecting a type of biomass for biofuel production.

Assmann et al. (2012) summarised plant biomass as presented in Table 2.3.

Table 2.3 Types and Examples of Plant Biomass

Woody Biomass	Non-Woody biomass	Processed waste	Processed fuels
• Trees • Shrubs • Tea and coffee bushes • Sweepings from forest floors • Bamboo • Palms	• Energy Crops – sugar cane • Cereal straw • Cotton, cassava, tobacco stems and roots • Bananas, plantains and the like • Soft stems (pulses and potatoes) • Swamp and water plants	• Cereal husks and cobs • Bagasse • Wastes from pineapple and other fruits • Nutshells, flesh and the like • Plant oil cake • Sawmill wastes • Industrial wood bark and logging wastes • Black liquor from pulp mills • Municipal waste	• Charcoal from wood and residues • Briquette and densified biomass • Methanol and ethanol • Plant oils from palms, rape, sunflower and the like • Producer gas • Biogas

Adapted from Assmann et al. (2012)

2.8.2 Wood

The term wood denotes a solid lignocellulosic substance that is naturally produced in the trees and certain shrubs. Lignocellulosic biomass is a promising alternative energy source. The advantage of its application as an alternative biomass includes its universal availability and its nature of being environmentally benign (Gazi, 2019). Ots et al. (2017) acknowledges that the use of low quality wood for electricity production has reduced the impact of emissions on the environment. Furthermore, it is carbon natural and, of course, renewable (Bellouard et al., 2019). Plantations in tropical and sub-tropical regions, including temperate regions, are observed as a solution for the increasing demand for biomass, to the extent that tree breeding programmes have been conducted with various trees in the interest of producing high volumes and lignin concentration for fuelwood (Bouvet et al., 2020).

In general terms, lignocellulose comprises of three distinct elements that constitute roughly 85 to 90% of the biomass and the remaining elements are organic extractives and inorganic minerals. They are as follows (Pasangulapati et al., 2012; Gazi, 2019):

- Hemicellulose (20-30%): chiefly branched polysaccharides of C5 and C6 comprised of various sugar monomers such as glucose, xylose, mannose galactose and arabinose and uronic acids.
- Cellulose (40-50%): a long linear polysaccharide with a β (1–4) glucose chain links. They can also be integrated into biofuels such as bioethanol and other aliphatic compounds.
- Lignin (20-30%): considered to be the greatest source of aromatic compounds. It is a complex phenolic macromolecule consisting of phenylpropanols, chiefly coniferyl alcohol, p-coumaryl alcohol, and sinapyl alcohol. It is the cementing material that produces elasticity.

Woody biomass exists as a complex compound structure. For it to be used effectively as biomass, it requires the exposure of cellulose and hemicelluloses from the cell walls, which are encapsulated in lignin, the core constraint in the process of biodegradation of lignocellulosic both in aerobic and anaerobic states (Amirta et al., 2016).

Although wood has always been a common source of energy and a viable alternative to coal, it is however, associated with some unattractive factors, such as excessive moisture content. This in turn negatively impacts the heating value. The two types of water that exist in biomass are bound water, which is within the cell wall of the wood (cellulose and hemicellulose) and free water, which is situated in the cell lumina (Machmudah et al., 2020). Another significant

concern is the ash generated from combustions posing a detrimental threat to the environment and economy.

Woody biomass can be subject to biochemical and/or thermochemical processes. In the biochemical processes, anaerobic digestion applied in the absence of oxygen and bacteria is used to decompose the woody biomass. Methane or biogas is produced. Aerobic digestion makes use of ambient oxygen to decompose the woody biomass. The quality of the products is influenced by process parameters such as temperature. Fermentation can also be exploited. Thermochemical processes that can be applied to woody biomass include pyrolysis, gasification, liquefaction, the Fisher-Tropsch process and the hydrothermal upgrading process to produce bio-oils, gases and char (Dahiya & Krivov, 2014).

2.8.3 Energy crops

Energy crops are inexpensive and low-maintenance plants that are employed in the production of bioenergy. Dedicated energy crops are plants and aquatic species that are rich in oils, sugars and starches. They are cultivated specifically for bioenergy applications and not for food or feed. Energy crops are grown and harvested periodically, and this may transpire on an annual basis or even a five to seven-year cycle. Generally, perennial crops are characterised as higher lignin crops as compared to annual crops (Lewandowski et al., 2003). Examples of energy crops include but are not limited to, sugar beets, cereal crops, corn, and sugar cane (Brown, 2014). Dedicated crops are divided into three categories: herbaceous energy crops, short woody crops, and oleaginous crops. In the quest of diversifying alternative and renewable energy sources, energy crops are expected to increase in the near future (Johnson et al., 2013).

A variety of sugar and starch crops are candidates to produce biofuels. Some of the products that are obtainable from crop biomass include heat, electricity, ethanol and transport fuels (Chao et al., 2019; Johnson et al., 2013). Corn grain has the capability to be converted into ethanol via a biochemical process of fermentation where sugars are transformed into alcohols. Grain, sorghum, wheat, sugarcane and sugar beets also have the potential to produce ethanol (Jones & Mayfield, 2012; Dahiya & Krivov, 2014).

Various studies have highlighted a grave concern about the production of biofuels from energy crops. The biomass used for these technologies such as grain or maize potentially competes with food and feed production and this is a prevalent bone of contention in many spheres. Further to this, these crops have similar land and water requirements to those of food and feed crops, which exacerbates these debates (Theuretzbacher et al., 2013). The general sentiment

is that edible crops, land and water resources for the production of biofuels end up competing with food and feed production (Dalla Marta et al., 2014). This has motivated the interest of adapting for high-yield non-food energy crops (Lewandowski et al., 2003). Land availability, crop yields, and food security are fundamental factors that also require special attention in the application of energy from crops (Chao et al., 2019).

2.8.4 Algae

Algae is photosynthetic aquatic organisms that can be categorised into two groups namely microalgae and macroalgae. Like terrestrial plants, algae consist of chlorophyll that remedies the carbon dioxide that is present in the atmosphere. Algae is generally composed of the following major chemical components: lipids, carbohydrates, proteins and nucleic acids (Chia et al., 2018; Bouanati et al., 2020). According to Chen et al. (2019), algae can be used to generate hydrocarbons, ethanol, biogas, or hydrogen. It is probably the best potential source of bioenergy. The energy converted from sunlight in the course of photosynthesis is preserved as lipids or carbohydrates within the algae, which is are released from algae for energy supply. Algae biomass generally yields bio-oil which is roughly 250 times higher than that of soybeans and seven to 31 times more than that of palm oil (Chia et al., 2018; Hossain et al., 2008).

Algae is located in lakes, ponds, reservoirs and the ocean. Its growth depends on temperature, amount of sun, and nutrients such as carbon dioxide, oxygen, nitrogen and phosphorus (Chia et al., 2018). It can be cultivated in any type of land. Green algae has greater bioenergy content, lower dampness and lower ash content. In the recent years, microalgae has gained a lot of consideration as a suitable feedstock for biofuel production (El Shenawy et al., 2020). However, there are some challenges to maintain a consistent feedstock as it is affected by seasonal changes, temperature and sunlight intensity. It requires drying to preserve it for production in winter where it is not available in great quantities as compared to summer, and this is rather costly. Summer productivity can be three to eight times higher than that of the winter (Wahlen et al., 2019).

Many authors have highlighted the significant and applaudable characteristics of algae, such as its high calorific value, it is vastly distributed, has a high production rate and a shorter life cycle than any other kind of biomass feedstock that can produce biodiesel (Chowdhury & Freire, 2015; El Shenawy et al., 2020; Wahlen et al., 2019; Zhao et al., 2016). Further to this, algae to biofuels does not compete with food production and it can be cultivated in marginal lands (Wahlen et al., 2019). The lipid amount and the carbohydrate content that are transformed into biofuels are very high in microalgae (Chia et al., 2018).

There are two techniques of algae cultivation, namely open pond and horizontal tubular photobioreactors. Both systems have unique advantages and disadvantages associated with them. The open pond system is economically viable, as it requires less energy to be established and operated. Furthermore, scaling them up is rather simple. They are, however, susceptible to contamination and evaporation owing to that fact that they are not covered. The horizontal tubular photobioreactor systems are intricate and more costly to erect and operate but they are superior in controlling the species composition and growth (Resurreccion et al., 2012).

2.8.5 Municipal solid waste

The present population produces a massive amount of MSW. The generation rate is predicted to sit at 2.2 billion tons per annum by 2025 globally (Ascher et al., 2019). This is a fundamental concern in most developed and underdeveloped countries because it is associated with grave environmental problems (Moghadam et al., 2009; Khoshnevisan et al., 2020). The disposal of this waste is also a considerable challenge because a major portion of it is either not collected or is just disposed of in landfill without undergoing appropriate treatment. Furthermore, some solid waste ends up being dumped in streets, on riverbanks and in oceans. This poses a fundamental threat not only to the environment, but health problems to humankind such as malaria and cholera from water contamination, which is a consequence of unregulated waste disposal. It is for this reason that the production of bioenergy from MSW has gained attention (Samun et al., 2017).

MSW is composed of heterogenous non-biodegradable materials ranging from metals, plastics, paper, textiles, rubber, and wood construction waste, to glass, garden waste, as well as biodegradable organic matter, predominantly composed of kitchen and garden wastes (Li et al., 2012). Table 2.4 shows the typical energy content of various MSW components.

Table 2.4 MSW energy content

Biogenetic	Energy content (MJ/ton)	Non-biogenic	Energy content (MJ/ton)
Leather	16,7	Polyethylene terephthalate (PET)	23,8
Textiles	16,0	High-density polyethylene (HDPE)	44,2
Wood	11,6	Polyvinyl chloride (PVC)	19,1
Food	6,0	Low-density polyethylene/linear low-density polyethylene (LDPE/LLDPE)	28,0
Yard trimmings	7,9	Polypropylene (PP)	44,2
Newspaper	18,6	Polystyrene (PS)	41,4
Cardboard	19,2	Rubber	31,2
Mixed paper	7,8	Other	23,8

Adapted from Chen et al. (2016)

The composition of the organic fraction of MSW entails: starch, lignocelluloses, lipid, protein, and pectin. Starch, together with lignocelluloses, have a high potential for being transformed into ethanol; on the other hand, the organic elements such as lipid, protein, and pectin, are converted into biogas (Mahmoodi et al., 2018). It is worth noting that the composition of MSW is affected by different factors, including culture, location, climatic and geographic conditions, collection frequency, and degree of economy and development of a given society (Mahmoodi et al., 2018; Moghadam et al., 2009).

The efficient methods to manage solid waste, in order to produce energy and value-added products, include but are not limited to (Samun et al., 2017):

- Chemical
- Fermentation
- Gasification
- Pyrolysis
- Hydrolysis
- Incineration

Figure 2.4 represents the general management methods of MSWs and possible ways for their valorisation.

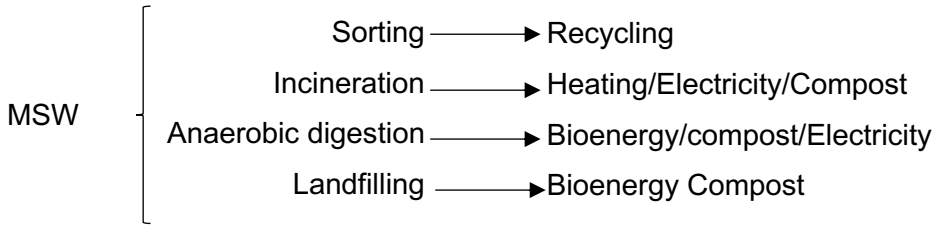

Figure 2.4 Management methods of MSWs and possible ways for their valorisation.

Adapted from Shan et al. (2010)

Despite the favourable attributes of incineration of MSW, such as heat recovery, there are however, various drawbacks of incineration as it produces a massive amounts of flue gas and hazardous fly ash. Recently, pyrolysis and gasification technologies have emerged to address these drawbacks and enhance energy output (Li et al., 2012).

One other effective method of handling MSW is to promote source separation, where the organic segment can be separated and transformed into biomethane. Just like energy crops and woody biomass, there are two principal biological ways of processing the organic material of MSW, namely aerobic composting and anaerobic digestion. This is where the biological degradation of biodegradable matter largely occurs. The anaerobic digestion can be further classified into dry or wet processes; this is based on the content of water in the waste. The wet process is analogous to conventional anaerobic sludge digestion. In the aerobic digestion composting, the term composting denotes a microbial degradation that ingests oxygen and produces a humus-rich material. The anaerobic digestion is analogous of microbial digestion; the difference is that it is conducted in the absence of oxygen. The bacterial decomposition of the organic substance produces a biogas that is rich in methane. This biogas is collected and supplied to a generator, where it is combusted and used to generate electrical energy (Visvanathan, 2010). The use of biogas in stoves and gas lamps at homes is implemented in various developing countries, whereas producing power from upgraded biogas is common in developed countries (Samun et al., 2017; Cesaro et al., 2020).

2.8.6 Sewage sludge

Sewage sludge is a renewable carbonaceous by-product of wastewater treatment. It is a residue of the primary and secondary water treatment processes (Zhang et al., 2017; Prestigiacomo et al., 2019). The typical sewage composition is: protein (18–40%), lignin (23–29%), lipids (6–19%), and carbohydrates (10–15%) (Su et al., 2019). Sludge contains various contaminants both organic and inorganic in nature. The inorganic component in sludge

includes substances such as heavy metals comprising of copper, zinc, nickel, cadmium, lead, arsenic, chromium, selenium and so forth (Aktar, 2009). The organic constituents include components such as pathogens, phthalates, pesticides, alkylphenols, monocyclic aromatics, surfactants, hormones, pharmaceuticals, nanoparticles, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), absorbable organ halogens (AOX) and many other deleterious substances (Chen et al., 2020; Kacprzak et al., 2017). The components removed during wastewater treatment include grit, screenings, and sludge, with sludge being the greatest component; therefore, its handling and disposal techniques remain a fundamental centre of focus (Fytili & Zabaniotou, 2008).

The sludge stemming from wastewater treatment facilities is predominately liquid or semisolid liquid with varied content depending on the region it emanates from (Fytili & Zabaniotou, 2008). The energy content of the solid component in sewage sludge that has endured dewatering on a dry basis is approximately 12-20 $MJkg^{-1}$ (Mujahid et al., 2020). The typical elemental analysis of sewage sludge with a moisture content of 75,8% according to Prestigiacomo et al. (2019) is detailed in Table 2.5.

Table 2.5 Elementary analysis of sewage sludge

Elemental Analysis	Value
C	43,39
H	6,48
N	5,04
S	0,86
HHV (MJ/kg)	16,13
Cd (mg/kg)	<0,1
Cu (mg/kg)	150
Ni (mg/kg)	17,4
Pb (mg/kg)	55,4
Zn (mg/kg)	331
Hg (mg/kg)	<0,1
Cr (mg/kg)	24,3
Organic content	89,1

Adapted from Prestigiacomo et al. (2019)

Sewage sludge from wastewater treatment plants has been rising due to insufficient wastewater treatments facilities to keep up with the rate of urbanisation. This has emerged a severe discomfort (Chen et al., 2020). The sludge has a considerable high water content, which is roughly 97-98% (Kacprzak et al., 2017). The cost of sewage sludge management accounts for approximately 50% of the entire operating costs of the wastewater treatment plant (Kacprzak et al., 2017). The solid content of sewage sludge that has undergone a dewatering

process is approximated at 10-20wt%, subject to the dewatering methods employed (Mujahid et al., 2020). The characteristics of municipal sewage sludge are shown in Table 2.6.

Table 2.6 Characteristics of municipal sewage sludge is as follows:

	Sludge Type		
Parameter	**Primary Sludge**	**Activated sludge**	**Secondary sludge**
Total dry solids, TS (%)	2-9	6-12	0,8-1,2
Volatile solids, VS (%)	60-80	30-60	59-68
Grease and fats (%)	7-35	-	5-12
Protein (%)	20-30	15-20	32-41
Cellulose (%)	8-15	8-15	7-9,7
Phosphorus (%)	0,8-2,8	1,5-4	2,8-11
Nitrogen (%)	1,5-4	1,6-6	2,4-5
Potassium (%)	0-1	0-3	0,5-0,7
pH	5-8	6,5-7,5	6,5-8
Energy MJ/kg	23-29		19-23

Adapted from Gao et al. (2020); Tyagi & Lo (2013)

The wastewater treatment ordinarily comprise of biological, chemical and thermal processes as well as prolonged storage with the intention of removing pathogens and shrink sludge quantity (Đurđević et al., 2019). The following process methods are employed to treat sewage sludge for the production of suitable end products or disposal (Aktar, 2009):

- sludge pasteurisation,
- mesophilic anaerobic digestion,
- thermophilic aerobic digestion,
- composting,
- lime stabilisation of liquid sludge,
- liquid storage,
- dewatering storage and,
- thermochemical treatments.

Traditional sewage sludge disposal techniques involve agricultural applications, ocean pumping, landfilling and incineration. Some of these techniques entail moisture contents of less than 60 wt%, thus making dewatering a necessity for these procedures. The disposal methods of sewage sludge, however, are no longer recommended owing to land limitations, soil, marine, and environmental pollution, stringent regulations and high costs (Wu et al., 2017; Samolada & Zabaniotou, 2014). These stringent regulations have controlled the amount of sewage sludge and other organic wastes that may be disposed of in landfills (Kacprzak et al.,

2017). There are regulations in place regarding the quality of the effluent discharge of sewage treatment works. These regulations enforce restrictions for the concentration of the following substances: total suspended solids, phosphorus, nitrogen, mercury and phenols (Werther & Ogada, 1999). In actual fact, it is strongly prohibited to dispose of untreated sludge for various valid reasons. The most imperative reasons are the inevitable malodorous gases associated with sewage sludge and the existence of various pathogens species that pose a serious threat to human health, animals, plants, soil and water. This is because there are living organisms in sewage sludge, such as bacteria, viruses, and protozoa and parasitic helminths. The heavy metals in the sewage sludge are also dangerous to both plants and animals (Werther & Ogada, 1999; Kacprzak et al., 2017).

Dried sewage sludge has an organic matter content of 50-70% and 39-50% mineral content, with 1-4% being inorganic carbon, 3,4-4% nitrogen, 0,5-2,5% phosphorus and the remaining amounts accounts for nutrients and micronutrients. The organic matter in the sewage sludge mineralises rapidly as a result of the lignin or cellulose in it. There is a substantial amount of nitrogen and phosphorus concentration in sewage. This characteristic indorses sewage to be suitable as a fertiliser in agricultural applications (Gao et al., 2020). The drying procedures include naturally drying which can make use of either, solar energy, thermal or mechanical drying. However, mechanically dewatered sludge still has a rather large moisture content of roughly 80 wt%, and further dewatering remains necessary. Thermal drying consumes a significant amount of energy; thus the methods become very expensive (Zhang et al., 2018).

2.9 Municipal water treatment

Inevitably, water is an essential constituent of the planet earth, and plays a very important role in the proper performance of the earth's ecosystem (Bouvet et al., 2020). Wastewater science and engineering have evolved over the past decades, with some developing countries still catching up with the latest technologies. Previously, untreated wastewater used to be discharged on land or in streams; however, with the impetus for innovation of recent technologies for the treatment of wastewater, coupled with stringent regulations, the disposal of untreated wastewater is no longer an option. In the distanced past, night soil which in modern language is better known as human waste, used to be deposited in buckets that were placed in the streets for collection and disposed of in agricultural lands. As it became unfeasible to transport large quantities for land disposals, this system was shadowed by the invention of the flushable toilet, where drainage systems were used to transport sewage and storm sewers to wastewater facilities for appropriate treatment procedures (Riffat, 2012).

Sewer sheds are typically located on fairly flat terrain in hotter climates. They yield septic wastewater with fewer biodegradable fragments, while municipalities located on hilly regions with sharp terrain and lower temperatures will naturally have fresher unaltered wastewater. Municipal wastewater facilities can be classified as low, medium or large strength, subject to the volume of inflow and infiltration experienced (Mannina et al., 2018).

Water treatment may be organised into different methods depending on the nature of pollutants and the degree of the desired removal. They are namely:

- Physical treatment methods – techniques entailing the separation of liquids and suspended solids where sedimentation, screening, and filtration plays a critical role (Cheremisinoff, 2001; Riffat, 2012).

- Chemical treatment methods – Chemical reactions are induced through the introduction of chemicals in the sewage with the intention to convert or destruct contaminants. Some of these chemicals methods include coagulation or flocculation for the eradication of solids, disinfection aimed at destroying pathogens, and chemical precipitation for the elimination of phosphorus (Riffat, 2012).

- Biological treatment methods – The purpose of biological treatment is to alleviate and eradicate nitrogen, phosphorus and biodegradable organic matter from wastewater; legitimate measures of microorganisms indigenous to wastewaters are incorporated to convert and destroy contaminants. These include activated sludge process, membrane bioreactor, trickling filter, and so forth (Riffat, 2012).

- Energy-intensive treatment methods – This includes electrochemical techniques. This treatment method has a dual purpose which is sterilisation for providing a palatable quality of water for human consumption, and processing sludge for volume reduction and adequate sludge quality (Cheremisinoff, 2001).

Municipal wastewater treatments generally comprise of preliminary treatment, primary treatment, secondary treatment, tertiary or advanced treatment, which refer to a higher degree of wastewater treatment, many occasionally may be implemented at certain municipalities depending on the complexity of the wastewater.

2.9.1 Preliminary wastewater treatment

Preliminary wastewater treatment typically involves screening and grit elimination. At the screening section, coarse material such as rags and twigs are removed as they have the potential to hinder the mechanical equipment's efficiency. The dense matter such as solids that settle in channels are removed through grids. Floatation is also performed for removal of oils and grease. The pre-treatment process generally alters the quality of the wastewater to a certain degree (Mannina et al., 2018; Riffat, 2012). Figure 2.5 demonstrates the typical wastewater process.

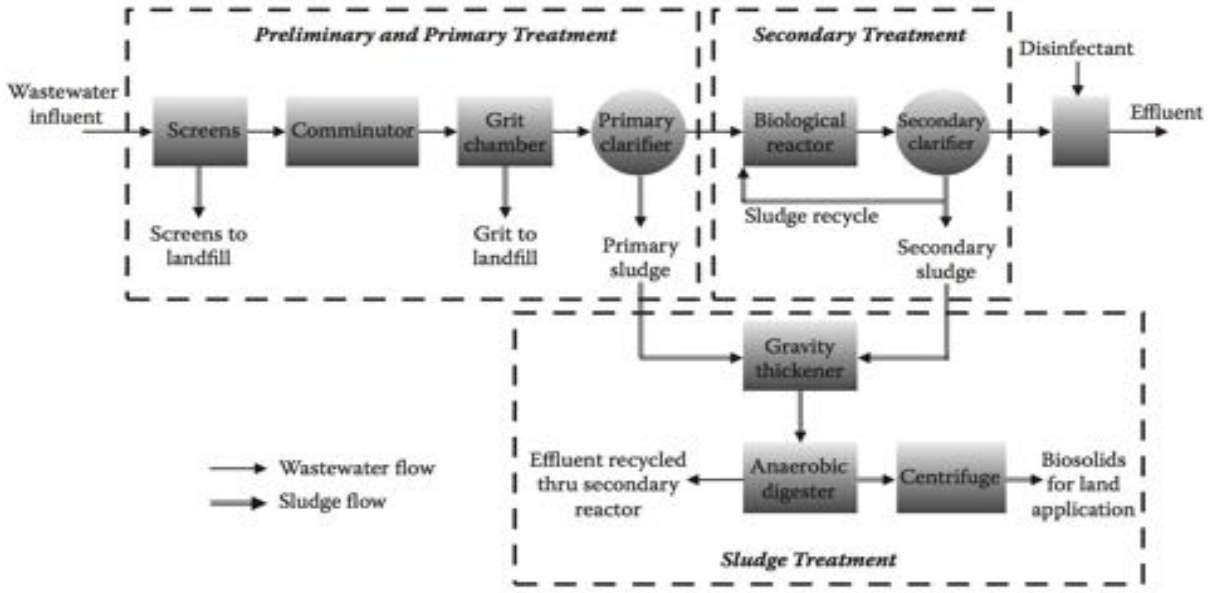

Figure 2.5 A typical wastewater flow diagram that includes a sludge digester

Adapted from Riffat (2012)

2.9.2 Primary wastewater treatment

Primary wastewater treatment entails the elimination of a fraction of suspended solids by gravity sedimentation of the effluent of the preliminary treatment. Primary clarifiers are used to perform this action. Settleable solids are also removed at this stage including more than half of the suspended solids. The residue of this stage is called primary sludge (Mannina et al., 2018).

Enhanced primary treatment may also be taken advantage of in the event when it is required. This entails the use of chemical coagulants to achieve coagulation and flocculation of solids in the interest of attaining further solid elimination in the sedimentation tank (Riffat, 2012).

2.9.3 Secondary wastewater treatment

The conventional secondary wastewater treatment is conducted by making use of a biological treatment method for the degradation of organic matter and to decrease the quantity of solids (Mannina et al., 2018). This process is conducted in a bioreactor; subsequent to that, a sedimentation tank or a secondary clarifier is used. Activated sludge treatment and trickling filter are achieved in this stage of treatment (Riffat, 2012).

Nutrient removal in the secondary treatment may be employed in the event that nutrients such as nitrogen or phosphorus need to be obtained. Supplementary reactors may be essential to achieve this (Riffat, 2012).

2.9.4 Tertiary wastewater treatment

Tertiary treatment comprise of a process such as granular media filtration, which is exploited for the removal of residual suspended solids and sterilisation for pathogen mitigation. Supplementary nutrient removal is further conducted during this stage. The advance treatment process is performed to manipulate the removal of further wastewater constituents, depending on the complexity or toxicity of specific compounds or for water recycling applications. Some examples are activated adsorption for the elimination of volatile matter and ion exchange for the mitigation of particular ions (Riffat, 2012).

2.10 Benefits of using sewage sludge as a biomass source

The principal procedures of sludge management are landfill disposals and incineration. With land availability being a great obstacle and ecological degradation as a consequence of air pollutants from residues of incineration, aspirations of transitioning towards sustainability have arisen, with sludge now considered as an ideal source of bioenergy (Elmi et al., 2020). Sewage sludge has been deemed a favourable feedstock because it is rich in volatile matter, thereby qualifying it as a potential bioresource as a liquid fuel (Huang et al., 2014).

Sewage is a non-food biomass source, and therefore does not compete with food and feed manufacturing, since the connotation of utilising biomass for fuel generation as opposed to food and feed has long been a bone of contention (Asomaning et al., 2018).

According to Prestigiacomo et al. (2019), bio-oil from sewage sludge is regarded as a cheap alternative to microalgae. The bio-oil obtained from microalgae in the absence of a catalyst is typically more viscous at room temperature and has substantial sulphur, nitrogen and oxygen contents, therefore requiring further upgrading in order to be used as a fuel. Upgrading involves

a catalyst using the following hydrogenolysis processes: hydrodeoxygenation (HDO), hydrodeazotation (HDN) and hydrodesulphurisation (HDS), in order to reduce the high sulphur and nitrogen and oxygen content in the bio-oil. However, the processes are too expensive and the cost depends on the molecular weight and heteroatom quantity in the bio-oil (Prestigiacomo et al., 2019). Prestigiacomo et al. (2019) found that when using ACF1600 as a catalyst, sewage sludge performed better than microalgae and the bio-oil obtained had the lowest O/C and highest H/C.

2.11 Disadvantages of using sewage sludge as a biomass source

One of the obstacles in the application of thermochemical conversion of sewage sludge is the bound water that is encapsulated in the microorganisms of the sludge, particularly in the operation of pyrolysis, where a substantial amount of energy is required to drastically reduce the water content of 80-90%. This makes fast pyrolysis of sewage sludge arduous. However, the liquefaction application of sewage sludge does not require additional drying as it makes use of the available water, which acts as a solvent in the hydrothermal process. The high energy is related to the pre-drying step that can be circumvented by using HTL as opposed to pyrolysis (Akhtar & Amin, 2011).

2.12 Thermochemical treatments of sewage sludge

Thermal processing is a promising technique to manage sewage sludge as it has the potential to valorise sewage sludge into useful products while addressing the environmental and health threats as a consequence of excess sludge (Chen et al., 2020). The advantage of thermal treatments applications include pathogen demolition and depression of sludge volume (Park et al., 2019).

There are four broad pathways of thermochemical processing, namely combustion, pyrolysis, gasification and liquefaction (Basu, 2010). Table 2.7 displays the comparison of the four thermochemical conversions.

Table 2.7 Comparison of Thermochemical Techniques

Process	Temperature (ºC)	Pressure (MPa)	Catalyst	Drying
Liquefaction	250-330	5-20	Essential	Not required
Pyrolysis	380-530	0.1-0.5	Not required	Necessary
Combustion	700-1400	>0,1	Not required	Not essential
Gasification	500-1300	>0,1	Not required	Necessary

Adapted from Basu (2010)

The extreme water content in sewage sludge limits the efficient and financial application of conventional treatments; hence dewatering is necessary for some applications (Park et al., 2019). Other methods include steam reforming and transesterification.

2.12.1 Combustion

Combustion is a high-temperature reaction that is exothermic in nature and involves the reaction of excess oxygen and hydrocarbons present in biomass. Water and carbon dioxide are the two pivotal components of combustion. The heat released through combustion is considered the biggest source of human energy consumption, which sits at more than 90% of the energy from biomass (Basu, 2010). At lower temperatures, development of hydrocarbons occur in the fluidized bed reactors. The flame temperature can be above 2000ºC, depending on the fuel's moisture content, heating value and the volume of air utilised in the process as well as the construction of the furnace (Hornung, 2014).

Combustion is an attractive option for sewage sludge because it reduces the volume of sewage sludge and the toxic compounds in it, and minimises its odour (Kosowska-Golachowska et al., 2020). In some countries, co-combustion is of dried sewage sludge with coal is seen as a solution to utilising the continuously growing volumes of sludge; however, this is not a solution for the problem of environmental pollution and non-renewable resources (Coskun et al., 2020).

2.12.2 Gasification

Gasification is a thermochemical process that converts any carbonaceous fuel, such as dried sewage sludge into a useful and convenient gaseous product that possesses a tolerable heating value or chemical feedstock. The gasification process is generally operated at high temperatures of 800-1800°C, depending on the characteristic of the feedstock and the melting temperature of the ash. Gasification involves removing oxygen from the carbonaceous matter to increase its energy density because a valuable gaseous fuel contains minimal oxygen content hence, dehydration or decarboxylation is imposed (Basu, 2010).

As much as combustion also converts carbonaceous matter into gaseous products, the definition of gasification does not extend to combustion because products from combustion, for example flue gas, do not have valuable residual heating value. The fundamental difference between the two applications is that gasification retains energy into chemical bonds, whereas combustion releases it. Furthermore, the amount of oxygen used in the reaction is different. Gasification is conducted in an oxygen-deficient environment, whereas combustion is conducted in excess air (Basu, 2010).

Gasification is achieved through a medium of reaction that can either be a gas or supercritical water (SCW). Examples of these gaseous mediums are air, oxygen, subcritical steam, or a mixture of these. Gasification is usually conducted in one of the three main types of gasifiers (Basu, 2010):

- Moving bed
- Fluidised bed
- Entrained flow

The main advantage of gasification of biomass is that the operation efficiency is increased after the conversion into useful gaseous fuels. The fuel can be employed in various applications such as city gas, burning in utility boilers, gas turbines or gas engines to generate electricity. The key disadvantages are that the conversion is complex, as the fuel gas that is produced cannot be conveniently stored and transported (Badeau & Levi, 2009).

2.12.3 Pyrolysis

Pyrolysis is the thermal decomposition of biomass, using high temperatures in the total absence of oxygen, into gas, liquid and solid phases (Muvhiiwa et al., 2019; Mei et al., 2020). Large hydrocarbons are broken down into smaller molecules during the reaction. Pyrolysis is typically characterised by three variations namely (Basu, 2010):

- Fast pyrolysis,
- Slow pyrolysis and
- Torrefaction or mild pyrolysis

Fast pyrolysis occurs in a matter of seconds to yield bio-oils. The essential characteristics of fast pyrolysis include very high heating and transfer rates, requires fine ground biomass feed, controlled temperatures and short residence times (Hornung, 2014). Slow pyrolysis produces both gaseous and solid products. It is also termed carbonisation owing to similarities in its process parameters of long residence time and lower temperatures. It is typically operated in temperatures that are around 400ºC, which are lower compared to those fast pyrolysis. Torrefaction is conducted in atmospheric conditions. The final product is a solid dry black substance which is called torrefied biomass or biochar, which has a higher energy density in comparison to raw biomass owing to the lowered weight and volume. After torrefaction, it becomes possible to contain and transport the biochar for further processing (Hornung, 2014). In the report of Ledakowicz et al. (2019), pyrolysis is regarded as the most optimal method for treatment of sewage sludge in comparison to other conventional thermal treatments, which

include incineration and gasification. Their motivation for their statement is that pyrolysis is a zero-waste method, possessing a higher potential in resolving the wastewater challenge compared to gasification and incineration methods. They added that pyrolysis is characterised by acceptable gas emissions and products yield from sewage sludge pyrolysis, such as biochar, could be used for soil remediation purposes, which are beneficial when applied to grow media (Ledakowicz et al., 2019). However, Mei et al. (2020) observed that in practice, pyrolysis liquid is of poor quality, the volume after pyrolysis is too little to be dispatched to refinery, and furthermore, it is exhausting to seek a market for an untreated oil that is a byproduct. The greatest hurdle with the utilisation of pyrolysis and the latter thermochemical methods for the treatment of sewage sludge is the drying that remains essential. This necessary expense accounts for half of the operation costs (Mei et al., 2020).

2.12.4 Transesterification

Transesterification is a process where non-edible oil or vegetable oil is reacted with an alcohol. Ethanol and methanol are the alcohols normally used owing to their inexpensiveness. This reaction is used to convert triglycerides into alkyl esters and glycerol (Thangarasu & Anand, 2019). Transesterification consists of an equilibrium reaction entailing numerous consecutive reversible reactions. The reactions may be carried out under mild conditions in a batch process as a continuous or semi-continuous process subject to process conditions and type of process. There are generally two classifications of transesterification, namely one that includes a catalyst and the other without a catalyst. Acid and base catalysts may be further classified into homogeneous, heterogeneous, and enzymatic catalysts. The disadvantage of a homogeneous catalyst is soap formation and the costly separation process of the catalyst, making heterogeneous and enzymatic catalysts preferable. Furthermore, homogeneous catalysts are reusable, and easy to purify (Thangarasu & Anand, 2019). Products obtained are biodiesel soup, mixtures of esters, alcohols, salts, glycerol and monoglycerides. Transesterification may occur in a range of temperatures. To reduce the operating costs, it is preferable to carry out the process at ambient temperatures (Bart et al., 2010; Mumtaz et al., 2017).

The biodiesel industry has given attention to the conversion of sewage sludge into biodiesel products; it is an attractive route since sewage sludge is an inexpensive and a readily available feedstock. Sewage sludge is reported to be more feasible when the lipid concentration exceeds 10%. For efficient biodiesel production, a solid alkaline catalyst is widely utilised as they can be filtered effortlessly and reused. Wu et al., 2016, in their research reported ta yield of biodiesel 6.8% using alkali catalysts and methanol to sewage sludge mass ratio of

10:1(w/w), the mass fraction of KOH at 25%, the dosage of the catalyst was 3% (wt/wt), and the temperature was 65ºC.

2.12.5 Steam reforming

Steam reforming is another example of a thermochemical technology used for the production of hydrogen (García, 2015). Natural gas is the leading stream reforming feedstock globally and accounts for 80-85% hydrogen production (Zhang et al., 2019). Additional non-renewable feedstock for steam reforming are methanol, liquified petroleum gas, naphtha, jet fuel and diesel (García, 2015). Bio-derived alcohol can also be employed in steam reforming as a feedstock. Generally, alcohols have a large H/C ratio and hydrogen produced at low temperature compared to methane reforming. Steam reforming is an equilibrium-restricted reaction (Huuhtanen et al., 2013). The thermodynamics study envisages that temperatures that are higher than 600ºC coupled with a steam/carbon ratio greater than three are essential in order to prevent carbon formation (He et al., 2013).

Steam reforming research is not widely published where steam reforming is applied to sewage sludge as the fundamental treatment method. However, it is used as a supplementary method with pyrolysis in the interest of enhancing the products. Practically, this entails using recycled steam that was generated during the drying and pyrolysis processes for the purpose of saving costs (Mei et al., 2020).

2.12.6 Supercritical fluid extraction

Supercritical fluid extraction can be defined as a process of separating a unique component known as an extract from another component known as the matrix. In this process, supercritical fuels play a significant role as extracting solvents. Extraction is typically from a solid matrix however, it is also possible to have extractions in liquid mediums. Supercritical fluid extraction can either be employed analytically for sample preparation or on a broader scale to strip undesired material substance from products (decaffeination) or collect a desired product such as bio-oils. The most common extraction fluid is carbon dioxide in high pressure and at times modified by solvents namely methanol or ethanol to extract products from natural materials. Unlike other processes, the extraction method does not leave solvent residue behind. Carbon dioxide is favourable as a supercritical fluid owing to its nature of being inexpensive, inert, odourless, inflammable, tasteless and low critical conditions (Sapkale et al., 2010).

2.12.7 Hydrothermal processing

The term hydrothermal denotes a conversion that takes place in the presence of water at relatively high pressures and temperature (Hornung, 2014). In hydrothermal processing of sewage sludge, water has a duel function. It can either function as a reactant or play the role of a critical solvent in the conversion into valuable products in the absence of supplementary water. This process is very attractive because it does not require additional drying, which in turn seeks to save energy costs, compared to other applications such as pyrolysis and oil extraction (Chen et al., 2020). The hydrothermal method can be divided into three processes according to the operating temperature: hydrothermal carbonisation (HTC), hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG). The fundamental objective of hydrothermal processing is to yield gaseous, liquid and solid energy products (Park et al., 2019). The quantity and quality of yield are subject of the following parameters, reaction time, pressure, solvents, and catalyst composition (Chen et al., 2020).

2.12.8 Hydrothermal carbonisation (HTC)

HTC is the decomposing of organic matter under high temperatures in the presence of water to yield a solid carbon fuel called biochar. An aqueous solution is also produced, which contains phenolic compounds, and the remainder is gas. Char traditionally signifies an organic complex solid that has a high carbon content and is a mixture of products of thermal decomposition or partial oxidation of any organic substance. HTC shares the same temperature ranges as HTL: between 180ºC and 320ºC (Park et al., 2019; Chen et al., 2020). The significant difference is that HTL generates bio-oil (Chen et al., 2020). The governing mechanisms in HTC are dehydration and decarboxylation. Bio-oil from HTC can be applied in phosphorus recovery when necessary (Chen et al., 2020).

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2.12.9 Hydrothermal gasification (HTG)

HTG has been discovered to be a fitting hydrotreatment for biomass, such as sewage sludge, that has a significant water content at a temperature above 400ºC. This technology takes advantage of the high water content and applies it as a reaction medium. This is beneficial, as it reduces the operation costs, since drying is considered unnecessary. Typical HTG involves both supercritical water gasification (SCWG) and subcritical water gasification (subCWG). This technology converts wet feedstock into clean energy such as methane and hydrogen. HTG has been reported to decompose organic pollutant in sewage sludge and produce a synthetic gas as recovered energy. In comparison to pyrolysis, HTG is operated at a lower temperature and has the capacity to alleviate pollutants such as polycyclic aromatics in the product. Although char and tar are inevitable by-products of HTG, in the hydrothermal drying method,

these by-products are produced in greater quantities. This is due to the intensive solubility and reactivity of the organic substance formed in SCW and subCW, resulting in restricted char and tar formation. Char and tar formation invite problems such as low efficiency for syngas production, blockages in the reactors and hinders the performance of heterogeneous catalysts (Wang et al., 2019).

2.12.10 Hydrothermal liquefaction (HTL)

HTL, also known as hydrous pyrolysis, is a promising technology for producing advanced biofuels and other value-added products through the conversion of biomass such as sewage sludge and various organic matter, including woody biomass, industrial wastes, food wastes, algae, arboreous crops, wastes from the forestry industry, and so forth (Thomsen et al., 2020; Dimitriadis & Bezergianni, 2017). This is conducted in a hot and pressurised environment between 200ºC and 450ºC and 5-15 MPa (Kumar et al., 2018; Park et al., 2019; Chen et al., 2020). HTL has also been excellent in eliminating substances of emerging concern, such as nitrogen and chorine, through denitrogenation and dechlorination (Chen et al., 2020). It is supported by the hydrolytic cleavage of the bio constituents of wet sludge and by the transformation of depolymerised products to basic organic molecules. The oils yielded in this process are also referred to as bio-oil. The process also has by-products, such as an aqueous phase, and a non-volatile solid component (Park et al., 2019). The favourable products are attained through manipulating of process parameters such as temperature, pressure, solvents, moisture, content, time and catalyst (Kumar et al., 2018).

HTL starts with solvolysis of biomass in micellar kinds, followed by a thermal depolymerisation into smaller fragments. HTL is a process that mimics the generation of fossils fuels under the depths of the earth, except that it is conducted in minutes, yielding bio-oil which is lower in oxygen content in comparison to that of pyrolysis (Jazrawi, 2014) . HTL follows a complex set of reactions. The process mechanism entails the hydrolysis of biopolymers into water-soluble oligomers, followed by the disintegration of intramolecular and intermolecular hydrogen bonds to form basic monomers such as glucose and other products like acetaldehyde, acetic acid, and furfural compounds (Kumar et al., 2018).

During HTL, polysaccharides endure hydrolysis and transform into monosaccharides, which further experience isomerisation, cyclisation and dehydration to generate phenols or cyclic ketones. Carbohydrates are responsible for the formation of aromatics via ring opening and further reactions entailing cyclisation and condensation (Liu et al., 2013). The N-containing compounds comprise of pyrroles, pyrazines, and amines. Proteins go through hydrolysis to form amino acids, which take one of two routes: decarboxylation to form carbonic acid and

amines or deamination reaction to form ammonia and organic acids (Peterson et al., 2008). Pyrazine, pyrrole, indoles and aromatic amides are also generated through cyclisation and condensation. The production of polycyclic nitrogenous compounds is achieved through Maillard reactions between sugars and amino acids, from carbohydrate and protein hydrolysis, respectively (Kumar et al., 2018).

SubCW generally has restricted interaction with sewage sludge due to low diffusivity capabilities and consequently performs as a reactant in the process. SCW, conversely, has greater diffusivity capabilities and expands the interaction rate of the solvent and sewage sludge (Chen et al., 2020). SCW exhibits favourable physiochemical properties for the conversion of sewage sludge during the HTL process. These properties including density, mass and heat transfer, viscosity, solubility and reactivity. These properties can be adjusted by altering key process parameters such as pressure and temperature (Mujahid et al., 2020). This is founded upon the fact that HTL is substantially dependent on pressure. The conversion is greatly intensified when water approaches the supercritical point (Chen et al., 2020).

2.12.10.1 Benefits of HTL of sewage sludge

- Unlike other thermochemical routes, the drying of sewage sludge is unnecessary as HTL is capable of processing wet feedstock, thus saving process costs (Conti et al., 2020).
- It is possible to use a feedstock with a moisture content of 30% and above (Durak & Genel, 2020).
- Water can serve independently as a reactant and catalyst in the HTL of sewage sludge (Hornung, 2014).
- The addition of a catalyst is not necessary but may be considered for improving yields (Hornung, 2014).
- HTL yields bio-oils that have higher energy density and superior quality in terms of their thermal and the storage stabilities. Furthermore, the bio-oil has less oxygen content and produce higher bio-oil yields, lower coke and lower energy consumption in contrast to fast pyrolysis (Mujahid & Kim, 2020; Bridgwater et al., 1999).
- HTL plays a vital role in the destruction of micropollutants that are present in the sludge (Thomsen et al., 2020).
- Compared to other thermochemical techniques, HTL can be achieved at lower temperatures, between 250ºC and 400ºC, and in shorter reaction times of 5-20 minutes (Eggers, 2012).

- HTL yields better quality of bio-oil with a high heating value and low moisture content (Xiu & Shahbazi, 2012)

2.12.10.2 Disadvantages of HTL

One of the fundamental challenges in the commercialisation of this technology is that it is uneconomical when compared to the costs of gasoline and diesel production. Furthermore, the reactors required that can manage high capacity water handling are costly and complex (Zhang et al., 2010). The poor conversion, inadequate yields and deprivation in the underlying comprehension of the complex mechanisms restrains the progression of the process commercially (Midgett, 2008). HTL experiments are typically conducted in in batch reactors and more work needs to be developed in moving towards continuous HTL techniques (Ponnusamy et al., 2020).

2.13 Operating parameters on HTL

2.13.1 Temperature

Temperature is a paramount parameter in the HTL process. It naturally enhances the synergetic effect on yielded products. When temperatures rise above activation energy, extensive fragmentations of bonds coupled with depolymerisation of biomass is promoted. This consequently intensifies the concentration of free radicals and repolarisation of fragmented molecules (Akhtar & Amin, 2011). In simple terms, high temperatures aid the decomposition of biopolymers and reformation of new compounds. The metamorphosis starts at 100 ºC with the dissolution of water-soluble compounds, followed by hydrolysis where monomeric bonds are broken – this occurs at temperatures greater than 150ºC. Subsequently, the slurry that emerges is liquified from approximately 200 ºC and 1 MPa (Durak & Genel, 2020).

Increasing temperatures beyond the supercritical point of water endorses higher yields of gaseous products and biochar. This reveals that excessive temperatures tend to promote repolymerisation and decomposition of intermediate products. Essentially, secondary reactions are triggered, initiating intermediate products to endure secondary reactions, thus encouraging the production of a supplementary gaseous phase (Xue et al., 2016). Furthermore, high temperatures, particularly those approaching SCW conditions, prohibit further bio-oil formation because the properties of water changes drastically near supercritical conditions, suppressing bio-oil yields and promoting gas formation (Akhtar & Amin, 2011; Chen, 2018; Yang et al., 2018; Chen et al., 2019; Biswas et al., 2017). In contrast to the bio-oil yield, the solid phase tends to increase when extreme temperatures are applied. Furthermore, an increase in temperature correlates to higher calorific value and quality of bio-oil.

Xu et al. (2018) in their work elucidated how the yields and compositions of the various products varied as the temperature increased the during HTL of sewage sludge at a temperature range of 260 ºC to 350ºC, using 10 minutes' residence time. Their results revealed that there were improvements in the bio-oil yield when there was an increase in temperatures. However, they noted that there was a point when the yields began to decrease when the operating temperature was approaching 350ºC. They recorded a maximum yield of 22,9 wt% at 340ºC. A similar situation was demonstrated in the work of Durak & Genel (2020), where they established that temperature is an effective parameter of the quantity and quality of the yield. At a temperature range of 220-300ºC, they obtained the highest yield at 280ºC for light bio-oil and 300ºC for heavy bio-oil. This suggested that at temperatures exceeding 280ºC, polymerisation reactions are favourable for light bio-oil development; however, for heavy bio-oil, both depolymerisation and polymerisation are effective with an increase of temperature.

Several authors have reported their optimum temperature for attaining the highest bio-oil yield, and favourable quality is different for each biomass feedstock because each biomass is unique (Xue et al., 2016; Yin et al., 2010; Qu et al., 2003; Jena et al., 2011; Anastasakis & Ross, 2011; Durak & Genel, 2020). Figure 2.6 shows results obtained by various authors in the quest to examine the effect of temperature in using various biomasses.

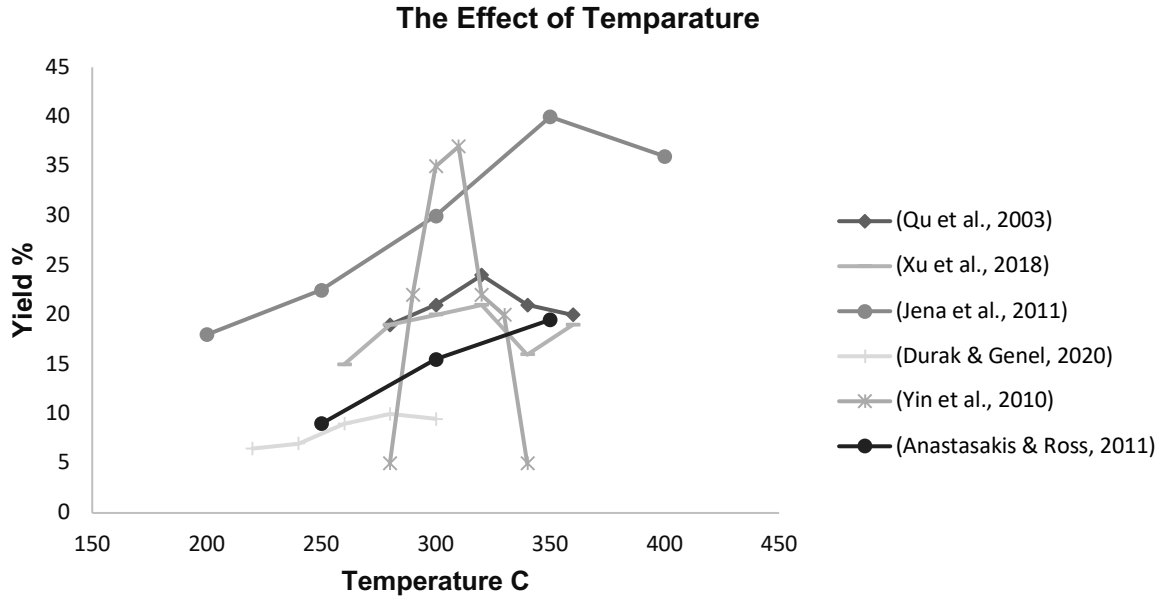

Figure 2.6 Variation in yield of bio-oil produced from biomass as a function of temperature in HTL adapted from various authors

2.13.2 Moisture content

The ratio of water and biomass is deemed to be an important parameter. There are three systematic methods to vary the moisture content during HLT. One requires the fixing of the water volume and varying the quantity of dried feedstock in each experiment. The second

entails loading varied volumes of slurry and fixing the solid contents. The third method is to fix the mass of the dried feedstock and vary the water quantity (Feng et al., 2018). Substantial moisture content is fitting for the enhancement of products of HTL, in particular the bio-oil yields. High bio-oil yields are a consequence of superior extraction of biomass when the solvent medium is substantial (Akhtar & Amin, 2011). According to Wang et al. (2008), high moisture contents reduce the volume of remaining residues. This diminution can be evident in the gas yields since the gaseous phase decreases with an increase in the moisture content (Karagöz et al., 2006). Pyrolysis generally produces more gases than HTL, implying that moisture content enhances the stability and solubility of fragmented compounds. During HTL, solvents extract the biomass component, which enhances the dissolution of biomass fragments. At low moisture contents, the interactions between the biomass and water are hindered, which suppresses dissolution of the biomass. Edifor et al. (2020), however, without conducting a moisture content verse yield investigation, did not support this narrative. They claimed that increasing the solid concentration can potentially increase yields and conversion. They based their argument on their finding that the solid concentration in sludge notably affects the stability of the sludge. The term stability in their work is defined as “the ability of particles to continuously remain suspended in the slurry”.

Conversely, it has also been observed that extremely high moisture contents are unfavourable as they tend to also hinder the yield of bio-oils significantly (Akhtar & Amin, 2011). Qian et al. (2017) studied the effect of moisture content of sewage sludge under isothermal (400ºC, 60 min) and fast conditions (500ºC, 1 min) and discovered that the moisture content does have a significant effect on the product yield. They used six different moisture contents between 75 and 97,7 % and proved that both isothermal and fast conditions had the largest bio-oil yield when the moisture content was 85%. This seeks to support the notion that extreme moisture contents are inclined to prohibit satisfactory yields. There exists a threshold where hydrolysis and repolymerisation reactions begin to compete and this results in a retarded bio-oil yield. Therefore it is imperative to select an optimal biomass to water ratio (Xue et al., 2016). This relationship is displayed in Figure 2.7 Demonstrates the relationship of moisture content and various yields obtained in the HTL of *hyacinth*.

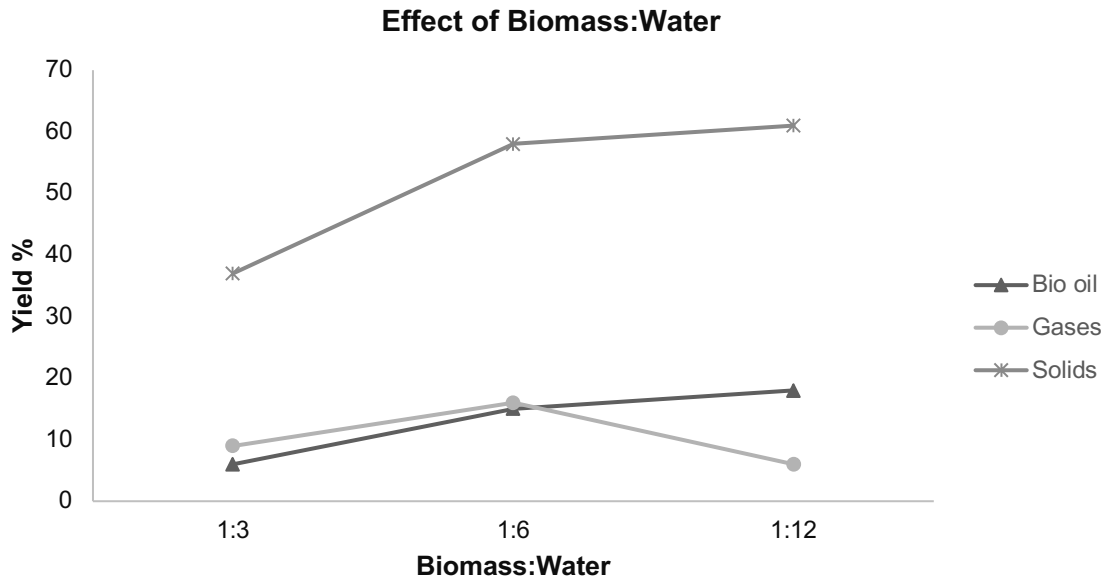

Figure 2.7 Effect of biomass:water ratio on the HTL of *hyacinth*

Adapted from Xue et al. (2016)

2.13.3 Catalyst

Catalysts have a considerable impact on the quality and quantity of products yielded (Durak & Aysu, 2016). The purpose of adding a catalyst in HTL processes is to effectively intensify the process's efficiency by achieving a reduced oxygen content in bio-oil, decrease the char and tar production, increase the bio-oil yield and improve the quality of products. Catalysts can be classified as heterogeneous or homogenous. Homogenous catalysts share the same phase as the reactants. Conversely, heterogeneous catalysts possess a different phase to one or more of the reactants.

Homogenous catalysts that have been commonly employed in HTL operations include alkali salts such as KOH, K_2CO_3, NaOH, and Na_2CO_3 (Durak & Genel, 2020). The HHV of bio-oil obtained from alkali catalytic HTL is always higher than the non-catalytic HTL (Nagappan et al., 2021). Alkali salts are economical in the application of HTL and play a fundamental role in effectively lowering the formation of biochar and tar and improve the bio-oil yield by accelerating the water gas shift reaction. The complex mechanism entails the generation of esters via a decarboxylation reaction between the hydroxyl groups in biomass and the formate ions in alkali carbonates. Subsequent to ester formation, there are various reactions such as dehydration, deoxygenation, decarboxylation and dehydration of micellar-like matter followed by cyclisation, polymerisation and condensation (Arturi et al., 2016).

NaOH as a catalyst is beneficial owing to less biochar associated with its use. The OH^{-1} ion neutralises the molecules, giving rise to polymerisation in char formation. Demirbaş (2000), Durak & Genel (2020), and Huang et al. (2013) have all revealed that K_2CO_3 is superior to KOH for HTL practices. K_2CO_3 reacts with water and the reaction produces bicarbonate, which acts as a catalyst to enhance the yield of bio-oil. This notion was supported by Karagöz et al. (2005), who based their findings on the performance of the catalysts in converting biomass and yielding of the bio-oil. They ranked the catalysts as follows: K_2CO_3 > KOH > Na_2CO_3 > NaOH. The study of Bi et al. (2017) also found K_2CO_3 to be the best performing catalyst amongst five other catalysts (KOH, formic acid, Ni/Si-Al, Ni_2P and zeolite) in the liquefaction of sorghum bagasse conducted at 300ºC and 350ºC yielding 61,8% bio-oil.

The incorporation of homogeneous alkali salts as catalysts during HTL is considered advantageous; however, their participation also tends to increase the pH and consequently reduce the dehydration reaction, which results in unstable and unsaturated molecules. Furthermore, the other disadvantage is related to the exorbitant costs of separation during the recovery of the catalysts (Kumar et al., 2018). Alkali catalysts are also infamous for instigating corrosion in HTL reactors (Murakami et al., 1990).

Organic acids are part of homogeneous catalysts. In contrast to alkali catalysts, organic acids as catalysts improve the flow properties of bio-oil; however, they yield more gaseous products, increase the sulphur content in HTL products and are not efficient in decreasing the heteroatom in bio-oil (Xu et al., 2018).

Heterogeneous catalysts are more common in HTG as opposed to HTL. They include rare metals such as Pt, Pd, Mo, Ni, Ru. Other metals that have been employed include metal oxides such as ZrO2 owing to MnO, MgO, NiO, ZnO, CeO_2, and La_2O_3. Nanocatalysts have also been examined. Their incorporation revealed an improvement in the bio-oil yield at lower operating temperatures in HTL (Kumar et al., 2018). Zhou et al. (2016) found that catalysts containing Ru and Pt elements are expensive and opted for CuZnAl in the HTL of rice straw in mixtures of water and ethanol. In comparison to homogeneous catalysts, heterogeneous catalysts are generally associated with lower bio-oil yields (Zhou et al., 2016). Interestingly, some studies have proved this phenomenon incorrect, such as the study of Nagappan et al. (2021), which applied both homogeneous and heterogeneous catalysts, KOH and HCOOH and FeS. FeS was discovered to yield higher bio-oil compared to the homogeneous catalysts (Nagappan et al., 2021). Some of the favourable attributes of heterogeneous catalysts are that they do not corrode reaction vessels and their recovery process is cheaper and easier (Murakami et al., 1990; Nagappan et al., 2021).

Among many positive impacts emanating from the use of catalysts reported by various authors such as Shah et al. (2020**),** they noted that the inclusion of a catalyst in HTL of sewage sludge reduced the nitrogen content in bio-oil and bio-oil expressed the highest energy recovery of 74%. Only a few studies discovered that the addition of a catalyst did not produce impressive results (Nagappan et al., 2021).

2.13.4 Solvents

Water plays a significant role in HTL as a solvent, catalyst and reactant (Kruse & Dinjus, 2007). Water has earned the name “universal solvent” owing to its ability to dissolve more substances than any other solvent. However, at standard conditions, water fails to dissolve organic compounds and can only achieve this at overcritical conditions (Durak & Aysu, 2016). Bound water does not have the same solubility as free water, which significantly hinders the mixing between organics and solvents (Yang et al., 2019).

In HTL, the solvent has a paramount function in achieving desirable bio-oil yields and qualities. Excluding subCW or SCW, the universally applied solvents are alcohols such as methanol, ethanol, propanol and isopropyl alcohol. Others such as phenol, acetone, ethylene glycol, ethylene carbonate, tetralin and toluene have also been examined. Supercritical alcohols have been found to have the following advantages in comparison to subCW and SCW:

- Better solubility – Alcohols, relative to water, are superior solvents of bio-oils. The dielectric of constant of alcohols is significantly inferior to that within subCW and SCW conditions, making it a better solvent (Brand et al., 2013).
- Easier product separation – Aqueous products in HTL by either subCW or SCW separate into two distinct factions, soluble or insoluble; however, the converse takes place when an organic solvent is used. A single aqueous phase manifests and bio-oils can be recovered conveniently through alcohol drying (Brand et al., 2013).
- Lower corrosivity – In comparison to supercritical alcohols, subCW is more corrosive close to its critical state (374°C and 22 MPa) (Brand et al., 2013; Huang et al., 2011).
- Supercritical alcohol possesses properties of hydrogen donor and hydroxylalkylation agent – “to depolymerize biomass, a deoxygenation agent to remove oxygen from biomass via H_2O formation, and a radical quenching agent to retard repolymerization and formation of char/tar” (Brand et al., 2013).
- Heavy metals: Solvent substantially impacts the redistribution of heavy metals during sewage sludge HTL (Xu et al., 2018).

- Elimination of cross-linked and reversable reactions – The inclusion of a solvent seeks to dilute the concentration of products hindering cross-link and reversible reactions (Liu & Zhang, 2008).
- Lower energy consumption – Supercritical alcohol performs better than water in the conversion of low-rank carbon (Liu & Zhang, 2008).
- Superior bio-oil qualities – Pure water as a solvent is associated with lower bio-oil yields, high oxygen content and low HHVs (Feng et al., 2018).

A study conducted by Liu & Zhang (2008) investigated the effect of various solvents (water, acetone and ethanol) at 250-550°C and a pressure of MPa for 20 minutes. Their results revealed that solvent type has a significant effect on products of HTL. Acetone was found to exhibit the highest conversion rate, while ethanol achieved the highest yield of 26,5% at 350°C. Brand et al. (2013) conducted experiments at 345°C for 30 minutes and maintaining a pressure of 5 MPa to investigate the performance of ethanol. The ratio of biomass (pine sawdust) and solvent from 0,06 to 0,25 g/g was used. The outcome showed that the conversion rose gradually from 82,2% to 85,3% and the bio-oil yield increase from 46,6 wt% to 56,4 wt%. Caporgno et al. (2016) in their study observed that a higher the ethanol:water ratio promoted a greater bio-oil yield. Further to that, they observed that the effects of the ethanol are more noticeable when rations are 3:10 and higher. Solvent ethanol decreased solid by-products and increased the conversion of microalgae (Caporgno et al., 2016). In their work, Huang et al. (2014) obtained a higher yield of oil with acetone as a solvent when compared to ethanol and methanol. The order of efficiency was methanol > ethanol > acetone. They found that ethanol and methanol tend to yield ester compounds while acetone favoured ketone production. Among all supercritical organic solvents – methanol, ethanol, propanol, butanol, and pentanol – ethanol is perceived as more effective in liquefaction furthermore it has been suggested to be employed in the HTL of sewage sludge because of its renewable nature (Huang et al., 2011).

Ethanol has gained a lot of interest as a co-solvent in HTL (Huang & Yuan, 2015). Isopropyl alcohol and ethylene glycol are also favourable due to their small autogenous pressure at high temperatures and high solubility. Ethylene glycol does not entirely penetrate the oil phase, therefore making it simple to separate in the bio-oil. Isopropyl alcohol, on the contrary, partitions into both the oil and aqueous phase, but it is relatively simple to strip it from the oil as it possesses rather high volatility (Han et al., 2019).

2.13.5 Biomass type

Biomass type is a pivotal parameter in the HTL treatment. Different types of biomasses comprise of several peculiar compositions, making biomass reactions in HTL remarkably unique. Even when identical reaction parameters are imposed, this uniqueness is also reflected in the properties of products yielded, which hugely lean on the type of biomass type exploited (Xue et al., 2016). There are several distinct types of biomasses worldwide; however, what is common about them is that they all consist of the following elements (Gollakota et al., 2018):

- C – Carbon is the most essential constituent in biomass, indicating the overall heating value.
- H – Hydrogen is converted into water, which contributes to overall heating value.
- N – Nitrogen contributes significantly to the degradation of biomass.
- S – Sulphur is related to gaseous emissions and corrosion.
- O – Oxygen must be limited as it controls the heating value of bio-oil. It is measured by subtracting 100 from the former elements and ash.

The use of biomass highly depends on different factors such as availability, climate and costs. Out of the many available biomass, lignocellulosic and algal biomass are the most well known in the application of HTL. The key components of lignocellulosic biomass are cellulose, hemicellulose and lignin (Wu et al., 2020). The components of algal biomass are carbohydrates, protein and lipid (Ali et al., 2020). Various types of waste, such as agricultural and municipal waste, have also been widely used in HTL application. Sewage sludge has been successfully investigated as a reliable feedstock for the production of exceptional bio-oils through HTL. According to Prestigiacomo et al. (2020), sewage sludge is equivalent to microalgae in terms of their conversion efficiency and opting for their use would potentially reduce 40% of the operating costs of the process.

Bio-oil yields of an outstanding quality remain the core objective of the HTL process. Generally, yields from biomass can range from 10%-60%, and in some exceptional cases, above 80%. Figure 2.8 is a graph propagated by Dimitriadis & Bezergianni (2017) displaying a combined distribution of yields attained from various publications of diverse feedstocks, namely wood algae and wastes. The graph demonstrates that 50% of publications on wood HTL obtained yields of the range 20-30%. Yields obtained from algae were found to be dispersed, however; 25% of the yields obtained a 25% yield. The wastes had an even greater dispersion, in the range of 35-45%.

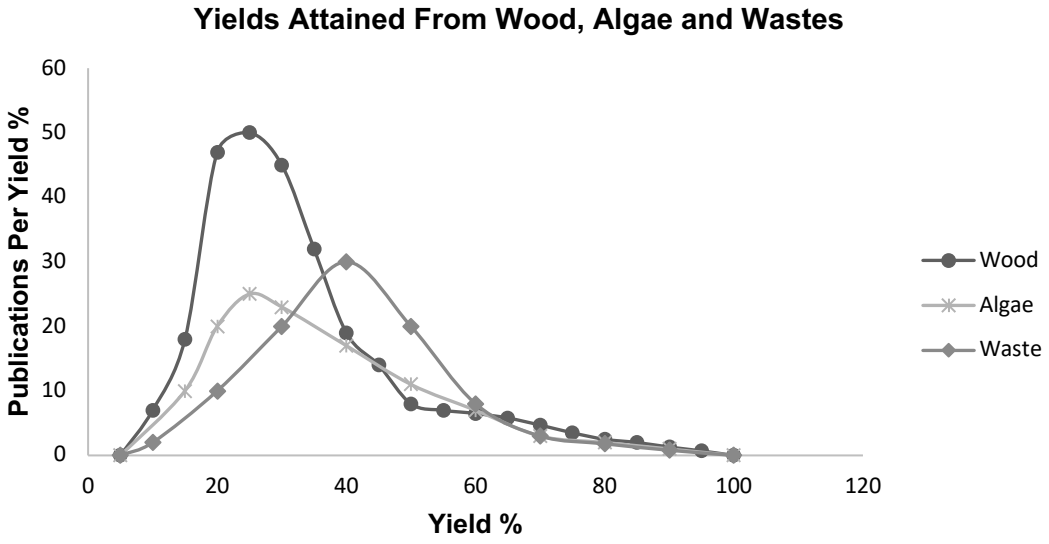

Figure 2.8 Combined distribution of yields of HTLs of wood, algae and wastes attained from various literature

Adapted from Dimitriadis & Bezergianni (2017)

There are recent trends in co-liquefaction with the intention to increase bio-oil yield, control the properties of bio-oil and utilise a selection of biomasses readily available. It is trusted that a synergistic effect on bio-oil yield emerges from effective collaboration among disintegrated products and intermediates from combined biomass. The degree of synergistic effect leans on the mixing ratio of variant biomass and HTL process conditions such as temperature and holding period (Yang et al., 2017). Various biomass types have been hydrothermally co-liquefied, such as microalgae, macroalgae, rice husk-straw, aspen/pinewood sawdust, plastics, spent coffee grounds, spent mushroom compost, sewage and pulp/paper sludge, animal manure and crude glycerol (Yang et al., 2019).

2.13.6 Residence time

HTL residence time is the period granted for reactions to be achieved in the HTL of biomass, which does not include the cooling and heating periods (Dimitriadis & Bezergianni, 2017; Leng et al., 2020). Sufficient residence time is regarded as a significant factor in conversion and yield of bio-oils (Leng et al., 2020). Increasing residence time results in favourable bio yield; however, there is a threshold, as a further increase has a negative impact. The threshold places reliance on operating parameters such as catalyst type, feed, temperature etc (Dimitriadis & Bezergianni, 2017).

Wang et al. (2018) explored various holding times from 0-8 hours on HTL of sewage sludge at 27ºC using CuSO4 as a catalyst. When the holding time was prolonged from 0-30 minutes, the bio-oil yield and conversion escalated from 17,08% and 67,49% to 47,45% and 97,74%, respectively. This illustrates that when HTL is conducted for an adequate time, sufficient decomposition and polymerisation of molecules take place. They experience a gradual decline of bio-oil yield from 30 minutes onwards. At eight hours, the bio-oil yield was 39,1%. This was due to further decomposition of bio-oil into a gaseous, aqueous and solid phase. The optimum residence time was 30 minutes.

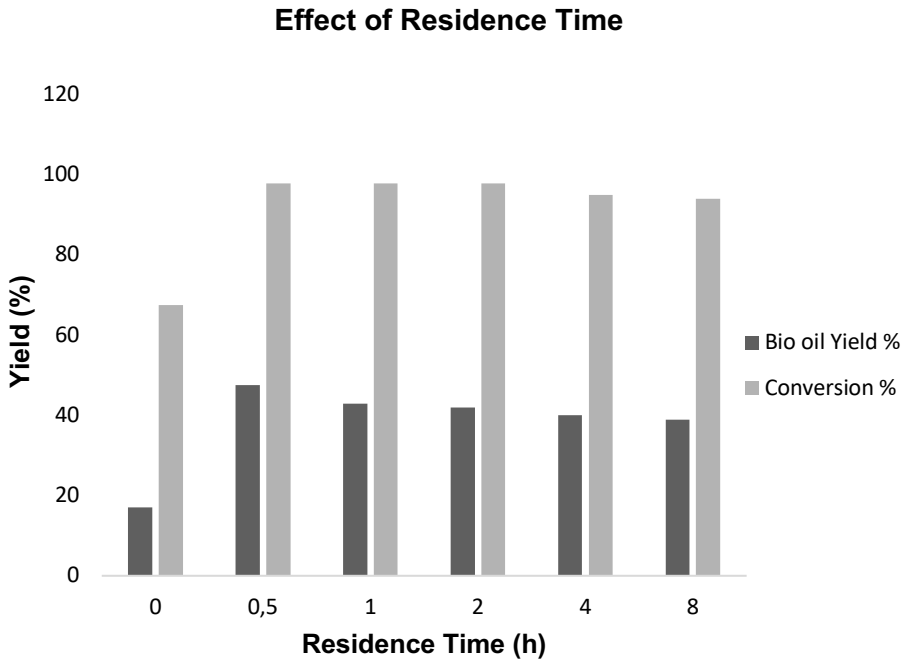

Figure 2.9 The effect of residence time on the catalytic HTL of sewage sludge

Adapted from Wang et al. (2018)

Malins et al. (2015) investigated the effects of residence time on the catalytic HTL of sewage sludge in increments of 30 minutes, starting from 10 minutes until 100 minutes at 300 ºC using FeSO4 a catalyst. The yield at 10 minutes was 43,7% and the conversion was 66,5%. Both yield and conversion slightly increased when the residence time was extended to 40 minutes. However, there was a slight decline in the value of energy recovery. When the process was prolonged to 100 minutes, the yield of bio-oil decreased to 40,3%; nevertheless, the conversion continued to increase. This was a result of the formation of by-products such as gas and biochar, as an increase in residence time promotes the further conversion of sewage sludge to other products.

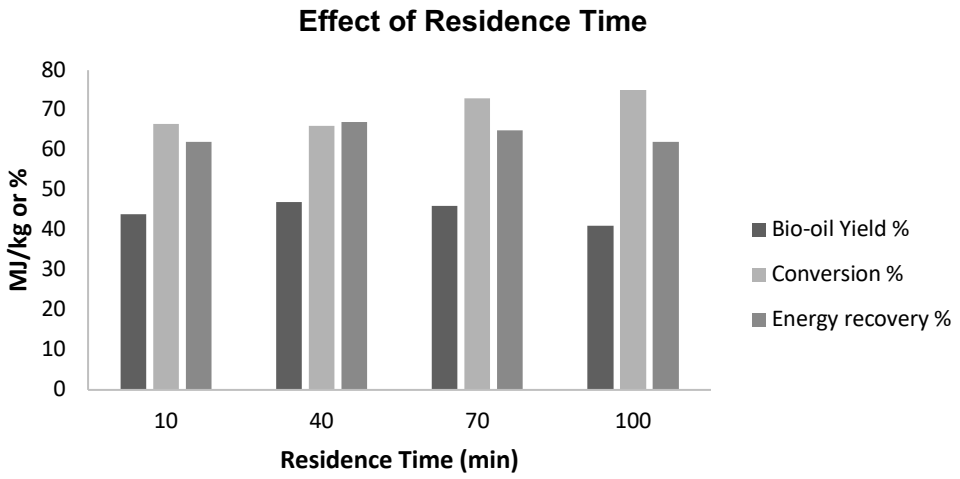

Figure 2.10 Effects of residence time on the catalytic HTL of sewage sludge

Adapted from Malins et al. (2015)

Jena et al. (2011) investigated the effect of holding time in the HTL of *Spirulina platensis* conducted at 350ºC from 0-120 minutes. Their results reflected that with an increase in holding time, the yield of bio-oil also increased; however, the increase was only until 60 minutes. After 60 minutes, the bio-oil yield diminished. The gaseous products in the first 60 minutes did not change significantly; however, between 60 and 90 minutes there was an increase from 18,2% to 27%. This increase from 60 to 90 minutes was due to lighter hydrocarbons transforming into gaseous products. Longer holding times tend to hinder bio-oil yields because light bio-oil converts to gases. With regard to the solid residue yield, the residence time had no impact; however, a gradual decrease in water-soluble substances was noted, which contributes to the increase in dehydration of carbohydrates (Jena et al., 2011).

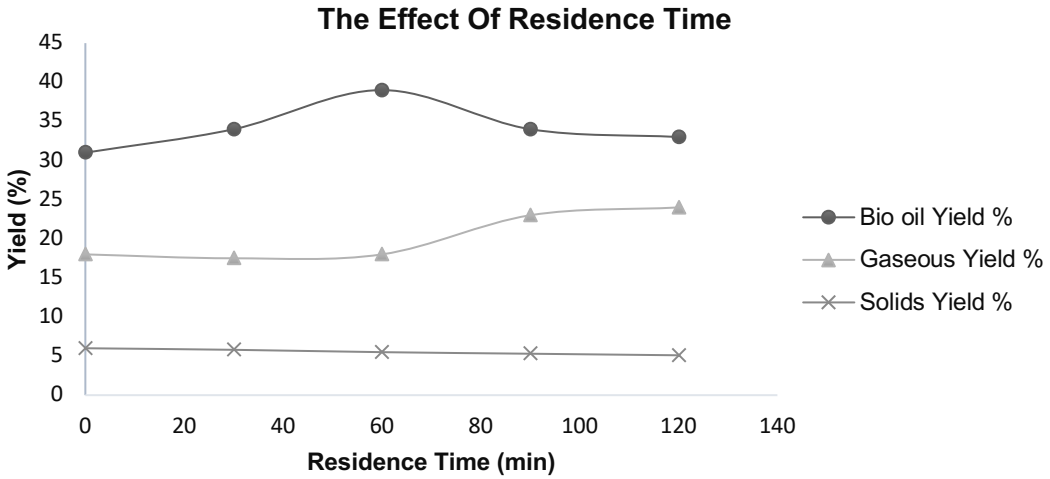

Figure 2.11 The effect of residence time in the HTL of *Spirulina platensis*

Adapted from Jena et al. (2011)

Analogous results were obtained by Li et al. (2020) in the HTL of macroalgae using reaction times from 15 minutes to 45 minutes at 280ºC. The bio-oil yield was highest at 30 minutes, where the conversion was 79,9%. Between 15 and 30 minutes, the bio-oil yield increased from 32,4 to 43.8%, followed by a minor decrease to 40,1% at 45 minutes. The difference in their results is that the solid residue did not maintain the same yield throughout reaction times. The yield of the solids considerably decreased between 15 and 30 minutes and dramatically increased at 45 minutes. It seems at 15 minutes, the biomass did not adequately decompose as at 30 minutes, as the conversion was 61,5%, as compared to 79,9% at 30 minutes. The increase of solids at 30 minutes demonstrates that polymerisation of products was enhanced, resulting in an increase in biochar.

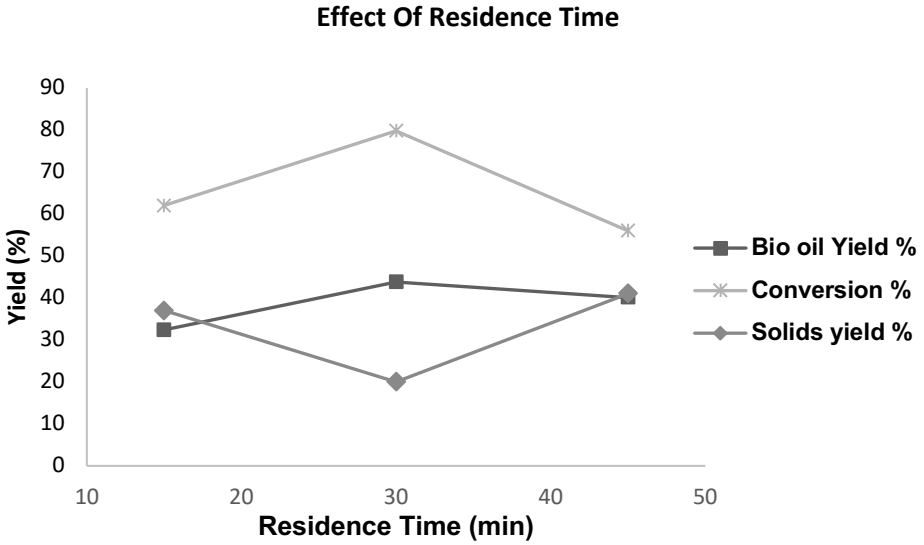

Figure 2.12 The effect of residence time on the HTL of macroalgae using reaction

Adapted from Li et al. (2020)

2.13.7 Pressure

In the HTL process, pressure is also a vital process parameter that has an influence on bio-oil yields. Pressure keeps the single-phase phase under both subcritical and supercritical conditions, consequently preventing great enthalpy inputs necessitating a phase modification in water (Xue et al., 2016). Two-phase processes need a great degree of heat to sustain the temperature of the system. Keeping the pressure beyond the critical pressure of the medium assists in promoting water density and manages the degree of hydrolysis and dissolution of biomass, which encourages favourable reaction pathways thermodynamically, such as the decomposition and extraction of biomass for the production of bio-oils (Xue et al., 2016; Akhtar & Amin, 2011; Wang et al., 2013).

As pressure intensifies during HTL, the properties of water, namely density, static dielectric constant and ion products, increase (Xue et al., 2016). Mediums with high density tend to penetrate effectively into components of biomass, which improves decomposition and extraction (Akhtar & Amin, 2011). Moreover, pressure impacts the ionic rate, which is fundamental in the production of the liquid phase, causing it to increase, while free radical reactions that promote gas formation decline. Pressure increase also influences an increase in the ion products that are responsible for hydrolysis rate (Akhtar & Amin, 2011).

Above supercritical conditions, pressure plays a negligible role in the yield of bio-oil and biogas due to the solvent density increase (which is instigated by high pressures) that encapsulates the C-C bonds of biomass. This cage effect prevents the bonds from breaking, subsequently decreasing fragmentations (Akhtar & Amin, 2011). Therefore modifications of pressure in supercritical HTL does not promote depolymerisation (Bai et al., 2019).

In contrast, Malins et al. (2015) reported a negligible improvement in bio-oil yield with increase of pressure (2-11 MPa) of sewage sludge. The highest yield obtained was 47,8%, with initial hydrogen pressure of 5 MPa at 300ºC. Further to that, other authors have discovered that subcritical conditions are more favourable as they yielded better results when process conditions were kept the same for both subcritical and supercritical conditions (Do et al., 2020).

2.13.8 Particle size

Particle size is reduced to improve biomass accessibility in order to achieve greater hydrolysis and fragmentation. However, this comes at a great energy cost. Particle size reduction entails increasing surface area and pore size (Mani et al., 2004). Particle size has a very low effect on HTL of biomass. This is due to subCW/SCW performing a duel role as a heat transfer medium as well as an extractant, consequently aiding in improving heat transfer in HTL and making particle size a secondary parameter (Akhtar & Amin, 2011). In the investigation of Zhang et al. (2009) on particle size (25,4 mm, 2 mm and 0,5 m) of perennial grass HTL conducted at 350ºC, they elucidated that the reduction size did not improve the yield of bio-oil and therefore there is no need to reduce the particle size. Since particle size imparts a negligible effect on HTL, it is not widely discussed in literature. Jayathilake et al. (2020), conducted HTL of wood and investigated the effect of particle size of particle radius (0,08, 0,1 and 1 mm) and in contrast, noted that decomposition rate became much slower when the particle size increased, since the reaction occurs on the outer surface of the particle. Compounds with a smaller radius yielded more bio-oil since they experience fast decomposition on the particle.

2.14 Bio-oils

Bio-oils are renewable liquid fuels obtained from biomass through different thermochemical procedures (Xu et al., 2011). They are suitable substitutes for conventional fuel oil or diesel that may be used in a variety of industrial applications such as boilers, furnaces, engines and turbines for the generation of electricity and heat. Alternatively, they can be employed in the production of various chemicals, adhesives, resins, plastics, wood flavours, and so forth (Xiu & Shahbazi, 2012). Generally, the upgrading of bio-oils remains essential as they are somewhat inferior to conventional petroleum-based fuels. For example, raw bio-oils cannot be used directly as transport fuels. They require proper upgrading to improve their properties before application (Xiu & Shahbazi, 2012).

2.14.1 Sewage sludge derived bio-oil characterisation

Bio-oil is a sophisticated combination of hundreds of organic compounds largely containing acids, alcohol, aldehydes, esters, ketones, phenols and lignin-derived oligomers. It has a dark brown appearance, is extremely viscous and has a distinctive odour. Bio-oils obtained from HTL typically have lower oxygen and moisture in comparison to those obtained from pyrolysis; however, bio-oil properties are different from heavy petroleum fuel oil (Park et al., 2021). The following are unfavourable attributes that limit their application.

- Low pH – Caused by degradation of organic acids, resulting in corrosion of reactors and piping (Park et al., 2021).
- Lower heating value – The heating is inferior in comparison to that of conventional fossil fuels oil due to high water content (Xu et al., 2011).
- Aging – Caused by secondary reactions that result in increasing of viscosity due to potential phase modification from subsequent reactions (Banks & Bridgwater, 2016).
- Biochar – Caused by imperfect char separation during the treatment, resulting in filter and engine blocking, alkali metal poisoning and oil aging.
- High viscosity – Results in high pumping costs and excessive pressure drop (Banks & Bridgwater, 2016).
- High water content – Since water is a reactant during the treatment, this results in decreased heating value, density, stability, increased pH and catalysts being harmed (Park et al., 2021; Xu et al., 2011).
- High oxygen content – Due to inevitable biomass composition, resulting in inadequate stability and inability to mix with hydrocarbons (Park et al., 2021).

- Nitrogen presence – Naturally coming from biomass and causes an unpleasant odour and poisoning of the catalyst during upgrading (Banks & Bridgwater, 2016).
- Toxicity – Due to biopolymer degradation, resulting in human toxicity on a very small scale (Banks & Bridgwater, 2016).
- Temperature sensitivity – Due to incomplete reactions, promoting phase separation and irreversible viscosity (Banks & Bridgwater, 2016).
- Poor volatility accompanying repolymerisation and week storage stability (Park et al., 2021).
- Presence of sulphur – Due to contamination in biomass. Results in catalyst poising in upgrading stage (Xu et al., 2011).
- Mechanical impurities – Harmful to storage, resulting in increase in viscosity (Xu et al., 2011).
- Immiscibility with petroleum owing to high water content (Park et al., 2021).

2.14.2 Element analysis of bio-oil from sewage sludge

An elementary analysis is a detection or determination of elements in a substance. The typical elemental analysis of bio-oil obtained in the HTL of sewage sludge is displayed in Table 2.8 and Table 2.9 respectively, where temperature and solvent type (methanol, ethanol and acetone) are varied. It is evident that an increase in temperature and solvent type has to some degree an effect on the elemental content and the heating value. Xu et al. (2018) noted a positive relationship between temperature and HHV and C content. High temperature also promotes deoxygenation (Huang et al., 2014). Initially, an increase in temperature favours the N- and S-containing organic compounds; however, denitrogenation and desulphurisation are triggered after 340ºC. An increase of temperatures promotes bio-oil quality as seen at 350ºC. N, S, O derived from proteins, lipids, carbohydrates and lignin in the sewage sludge feedstock are the lowest and the C and H content are higher.

Huang et al. (2014) performed HTL of sewage sludge at 360ºC using different solvents. They noticed a vast increase in C, H, and N, after HTL treatment in comparison to that of the raw sewage feedstock. The bio-oils from methanol and ethanol solvent obtained higher HHV values and C and H contents in comparison to the bio-oil from acetone solvent, and the O content however was extremely high. Bio-oil obtained in ethanol was found to be superior.

Table 2.8 Element content and heating rate of sewage sludge obtained at different temperatures

T	Element Content					HHV(MJ/kg)
	C	H	N	S	O	
260ºC	70,99	9,27	4,40	1,29	14,05	34,84
300ºC	72,36	9,10	4,49	1,46	12,59	35,35
340ºC	72,36	9,04	4,88	1,81	11,91	35,41
350ºC	73,12	9,20	4,43	1,67	11,58	35,94

Adapted from Xu et al. (2018)

Table 2.9 Element content and heating rate of sewage sludge obtained using different solvents

T	Element Content					HHVMJ/kg
	C	H	N	S	O	
Methanol	73,97	9,84	6,60	1,12	8,47	37,69
Ethanol	75,12	9,85	6,98	1,39	6,66	38,42
Acetone	70,21	4,42	5,56	1,05	18,78	26,74

Adapted from Huang et al. (2014)

2.14.3 Compound Composition in bio Oli Of Sewage Sludge

Sewage sludge bio-oil composition can be further clarified through the presentation of an ion chromatogram, which exhibits a vast number of organic compounds. The chromatogram is represented by a graph showing retention times relative to peak areas, and tentatively identified compounds with their formulas. Bio-oils from sewage sludge are characterised by an abundance of cyclic compounds, long chain fatty acid esters formed from lipids (triglycerides) via transesterification, and subsequent esterification reactions of free fatty acids with alcohols. Other esters and derivatives may be generated from the decomposition of carbohydrates and proteins from the sewage biomass. Nitrile compounds also have the potential to emerge from the dehydration of acid amides. The Maillard reaction may promote the generation of nitrogen-containing cyclic molecules such as pyridines and pyrroles, including N-containing ketones. Amides are the most abundant detectable products; they supposedly arise from incomplete hydrolysing reactions in such a short residence time (Huang et al., 2014; Xu et al., 2018).

Bio-oils from sewage sludge also typically comprise of long chain aliphatic hydrocarbons, moieties and aliphatic acids (Qian et al., 2017). According to Shah et al. (2020), in HTL of sewage sludge-obtained bio-oil, N-containing compounds, ketones, phenols, acids, and long-chain hydrocarbons are present. And in the work of Huang et al. (2014), they found that the

most abundant compounds in the bio-oil produced from sewage HTL where ethanol was a solvent are esters (heptadecanoic acid, ethyl ester (14,7%); 1,2-benzenedicarboxylic acid, disoctyl ester (8.97%); and octadecanoic acid, ethyl ester (7.96%)). The sulphur content in the bio-oils ranges from 1,05% to 1,39%, similar to that of fossil oil, which is in the range 0,05-5,0% (Miao & Wu, 2004).

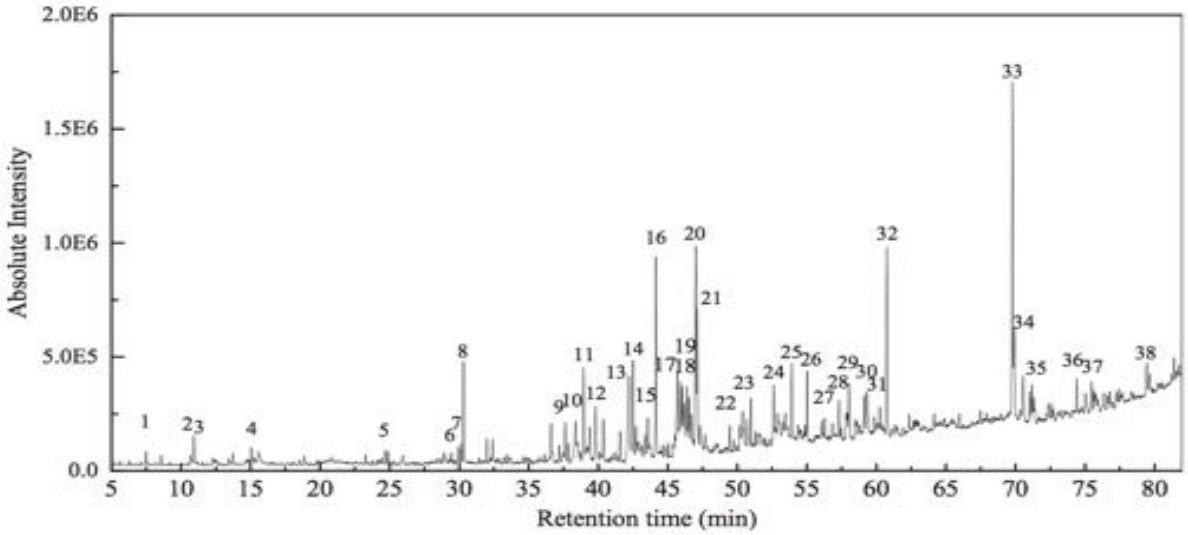

Figure 2.13 Total ion chromatography of bio-oil from sewage sludge HTL

Adapted from Xu et al. (2018)

Table 2.10 List of compounds emerging from bio-oil from sewage sludge HTL

NO.	Time (min)	Compounds	Relative peak area (%)	Molecular formula
1	7,50	Phenol	0,76	C_6H_6O
2	10,65	2-Pyrrolidinone	1,05	C_4H_7NO
3	10,92	p-Cresol	1,01	C_7H_8O
4	15,05	Phenol, 4-ethyl-	1,07	$C_8H_{10}O$
5	24,89	1H-Indole, 3-methyl-	0,82	C_9H_9N
6	29,95	1-Heptadecanamine, N,N-dimethyl-	1,21	$C_{19}H_{41}N$
7	30,13	Acetamide, N-(2-phenylethyl)-	1,02	$C_{10}H_{13}NO$
8	30,31	Phenol, 2,4-bis(1,1-dimethylethyl)-	5,03	$C_{14}H_{22}O$
9	37,64	Benzedrex	2,27	$C_{10}H_{21}N$
10	38,36	(3S,6S)-3-Butyl-6-methylpiperazine-2,5-dione	1,24	$C_9H_{16}N_2O_2$
11	38,95	n-Tridecan-1-ol	1,15	$C_{13}H_{28}O$
12	39,39	4-Cyanobenzoic acid, 2-phenylethyl ester	1,18	$C_{16}H_{13}NO_2$

NO.	Time (min)	Compounds	Relative peak area (%)	Molecular formula
13	42,22	Pentadecanoic acid	1,05	$C_{15}H_{30}O_2$
14	42,49	Pyrrolo[1,2-*a*]pyrazine-1,4-dione,hexahydro-3-(2-methylpropyl)-	7,46	$C_{11}H_{18}N_2O_2$
15	42,70	7-Ethyl-4,6-heptadecandione	0,76	$C_{19}H_{36}O_2$
16	44,14	n-Nonadecanol-1	2,64	$C_{19}H_{40}O$
17	45,91	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo [1,2-a:1′,2′-d]pyrazine	3,49	$C_{14}H_{22}N_2O_2$
18	46,18	L-Proline, N-valeryl-, heptadecyl ester	2,55	$C_{27}H_{51}NO_3$
19	46,52	Palmitoleic acid	0,74	$C_{16}H_{30}O_2$
20	47,01	Dibutyl phthalate	2,72	$C_{16}H_{22}O_4$
21	47,09	n-Hexadecanoic acid	2,93	$C_{16}H_{32}O_2$
22	49,47	Octadecanamide	0,99	$C_{18}H_{37}NO$
23	50,38	9-Octadecen-1-ol, (Z)-	1,35	$C_{18}H_{36}O$
24	52,61	2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3] undecane, 1-ethyl-	2,93	$C_8H_{17}NO_3Si$
25	53,92	Octadecanamide	3,27	$C_{18}H_{37}NO$
26	55,02	N-Methyldodecanamide	2,20	$C_{13}H_{27}NO$
27	56,27	Octanamide, N,N-dimethyl-	1,13	$C_{10}H_{21}NO$
28	57,83	Cyclo-(l-leucyl-*l*-phenylalanyl)	1,23	$C_{15}H_{20}N_2O_2$
29	58,03	Ergotaman-3′,6′,18-trione,9,10-dihydro-12′-hydroxy-2′-methyl-5’-(phenylmethyl)- ,(5’.alpha.,10.alpha.)-	1,78	$C_{33}H_{35}N_5O_5$
30	59,12	9-Octadecenamide, (Z)-	0,85	$C_{18}H_{35}NO$
31	59,86	Octadecanamide	0,85	$C_{18}H_{37}NO$
32	60,75	Phenol,2,2′-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	4,45	$C_{23}H_{32}O_2$
33	69,78	13-Docosenamide, (Z)-	10,73	$C_{22}H_{43}NO$
34	69,90	Cholest-4-ene	0,82	$C_{27}H_{46}$
35	73,19	4-Cyanobenzoic acid, tridec-2-ynyl ester	1,10	$C_{21}H_{27}NO_2$
36	75,l45	26-Norcoprostan-16,22-epoxy-3.alpha.,25-diol 3-*O*-acetyl-	1,40	$C_{28}H_{46}O_4$
37	75,94	.gamma.-Tocopherol	1,15	$C_{28}H_{48}O_2$
38	77,69	(+)-.gamma.-Tocopherol, O-methyl-	1,23	$C_{29}H_{50}O_2$
Total			79,60	

Adapted from Xu et al. (2018).

2.15 Bio-oil upgrading

The commercialisation of bio-oil as transport fuel has been limited due to the negative aspects that are illuminated in section 2.13.1. These negative aspects spring from the presence of extremely reactive oxygenated compounds found in bio-oil, such as acids, phenols, furans, aldehydes, sugars, and pyrolytic lignin fragments. Thus it is necessary to upgrade bio-oil to meet international fuel quality. Certain compounds modify the bio-oil characteristics and promote reactions such as esterification, phenol-aldehyde reactions, polymerization, and condensation (Xu et al., 2009). These reactions help to enhance the stability of bio-oil. Various methods of upgrading processes have been investigated. These processes may be divided into physical and chemical methods, they include:

- Hydrotreating/Hydrocracking
- Sub/supercritical fluid
- Solvent addition/esterification
- Emulsification
- Steam reforming
- Chemical extraction

CHAPTER 3

3 Materials and Method

This chapter delivers a comprehensive description of the experimental procedure that was followed in order to obtain results for this work. The list of apparatus and material used are presented. The equations of yields and conversion are elucidated. A schematic diagram of the entire experimental procedure of the HTL of sewage sludge is presented.

3.1 Apparatus

The following apparatus was used:

- Refrigerator
- Furnace
- Oven
- Grinder
- Measuring scale
- X5 Erlenmeyer flasks 250 ml
- X5 beakers
- X5 funnels
- X90 filtering paper
- X90 50 ml conical centrifuge tubes
- 20 ml measuring cylinder
- 10 ml measuring cylinder

3.2 Materials

3.2.1 Dichloromethane (DCM)

The DCM that was used for bio-oil extraction after the HTL of sewage sludge was purchased from Shalom Laboratory Supplies c.c. in Durban, KwaZulu-Natal.

3.2.2 Ethanol

The ethanol that was used as a solvent during the HTL of sewage sludge was purchased from Shalom Laboratory Supplies c.c. in Durban, KwaZulu-Natal.

3.2.3 Raw Material

The raw secondary sewage sludge that served as a feedstock in the HTL process was a by-product of an existing wastewater treatment plant in Howick, KwaZulu-Natal. Twenty litres was obtained and transported to Durban University of Technology School of Horticulture's nursery, where it was immediately dried by sun. The dried sludge was then ground into a homogenous mass using a grinder. A thermal gravimetric analysis was conducted on the homogenous

sample to determine the mass of volatile solids that was used in the calculation of the yield and conversion. The volatile solids were determined to be 46,7%. The dried sewage sample was stored in the refrigerator for the duration of the experimental work to prevent any further microbial activity.

Figure 3.1 Showing the drying process and the reduction of particle size of sewage sludge after grinding

3.3 Experimental setup and procedure

The hydrothermal liquefaction experiments were conducted in 60 ml batches assembled from 316 stainless steel batch pressure reactors that were procured from Simunye Engineering in Durban. The reactors were designed to endure a pressure and temperature of 40 MPa and 500ºC respectively. The particle size of the dried sewage sample charges was controlled by

grinding and sieving the dried sewage mass. De-ionised water (H_2O) and ethanol (E) were examined as solvents and their composition was varied in three steps in the following order: 1:0, 1:1 and 0:1 (H_2O:E). In the interest of investigating the effect of solvent content, the relevant solvent was carefully measured using a measuring cylinder, and then added into the dried feedstock. The mass of the dried feedstock was maintained at 1 g throughout the experiments and the volumes of the solvents were varied according to the desired solvent: feed ratio required on a wt/wt basis. The five solvent contents investigated were 75%, 80%, 85%, 90% and 95%. Six temperatures were explored: 220ºC, 250ºC, 280ºC, 310ºC, 340ºC, and 370ºC. Following the loading of the samples into the reactors, the reactors were flushed with nitrogen to displace the air inside and for the removal of any impurities. The reactors were then sealed using a spanner to tighten the nuts. They were then placed in a furnace that was maintained at a desired temperature. Residence times of 30 minutes were maintained for all the experiments. After 30 minutes, the reactors were removed from the furnace and were air cooled for an hour, and thereafter placed in a water bath for further cooling. After cooling, the reactors were tapped at least five times using a hammer for the elimination of CO_2 that had dissolved in the aqueous phase and to dislodge bio-oil that had stuck in the caps of the reactor. The contents of the reactor were then subjected to a separation process. DCM was used as an extraction medium in this process.

The analysis of solid content and gaseous content were not within the scope of this study; therefore the gases were not collected and the solid phase was safely discarded. The separation procedure that was followed is demonstrated in Figure 3.2. The reactors were opened using a spanner and the gaseous phase was released. The suspension from the reactors was washed with DCM into a beaker and then filtered with filter paper under vacuum to separate the liquids from the solids. The filtrate was poured into separation flasks using a funnel where two distinct layers partitioned naturally, allowing for simple separation. The layer comprising of DCM that contained the bio-oil was transferred into a pre-weighed 50 ml conical centrifuge tube, then placed in the oven overnight at 60ºC to obtain the produced bio-oil. The bio-oil mass was measured using a measuring scale and sent for GCMS analysis.

3.4 Calculation of bio-oil and biochar yield and conversion

Bio-oil yield $= \mathbf{y_{bo}} = \frac{\mathbf{m_{bo}}}{\mathbf{m_{vs}}} \times \mathbf{100}\%$ **Equation 3. 1**

Biochar yield = $\mathbf{y_{bc}} = \frac{\mathbf{m_{bc}}}{\mathbf{m_{vs}}} \times \mathbf{100}\%$ **Equation 3. 2**

Hydrothermal liquefaction Conversion $= \mathrm{x} = \left(1 - \frac{\mathrm{m_{bc}}}{\mathrm{m_{vs}}}\right) \times 100\%$ **Equation 3. 3**

Where: m_{bo} is the mass of bio-oil produced

m_{vs} is mass of volatile solids.

m_{bc} is the mass of biochar = (mass of solid residuals – mass of non-volatile solids)

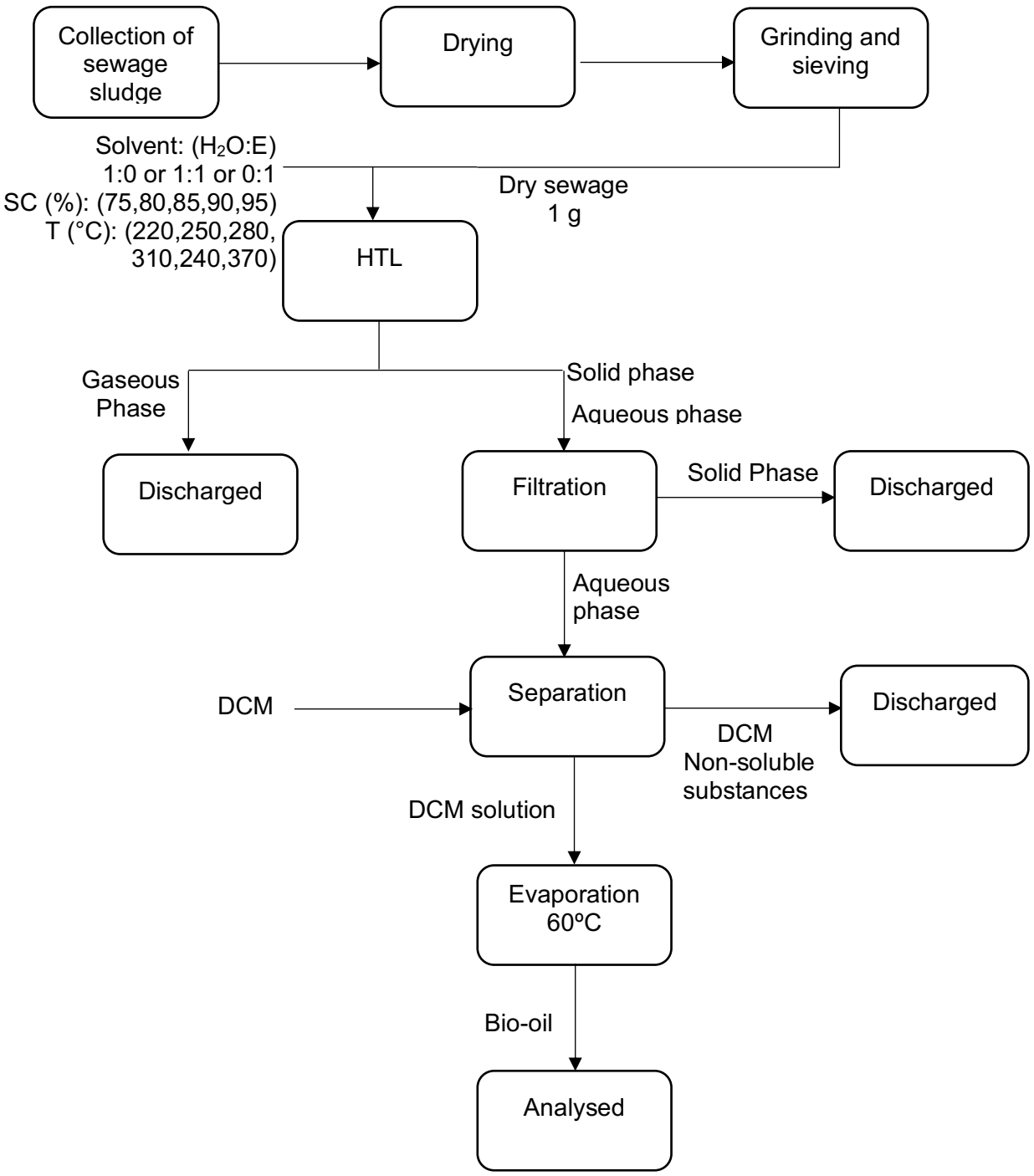

Figure 3.2 Schematic diagram of the experimental procedure that was executed for the HTL of municipal sewage sludge

CHAPTER 4

4 The effect of operating conditions on bio-oil yield and conversion

This chapter presents the results and discussion of the effect of process parameters on the bio-oil yield obtained in the batch HTL of municipal sewage sludge, where the temperature, solvent content and solvent type were varied. The influence of process parameters on the conversion and the biochar is also discussed. Unless otherwise stated, the term “yield” refers to the yield of bio-oil. In this work, the gases, solids and the aqueous phase that was not soluble in DCM were not analysed. The solid yields were recorded in the interest of determining conversion.

4.1 Introduction

HTL is a method of thermochemical conversion of biomass that has gained considerable attention and has been deemed a promising route. Between the 1970s and 1980s, HTL was customarily termed direct biomass liquefaction. It is ultimately pyrolysis that is conducted in an atmosphere of compressed, hot liquid water where the use of a catalyst is not compulsory (Elliott et al., 2015). Most of the research conducted on HTL reports on the results obtained from batch processes. HTL is typically conducted in moderate temperatures and very high pressures. Owing to the intense pressure, the solvent remains in the liquid state and at this environment, the dielectric constant rises with a decrease in the density relative to solvent at usual pressure and temperature (Jazrawi et al., 2013). The chief products of HTL include bio-oil with a relatively high heating value, biochar, gaseous products and aqueous products (Toor et al., 2011). Low bio-oil yields, harsh reaction conditions and inferior bio-oil quality are the driving forces of utilising organic solvents such as ethanol, methanol, propanol and acetone as the reaction medium during HTL. The advantages of their applications are (i) superior dissolution, (ii) promotes deoxygenation reactions that reduce the acidity of bio-oils and enhanced energy content (iii) moderate operating conditions, (iv) stabilisation of reaction intermediate, which curbs the formation of biochar (Zeb et al., 2017; Zhao et al., 2021). Notwithstanding the fact that organic solvent has a synergistic effect on the bio-oils yields, the use of pure organic solvent tends to hinder the fundamental initial step in HTL, which is hydrolysis (Cheng et al., 2010).

4.2 Experimental Procedure

The municipal sewage sludge was dried by sun for 72 hours. Thereafter, the dried sludge was ground to reduce the surface area. Once homogeneity in the sewage particle size was obtained, a thermal gravimetric analysis was conducted on a sample to determine the volatile content for yield and conversion calculations. The TGA and its derivative provided the loss of

the weight of the dried sewage sample with temperature. This graph is available in Figure 8.1.1 in the appendix, where it illustrates the moisture content (which accounts for the bound water) and the volatile matter. The HTL treatment was then conducted and DCM was used as an extraction medium. Three phases were achieved: a gaseous phase, an aqueous phase containing bio-oil, and a solid phase consisting of unreacted solids. Temperature, solvent content and solvent type were varied as 220ºC, 250ºC, 280ºC, 310ºC, 340ºC and 370ºC, 75%, 80%, 85%, 90%, and 95% and pure H_2O, H_2O/E and pure ethanol respectively. E denotes the solvent ethanol. The bio-oils achieved were weighed and analysed. The yield and conversion in this work are based on the experimental yield as opposed to the industrial yield, hence the calculations were performed considering the mass of volatile solids as opposed to the mass of the total feedstock. The volatile component of the municipal sewage sludge was determined to be 46,7%.

4.3 The effect of process parameters on the yield of bio- oil

4.3.1 The effect of temperature on the yield of bio-oil

Temperature was a highly influential parameter in the experiments of HTL of municipal sewage sludge. It supplied essential heat energy to enhance the fragmentation of bonds and intensified the synergetic effect on yielded products. Temperature also played an immense role in the pressure of the system as the experiments were conducted in a closed batch environment. The pressure exerted on feedstock was essentially the vapour pressure of the solvent employed since the gaseous phase could not escape during the reaction.

Figure 4.1 depicts the effect of temperature at various solvent contents (75-95%) (a) when pure H_2O, (b) co-solvent H_2O/E and (c) pure ethanol were alternately applied as solvents at a constant residence time of 30 minutes. The temperatures explored ranged from 220°C to 370°C and lie within the realms of subcritical conditions for pure H_2O; however after 241°C, ethanol reaches supercritical conditions. The critical point for mixed H_2O/E on a ratio of (1:1) is approximately 314°C and 11 Mpa. The addition of ethanol resulted in a much milder critical point than that of pure H_2O ,which is 374°C and 22,1 Mpa (Li et al., 2018). Generally, it is evident from Figure 4.1 that the trend of the bio-oil yields in all the experiments emulates a bell-like shape. For all the various solvent types and solvent contents, an analogous pattern is maintained, where the yields are found to initially increase until a certain temperature, and then a subsequent notable decline is witnessed. In Figure 4.1a, where pure H_2O was used as a solvent, this general trend of increasing bio-oil yields followed by a sharp decline occurs when temperatures approach 310°C, and for temperatures exceeding 310°C, the bio-oil yields are hindered. At solvent content of 75% for example, the bio-oil yields initially increase from 14,99

wt% at 220°C until 23,55 wt% at 310°C. Thereafter, the yields started to decrease back to 14,99 wt% and further to 8,57 wt% when temperatures increased from 340°C to 370°C. It is also worth noting that there are two conditions on Figure 4.1a, at solvent content of 80% and 90%, where the yields began to decline after 340°C and 280°C respectively. That was the only instance when the yields did not conform with the trend of decreasing only after reaching 310°C. This slight divergence in the typical trend, however, does not emerge as a fundamental discrepancy because both temperatures, 280°C and 340°C, are close to 310°C, in fact, 310°C is located between them. The preliminary enhancement of bio-oil yields in all the experiments as presented in Figure 4.1a across the various solvents contents is because subcritical water has the capability to promote hasty liberation of intracellular free fatty acids and neutral lipids by fragmenting cell walls, thereby endorsing supplementary hydrolysis of complex carbonaceous compounds catalysed by H^+ and OH^- ions (Jena et al., 2011). Furthermore, the density and polarity progressively declines with the escalation in temperature and pressure consequently augmenting the solubility of hydrophobic organic compounds (Li et al., 2018). The increase in bio-oil yields is also informed by the increase of pressure as temperature increases. Pressure increases the solvent density resulting in efficient penetration into the sewage feedstock thereby enhancing the decomposition and extraction (Akhtar & Amin, 2011). The trend of these results was consistent with those obtained by Xu et al. (2018) who in their work performed HTL of sewage sludge at temperature range 260-350ºC using 10 minutes residence time.

The subsequent deterioration of bio-oil yield, which is demonstrated in all experiments as the temperatures increase to from 310°C to 370°C, is a result of intermediate products subjected to further diverse secondary reactions such as refragmentation, isomerisation, and dehydration, which favour the yield of supplementary gaseous products as opposed to liquid products. Typically, the intermediate liquid yields undergo decarboxylation and extensive re-fragmentation of bonds from steam reforming/gasification, which in turn increase the gaseous products (Xu & Lancaster, 2008). It is also widely accepted in the literature that close to supercritical conditions, the properties of solvent are drastically modified. Extremely hot pressurised conditions hinder oil formation and advance the gaseous yields; that is why relatively low bio-oil yields were obtained when the temperature was beyond 310°C, which is close to supercritical conditions of mixed H_2O/E (314°C). In addition to that, at supercritical conditions, pressure has less of an influence on the yield of bio-oils; therefore, reduced bio-oil yields are prevalent after 314°C and the formation of gaseous products are favoured (Akhtar & Amin, 2011).

It is interesting to note that in Figure 4.1a, the solvent content had a negligible effect on the bio-oil yields for temperatures 220°C and 370°C. This is revealed by the consistent bio-oil yields of 14,99 wt% from 75% solvent content followed by a trivial drop to 12,58 wt% for temperature 220°C and bio-oil yield of 8,57 wt% for 370°C. At both these temperatures, the yield of bio-oils was determined to be the least. Generally, low temperatures such as 220°C are inclined to form more solid products and this could potentially be as a result of insufficient synergy or inadequate fragmentation of the sewage sludge biomass, which retard the formation of bio-oils. At 370°C, the reactions facilitate the generation of more gaseous products as opposed to bio-oils.

The general bio-oil yield pattern, of first increasing then decreasing as temperature climbs, was typically maintained in both Figure 4.1b where a co-solvent of H_2O/E on the ratio of (1:1) was employed as a solvent, and 4.1c, where pure ethanol was explored. The optimal solvent contents when the co-solvent H_2O/E was employed was typically 85% and 80% when pure ethanol was a solvent.

4.3.2 The effect of solvent content on the yield of bio-oil

Figure 4.1 also demonstrates the effect of the solvent content on the bio-oil yield. The solvent content is varying mass ratios of dried sewage (g) and solvent (wt/wt). The dried feedstock was maintained at 1 g and the solvent volumes were altered to achieve the desired solvent content between 75% and 95%. To some extent, the solvent content had a meaningful impact on the yield of bio-oils; however, in comparison to temperature, the solvent content was not as sensitive. Narrowing down to Figure 4.1c for a more concise evaluation, since the trend of yields with respect to solvent content are analogous for the three graphs, it is undoubtedly appreciated that there is an observable pattern across the various temperatures. As it was discovered with temperature, a correlative tendency was witnessed with the solvent content, where the yields initially rise and then encounter a regression, and this is predominant in almost all the temperatures. This can be demonstrated using temperatures of 280°C and 310°C where the yields climbed from 21,41 wt% to 27,84 wt% and 29,98 wt% to 34,26 wt% respectively when the solvent content increased from 75-80%. A decline to 10,71 wt% and 21.41 wt% respectively was achieved at maximum solvent content of 95%. This tendency reoccurred in almost all the temperatures, even when the solvent type was either pure H_2O or a co-solvent H_2O/E, as shown in Figure 4.1a and Figure 4.1b. At low solvent contents, HTL tends to behave analogously to pyrolysis (Akhtar & Amin, 2011). It has become evident from the results illustrated by Figure 4.1 that low solvent contents coupled with low temperatures naturally yield low bio-oils and higher solid products. This is possibly as a consequence of an insufficient degree of hydrolysis and compounds are barely fragmented when the temperature is low. Very

large solvent contents such as 95% are likewise not conducive to implement on HTL processes, as they tend to dilute the intermediate of bio-oils, hindering the polymerisation hence oil formation (Wang et al., 2021).

As was already enunciated, extremely high temperatures facilitate the generation of more gaseous products; therefore, a combination of high temperatures and high solvent content would not yield synergistic effects and this occurrence is demonstrated by almost all the graphs of Figure 4.1. In the interest of comparing the effect of the lowest temperatures (220°C) and excessive temperatures (370°C) at constant solvent contents, Figure 4.1 is a perfect juxtaposition. It is incontrovertible that lower temperatures yielded slightly greater bio-oil yields as compared to higher temperatures. For example, Figure 4.1 (a) at solvent content of 75%, when comparing the two extreme temperatures (220°C and 370°C), the bio-oil yields were 14,99 wt% and the 8,57 wt% respectively. This phenomenon of obtaining higher bio-oil yields at the lowest temperatures and lower bio-oil yields at the highest temperature is conventionally authentic and this is evident from Figure 4.1.

The temperature of 310°C emerged categorically as the optimal temperature across the various solvent contents. The best yield, which was the overall highest in all 90 experiments, was achieved when a combination of H_2O/E performed as a co-solvent at 85% solvent content and 310°C, which amounted to 40,69 wt%. The lowest bio-oil yield obtained was 6,42 wt%, as seen from Figure 4.1a, where pure H_2O was a solvent at extreme conditions of 370°C and 95% solvent content. The order of efficiency of solvent content is as follows: 85% > 80% > 75% > 90% > 95%.

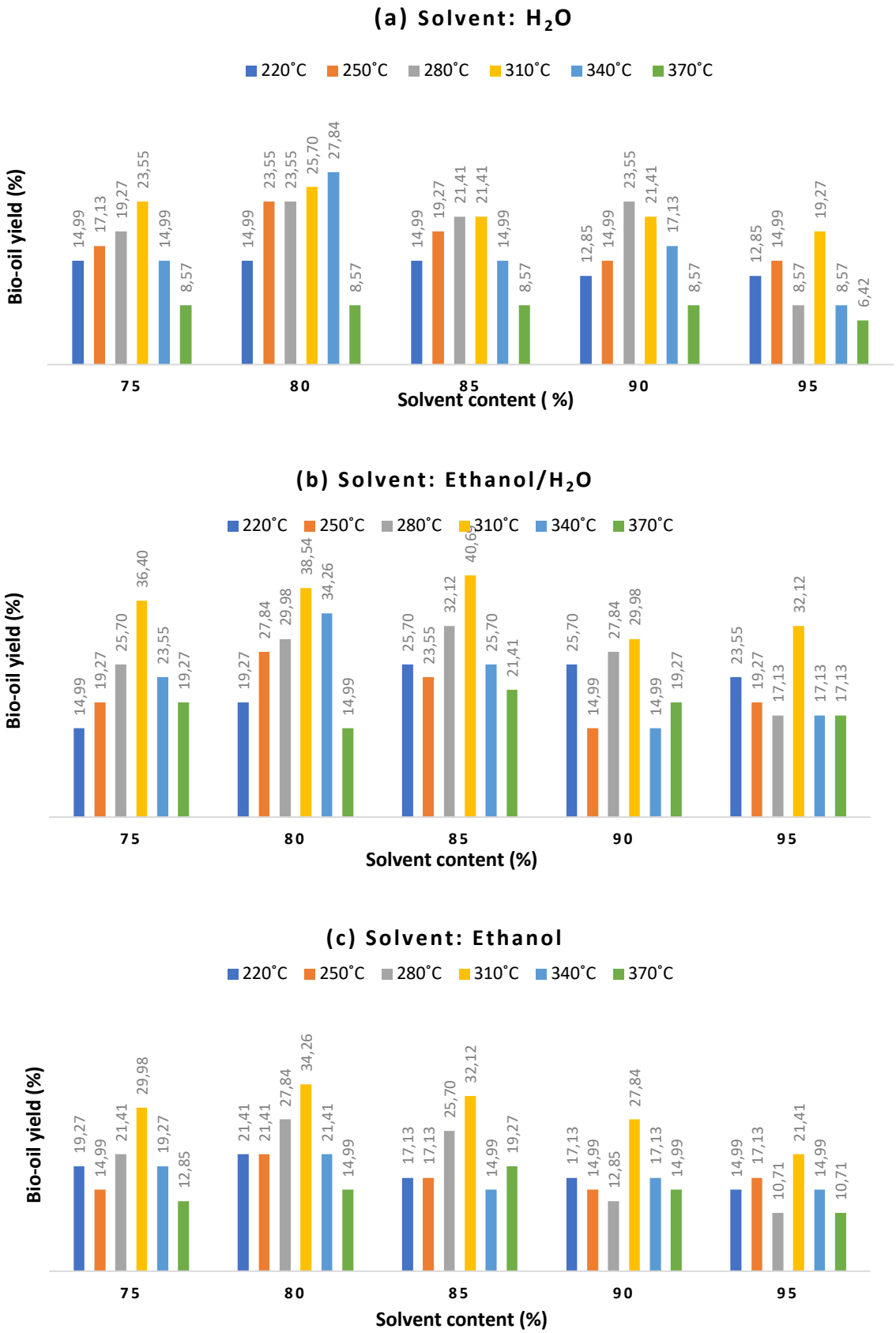

Figure 4.1 The effect of temperature on the bio-oil yield at various solvent contents (75-95%) when (a) pure H_2O, (b) co-solvent H_2O/E and (c) pure ethanol were interchangeably applied as solvents at a constant residence time of 30 minutes

4.3.3 The effect of solvent type on the yield of bio-oil

Solvent type plays a critical role in the HTL of sewage sludge. There are advantageous connotations of exploiting organic solvents. Among others, the advantages include, superior dissolution and stabilisation of weak polar and non-polar reaction intermediates. They are also effective in moderate process conditions and yield bio-oils with enhanced energy density and lower acidity (Zhao et al., 2021).

Figure 4.2 represents the effect of the three solvents investigated (which are pure H_2O, co-solvent H_2O/E and pure ethanol) on the bio-oil yield at various temperatures (a-e) and various solvent contents (75-95%). In the 90 experiments conducted, the results show that bio-oils derived using pure H_2O solvent were overall the least effective in yielding high bio-oil quantities. This revelation was not astonishing as it was expected, based on the DCM solutions obtained after the separation process of the aqueous phase. The DCM solutions extract for experiments where pure H_2O was a solvent were always the most transparent when juxtaposed beside the other DCM solutions derived from H_2O/E and pure ethanol (refer to Figure 8.1.2 in the appendix). The lower yields obtained when pure H_2O was a solvent was therefore anticipated. This was typically the trend in all the various solvent contents and temperatures as shown in Figure 4.2. The production of bio-oils was hindered when pure H_2O performed as solvent owing to enhanced self-condensation reactions. These results are in agreement with Feng et al. (2018) and Jena et al. (2011).

After evaluating all the temperatures (220-370°C) and the solvent contents (75-95%), the combination of H_2O/E gave rise to a synergetic effect. It is safe to pronounce without any reservations that H_2O/E was predominantly the solvent that yielded the highest bio-oils. This was evident in all the experiments. On all occasions where H_2O/E was employed, the yields would generally be enhanced, demonstrating that H_2O/E favours sewage liquefaction. This is extremely advantageous in that costs are reduced when using H_2O/E as a co-solvent as opposed to pure ethanol, since water is more cost-effective. Furthermore, co-solvent H_2O/E is associated with lower toxicity and renewability in comparison to pure ethanol (Zhao et al., 2021). The density and dielectric constant of H_2O/E mixture is effective in dissolving sewage. The mixture of alcohol and water generally has the potential to reduce the generation of high boiling point intermediates (Feng et al., 2018). The role of water in the mixed solvent is to fragment the cell wall and consequently liberate the organic component, which is encapsulated by the wall, and thereafter hydrolysing the cell membrane. The ethanol subsequently stimulates the solubility of the organic component and free radicals as the hydrogen donor to enhance the generation of bio-oils (Feng et al., 2018).

Pure ethanol was the second-best performing solvent. The top three highest bio-oil yields were 40,69 wt%, 38,54 wt% and 36,40 wt%. They were derived with the co-solvent H_2O/E at 310°C with solvent content 85%, 80% and 75% respectively. Similar results were reported by Biswas et al. (2020), who determined that HTL with co-solvent of water and ethanol (1:1) displayed a synergistic effect on depolymerisation of macroalgae, producing higher yields of bio-oils compared to pure solvents.

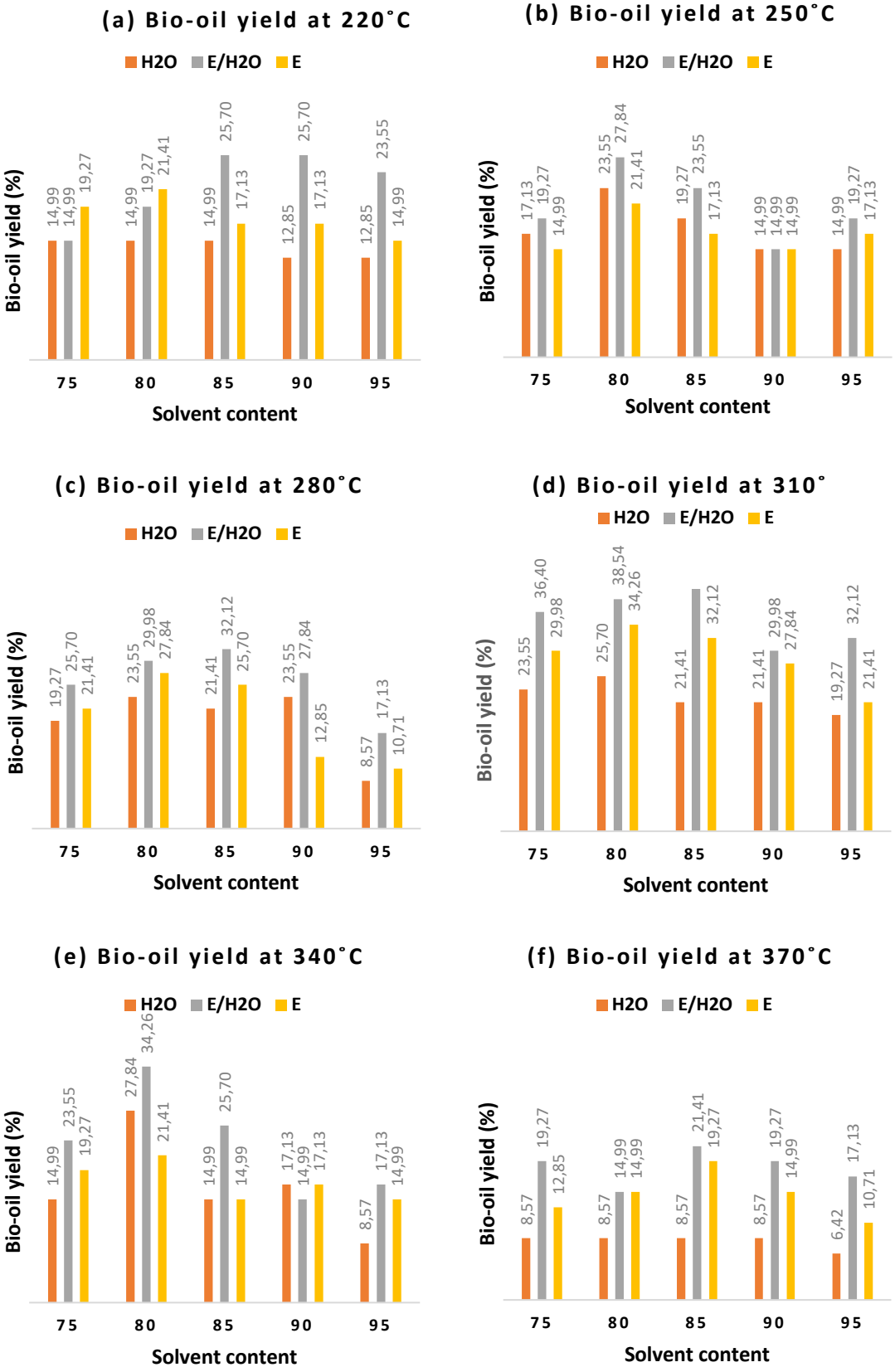

Figure 4.2 The effect of solvent type on the bio-oil yield at various solvent contents (75-95wt%) where (a) Temperature 220˚C (b) Temperature 250˚C (c) Temperature 280˚C (d) Temperature 310˚C (e) Temperature 340˚C (f) Temperature 370˚C at a constant residence time of 30 minutes

4.4 The effect of process parameters on the municipal sewage sludge conversion

4.4.1 The effect of temperature on the municipal sewage sludge conversion

Temperatures essentially supply heat energy for the fragmentation of biomass linkages (Li et al., 2020). The results obtained categorically demonstrate that temperature plays a consequential role in the conversion of sewage sludge. This is evident from Figure 4.3 which displays the effect of temperature on the conversion when applying different solvents. The conversion trend is analogous to that observed in Figure 4.1 of the bio-oil yields. The conversion initially increases with the increase of temperature, and subsequently a decline when the temperature is elevated further is observed. This transpired as a result of depolymerisation and re-polymerisation of active intermediates (Yan et al., 2019). Among the six temperatures investigated, the intermediate temperature, 310ºC, gave the highest conversions. The top three which were also the overall top conversions, were 85,65%, 83,51% and 81,37%. The corresponding solvent contents were 90%, 80% and 85% at 310ºC. These results agree with those obtained by Li et al. (2020) in the HTL of sewage sludge.

4.4.2 The Effect of solvent content on the municipal sewage sludge conversion

A uniform pattern is sustained when the solvent content is considered. For example, in Figure 4.3a, at 85% solvent content, the conversion increased from 47,11% to 68,52% between 220ºC and 310ºC. Thereafter the conversion experienced a decrease to 64,24% and 42,83% when the solvent content increased to 90% and 95%. This is because excessively high solvent content tends to hinder dehydration reactions, thereby affecting the conversion (Qian et al., 2017). The top three conversions achieved when the temperature was 310ºC also demonstrates that high conversion was attained when the solvent content was at the intermediate region. Malins et al. (2015) also investigated the influence of solvent content on the HTL of sewage sludge at 300ºC and the results they obtained revealed that the conversion increased with increased solvent content.

4.4.3 The Effect of solvent type on the municipal sewage sludge conversion

The highest conversion was commonly achieved when the co-solvent H_2O/E was employed. This is apprehensible on Figure 4.4, which illustrates the influence of solvent type on the conversion. The highest conversion across all the runs was 85,65% at 310ºC, 90% solvent content using the co-solvent. The order of superiority of solvent are H_2O/E > pure ethanol > pure water. This highly correlates with what was achieved for the bio-oil yields. This concurs with the study of Li et al. (2020) who performed HTL on macroalgae and observed that with water as a solvent the conversion was lowest compared to when organic solvents were employed. This is because there was insufficient biomass decomposition.

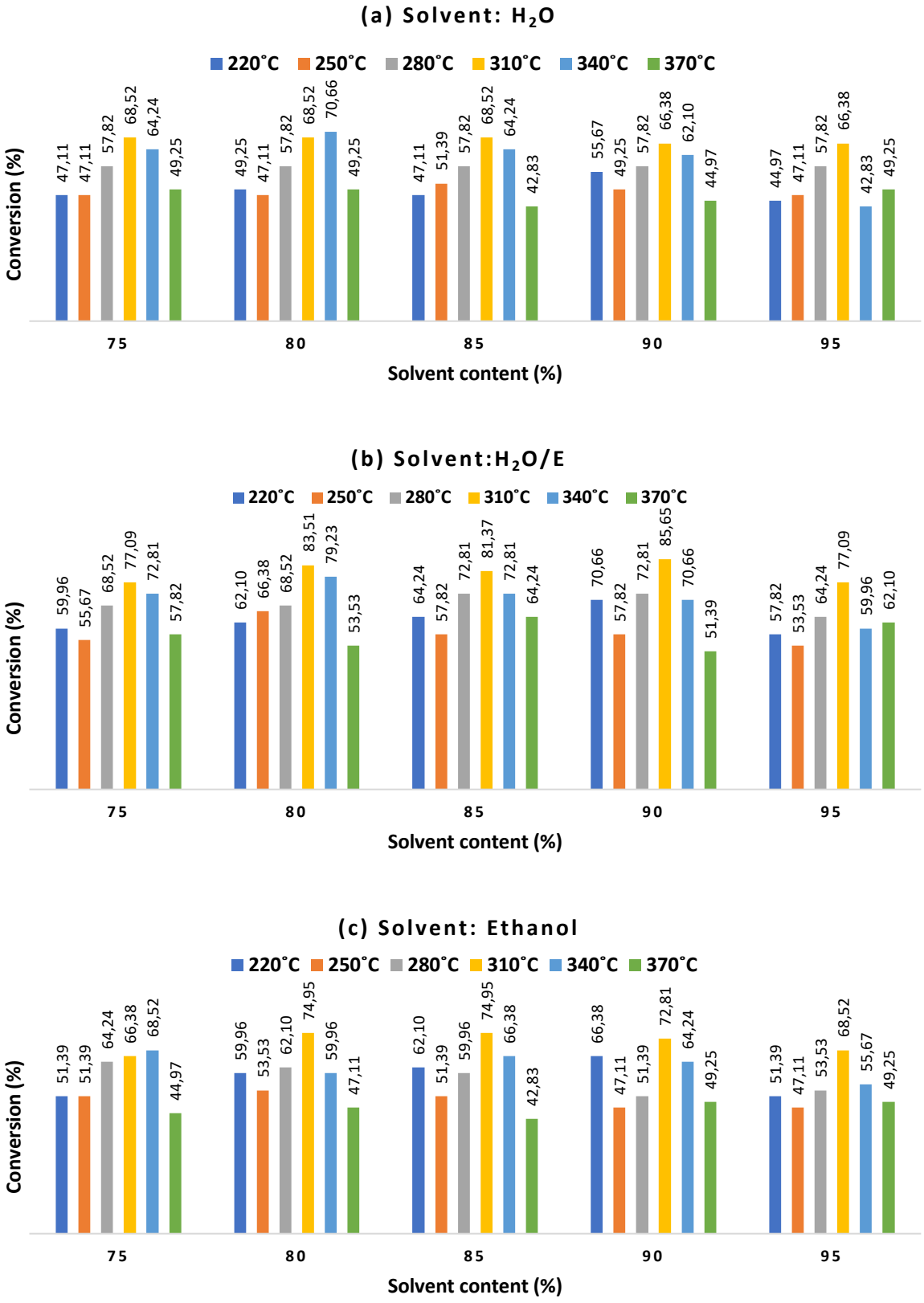

Figure 4.3 The effect of temperature on the municipal sewage sludge conversion at various solvent contents (75-95wt%) when (a) pure H_2O, (b) co-solvent H_2O/E and (c) pure ethanol were alternately applied as solvents at a constant residence time of 30 minutes

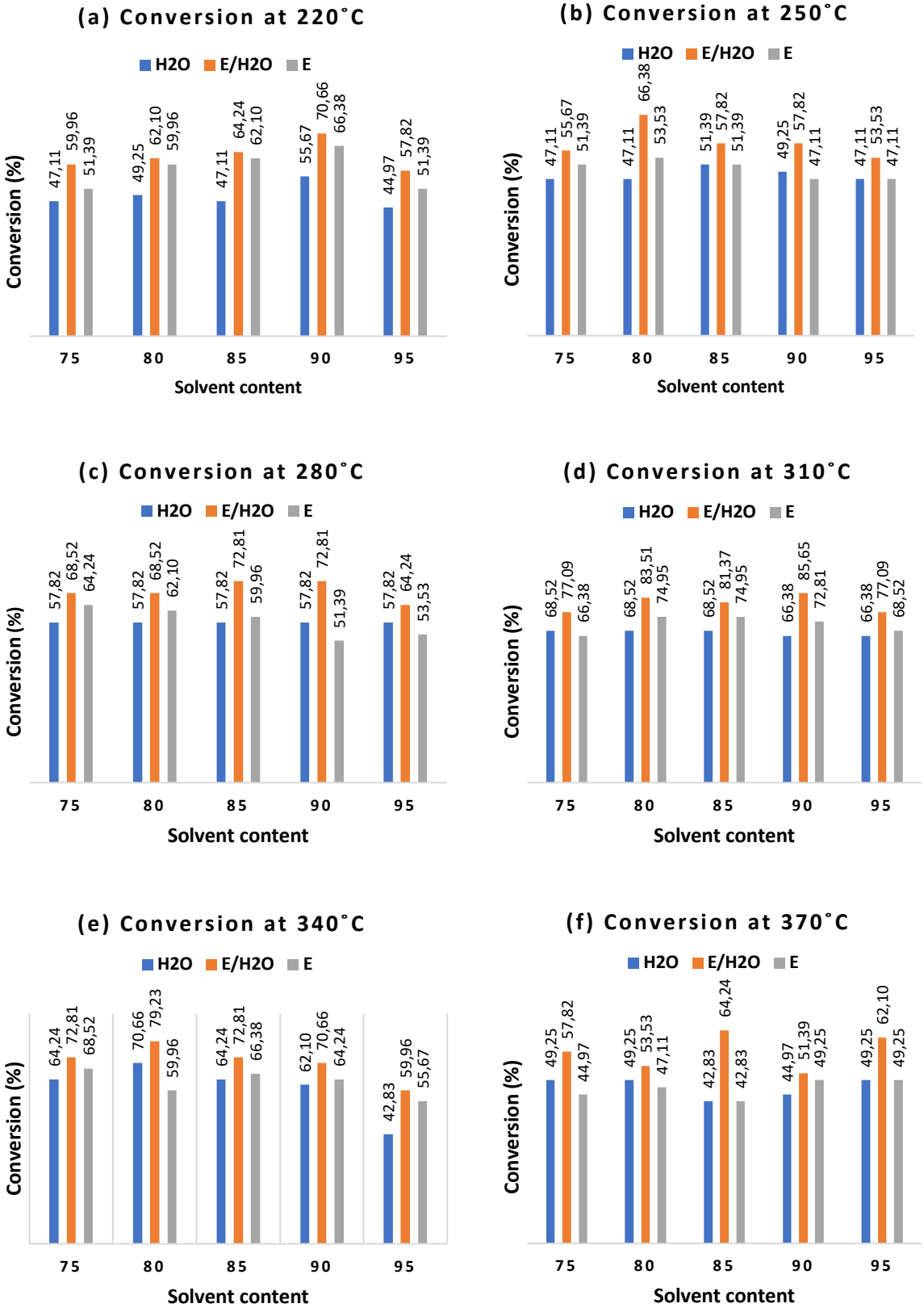

Figure 4.4 The effect of solvent type on the municipal sewage sludge conversion with (a) Temperature 220˚C (b) Temperature 250˚C (c) Temperature 280˚C (d) Temperature 310˚C (e) Temperature 340˚C (f) Temperature 370˚C and at a constant residence time of 30 minutes

According to Xu et al. (2011), the volatility of biomass has a direct influence on the conversion. Biomass with higher volatility is inclined to higher conversions. Furthermore, biomass with a sufficient volatile component is associated with pleasant bio-oil and biogas yields. High ash content in biomass increases biochar formation during HTL. The biochar yields for the 90 runs are presented in Figure 4.5. The graphs demonstrate that biochar formation was prevalent in the lower region of the temperatures (220-250ºC) and significantly low in the mid regions (280-310ºC). Towards the excessive temperatures (340-370ºC), a slight increase of the biochar yields was experienced. Lower temperatures favoured substantial biochar formation due to inefficient decomposition of biomass, as the thermal energy of the system was depressed. At higher temperatures, the lower yield of solids were attained owing to the conversion of larger fragments of biomass into smaller ones by cracking reactions (Shah et al., 2020). Wang et al. (2019) reported on the formation of biochar from dried sewage sludge liquefaction as a function of time. They obtained analogous results. At lower temperatures such as 300ºC, they obtained the highest biochar yield, and with the increase in temperature, the amount of biochar decreased. They elucidated that with further increase in temperatures, there were free radical reactions that were triggered, hence promoting gasification reactions, and superior decomposition was more feasible. As temperature became too excessive, side reactions were instigated, hence intermediate products re-polymerise, forming more biochar (Wang et al., 2019).

4.5 Summary

The temperature of 310°C emerged categorically as the optimal temperature across the various solvent contents. The best yield, which was the overall highest in all 90 experiments, was achieved when H_2O/E performed as a co-solvent at 85% solvent content and 310°C, which amounted to 40,69 wt%. Bio-oils derived by the use of pure H_2O solvent were overall the least effective in yielding high bio-oil quantities. The lowest bio-oil yield obtained was 6,42 wt% pure H_2O was a solvent at extreme conditions of 370 °C and 95% solvent content. The order of efficiency of solvent content was as follows: 85% > 80% >75% > 90% > 95%. Among the six temperatures investigated, the intermediate temperature, 310ºC, gave the highest conversions. The highest conversion across all the runs was 85,65% at 310ºC, 90% solvent content using the co-solvent H_2O/E. The order of superiority of solvent is H_2O/E > pure ethanol > pure water.

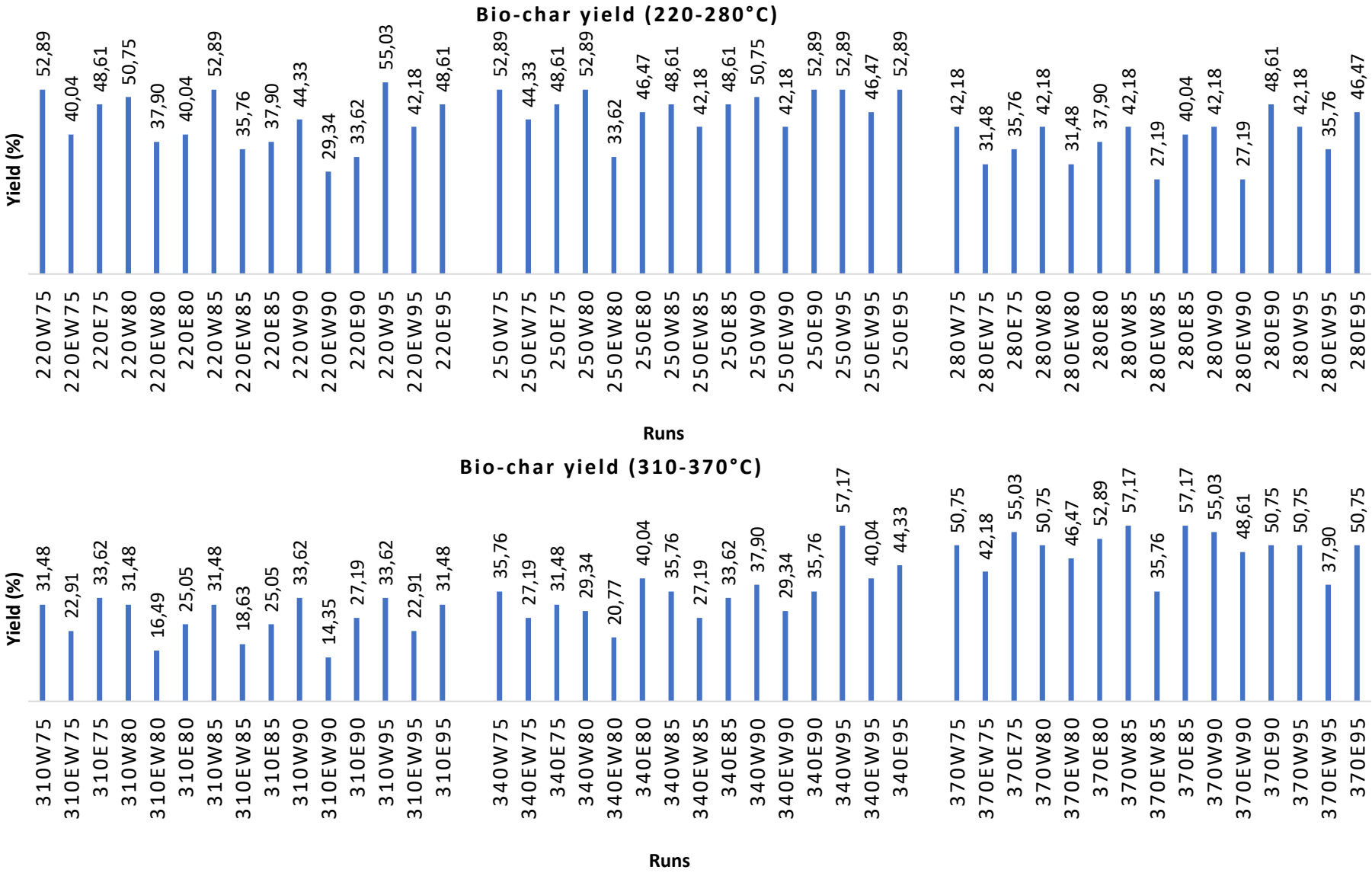

Figure 4.5 The yield of biochar in the various runs

CHAPTER 5

5 Effect of operating conditions on the compound distribution

5.1 Introduction

The bio-oils obtained from HTL of municipal sewage sludge are complex mixtures of hydrocarbons, esters and fatty acids, and compounds containing oxygen (O) or nitrogen (N), such as amines and phenols. These N-compounds are produced through various reactions, including dimerisation of amino acids or Maillard reactions between amino acids and sugars, which are formed by hydrolysis of proteins and carbohydrates (Xu et al., 2018). The chief reactions in the HTL of municipal sewage sludge also include esterification of solvent ethanol and the acids retrieved from deamination of amino acids, which is an intermediate product from the degradation of proteins and alcoholises of intermediate products. There are several other potential reactions that may occur during the liquefaction of sewage sludge; however, sewage sludge has a very complex composition. Therefore, trying to identify the exact reaction pathways remains an intricate task (Zhai et al., 2014). The bio-oils obtained from the HTL of municipal sewage sludge have been considered as a possible alternative to traditional fossil fuels (Hu et al., 2019). However, it is necessary to upgrade the raw bio-oil to meet a certain standard, as it has a high presence of nitrogen, oxygen and acidity, which limits its application (Park et al., 2021).

5.2 Analytical technique

The bio-oils that were retrieved from the HTL of sewage sludge were analysed using a gas chromatography-mass spectrometer (GCMS-QP2010 Ultra), in the interest of determine the product distribution of various products of different molecular structures and molecular weights in the bio-oil samples obtained from the 90 experiments under various process conditions. In total, there were 887 unique chemical compounds detected from the 90 experiments and an average of 43 chemical compounds emerging from each sample. All the compounds that emerged from the chromatogram were accounted for, regardless of how minute the concentration appeared to be. The details attained from the chromatograms were used to determine the effect of various process conditions on the distribution of the products. The bio-oils obtained in the HTL of municipal sewage sludge had indistinguishable physical characteristics. They appeared extremely dark brown, highly viscous in nature, and were associated with a repulsive odour.

5.3 The distribution of functional groups at the optimal operating conditions

The bio-oils comprised of complex combinations of diverse chemical compounds encompassing distinct physiochemical properties and assorted chemical groups. Consistent with Ates & Erginel (2016) and Tong et al. (2020), who performed HTL of sewage sludge, the principal chemical compounds in the bio-oils comprised of long-chain and branched hydrocarbons, carboxylic acids, alcohols, phenols and some N-containing compounds. The compounds that emerged were typically classified in groups as follows:

- Aliphatic hydrocarbons: (chain, branched and cyclic) alkanes, alkenes and alkynes.
- Aromatic hydrocarbons: benzene and phenol derivatives
- Carboxylic acids
- Esters
- Nitrogenated compounds such as amines and amides
- Oxygenated compounds such as ketones, alcohols and aldehydes

Figure 5.1 demonstrates the distribution of the chemical compounds according to the varied functional groups with respect to the optimal process conditions where the temperature was 310ºC, solvent content was 85% and the solvent employed was H_2O/E. The chemical compounds were categorised into five groups, namely: (1) aliphatic hydrocarbons, (2) aromatics, (3) acids, (4) acid esters, (5) N-containing compounds and (6) O-containing compounds. This classification is represented in Table 5.1, where the distinct functional groups with the relevant compounds are listed. The peak areas of the different compounds belonging to the same group were ultimately added. The sum of all the groups added up to 100%. The detailed ion chromatogram of the bio-oil obtained from this run is presented in 8.2.1in the appendix. The fatty acids and the aliphatic hydrocarbons were the highest at 33,99% and 32,66% respectively. It is evident from Figure 5.1 that the groups emerged in the following order of prevalence: fatty acids > aliphatic hydrocarbons > O-containing compounds > N-containing compounds > aromatics > acid esters. This product distribution is consistent with the results obtained by Shah et al. (2020) where they performed HTL on high ash-containing sewage sludge at the subcritical and supercritical conditions (350ºC and 400ºC). In total, 41 chemical compounds emerged from this run, and the prominent chemical compounds in the aliphatic hydrocarbons were heptadecane 11,32%, pentadecane 7,24% and heptadecane, 2,6,10,15 tetramethyl, 3,63% as displayed in Table 5.1. These long-chain aliphatic hydrocarbons (C_{15}-C_{20}) may be as a result of decarboxylation of fatty acids. The prime fatty acids were tridecanoic acid (14.84%), dodecanoic acid (10,69%) and decanoic acid (2,41%). Out of the 41 chemical compounds, these 6 compounds alone accounted for 50,13% of the total compounds. This is consistent with Qian et al. (2017), who also obtained a substantial

portion of aliphatic hydrocarbon moieties and aliphatic acids when they performed HTL on sewage sludge. Further to that, Xu et al. (2018) also obtained long-chain hydrocarbons (C_{10}-C_{22}), which accounted for 57,35% of the total peak area.

The acids emerged remarkably. They could have been generated from hydrolysis of lipids, and the acid esters could potentially have been derived from esterification reactions where alcohols formed by cellulose react with acids. As much as the bio-oil derived at the optimal conditions contains almost a third of the compounds compared to those present in gasoline, namely alkanes/cycloalkanes, alkenes and aromatics, the high presence of acids are unfavourable. The presence of phenols (which are classified under aromatics) directly impacts the quality of the bio-oil, as they significantly reduce the heating value of the oil. When retrieved, phenols can be applied as a substitute for the costly petroleum-based phenols as cheap renewable resins (Arazo et al., 2017). Table 5.1 also reflects that the bio-oil has a relatively high content of O-containing compounds (aldehydes, alcohols and ketones) and N-containing compounds (amides and amines), which account for 16,05% and 8,12% respectively. This has a negative impact on the quality of the bio-oil, indicating that further upgrading is necessary. The N-containing compounds were either formed by incomplete hydrolysis, decarboxylation, deamination, depolymerisation, dehydration or decomposition of protein in the sewage sludge (Biller & Ross, 2011; Biswas et al., 2017). This necessitates the upgrading of the bio-oils either by deamination, dehydroxylation and decarboxylation techniques (Xu et al., 2018).

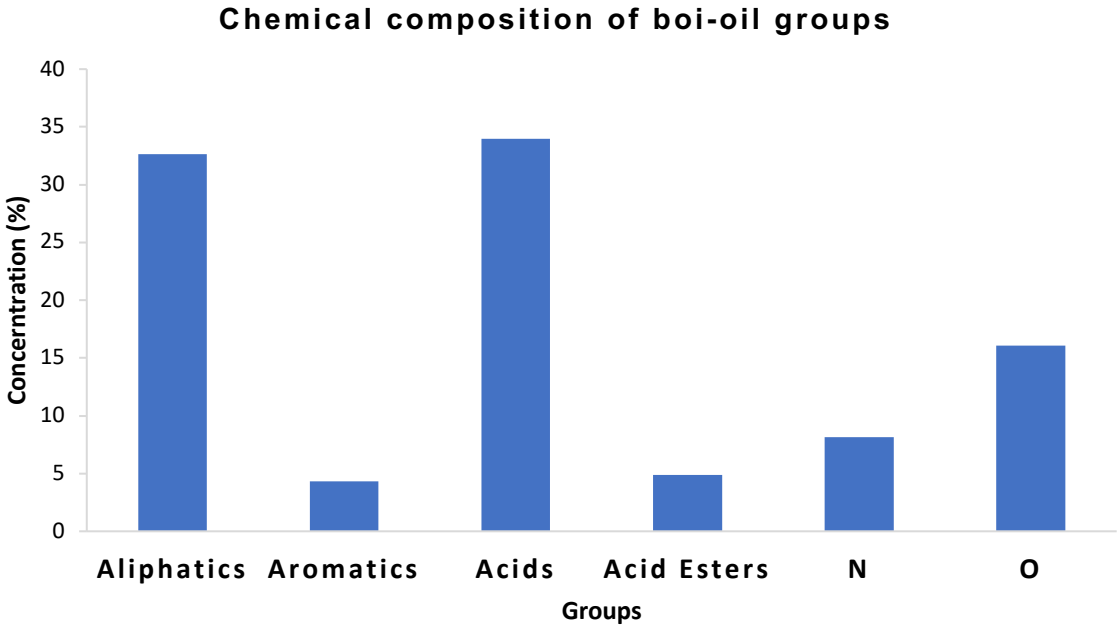

Figure 5.1 The chemical composition of bio-oil obtained at the optimal conditions: 310ºC H2O/E solvent and 85% solvent content.

Table 5.1 Chemical compounds obtained from the bio-oil sample at optimal process conditions 310ºC H2O/E solvent and 85% solvent content

	Aliphatic Hydrocarbons	
1	Dodecane (CAS)	1
2	Tridecane (CAS)	0,26
3	2-Methyl-7-nonadecene	0,49
4	Tetradecane (CAS)	1,99
5	Heptadecane, 2,6,10,15-tetramethyl- (CAS)	3,63
6	2-methyloctacosane	0,65
7	Pentadecane	7,24
8	Hexadecane, 2,6,10,14-tetramethyl- (CAS)	0,95
9	1-HEPTENE, 2-PENTYL-	2,32
10	Heptadecane	11,32
11	2,6,10-TRIMETHYLPENTADECANE	2,81
		32,66
	Aromatics	
12	1-[p-Tolylsulfonyl]-2-methylaziridine	0,57
13	N-Ethylamphetamine acetate	1,03
14	Benzene, (2,3-dimethyldecyl)- (CAS)	0,55
15	3-(Hydroxy-phenyl-methyl)-2,3-dimethyl-octan-4-one	0,5
16	PHENOL, 2,4-BIS(1,1-DIMETHYLETHYL)-	1,67
		4,32
	Fatty Acids	
17	Decanoic acid (CAS)	2,41
18	Undecanoic acid (CAS)	1,94
19	Dodecanoic acid (CAS)	10,69
20	9-Octadecenoic acid (Z)- (CAS)	2,58
21	Tridecanoic acid (CAS)	14,82
22	Tetradecanoic acid	1,55
		33,99
	Acid Esters	
23	Heptadecanoic acid, ethyl ester (CAS)	0,96
24	2-Pyrrolidinecarboxylic acid-5-oxo-, ethyl ester	3,92
		4,88
	N-containing compounds	
25	1,5-Di-O-acetyl-7-O-[2-deoxy-3,4,6-tri-O-methyl-2-(N-methylacetamido)-.alpha.-d-glucopyranosyl]-2,3,4,6-tetra-O-methyl-l-glycer	0,58
26	2-Piperidinone	2,49
27	3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,5-dione, N-acetyl-	0,81
28	Hexacosylamine, N,N-dimethyl-	1,49

29	3-Piperidino-2-pentene	0,43
30	3,4-Dihydroxyproline	1,09
31	1-(Cyclopropyl-nitro-methyl)-cyclopentanol	0,68
32	2-Pyrrolidinone (CAS)	0,55
		8,12
	O-containing compounds	
33	1,2,3-Propanetriol (CAS)	1,17
34	Trimethylsilyloxycyclobutane	1,38
35	Tridecanol, 2-ethyl-2-methyl-	2,36
36	3-Hydroxybutanal, TBDMS derivative	0,62
37	n-Nonadecanol-1	6,53
38	2-Dodecenal (CAS)	0,82
39	2,3,7-TRIMETHYLOCTANAL	0,83
40	Docosyl octyl ether	2,05
41	1-Butyl(dimethyl)silyloxypropane	0,29
		16,05
Total		**100,00**

5.4 The effect of process conditions on the functional groups

5.4.1 The effect of temperature on the functional groups

Figure 5.2a displays the effect of temperature on the product distribution where the products are classified into respective functional groups that were obtained at the optimal process conditions where the temperature was 310°C, solvent content was 85% and the solvent employed was H_2O/E. The chromatograms and detailed chemical composition tables are presented in chapter 8.3 in the appendix. Interestingly, the pattern of the distribution of functional groups obtained for the optimal conditions in Figure 5.1 was consistent with that of the graph shown in Figure 5.2a at various temperatures. As much as the narrative that the increase of temperature promotes intensification of the concentration of free radicals is well acknowledged, the composition of sewage sludge is extremely sophisticated, making it very difficult to identify the precise reaction pathways. There are many possible routes; some compounds can be generated by reactions such as hydration or dehydration, hydrolysis, esterification, cracking, decarboxylation of carboxylic acids (Zhai et al., 2014).

The concentration of aliphatic hydrocarbons and fatty acids in Figure 5.2a ultimately materialised as the most dominant functional groups, and combined they accounted for more than 60% of the bio-oil composition. The concentration of aliphatic hydrocarbons decreased with an increase in temperature; however, at 370ºC there was an abrupt and unexpected rise. This rise in the aliphatic hydrocarbons at 370ºC corresponded with a sharp decline in the

amount of carboxylic acids. The formation of aliphatic hydrocarbons at 370ºC suggests that fatty acids in sewage sludge encountered decarboxylation reactions (Tong et al., 2020). Contrary to the trend of aliphatic hydrocarbons, the acids experienced an initial increase from 32,17% to 45,51% at 220ºC and 250ºC respectively. As the temperature continued to increase beyond 250ºC, the concentration of the acids were found to decrease. This possibly means that increase in temperatures favours decarboxylation/decarbonylation or deoxygenation reactions (Shah et al., 2020).

The N-containing compounds such as amides and amines also emerged, notably followed by O-containing compounds, which comprise of ketones, alcohols, and aldehydes. The rise of N-containing compounds with an increase in temperature may be due to the promotion of a Maillard reactions between polysaccharides from carbohydrates and amino acids from proteins (Shah et al., 2020). Generally, bio-oils produced through HTL of sewage sludge have a significant nitrogen content, which limits the subsequent utilisation of the oils (Ellersdorfer, 2020). Acid esters were unexpectedly one of the inconsequential functional groups, followed by the aromatic compounds. The O-containing compounds increased with an increase in temperature. This could be explained by the simple logic that as temperature increases, chain breaking and cracking reactions are instigated to produce oxygenates such as aldehydes, ketones and alcohol (Tong et al., 2020). The presence of N- and O-containing compounds is a fundamental drawback, as these compounds not only compromise the quality of the bio-oils, but also impact the storage stability. Catalytic upgrading would be necessary to control and eliminate the nitrogen through hydrodenitrogenation processes. This would highly manage NO_x emissions when the bio-oil undergoes combustion (Zhai et al., 2014).

5.4.2 The effect of solvent content on the functional groups

Figure 5.2b represents the effect of solvent content on the functional groups that materialised at the optimal conditions when the temperature was 310ºC and the solvent was H_2O/E. The chromatograms and detailed chemical composition tables are presented in chapter 8.4 in the appendix. The aliphatic hydrocarbons tended to encounter an overall decrease with increased solvent from 50,47% to 22,46%. The acids, on the other hand, experienced an overall increase when taking into consideration the extreme condition when the temperature was 220 ºC and 370 ºC. According to Li et al. (2018), this is because the concentration of free radicals increased with an increase in the solvent content. It is interesting to note that the change in the solvent content has an influence on the N- and O-containing compounds. These compounds are found to be significantly lower compared to when the temperature was varied. Temperature has a greater influence on the changes of the product distribution compared to solvent content. At 280ºC, there was a significant surge in the total concentrations of the esters.

This surge is a result of esterification reactions that occurred between the acids and the ethanol.

5.4.3 The effect of solvent type on functional groups

The chromatograms and detailed chemical composition tables are presented in chapter 8.5 in the appendix. In Figure 5.2c, it was unexpected that the acid esters would not be influenced by the ethanol content in the solvent. As the ethanol content increased from 50% to 100%, the acids experienced a decrease and this decrease in acids was expected to promote additional acid esters via the esterification reactions between ethanol and the fatty acids. The increase in the ethanol content had a remarkable impact on the quality of bio-oil. This is reflected in the quantity of N- and O-containing compounds, which significantly decreased from 12,39% to 1% for N-containing compounds and from 17,19% to 5,4% for the latter. This shows that increasing solvent content, ethanol, in particular, influenced the composition of bio-oils. Chen et al. (2012) also observed a similar trend when used ethanol-water in the direct liquefaction of *Dunaliella teriolecta.* Furthermore, it is widely accepted in literature that co-solvents on HTL of biomass are inclined to enhance bio-oil quality (Li et al., 2018). Feng et al. (2018) also validated this when they mentioned that bio-oils obtained from liquefaction in pure water are inclined to high oxygen content. This is because water seeks to promote hydrolysis, while ethanol promotes dissolution reactions (Zhao et al., 2021).

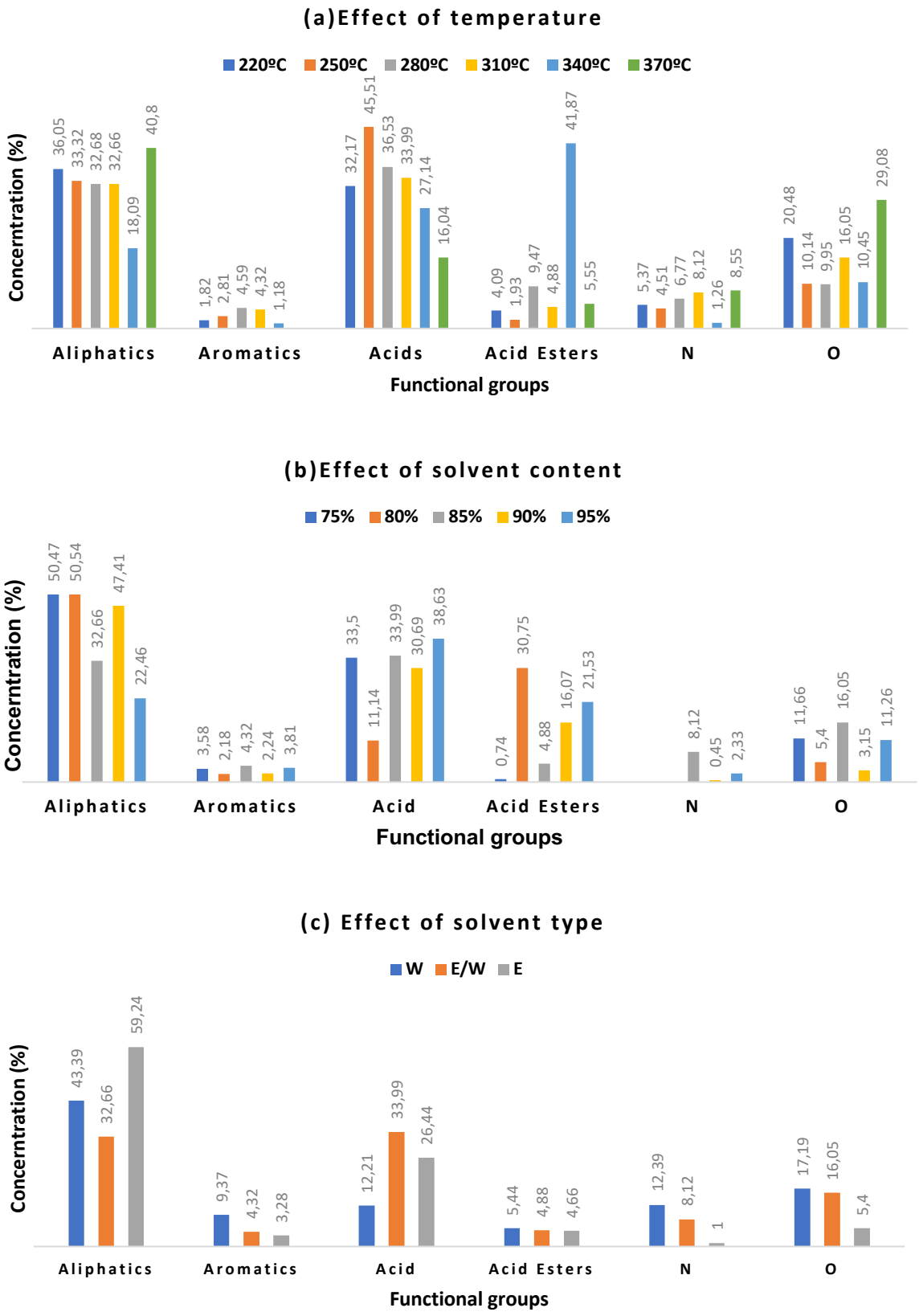

Figure 5.2 The effect of process parameters on the functional groups with respect to the optimal process conditions run 310EW75, (a) the effect of temperature when solvent content of 85% and solvent H_2O/E is kept constant, (b) the effect of solvent content when the temperature 310ºC and solvent H_2O/E is kept constant, (c) the effect of solvent type when solvent content of 85% and temperature 310ºC is kept constant

5.5 The effect of process conditions on the dominant compounds obtained from the optimal process conditions

At the run where optimal process conditions were obtained, where the temperature was 310ºC, the solvent type was H_2O/E and the solvent content was 85%, there were chemical compounds that were found to be dominant out of all the other products that emerged. These compounds include aliphatic compounds such as pentadecane ($C_{15}H_{32}$), heptadecane ($C_{17}H_{36}$), hexadecane 2,6,10,14-tetramethyl ($C_{20}H_{42}$), and an acid called decanoic acid ($C_{10}H_{20}O_2$). The behaviour of the compounds was evaluated across the optimal conditions. The effect of temperature, solvent content and solvent type were investigated, and the results are presented in Figure 5.3. To the best of the researcher's knowledge, no one has performed an investigation into how specific compounds, in particular pentadecane, heptadecane, hexadecane 2,6,10,14-tetramethyl, and decanoic acid are effected by process conditions such as temperature, solvent type and solvent content in a HTL treatment of sewage sludge or any other feedstock.

5.5.1 The effect of temperature on the dominant compounds obtained from the optimal process conditions

Figure 5.3a demonstrates the effect of temperature on the distribution of the dominant compounds at 85% solvent content using H_2O/E. It appears that the temperature had an influence on the distribution of the various compounds. Dodecanoic acid featured as the most dominant compound and emerged substantially across all the different temperatures. Dodecanoic acid manifested the strongest when the temperature was 250ºC. The corresponding concentration was 13,06%; afterwards, there was a gradual decline to 4,87% at 340ºC. This suggests that when H_2O/E is a solvent, at 85% solvent content, dodecanoic acid is likely to be derived in higher quantities when the operating temperature is moderate, around 220ºC and 250ºC. Pentadecane experienced a gradual incline from 4,5% to 9,36% at 220ºC and 370ºC respectively. Similar to heptadecane, pentadecane encountered an initial increase in the concentration from 3,42% to 11,32% from 220ºC to 310ºC; however, this phenomenon did not emerge at 340ºC and 370ºC. This is interesting to note because the region of 310ºC is the supercritical region of solvent H2O/E. This advances the idea that at supercritical conditions, the heptadecane could be inclined to depolymerisation reactions forming pentadecane or hexadecane derivatives. Hexadecane 2,6,10,14-tetramethyl was the least emerging compound with a maximum of 3,99% at 370ºC.

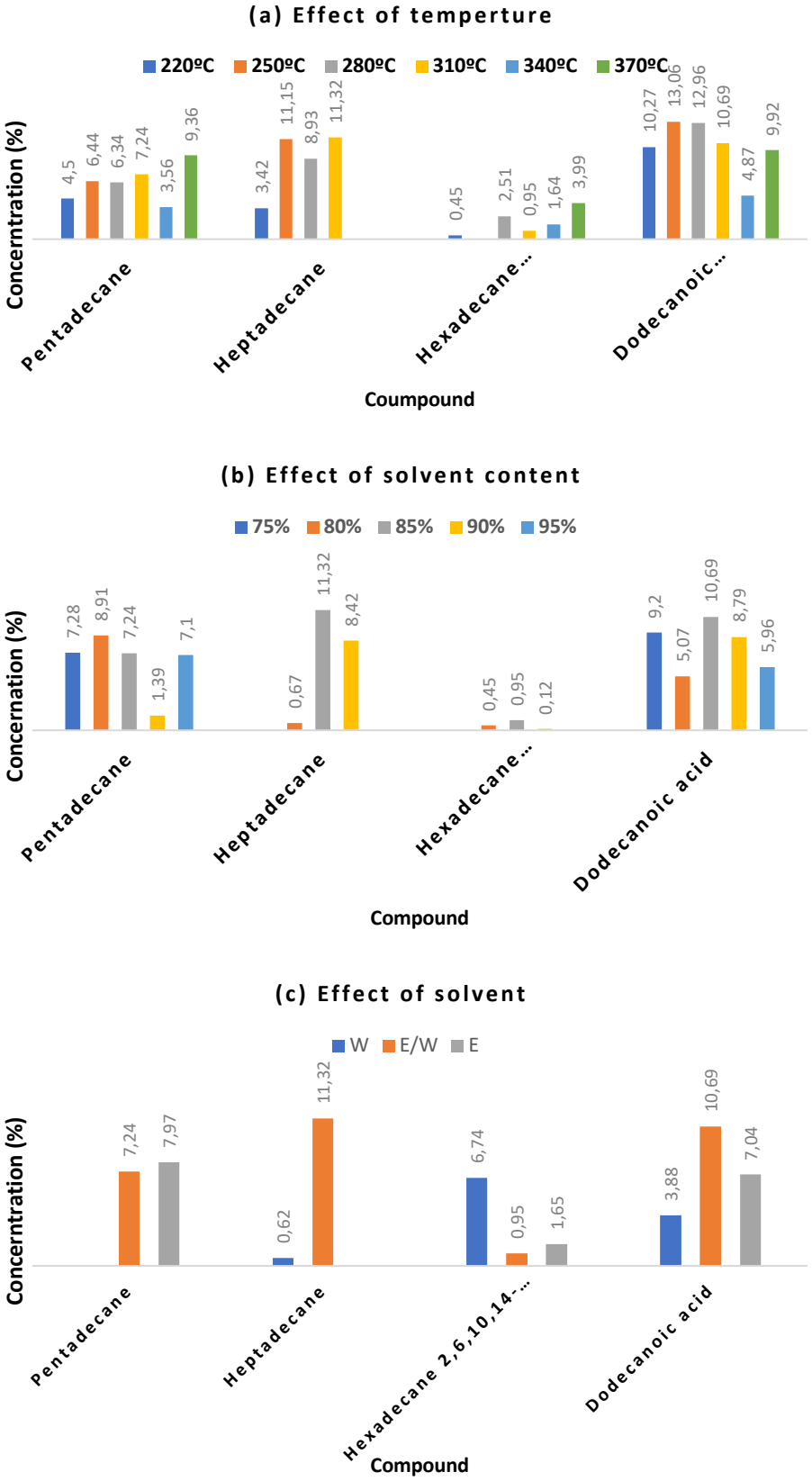

Figure 5.3 The effect of process conditions on the dominant compounds with respect to the optimal process conditions run 310EW75 (a) the effect of temperature when solvent content of 85% and solvent H_2O/E is kept constant, (b) the effect of solvent content when the temperature 310ºC and solvent H_2O/E is kept constant, (C) the effect of solvent type when solvent content is 85% and temperature 310ºC is kept constant

5.5.2 The effect of solvent content on the dominant compounds obtained from the optimal process conditions

Figure 5.3b presents the effect of solvent content on the distribution of the dominant compounds when H_2O/E was employed as a solvent at 310ºC. Pentadecane and dodecanoic acid emerged in all the various solvent contents, while heptadecane and hexadecane 2,6,10,14-tetramethyl did not emerge at the extreme solvent content of 75% and 95%. Apart from the divergence at 90% solvent content, based on the results, it is safe to state that solvent content had a negligible influence on the concentration of pentadecane. Dodecanoic acid sustained an overall decline when the solvent content increased from 85% to 95%. The decrease was from 9,2% to 5,96%, implying that esterification reactions were advanced. This increase is owing to the rise of the alcohol (ethanol) volume, hence promoting intense esterification reactions between the acid and the alcohol. Li et al. (2018) also supported this narrative.

5.5.3 The effect of solvent type on the dominant compounds obtained from the optimal process conditions

Figure 5.3c represents the influence of the solvent type on the dominant compounds when the solvent content was 85% and the temperature 310ºC. It is evident that the formation of pentadecane was favoured by the addition of ethanol in the solvent, since it did not emerge when pure water was employed as a solvent. It is also notable that when the content of ethanol increased from 50% to 100%, the concentration rose slightly to 7,24% and 7,97% respectively, signifying that an increase in ethanol content to 100% has little effect on the production of pentadecane. When the solvent was a mixture of H_2O and ethanol, heptadecane emerged strongly and was the highest overall with a concentration of 11,32%, followed by dodecanoic acid (10,69%). When considering the total concentration, it is evident that when the co-solvent was employed, generally, the total highest concentrations were obtained, followed by pure ethanol and lastly pure H_2O. It is very interesting to note that this trend was maintained even when the bio-oil yields were concerned. The highest bio-oil yields were obtained when using H_2O/E>ethanol>H_2O.

5.6 The product distribution of the top seven compounds overall

An investigation was conducted across all the 90 bio-oil samples that were derived from all the HTL runs to determine the compounds that emerged supremely overall. The compounds were determined by adding the total concentration achieved across all 90 runs. The leading totals were then deemed the dominant compounds overall. Their distribution in all the experiments was then explored, seeking for specific process conditions that predominately favoured their

production and the influence of process conditions in the trend of their formation at a specific temperature. The top seven compounds are tabulated in Table 5.2 with their corresponding molecular formula and the grand cumulative total. The denotation of the specific experiment/run was presented in the order of temperature, solvent type and the content type, for example, experiment 310WE85 denotes chemical compounds achieved when the process conditions were: temperature of 310 ºC, the co-solvent of H_2O/E and a solvent content of 85%. Figure 5.4 displays the distribution of the total concentrations obtained in the 90 experiments relative to temperature. This indicates the temperature range that favoured the formation of certain compounds.

Table 5.2 The highest seven accumulative total concentration

Compound Name	**Molecular formula**	**Total concentration across 90 experiments**
Dodecanoic Acid	$C_{10}H_{20}O_2$	486,35
Heptadecane	$C_{17}H_{36}$	448,68
Hexadecane	$C_{16}H_{24}$	428,9
Pentadecane	$C_{15}H_{32}$	322,65
Eicosane	$C_{20}H_{42}$	314,67
Hexadecane 2,6,10,14-tetramethyl	$C_{20}H_{24}$	308,18
9-Octdecanoic Acid	$C_{18}H_{34}O_2$	284,98

Dodecanoic acid, which is widely known as lauric acid, is a non-expensive saturated fatty acid derived from various vegetable fats, in particular coconut extract and seeds. It can be comprehensively utilised in food production, soaps and shampoos (Desgrosseilliers et al., 2013). The distribution of dodecanoic acid is presented in Figure 5.5. Dodecanoic acid was the most dominant compound and appeared in almost all the 90 bio-oil samples. It is noteworthy that whenever ethanol was in the solvent, whether pure or 50% composition, there were generally higher concentrations of decanoic acid. Out of the 12 times the concentration of decanoic acid exceeded 10%, 11 of those times occurred when ethanol was participating as a solvent. This suggests that when ethanol is in the solvent, dodecanoic acid production is a highly favoured probability. According to Figure 5.4, the temperature that favoured the production of dodecanoic acid the most was 280ºC, yielding a total concentration of 100,44.

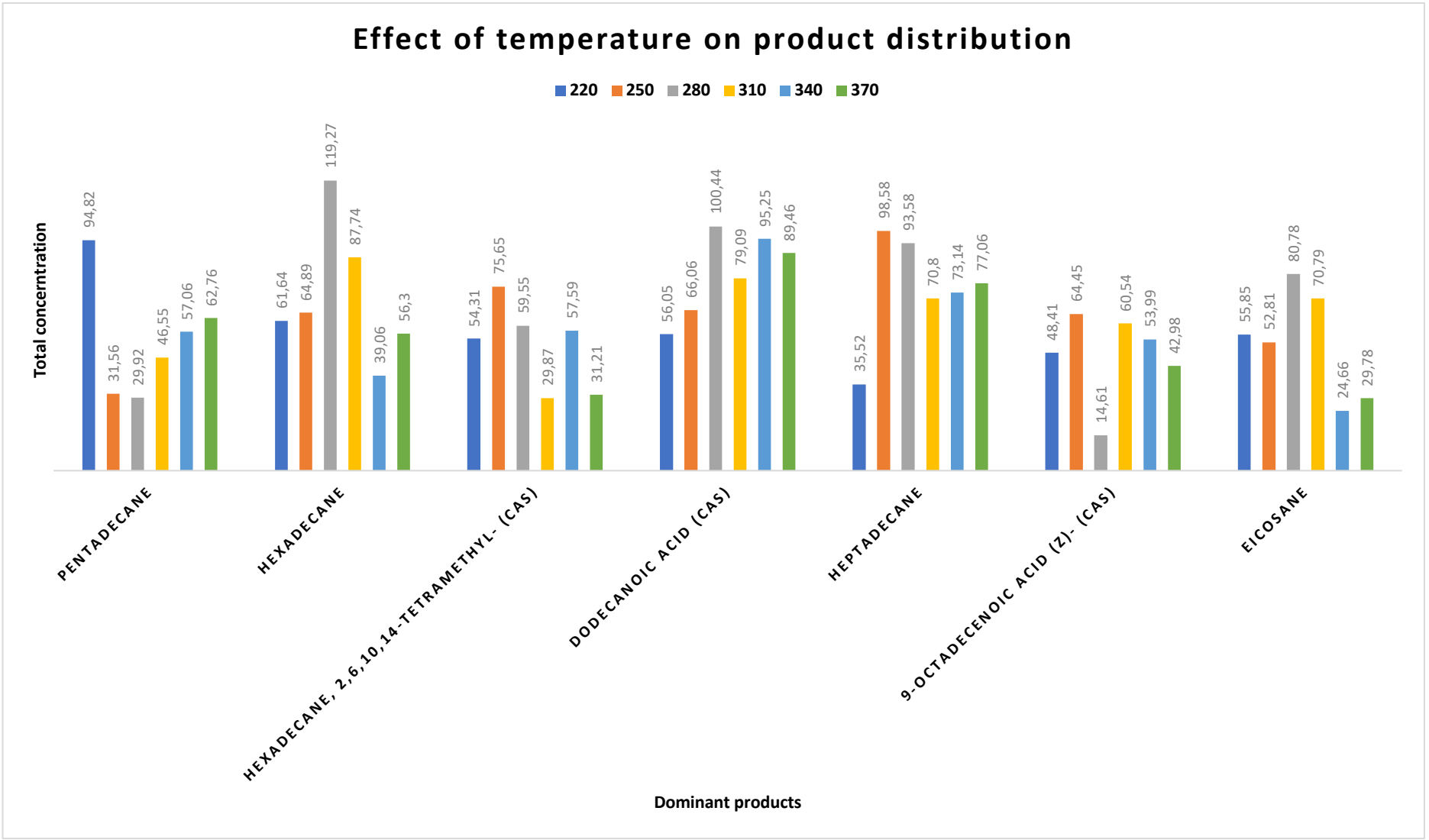

Figure 5. 4 The effect of temperature on the product distribution of the overall dominant products

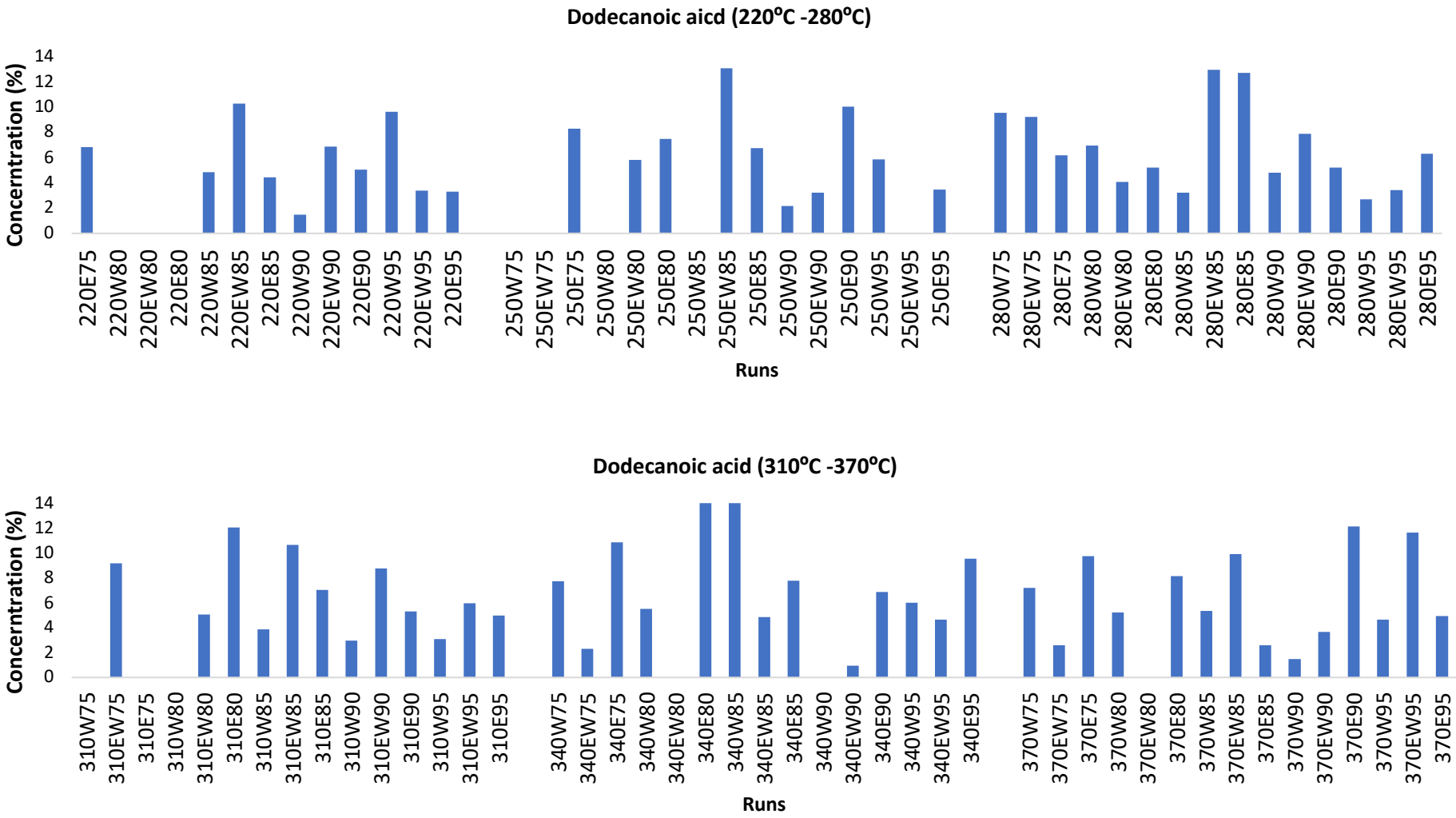

Figure 5.5 The distribution of dodecanoic acid

The product distribution of heptadecane, pentadecane, eicosane, hexadecane 2,6,10,14-tetramethyl hexadecane and 9-octadecanoic acid are presented in chapter 8.6 in the appendix. A prevalent trend was observed: when pure ethanol was employed as a solvent, heptadecane tended to strongly emerge. The top three concentrations where heptadecane emerged supremely were at the following runs: 310E95, 220E95 and, 340E90, where the concentrations were 21,03%, 19,48% and 17,99% respectively. It is categorical that ethanol promoted the production of heptadecane. The highest total concentration of heptadecane was 98,58 and was obtained when the temperature was 250ºC. This reveals that temperatures that promote the formation of heptadecane are prevalent at lower temperatures but not below 250ºC.

Hexadecane generally surfaced amicably in the region of the temperature 280ºC, which was the highest total concentrations obtained. This suggests that moderate temperatures favour more hexadecane yield. The highest concentration obtained was at 280ºC, when pure ethanol was a solvent at 95% solvent content. Pentadecane features favourably at lower temperatures, with the highest concentration being 21,68%, achieved at 220ºC with pure water as a solvent and 75% solvent content. It did not, however, evolve satisfactorily in the mean temperatures. The overall highest recorded concentration out of the 887 compounds was obtained by eicosane 36,52% at a temperature of 220ºC solvent H_2O/E and content of 95%. Contrary to the evolution of pentadecane, eicosane sustained a satisfactory yield in the mean temperature region. Lower temperatures favoured the formation of hexadecane 2,6,10,14-tetramethyl. The highest total concertation was obtained at 250ºC, when H_2O/E was a solvent at a content of 90%. Lastly, 9-Octdecanoic acid surfaced remarkably when pure ethanol as was used as a solvent. The top concentrations were 16,1%, 16,01% and 14,6%, all obtained when the solvent was pure ethanol.

5.7 Summary

In the HTL of municipal sewage sludge at different operating conditions, aliphatic hydrocarbons and fatty acids dominated the bio-oil constituency across the different runs. This is consistent with Qian et al. (2017), who also performed HTL on sewage sludge. O- and N-containing compounds also emerged notably, which was a disadvantage because they hinder the bio-oil quality. The acid esters however did not surface effectively, as they were expected to compared to the work obtained by Huang et al. (2014). The extreme temperatures such as 370 ºC promoted decarboxylation or decarbonylation of acids into hydrocarbons. Pentadecane ($C_{15}H_{32}$), heptadecane ($C_{17}H_{36}$), hexadecane 2,6,10,14-tetramethyl ($C_{20}H_{42}$), emerged as the most common aliphatic hydrocarbon compounds obtained at the optimal operating conditions, including decanoic acid ($C_{10}H_{20}O_2$). Across all 90 runs, the top seven compounds were determined to be dodecanoic acid, heptadecane, pentadecane, eicosane, hexadecane

2,6,10,14-tetramethyl hexadecane and 9-octadecanoic acid. The manifestation of these compounds was influenced by either temperature, solvent type or content. The compound that overall appeared the most when all the concentrations throughout the 90 runs was dodecanoic acid. The high acidity and manifestation of the O- and N-containing compounds indicates that the bio-oils obtained need to undergo further upgrading before they can be utilised in any application.

CHAPTER 6

6 Conclusion and recommendations

6.1 General conclusions

The objectives of this study as stated in the introduction were to:

- Investigate the effect of operating parameters on the yield of bio-oil.
- Investigate the effect of operating parameters on the conversion of municipal sewage sludge.
- Determine the effect of operating parameters on the product distribution in the bio-oil produced.

Out of the three process parameters investigated, which were temperature, solvent content and solvent type, temperature was found to have the greatest effect on the bio-oil yield and the conversion of sewage sludge followed by the solvent type and lastly solvent content. The yield of bio-oil initially increased with increase in temperature up until the intermediate temperature of 310°C, then afterwards started to decline with further increase in temperature. The same pattern of bio-oil yields was observed for the effect of solvent content. The co-solvent water and ethanol was determined to have a synergistic effect, however, when pure ethanol was used the yields decreased. The lowest yields were achieved when pure water was used as a solvent. The optimal process conditions were obtained at intermediate process conditions, namely: temperature of 310°C, solvent content of 85%, and a mixture of H_2O and ethanol as a co-solvent at a ratio of 1:1. The highest bio-oil yield obtained was 40,69 wt%. The lowest bio-oil yield obtained was 6,42 wt% where pure H_2O was a solvent at 370°C and 95% solvent content.

An analogous trend for yield was also observed for conversion. Among the six temperatures investigated, the intermediate temperature, 310ºC, gave the highest conversions. Higher conversions were obtained when ethanol and water were used as a co-solvent. The order of solvent performance is H_2O/E > pure ethanol > pure H_2O. The conversion increased with an increase in solvent content and then typically decreased after 85%. The highest conversion across all the runs was 85,65% at 310ºC, 90% solvent content using the co-solvent H_2O/E.

Across the different runs, aliphatic hydrocarbons and fatty acids were the most common products in the bio-oils. Across all the 90 runs, the seven most predominant compounds in the order of highest to lowest were: dodecanoic acid, heptadecane, hexadecane, pentadecane, eicosane, hexadecane, 2,6,10,14-tetramethyl, and 9-octadecanoic acid. The production of these compounds was highly influenced by either temperature, solvent type or

content with temperature and solvent type having a greater influence. The high acidity and formation of the O- and N-containing compounds in the bio-oils obtained implies that further upgrading is necessary before the bio-oils can be used in any application.

6.2 Recommendations and future work

The study was aimed at valorising municipal sewage sludge using hydrothermal liquefaction technology. In this study, the scope did not include the investigation of some process parameters, therefore it is for this reason, the following are recommendations drawn from this study for future investigation.

- Work needs to be exhausted on co-liquefaction of different biomasses and identification of suitable catalysts and solvents that will have a synergistic effect on yield and conversion.
- As has been established from this study that aliphatic hydrocarbons and fatty acids were the dominant products in the bio oils, a study needs to be done on how to manipulate process conditions to target specific valuable products.
- In the future, more comprehensive work needs to be developed in moving towards continuous HTL techniques since HTL experiments are typically conducted in batch reactors, especially for commercialisation purposes.

CHAPTER 7

7 References

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CHAPTER 8

8 Appendices

8.1 Experimental Data

The runs are denoted in the following order: temperature/solvent type/solvent content. For example, the optimal process conditions were:

- temperature: 310 °C,
- solvent type: EW and
- solvent content: 75%

Therefore, the run/experiment corresponding to the optimal conditions is denoted by 310EW75, where E and W represent ethanol and water respectively.

8.1.1 Sample calculation

Constants: Mass of dried sewage sample charged per experiment 1g

Mass of volatile solids: 0,467

Bio-oil yield= $\mathbf{y_{bo}} = \frac{\mathbf{m_{bo}}}{\mathbf{m_{vs}}} \times \mathbf{100}\%$ **Equation 3. 4**

Biochar yield =$y_{bc} = \frac{m_{bc}}{m_{vs}} \times 100\%$ **Equation 3. 5**

Hydrothermal liquefaction Conversion $x_{bc} = \left(1 - \frac{m_{bc}}{m_{vs}}\right) \times 100\%$ **Equation 3. 6**

Where: m_{bo} is the mass of bio-oil produced

m_{vs} is mass of volatile solids.

m_{bc} is the mass of biochar = (mass of solid residuals – mass of non-volatile solids)

Run 1 (220W75): T=220 °C, solvent type: H2O and solvent content is 75% (220W75)

m_{bo}= 0.07 g

m_{vs} = 0.467 g

m_{bc} =0.25 g

$y_{bo} = \frac{m_{bo}}{m_{vs}} \times \frac{0.07}{0.467} \times 100$ =14,99%

$y_{bc} = \frac{m_{bc}}{m_{vs}} \times \frac{0.247}{0.467} \times 100$= 52,89%

$x = \left(1 - \frac{m_{bc}}{m_{vs}}\right) \times \left(1 - \frac{0.247}{0.467}\right) \times 100$= 47,11%

Table 8.1.1 Raw data

T (C)	Solvent content (%)	Solve type W:water E:ethanol	Mass of bio-oil m_{bo} (g)	Mass of biochar m_{bc} (g)	Bio-oil Yield (%)	Sewage Conversion (%)
220	75	W	0,07	0,247	14,99	47,11
		W:E	0,07	0,187	14,99	59,96
		E	0,09	0,227	19,27	51,39
	80	W	0,07	0,237	14,99	49,25
		W:E	0,09	0,177	19,27	62,10
		E	0,10	0,187	21,41	59,96
	85	W	0,07	0,247	14,99	47,11
		W:E	0,12	0,167	25,70	64,24
		E	0,08	0,177	17,13	62,10
	90	W	0,06	0,207	12,85	55,67
		W:E	0,12	0,137	25,70	70,66
		E	0,08	0,157	17,13	66,38
	95	W	0,06	0,257	12,85	44,97
		W:E	0,11	0,197	23,55	57,82
		E	0,07	0,227	14,99	51,39
250	75	W	0,08	0,247	17,13	47,11
		W:E	0,09	0,207	19,27	55,67
		E	0,07	0,227	14,99	51,39
	80	W	0,11	0,247	23,55	47,11
		W:E	0,13	0,157	27,84	66,38
		E	0,10	0,217	21,41	53,53
	85	W	0,09	0,227	19,27	51,39
		W:E	0,11	0,197	23,55	57,82
		E	0,08	0,227	17,13	51,39
	90	W	0,07	0,237	14,99	49,25
		W:E	0,07	0,197	14,99	57,82
		E	0,07	0,247	14,99	47,11
	95	W	0,07	0,247	14,99	47,11

		W:E	0,09	0,217	19,27	53,53
		E	0,08	0,247	17,13	47,11
280	**75**	**W**	0,09	0,197	19,27	57,82
		W:E	0,12	0,147	25,70	68,52
		E	0,10	0,167	21,41	64,24
	80	**W**	0,11	0,197	23,55	57,82
		W:E	0,14	0,147	29,98	68,52
		E	0,13	0,177	27,84	62,10
	85	**W**	0,10	0,197	21,41	57,82
		W:E	0,15	0,127	32,12	72,81
		E	0,12	0,187	25,70	59,96
	90	**W**	0,11	0,197	23,55	57,82
		W:E	0,13	0,127	27,84	72,81
		E	0,06	0,227	12,85	51,39
	95	**W**	0,04	0,197	8,57	57,82
		W:E	0,08	0,167	17,13	64,24
		E	0,05	0,217	10,71	53,53
310	**75**	**W**	0,11	0,147	23,55	68,52
		W:E	0,17	0,107	36,40	77,09
		E	0,14	0,157	29,98	66,38
	80	**W**	0,12	0,147	25,70	68,52
		W:E	0,18	0,077	38,54	83,51
		E	0,16	0,117	34,26	74,95
	85	**W**	0,10	0,147	21,41	68,52
		W:E	0,19	0,087	40,69	81,37
		E	0,15	0,117	32,12	74,95
	90	**W**	0,10	0,157	21,41	66,38
		W:E	0,14	0,067	29,98	85,65
		E	0,13	0,127	27,84	72,81
	95	**W**	0,09	0,157	19,27	66,38
		W:E	0,15	0,107	32,12	77,09
		E	0,10	0,147	21,41	68,52

340	75	W	0,07	0,167	14,99	64,24
		W:E	0,11	0,127	23,55	72,81
		E	0,09	0,147	19,27	68,52
	80	W	0,13	0,137	27,84	70,66
		W:E	0,16	0,097	34,26	79,23
		E	0,10	0,187	21,41	59,96
	85	W	0,07	0,167	14,99	64,24
		W:E	0,12	0,127	25,70	72,81
		E	0,07	0,157	14,99	66,38
	90	W	0,08	0,177	17,13	62,10
		W:E	0,07	0,137	14,99	70,66
		E	0,08	0,167	17,13	64,24
	95	W	0,04	0,267	8,57	42,83
		W:E	0,08	0,187	17,13	59,96
		E	0,07	0,207	14,99	55,67
370	75	W	0,04	0,237	8,57	49,25
		W:E	0,09	0,197	19,27	57,82
		E	0,06	0,257	12,85	44,97
	80	W	0,04	0,237	8,57	49,25
		W:E	0,07	0,217	14,99	53,53
		E	0,07	0,247	14,99	47,11
	85	W	0,04	0,267	8,57	42,83
		W:E	0,10	0,167	21,41	64,24
		E	0,09	0,267	19,27	42,83
	90	W	0,04	0,257	8,57	44,97
		W:E	0,09	0,227	19,27	51,39
		E	0,07	0,237	14,99	49,25
	95	W	0,03	0,237	6,42	49,25
		W:E	0,08	0,177	17,13	62,10
		E	0,05	0,237	10,71	49,25

Below is Figure 8.1.1 representing the thermo gravimetric analysis (TGA) of dried municipal sewage sludge

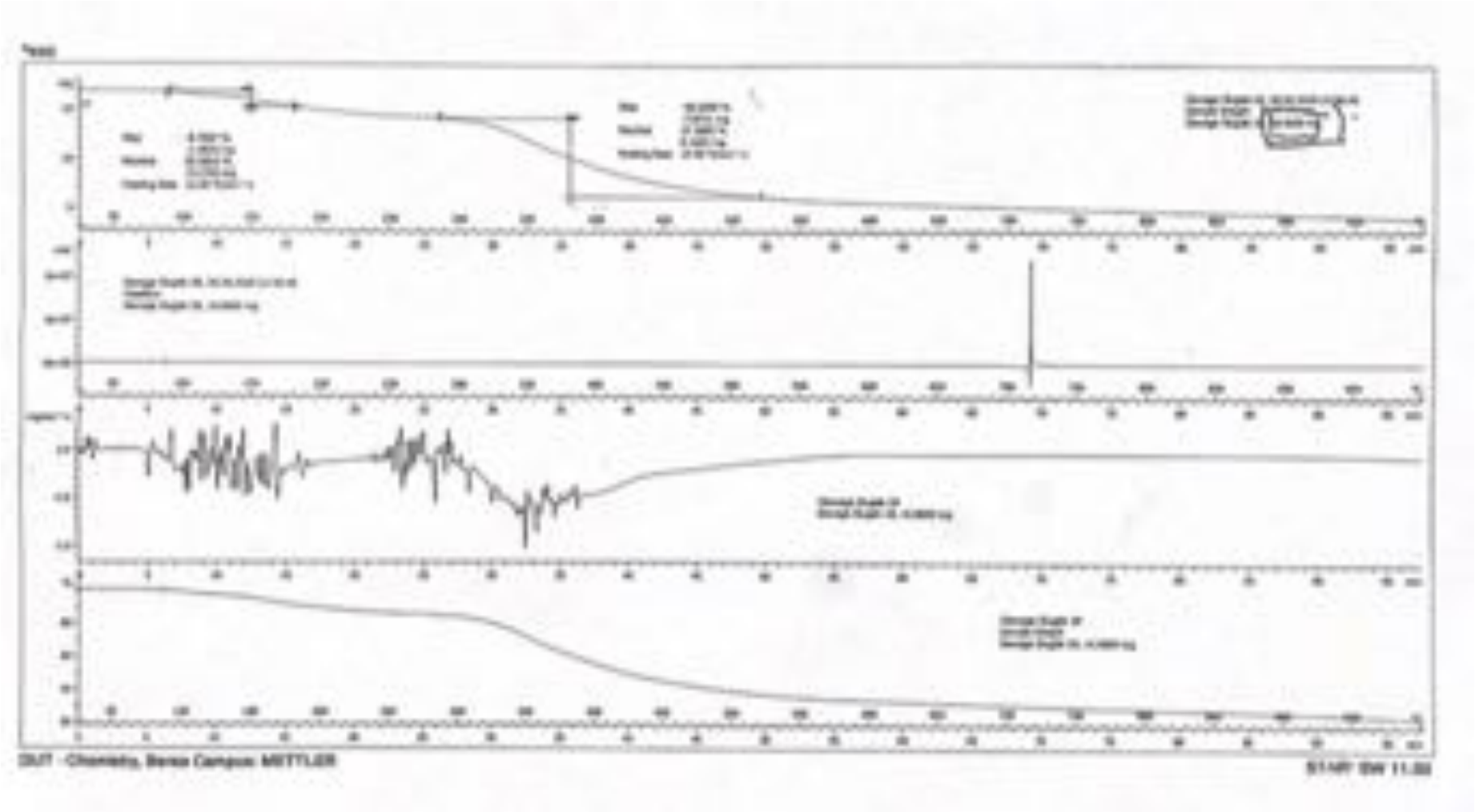


Figure 8.1.1 Thermo gravimetric analysis (TGA) of dried municipal sewage sludge

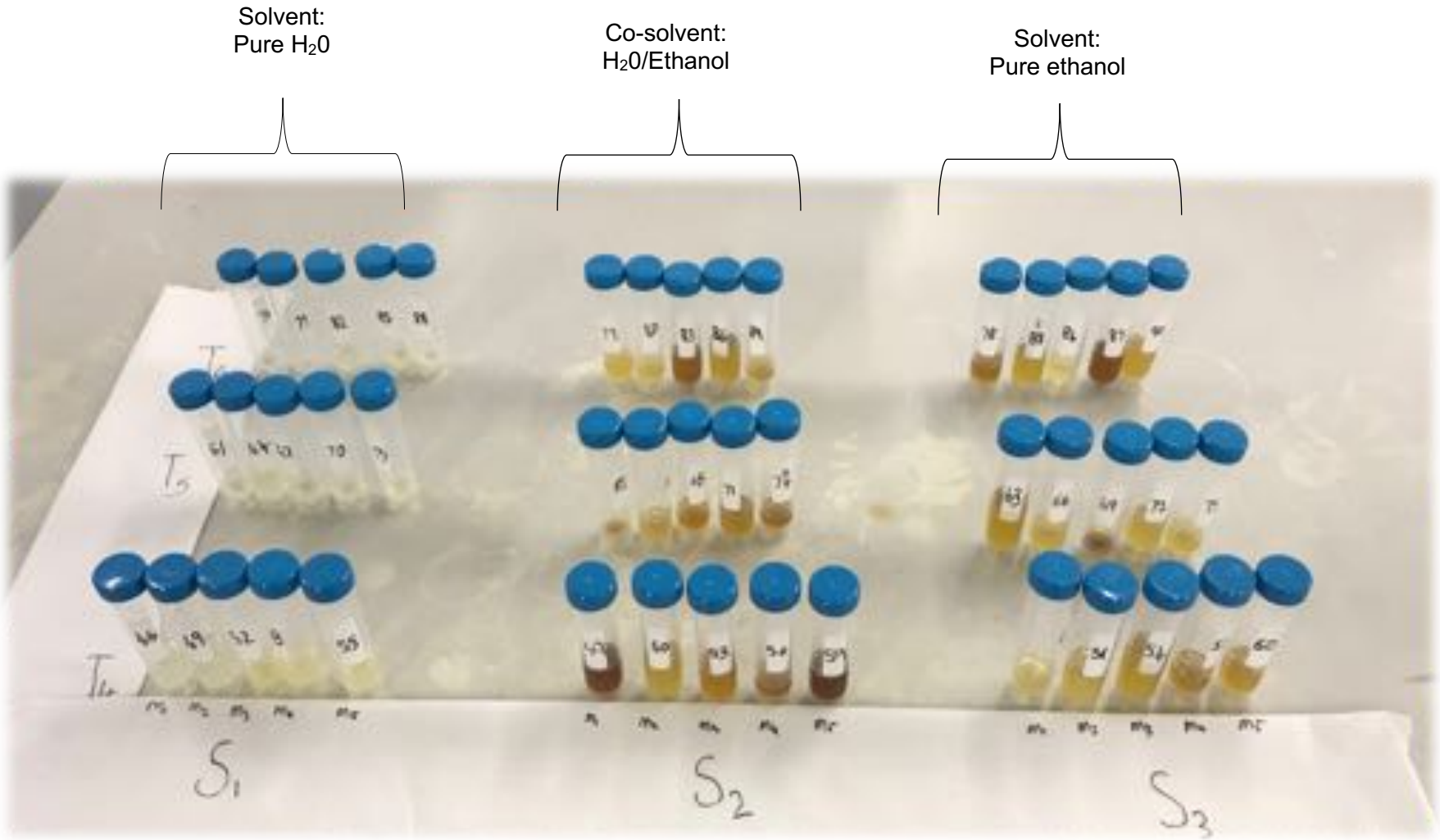
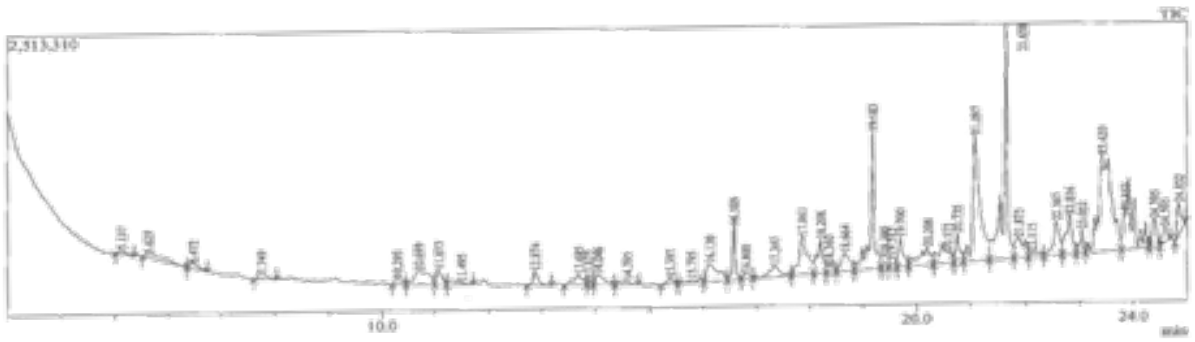


Figure 8.1.2 DCM solution obtained from the different process parameters

8.2 Product Distribution Data

8.2.1 GCMS for optimal process conditions – Run: 330EW85



Peak Report TIC

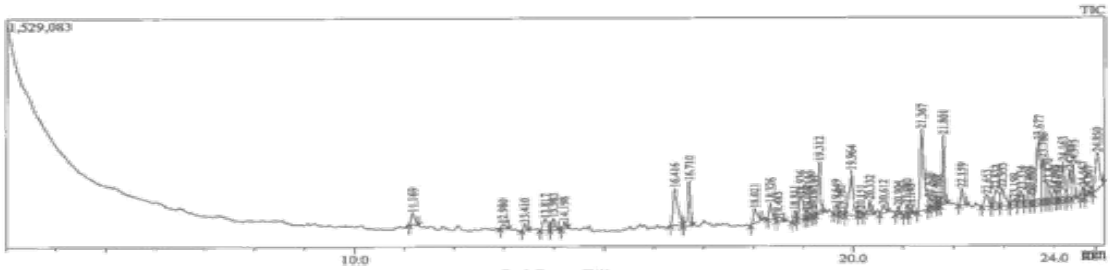
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	5.137	5.015	5.355	287848	0.29	32399	0.29	8.88		1-Butyl(dimethyl)silyloxypropane
2	5.629	5.515	6.355	1164740	1.17	37564	0.34	31.01		1,2,3-Propanetriol (CAS)
3	6.472	6.355	6.735	567268	0.57	46683	0.42	12.15		1-[p-Tolylsulfonyl]-2-methylaziridine
4	7.749	7.595	8.035	553436	0.55	47632	0.43	11.62		2-Pyrrolidinone (CAS)
5	10.293	10.195	10.455	573618	0.58	53906	0.48	10.64		1,5-Di-O-acetyl-7-O-[2-deoxy-3,4,6-tri-O
6	10.699	10.455	10.995	2480081	2.49	120193	1.08	20.63		2-Piperidinone
7	11.077	10.995	11.215	996986	1.00	132669	1.19	7.51		Dodecane (CAS)
8	11.495	11.215	11.715	675852	0.68	25822	0.23	26.17		1-(Cyclopropyl-nitro-methyl)-cyclopentan
9	12.874	12.715	13.175	820093	0.82	128448	1.15	6.38		2-Dodecenal (CAS)
10	13.685	13.415	13.835	1087235	1.09	88602	0.80	12.27		3,4-Dihydroxyproline
11	13.875	13.835	13.955	260945	0.26	56857	0.51	4.59		Tridecene (CAS)
12	14.046	13.955	14.355	1023574	1.03	85871	0.77	11.92		N-Ethylamphetamine acetate
13	14.595	14.355	14.795	495696	0.50	39097	0.35	12.68		3-(Hydroxy-phenyl-methyl)-2,3-dimethyl-
14	15.397	15.215	15.535	492988	0.49	59915	0.54	8.23		2-Methyl-7-nonadecene
15	15.795	15.535	16.015	549530	0.55	26843	0.24	20.47		Benzene, (2,3-dimethyldecyl)- (CAS)
16	16.130	16.015	16.455	2404670	2.41	155021	1.39	15.51		Decanoic acid (CAS)
17	16.589	16.455	16.715	1989646	1.99	494731	4.45	4.02		Tetradecane (CAS)
18	16.800	16.715	16.935	427126	0.43	55525	0.50	7.69		3-Piperidino-2-pentene
19	17.347	16.935	17.655	1374320	1.38	103054	0.93	13.34		Trimethylsilyloxycyclobutene
20	17.861	17.655	18.075	3904880	3.92	351209	3.16	11.12		2-Pyrrolidinecarboxylic acid-5-oxo-, ethyl
21	18.206	18.075	18.315	2320360	2.33	293900	2.64	7.90		Heptadecane, 2,6,10,15-tetramethyl- (CA
22	18.360	18.315	18.495	651976	0.65	74276	0.67	8.78		2-methyloctacosane
23	18.664	18.495	18.835	1939060	1.94	159917	1.44	12.13		Undecanoic acid (CAS)
24	19.183	18.835	19.335	7215914	7.24	1210497	10.88	5.96		Pentadecane
25	19.395	19.335	19.475	949912	0.95	127510	1.15	7.45		Hexadecane, 2,6,10,14-tetramethyl- (CAS
26	19.515	19.475	19.635	823065	0.83	106191	0.95	7.75		2,3,7-TRIMETHYLOCTANAL
27	19.700	19.635	19.855	1660792	1.67	259256	2.33	6.41		PHENOL, 2,4-BIS(1,1-DIMETHYLETH
28	20.206	19.855	20.315	2356438	2.36	156608	1.41	15.05		Tridecanol, 2-ethyl-2-methyl-
29	20.575	20.315	20.695	2315263	2.32	111530	1.00	20.76		1-HEPTENE, 2-PENTYL-
30	20.755	20.695	20.875	1294250	1.30	238320	2.14	5.43		Heptadecane, 2,6,10,15-tetramethyl- (CA
31	21.097	20.875	21.355	10658630	10.69	1137550	10.23	9.37		Dodecanoic acid (CAS)
32	21.658	21.355	21.795	11289568	11.32	2017689	18.14	5.60		Heptadecane
33	21.875	21.795	22.055	2044535	2.05	188084	1.69	10.87		Docosyl octyl ether
34	22.115	22.055	22.335	620649	0.62	52704	0.47	11.78		3-Hydroxybutanal, TBDMS derivative
35	22.567	22.335	22.675	2574360	2.58	300025	2.70	8.58		9-Octadecenoic acid (Z)- (CAS)
36	22.816	22.675	22.935	2806363	2.81	366155	3.29	7.66		2,6,10-TRIMETHYLPENTADECANE
37	23.052	22.935	23.115	960490	0.96	212146	1.91	4.53		Heptadecanoic acid, ethyl ester (CAS)
38	23.420	23.115	23.775	14776986	14.82	903594	8.12	16.35		Tridecanoic acid (CAS)
39	23.853	23.775	24.295	6509898	6.53	380699	3.42	17.10		n-Nonadecanol-1
40	24.395	24.295	24.495	1484460	1.49	254539	2.29	5.83		Hexacosylamine, N,N-dimethyl-
41	24.595	24.495	24.695	803780	0.81	144906	1.30	5.55		3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,
42	24.852	24.775	24.975	1547222	1.55	286869	2.58	5.39		Tetradecanoic acid
				99734503	100.00	11125006	100.00			

Figure 8.2.1 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained at the optimal conditions where the temperature was 310ºC, solvent H2O/E and 85% solvent content

8.3 The effect of temperature on the functional groups with respect to the optimal conditions.

Figure 8.3.1: Run 220EW85%
Figure 8.3.2: Run 250EW85%
Figure 8.3.3: Run 280EW85%
Figure 8.3.4: Run 340EW85%
Figure 8.3.5: Run 370EW85%

8.3.1 GCMS for optimal process conditions – Run: 220EW85

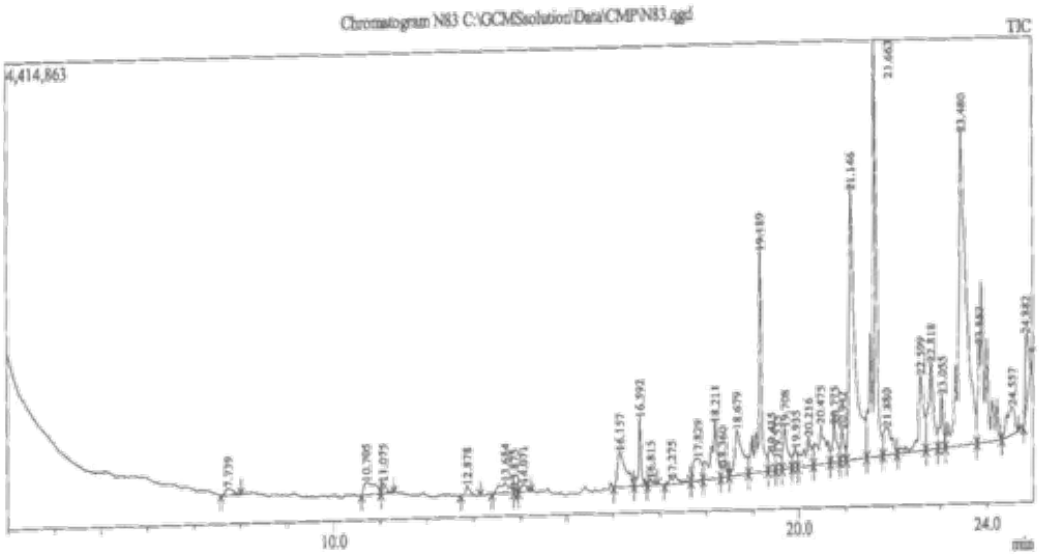


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	11.169	11.095	11.285	421830	1.40	80558	1.19	5.24		Dodecane (CAS)
2	12.980	12.925	13.090	166339	0.55	30556	0.45	5.44		Decane, 1,1'-oxybis- (CAS)
3	13.410	13.355	13.485	159530	0.53	47004	0.69	3.39		Heptadecane, 8-methyl- (CAS)
4	13.817	13.720	13.915	507809	1.68	76807	1.14	6.61		Methyl 2,2-dimethyldecanoate
5	13.983	13.915	14.085	384340	1.27	83352	1.23	4.61	V	Tridecane (CAS)
6	14.198	14.140	14.265	182558	0.60	51403	0.76	3.55		Formamide, N,N-dibutyl-
7	16.416	16.325	16.585	1686662	5.59	251497	3.72	6.71		Decanoic acid (CAS)
8	16.710	16.585	16.775	1051595	3.48	302216	4.47	3.48		Tetradecane (CAS)
9	18.021	17.940	18.145	549919	1.82	98429	1.45	5.59		Octadecanoic acid (CAS)
	18.326	18.265	18.435	424376	1.41	109017	1.61	3.89		2,6,10-Trimethyltridecane
	18.485	18.450	18.610	169625	0.56	27540	0.41	6.16		Benzeneacetic acid, 3-tridecyl ester
12	18.811	18.765	18.865	240723	0.80	72898	1.08	3.30		1-Dodecanol (CAS)
13	18.936	18.865	19.030	980739	3.25	160899	2.38	6.10	V	Undecanoic acid (CAS)
14	19.060	19.030	19.085	136613	0.45	49539	0.73	2.76	V	Hexadecane, 2,6,10,14-tetramethyl- (CA
15	19.130	19.085	19.165	403442	1.34	139964	2.07	2.88	V	n-Tridecan-1-ol
16	19.197	19.165	19.245	355618	1.18	108483	1.60	3.28	V	Tetracosane (CAS)
17	19.312	19.245	19.390	1356748	4.50	355213	5.25	3.82	V	Pentadecane
18	19.649	19.600	19.715	251198	0.83	61329	0.91	4.10		L-Serine, O-(phenylmethyl)- (CAS)
19	19.760	19.715	19.835	121350	0.40	31241	0.46	3.88	V	Phenol, 2,6-bis(1,1-dimethylethyl)-4-meth
20	19.964	19.840	20.095	1629022	5.40	302534	4.47	5.38		PHENOL, 2,4-BIS(1,1-DIMETHYLETE
21	20.151	20.095	20.205	137249	0.45	34727	0.51	3.95	V	Tridecanol (CAS)
22	20.332	20.205	20.405	309419	1.03	98021	1.45	3.16	V	11-Methyltricosane
23	20.612	20.535	20.690	254443	0.84	57000	0.84	4.46	V	Dodecane, 3-cyclohexyl-
24	20.904	20.845	20.940	192448	0.64	57771	0.85	3.33		2-methyloctacosane
25	21.080	21.020	21.115	235349	0.78	73652	1.09	3.20		1,3-Propanediol, ethyl tetradecyl ether
26	21.145	21.115	21.200	130836	0.43	44591	0.66	2.93	V	Benzene, (3-octylundecyl)- (CAS)
27	21.367	21.285	21.505	3098080	10.27	550632	8.14	5.63		Dodecanoic acid (CAS)
28	21.520	21.505	21.580	271627	0.90	76097	1.12	3.57	V	Nonahexacontanoic acid
29	21.616	21.580	21.670	211458	0.70	54613	0.81	3.87	V	1-Octadecene (CAS)
30	21.708	21.670	21.745	124407	0.41	42015	0.62	2.96	V	Heptadecanoic acid, ethyl ester (CAS)
31	21.801	21.745	21.875	1355007	4.49	469209	6.94	2.89	V	Hexadecane
32	22.159	22.095	22.255	429557	1.42	115667	1.71	3.71		trans-2-Dodecen-1-ol
33	22.653	22.555	22.750	451985	1.50	79663	1.18	5.67		Sedoheptulose, 2,3:4,5-dimethylene-
34	22.832	22.755	22.910	678367	2.25	109929	1.62	6.17		Tridecanoic acid
35	22.953	22.910	23.110	708305	2.35	119783	1.77	5.91	V	2,6,10-TRIMETHYLPENTADECANE
36	23.199	23.110	23.255	185173	0.61	44421	0.66	4.17		Dotriacontane (CAS)
37	23.334	23.255	23.390	359922	1.19	91601	1.35	3.93		Cyclooctasiloxane, hexadecamethyl-
38	23.493	23.390	23.510	345790	1.15	85926	1.27	4.02	V	Oxirane, hexadecyl-
39	23.550	23.510	23.585	271173	0.90	69148	1.02	3.92	V	1,3-Propanediol, dodecyl ethyl ether
40	23.677	23.585	23.735	2441502	8.09	418359	6.18	5.84	V	Tetracosanoic acid
41	23.766	23.735	23.835	1274540	4.22	295832	4.37	4.31	V	n-Pentadecanol
42	23.870	23.835	23.925	509338	1.69	121324	1.79	4.20	V	2-Methylhexacosane
43	24.005	23.925	24.035	350251	1.16	76650	1.13	4.57	V	Dichloroacetic acid, heptadecyl ester
44	24.074	24.035	24.105	253059	0.84	70824	1.05	3.57	V	Ethyl tridecanoate
45	24.163	24.105	24.230	1032805	3.42	261509	3.87	3.95	V	Heptadecane
46	24.302	24.230	24.340	858524	2.84	205211	3.03	4.18	V	Pentadecane, 2,6,10,14-tetramethyl-
47	24.375	24.340	24.455	728328	2.41	232898	3.44	3.13	V	Dotriacontane (CAS)
48	24.567	24.525	24.610	244300	0.81	78692	1.16	3.10	V	2-Methylhexacosane
49	24.667	24.610	24.710	115839	0.38	39414	0.58	2.94		Ethanol, 2-(dodecyloxy)- (CAS)
50	24.850	24.765	24.980	1439823	4.77	249692	3.69	5.77		3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2
				30178940	100.00	6765350	100.00			

Figure 8.3.1 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 220ºC, solvent H2O/E and 85% solvent content

8.3.2 GCMS for optimal process conditions – Run: 250EW85

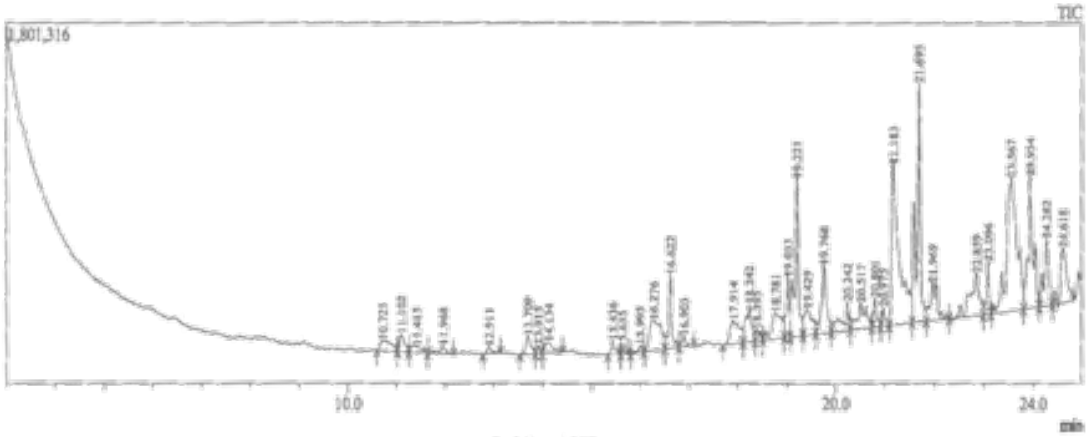


Peak Report TIC

	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
	7.739	7.575	8.015	779802	0.44	63083	0.31	12.36		2-Pyrrolidinone (CAS)
	10.705	10.595	11.015	2151175	1.22	118189	0.58	18.20		2-Piperidinone
2	11.075	11.015	11.295	688175	0.39	104911	0.51	6.56	V	Dodecane (CAS)
3	12.878	12.735	13.155	623993	0.35	95140	0.47	6.56		2-Hexyl-1-decanol
4	13.684	13.395	13.855	1487091	0.84	96123	0.47	15.47		3,4-Dihydroxyproline
5	13.875	13.855	13.955	146141	0.08	44583	0.22	3.28	V	DECANE, 3,8-DIMETHYL-
6	14.071	13.955	14.235	572267	0.32	70458	0.35	8.12	V	1H-Indole (CAS)
7	16.157	16.015	16.455	4258013	2.41	329450	1.62	12.92		Decanoic acid (CAS)
8	16.592	16.455	16.735	2567256	1.45	630929	3.09	4.07	V	Tetradecane (CAS)
9	16.815	16.735	16.955	399866	0.23	58027	0.28	6.89	V	Methyl pinidine
10	17.275	17.115	17.675	1000965	0.57	47653	0.23	21.01		7,7-Dimethyl-bicyclo[2.2.1]heptan-2-ol
11	17.829	17.675	17.935	2668590	1.51	214791	1.05	12.42		Undecanoic acid (CAS)
12	18.211	17.935	18.315	5197229	2.94	523888	2.57	9.92	V	Heptadecane, 2,6,10,15-tetramethyl- (CA
13	18.360	18.315	18.495	1048183	0.59	111741	0.55	9.38	V	Carbonic acid, octadecyl vinyl ester
14	18.679	18.495	18.915	5335075	3.02	430676	2.11	12.39	V	Undecanoic acid (CAS)
15	19.189	18.915	19.335	11382245	6.44	2112939	10.36	5.39	V	Pentadecane
16	19.415	19.335	19.495	1637602	0.93	194183	0.95	8.43	V	Benzene, (2,3-dimethyldecyl)-
17	19.535	19.495	19.635	1142456	0.65	152951	0.75	7.47	V	Pentatriacontane (CAS)
18	19.708	19.635	19.855	2754367	1.56	388118	1.90	7.10	V	PHENOL, 2,4-BIS(1,1-DIMETHYLETE
19	19.935	19.855	19.975	1017277	0.58	182497	0.89	5.57	V	Cyclopropanemethanol, 2-methyl-2-(4-m
20	20.216	19.975	20.315	3147255	1.78	276983	1.36	11.36	V	Disulfide, di-tert-dodecyl
21	20.475	20.315	20.675	4477629	2.53	338972	1.66	13.21	V	2-Cyclohexylnonadecane
22	20.775	20.675	20.875	2555616	1.45	419747	2.06	6.09	V	OCTACOSANE
23	20.942	20.875	21.015	1517538	0.86	290875	1.43	5.22	V	Pentadecane, 3-methyl- (CAS)
24	21.146	21.015	21.455	23086516	13.06	2479780	12.16	9.31	V	Dodecanoic acid (CAS)
25	21.663	21.455	21.795	19703384	11.15	3528751	17.30	5.58	V	Heptadecane
26	21.880	21.795	22.095	3042421	1.72	267279	1.31	11.38	V	2-Methyltetracosane
27	22.599	22.095	22.695	6030851	3.41	722245	3.54	8.35	V	Tridecanoic acid (CAS)
28	22.818	22.695	22.955	6465842	3.66	842716	4.13	7.67	V	Pentadecane, 2,6,10-trimethyl-
29	23.055	22.955	23.115	2359630	1.34	506388	2.48	4.66	V	Ethyl tridecanoate
30	23.480	23.115	23.795	35809167	20.26	2954925	14.49	12.12	V	Tridecanoic acid (CAS)
31	23.857	23.795	24.315	15274666	8.64	951539	4.67	16.05	V	n-Pentadecanol
32	24.557	24.335	24.695	3139244	1.78	261498	1.28	12.00		1-Tetradecanamine, N,N-dimethyl-
33	24.882	24.795	24.995	3247841	1.84	581829	2.85	5.58		Tetradecanoic acid (CAS)
34				176715368	100.00	20393857	100.00			

Figure 8.3.2 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 250ºC, solvent H2O/E and 85% solvent content

8.3.3 GCMS for optimal process conditions – Run: 280EW85

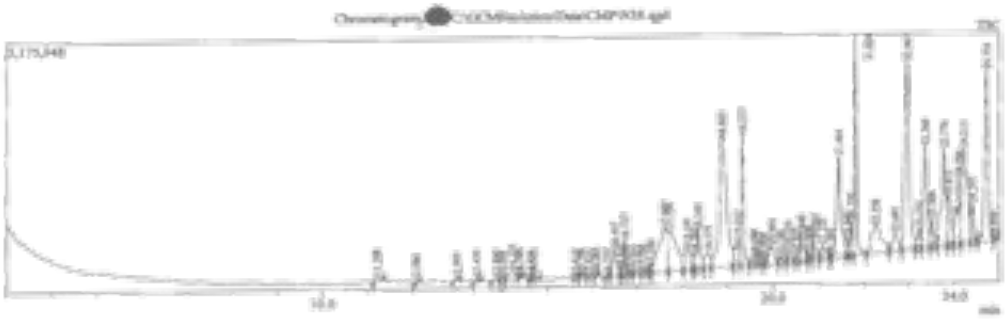


Peak Report TIC

	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
	10.721	10.595	11.015	845250	1.22	47564	0.58	17.77		2-Piperidinone
	11.102	11.015	11.255	678816	0.98	85382	1.04	7.95		Dodecane (CAS)
	11.415	11.255	11.635	530709	0.77	33010	0.40	16.08		CYCLOOCTANONE-2,2,8,8-D4
	11.968	11.635	12.175	429681	0.62	41232	0.50	10.42		5-Hydroxymethyl-2,2,5-trimethyl-1,3-diox
5	12.911	12.775	13.135	251700	0.36	35887	0.44	7.01		2-Ethyl-1-dodecanol
6	13.709	13.535	13.855	703635	1.02	90169	1.10	7.80		Isovaleric acid, undecyl ester
7	13.915	13.855	13.995	238436	0.34	43515	0.53	5.48		Pentadecane, 2,6,10-trimethyl-
8	14.134	13.995	14.415	672906	0.97	55232	0.68	12.18		1H-Indole (CAS)
9	15.436	15.335	15.595	397270	0.57	68993	0.84	5.76		CYCLOUNDECANE, 1,1,2-TRIMETHY
10	15.635	15.595	15.775	165223	0.24	27916	0.34	5.92		Tetradecane, 6,9-dimethyl- (CAS)
11	15.995	15.795	16.075	249956	0.36	34370	0.42	7.27		Octane, 2,6-dimethyl- (CAS)
12	16.276	16.075	16.495	2512962	3.64	152264	1.86	16.50		Decanoic acid (CAS)
13	16.622	16.495	16.795	1664567	2.41	342027	4.18	4.87		Tetradecane (CAS)
14	16.903	16.795	17.095	296585	0.43	50509	0.62	5.87		trans-2-Dodecen-1-ol
15	17.914	17.695	18.115	1662364	2.41	117319	1.43	14.17		Undecanoic acid
16	18.242	18.115	18.355	1519990	2.20	180183	2.20	8.44		2,6,10-Trimethyltridecane
17	18.395	18.355	18.515	386982	0.56	58950	0.72	6.56		PENTACOSANE
18	18.781	18.515	18.955	2002265	2.90	131047	1.60	15.28		Undecanoic acid (CAS)
19	19.033	18.955	19.075	1361035	1.97	319492	3.91	4.26		n-Tridecan-1-ol
20	19.221	19.075	19.335	4381096	6.34	745063	9.11	5.88		Pentadecane
21	19.429	19.335	19.595	1452726	2.10	129096	1.58	11.25		1-Dodecanamine, N,N-dimethyl- (CAS)
22	19.768	19.595	19.915	2501449	3.62	344836	4.22	7.25		PHENOL, 2,4-BIS(1,1-DIMETHYLETH)
23	20.242	19.915	20.295	1281306	1.85	129858	1.59	9.87		Hexadecane, 2,6,10,14-tetramethyl- (CAS)
24	20.517	20.295	20.735	1655169	2.39	129449	1.58	12.79		Dodecane, 2-cyclohexyl-
25	20.801	20.735	20.915	649302	0.94	137588	1.68	4.72		2-methyloctacosane
26	20.975	20.915	21.095	458030	0.66	90187	1.10	5.08		Hexadecane, 2,6,10,14-tetramethyl- (CAS)
27	21.183	21.095	21.555	8956957	12.96	807720	9.88	11.09		Dodecanoic acid (CAS)
28	21.695	21.555	21.835	6171892	8.93	1117884	13.67	5.52		Heptadecane
29	21.969	21.835	22.295	1920643	2.78	190912	2.34	10.06		Cedrane, 8-propoxy-
30	22.859	22.295	22.995	2702669	3.91	215447	2.64	12.54		2,6,10-TRIMETHYLPENTADECANE
31	23.096	22.995	23.155	940040	1.36	264279	3.23	3.56		Ethyl tridecanoate
32	23.567	23.155	23.815	10102853	14.62	648575	7.93	15.58		Octadecanoic acid (CAS)
33	23.954	23.815	24.135	4899482	7.09	707530	8.65	6.92		Ethyl tridecanoate
34	24.282	24.135	24.395	2087254	3.02	327885	4.01	6.37		2,3,7-TRIMETHYLOCTANAL
35	24.618	24.395	24.835	2380978	3.45	274228	3.35	8.68		3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,5

Figure 8.3.3 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 280ºC, solvent H2O/E and 85% solvent content

8.3.4 GCMS for optimal process conditions – Run: 340EW85

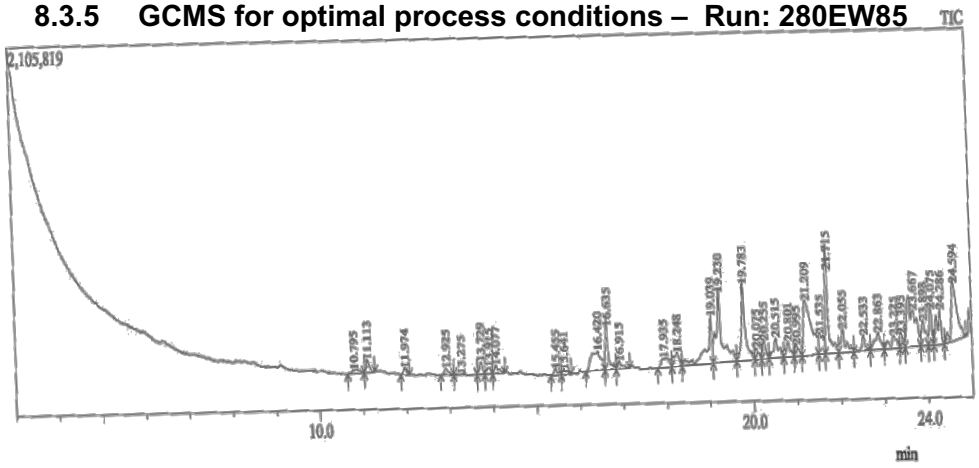


Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	11.208	11.125	11.375	864455	0.33	124578	0.30	6.94		2-Ethylhexyl benzoate
2	12.086	12.000	12.175	139964	0.05	31508	0.08	4.18		5-Hydroxymethyl-3,2,3-trimethyl-1,3-dio
3	12.989	12.895	13.085	103124	0.07	45969	0.10	4.80		Carbonic acid, decyl vinyl ester
4	13.430	13.350	13.530	443961	0.17	113486	0.27	3.91		Heptadecane, 8-methyl- (CAS)
5	13.890	13.740	13.945	628394	0.24	99907	0.24	6.29		Nonanoic acid
6	14.308	13.945	14.065	377601	0.14	68630	0.16	5.50		Tetradecane (CAS)
7	14.225	14.065	14.345	1588893	0.68	177739	0.42	10.07		Decanoic acid, ethyl ester (CAS)
8	14.390	14.345	14.470	276853	0.10	59907	0.14	4.62		Tridecanal (CAS)
9	14.636	14.580	14.665	152930	0.06	47748	0.11	3.20		2-Isopropyl-5-methyl-1-heptanol
10	14.713	14.665	14.825	307905	0.12	85292	0.20	3.61		NONANE, 3-METHYL-5-PROPYL-
11	15.610	15.570	15.695	2149118	0.08	33485	0.08	6.42		1-Methyl-2-oxopyrrolidine-4-carboxylic acic
12	15.746	15.695	15.805	269688	0.10	62484	0.15	4.32		Tridecane, 2-methyl- (CAS)
13	15.925	15.875	16.040	192652	0.07	22381	0.05	8.61		DODECANE, 2,6,11-TRIMETHYL-
14	16.085	16.040	16.135	202519	0.08	66510	0.16	3.05		Hexadecane, 2,6,10,14-tetramethyl- (CAS
15	16.330	16.270	16.385	143406	0.05	29942	0.07	4.79		9-Hexadecenoic acid (CAS)
16	16.495	16.385	16.610	3421097	1.29	577562	1.37	5.92		Decanoic acid (CAS)
17	16.640	16.610	16.670	407846	0.15	121087	0.29	3.37		Decanoic acid, ethyl ester (CAS)
18	16.727	16.670	16.785	2350756	0.89	726813	1.73	3.23		Tetradecane (CAS)
19	16.825	16.785	16.900	336528	0.13	69513	0.16	4.84		Carbonic acid, octadecyl prop-1-en-2-yl e
20	17.023	16.900	17.085	497123	0.19	67868	0.16	7.32		Dodecanal (CAS)
21	17.130	17.085	17.235	399260	0.15	60632	0.14	6.58		4,4-Dimethyl-cyclohex-2-en-1-ol
22	17.300	17.235	17.315	447945	0.17	142447	0.34	3.14		Hexadecane (CAS)
23	17.602	17.315	17.690	13056611	4.93	930253	2.21	14.04		9-Octadecenoic acid (Z)- (CAS)
24	17.734	17.690	18.020	11033907	4.20	859617	2.04	12.94		9-Octadecenoic acid (Z)- (CAS)
25	18.101	18.020	18.220	4548828	1.72	552775	1.31	8.23		Tetradecanoic acid (CAS)
26	18.260	18.220	18.290	1254285	0.47	331550	0.79	3.78		Tetradecane, 4-methyl- (CAS)
27	18.350	18.290	18.460	4567838	1.73	818889	1.94	5.58		2,6,10-Trimethyltridecane
28	18.575	18.460	18.640	2884705	1.09	350585	0.83	8.23		Tetradecane, 3-methyl- (CAS)
29	18.885	18.640	19.120	31823026	12.02	2716428	6.44	11.72		Tetradecanoic acid, ethyl ester (CAS)
30	19.217	19.120	19.280	4128678	1.56	600309	1.42	6.88		Hexadecane, 2,6,10,14-tetramethyl- (CAS
31	19.337	19.280	19.490	9427310	3.56	2769764	6.57	3.40		Pentadecane
32	19.579	19.490	19.640	1324143	0.50	205229	0.48	6.52		1-Dodecanamine, N,N-dimethyl- (CAS)
33	19.672	19.640	19.760	910841	0.34	147985	0.35	6.16		Tetradecanal (CAS)
34	19.800	19.760	19.840	482310	0.18	112953	0.27	4.27		2-Thiophenoacetic acid, 4-tetradecyl ester
35	19.990	19.840	20.120	3132920	1.18	387588	0.92	8.08		PHENOL, 2,4-BIS(1,1-DIMETHYLETH
36	20.180	20.120	20.290	796323	0.29	149460	0.35	5.06		Octacosyl trifluoroacetate
37	20.353	20.290	20.460	1351823	0.50	324241	0.77	4.31		11-Methyltriacontane
38	20.523	20.460	20.580	936000	0.35	157179	0.37	5.95		Threitol, 2-O-decyl-
	20.640	20.580	20.750	2513463	0.87	412279	0.98	5.61		Dodecane, 2-cyclohexyl-
	20.800	20.750	20.860	810588	0.31	170205	0.40	4.76		Pentadecane, 4-methyl-
41	20.922	20.860	21.040	1835285	0.69	418152	0.99	4.39		Iron, tricarbonyl[N-(phenyl-2-pyridinylm
42	21.103	21.040	21.240	1830974	0.69	304358	0.72	6.02		Pentadecane, 3-methyl- (CAS)
43	21.280	21.240	21.300	217019	0.08	67329	0.16	3.22		Dodecanal (CAS)
44	21.464	21.300	21.610	12896590	4.87	2083204	4.89	6.25		Dodecanoic acid (CAS)
45	21.640	21.610	21.680	1287780	0.49	387824	0.92	3.32		n-Pentadecanol
46	21.730	21.680	21.770	2394760	0.90	750095	1.78	3.19		Dodecanoic acid, ethyl ester (CAS)
47	21.824	21.770	22.080	14035471	5.30	4423645	10.49	3.17		Hexadecane
48	22.258	22.080	22.360	8598048	3.25	590655	1.40	14.56		Pentadecanoic acid (CAS)
49	22.495	22.360	22.830	3359815	1.27	388481	0.92	8.65		Octadecanoic acid (CAS)
50	22.967	22.830	23.130	25363906	9.58	3890878	9.22	6.52		Pentadecanoic acid, ethyl ester
51	23.252	23.130	23.270	2328325	0.88	447485	1.06	5.20		Ethyl tridecanoate
52	23.360	23.270	23.460	11752273	4.43	2130895	5.05	5.51		Pentadecanoic acid, ethyl ester
53	23.509	23.460	23.610	3044498	1.15	626837	1.49	4.86		9-Octadecen-1-ol, (Z)-
54	23.776	23.610	23.840	13863480	5.24	2029106	4.81	6.83		9-Octadecenoic acid (Z)- (CAS)
55	23.870	23.840	23.970	5427640	2.05	1034311	2.45	5.25		(Z)-Ethyl pentadec-9-enoate
56	24.094	23.970	24.140	1036271	3.07	1391305	3.30	5.85		Ethyl tridecanoate
57	24.215	24.140	24.360	17273069	6.52	2008759	4.76	8.59		1-Octadecanol (CAS)
58	24.397	24.360	24.510	3274854	1.24	820240	1.94	3.99		5-Decanone (CAS)
59	24.716	24.510	24.860	18818058	7.11	3525179	8.37	5.33		Pentadecanoic acid, ethyl ester
60	24.900	24.860	24.970	599020	0.07	53912	0.13	3.64		1H-Imidazole, 2-phenyl- (CAS)
				264784576	100.00	42188353	100.00			

Figure 8.3.4 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 340ºC, solvent H2O/E and 85% solvent content

8.3.5 GCMS for optimal process conditions – Run: 280EW85



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.795	10.655	11.035	304887	0.74	18350	0.36	16.62		Naphthalene (CAS)
2	11.113	11.035	11.275	398992	0.96	72849	1.45	5.48	V	Dodecane (CAS)
3	11.974	11.875	12.075	196877	0.47	39511	0.79	4.98		5-Hydroxymethyl-2,2,5-trimethyl-1,3-dio
4	12.925	12.795	13.095	246655	0.59	33534	0.67	7.36		Carbonic acid, allyl tetradecyl ester
5	13.275	13.095	13.635	75435	0.18	2898	0.06	26.03	V	Chloroacetic acid, 10-undecenyl ester
6	13.729	13.635	13.815	392034	0.95	68850	1.37	5.69		l-Alanine, N-methoxycarbonyl-, butyl este
7	13.915	13.815	13.995	258870	0.62	35909	0.71	7.21	V	Hexadecane (CAS)
8	14.077	13.995	14.275	336109	0.81	47164	0.94	7.13	V	Formamide, N,N-dibutyl-
9	15.455	15.335	15.575	228141	0.55	38802	0.77	5.88		cis-2-Methyl-7-octadecene
10	15.641	15.575	15.795	201200	0.49	24787	0.49	8.12		1-Iodo-2-methylundecane
11	16.420	16.135	16.575	1775974	4.28	104959	2.09	16.92		9-Octadecenoic acid (Z)- (CAS)
12	16.635	16.575	16.835	1194761	2.88	271201	5.39	4.41		Tetradecane (CAS)
13	16.915	16.835	17.135	324072	0.78	44680	0.89	7.25		Tridecanal (CAS)
14	17.935	17.795	18.115	762102	1.84	50267	1.00	15.16		Undecanoic acid (CAS)
15	18.248	18.115	18.355	769337	1.85	77693	1.54	9.90		Hexadecane, 2,6,10,14-tetramethyl- (CAS
16	19.039	18.355	19.075	2470999	5.96	264361	5.25	9.35		n-Pentadecanol
17	19.230	19.075	19.615	3881953	9.36	395512	7.86	9.82		Pentadecane
18	19.783	19.615	20.035	3035952	7.32	430095	8.55	7.06		PHENOL, 2,4-BIS(1,1-DIMETHYLETH
19	20.075	20.035	20.195	411770	0.99	63688	1.27	6.47		Tridecanol (CAS)
20	20.255	20.195	20.355	562135	1.36	108479	2.16	5.18		Eicosane
21	20.515	20.355	20.695	1074686	2.59	108324	2.15	9.92		Heptafluorobutyric acid, pentadecyl ester
22	20.801	20.695	20.935	643917	1.55	83335	1.66	7.73		Hexatriacontane (CAS)
23	20.995	20.935	21.115	424342	1.02	71976	1.43	5.90		Pentadecane, 8-hexyl- (CAS)
24	21.209	21.115	21.495	4113857	9.92	312649	6.21	13.16		Dodecanoic acid (CAS)
25	21.535	21.495	21.655	986127	2.38	122439	2.43	8.05		6-Tridecanol
26	21.715	21.655	21.955	2635060	6.35	566909	11.26	4.65		Hexadecane
27	22.055	21.955	22.295	1054536	2.54	142195	2.83	7.42		Tetradecanal
28	22.533	22.295	22.675	515138	1.24	90814	1.80	5.67		Sulfurous acid, butyl tridecyl ester
29	22.863	22.675	22.995	957334	2.31	95118	1.89	10.06		2,6,10-TRIMETHYLPENTADECANE
30	23.225	22.995	23.355	885842	2.14	70392	1.40	12.58		Hexadecane, 2,6,10,14-tetramethyl- (CAS
31	23.395	23.355	23.475	443517	1.07	87862	1.75	5.05		11-Hexadecen-1-ol, (Z)-
32	23.667	23.475	23.835	3553181	8.57	204572	4.06	17.37		n-Heptadecanol-1
33	23.898	23.835	24.015	960346	2.32	141069	2.80	6.81		n-Pentadecanol
34	24.075	24.015	24.135	856892	2.07	217576	4.32	3.94		Octadecane (CAS)
35	24.286	24.135	24.375	1338112	3.23	181222	3.60	7.38		Docosane (CAS)
36	24.594	24.375	24.855	3208781	7.74	342925	6.81	9.36		3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,
				41479923	100.00	5032966	100.00			

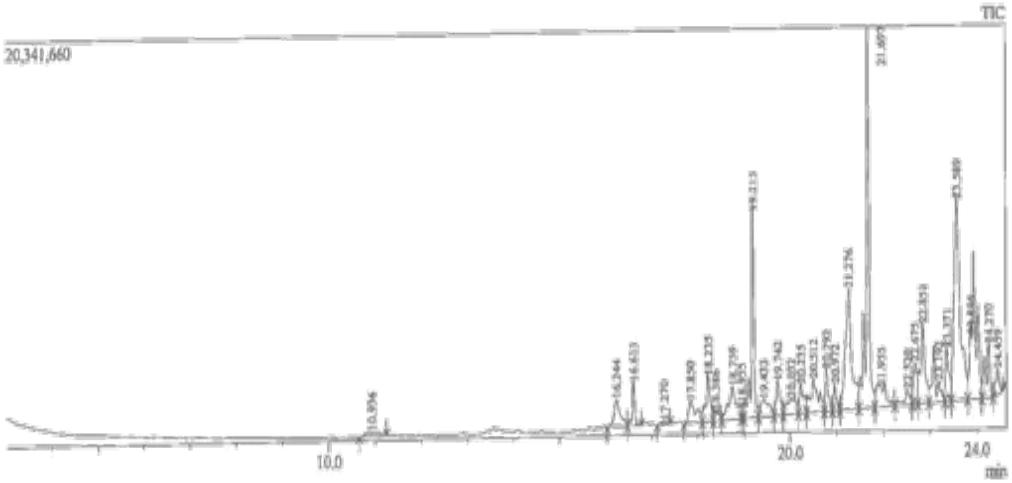
Figure 8.3.5 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 370ºC, solvent H2O/E and 85% solvent content

8.4 The effect of solvent content on the functional groups with respect to the optimal conditions

The data for run 310EW75% temperature 310°C is presented in Figure 8.2.1.

Figure 8.4.1: Run 310EW75%
Figure 8.4.2: Run 310EW80%
Figure 8.4.3: Run 310EW90%
Figure 8.4.4: Run 310EW95%

8.4.1 GCMS for optimal process conditions Run: 310EW75

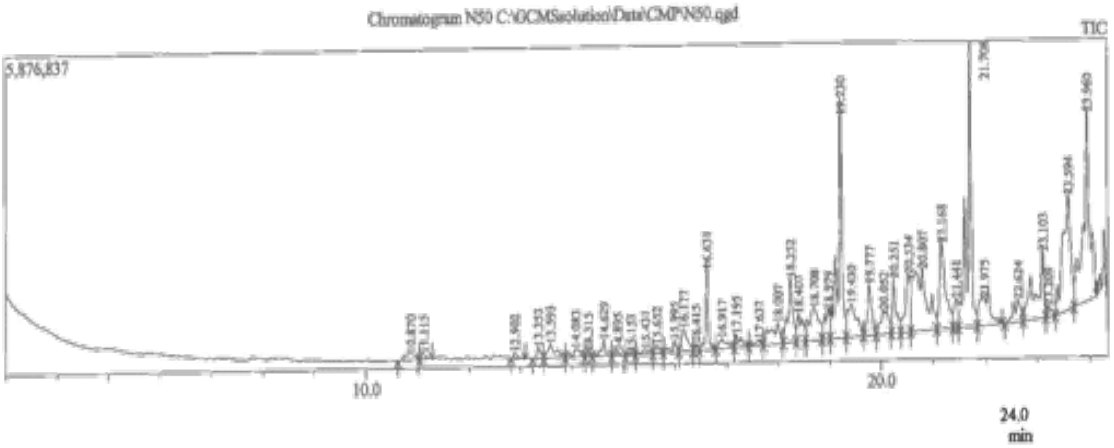


Peak Report TIC

	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.936	10.655	11.255	4633033	0.74	223046	0.26	20.77		Hexanoic acid, 1-cyclopentylethyl ester
2	16.244	16.035	16.475	12767363	2.03	1344886	1.59	9.49		Decanoic acid (CAS)
3	16.613	16.475	16.775	8608265	1.37	2327041	2.75	3.70		Tetradecane (CAS)
4	17.270	17.115	17.395	1540714	0.25	200823	0.24	7.67		1H-INDENE, OCTAHYDRO-2,2,4,4,7,7
5	17.850	17.695	18.095	13059689	2.08	1111989	1.31	11.74		9-Octadecenoic acid (Z)- (CAS)
6	18.235	18.095	18.335	15437798	2.46	2410754	2.85	6.40		Heptadecane, 2,6,10,15-tetramethyl- (CA
7	18.386	18.335	18.515	4443162	0.71	544598	0.64	8.16		2-methyloctacosane
8	18.759	18.515	18.935	20095079	3.20	1644525	1.94	12.22		Undecanoic acid (CAS)
9	18.955	18.935	18.995	2596969	0.41	771741	0.91	3.37		Tetracosane (CAS)
10	19.215	18.995	19.315	45708389	7.28	10541809	12.45	4.34		Pentadecane (CAS)
11	19.433	19.315	19.655	11835919	1.89	893390	1.06	13.25		Benzene, (2,3-dimethyldecyl)- (CAS)
	19.742	19.655	19.855	10633087	1.69	1692806	2.00	6.28		PHENOL, 2,4-BIS(1,1-DIMETHYLETH
	20.032	19.855	20.175	11368556	1.81	812986	0.96	13.98		Pentatriacontane (CAS)
14	20.235	20.175	20.355	10175784	1.62	1513971	1.79	6.72		Hexadecane, 1-iodo-
15	20.512	20.355	20.735	20350065	3.24	1689177	1.99	12.05		(1-METHYLUNDECYL)CYCLOHEXA
16	20.792	20.735	20.915	10063105	1.60	2118184	2.50	4.75		Pentadecane, 2-methyl- (CAS)
17	20.972	20.915	21.075	6303259	1.00	1360121	1.61	4.63		Pentadecane, 3-methyl- (CAS)
18	21.276	21.075	21.475	57726927	9.20	5945474	7.02	9.71		Dodecanoic acid (CAS)
19	21.697	21.475	21.815	85556813	13.63	18125063	21.40	4.72		Hexadecane (CAS)
20	21.955	21.815	22.235	16913642	2.69	1063875	1.26	15.90		14-.BETA.-H-PREGNA
21	22.520	22.235	22.615	7264431	1.16	763127	0.90	9.52		Eicosane (CAS)
22	22.675	22.615	22.735	11285384	1.80	1988196	2.35	5.68		Tridecanoic acid (CAS)
23	22.851	22.735	22.975	27561503	4.39	3998787	4.72	6.89		Pentadecane, 2,6,10-trimethyl-
24	23.192	22.975	23.315	18552344	2.96	1057115	1.25	17.55		Pentadecane, 8-hexyl-
25	23.371	23.315	23.455	14061244	2.24	2702875	3.19	5.20		9-Octadecen-1-ol, (Z)-
26	23.589	23.455	23.815	95588262	15.23	10165781	12.00	9.40		9-Octadecenoic acid (Z)- (CAS)
27	23.895	23.815	24.115	59121931	9.42	3655416	4.32	16.17		n-Nonadecanol-1
28	24.270	24.115	24.355	17592637	2.80	2741068	3.24	6.42		Docosane (CAS)
29	24.459	24.355	24.555	6866672	1.09	1272872	1.50	5.39		Dotriacontane (CAS)
				627712026	100.00	84681496	100.00			

Figure 8.4.1The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 310ºC, solvent H2O/E and 75% solvent content

8.4.2 GCMS for optimal process conditions – Run: 310EW80

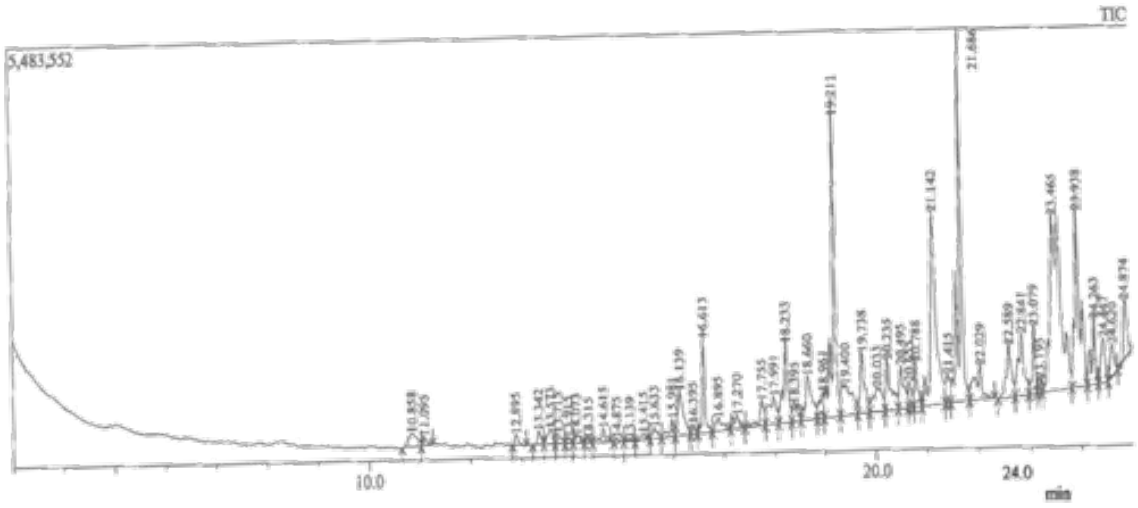


Peak Report TIC

R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
10.870	10.615	11.035	1654567	0.65	114940	0.36	14.40		Hexanoic acid, 1-methyloctyl ester (CAS
11.115	11.035	11.275	655852	0.26	108126	0.34	6.07	V	Dodecane (CAS)
12.902	12.815	13.095	555825	0.22	106105	0.33	5.24		Octadecane (CAS)
13.353	13.235	13.455	1153087	0.45	220113	0.69	5.24		Hexadecane, 2,6,10,14-tetramethyl- (CA
13.593	13.455	13.875	2893093	1.13	259403	0.82	11.15		Ether, hexyl t-butyl
14.083	13.875	14.255	1709778	0.67	152312	0.48	11.23		2-Isopropyl-5-methyl-1-heptanol
14.315	14.255	14.395	399550	0.16	96113	0.30	4.16		2-Isopropyl-5-methyl-1-heptanol
14.629	14.395	14.775	1700768	0.67	292433	0.92	5.82		Heptadecane
14.895	14.775	15.035	475731	0.19	91332	0.29	5.21		Eicosane (CAS)
15.153	15.035	15.235	419157	0.16	64802	0.20	6.47		Eicosane
15.431	15.235	15.575	971252	0.38	100336	0.32	9.68		2-Hexadecen-1-ol, 3,7,11,15-tetramethyl
15.652	15.575	15.775	937928	0.37	154525	0.49	6.07		Tridecane, 2-methyl- (CAS)
15.995	15.775	16.075	1548255	0.61	206701	0.65	7.49		Dodecane, 2,6,10-trimethyl- (CAS)
16.177	16.075	16.355	3467824	1.36	428239	1.35	8.10		Decanoic acid (CAS)
16.415	16.355	16.475	642898	0.25	127462	0.40	5.04		Oxalic acid, cyclohexylmethyl tridecyl es
16.631	16.475	16.795	5681936	2.23	1502657	4.74	3.78		Tetradecane (CAS)
16.917	16.795	17.155	1944307	0.76	179136	0.57	10.85		Dodecane (CAS)
17.195	17.155	17.435	1647100	0.65	219189	0.69	7.51		Hexadecane (CAS)
17.637	17.435	17.715	782742	0.31	102713	0.32	7.62		Hexadecane (CAS)
18.007	17.715	18.095	5031266	1.97	362824	1.14	13.87		Tetradecane, 5-methyl-
18.252	18.095	18.355	8057507	3.16	1199250	3.78	6.72		Heptadecane, 2,6,10,15-tetramethyl-
18.407	18.355	18.535	3813131	1.49	481953	1.52	7.91		HENTRIACONTANE
18.708	18.535	18.855	7991971	3.13	609008	1.92	13.12		Undecanoic acid (CAS)
18.979	18.855	19.015	4062820	1.59	560142	1.77	7.25		Tetracosane (CAS)
19.230	19.015	19.315	22734992	8.91	4131613	13.03	5.50		Pentadecane
19.430	19.315	19.655	7804427	3.06	604051	1.91	12.92		2,3,7-TRIMETHYLOCTANAL
19.777	19.655	19.895	5551947	2.18	940211	2.97	5.91		PHENOL, 2,4-BIS(1,1-DIMETHYLETI
20.052	19.895	20.195	5024703	1.97	439586	1.39	11.43		Pentatriacontane (CAS)
20.251	20.195	20.375	5159268	2.02	1003338	3.17	5.14		Eicosane
20.534	20.375	20.575	7650925	3.00	1086965	3.43	7.04		n-Nonylcyclohexane
20.807	20.575	21.075	21276707	8.34	1084599	3.42	19.62		Pentadecane, 2-methyl- (CAS)
21.168	21.075	21.375	12934833	5.07	1612810	5.09	8.02		Dodecanoic acid (CAS)
21.441	21.375	21.475	2649842	1.04	533935	1.68	4.96		Hexamethylene diacrylate
21.708	21.475	21.835	27437114	10.75	4682007	14.77	5.86		Hexadecane (CAS)
21.975	21.835	22.315	8251771	3.23	516848	1.63	15.97		Carbonic acid, decyl 2-ethylhexyl ester
22.624	22.355	22.715	4030568	1.58	402934	1.27	10.00		9-Octadecenoic acid (Z)- (CAS)
23.103	22.715	23.155	12901775	5.06	1209521	3.82	10.67		Pentadecanoic acid, ethyl ester
23.209	23.155	23.335	1175410	0.46	207544	0.65	5.66		2-Methyltetracosane
23.594	23.335	23.695	22493897	8.82	2142071	6.76	10.50		Pentadecafluorooctanoic acid, tetradecyl
23.960	23.695	24.135	29856181	11.70	3361107	10.60	8.88		Ethyl tridecanoate
			255132705	100.00	31698954	100.00			

Figure 8.4.2 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 310ºC, solvent H2O/E and 80% solvent content

8.4.3 GCMS for optimal process conditions Run: 310EW90

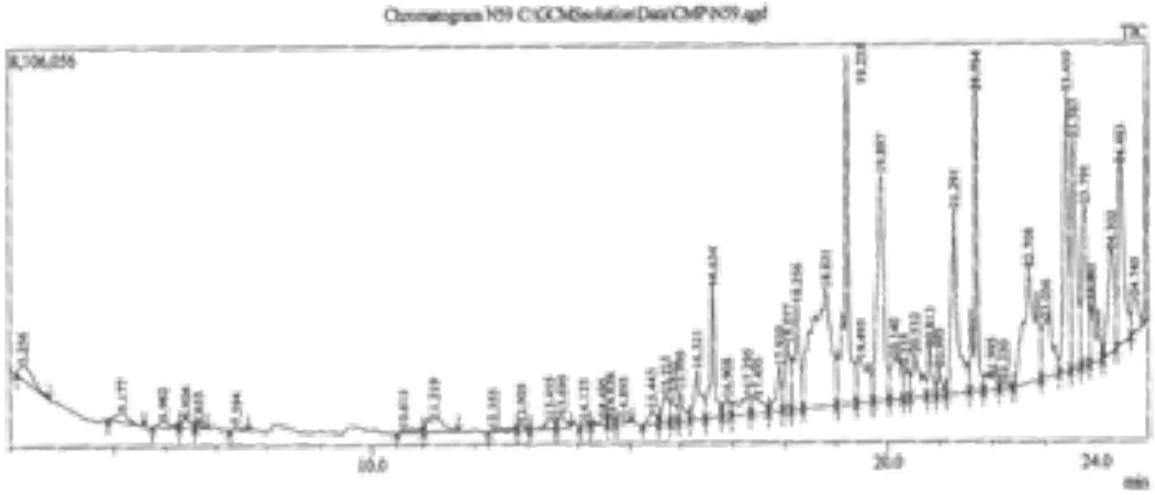


Peak Report TIC

R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
10.858	10.655	11.035	2176575	0.97	177052	0.55	12.29		Hexanoic acid, 1-cyclopentylethyl ester
11.095	11.035	11.255	742932	0.33	121979	0.38	6.09	V	Dodecane (CAS)
12.895	12.815	13.095	744593	0.33	144641	0.45	5.15		2-Hexyl-1-octanol
13.342	13.215	13.435	1042521	0.47	174344	0.54	5.98		pentadecane
13.573	13.435	13.655	1701963	0.76	205378	0.64	8.29		Ether, hexyl t-butyl
13.715	13.655	13.855	1006862	0.45	135479	0.42	7.43		di-2-Acetamido-2-methylsuccinic acid
13.915	13.855	14.015	518897	0.23	83122	0.26	6.24		Tetradecane (CAS)
14.073	14.015	14.235	882444	0.40	115189	0.36	7.66		4-Pentenoic acid, 2-methyl-, heptadecyl e
14.315	14.235	14.395	285080	0.13	52977	0.16	5.38		2-Isopropyl-5-methyl-1-heptanol
14.615	14.395	14.755	1076049	0.48	188951	0.59	5.69		Heptadecane, 8-methyl- (CAS)
14.875	14.815	15.015	264431	0.12	57710	0.18	4.58		Hexadecane, 2,6,10,14-tetramethyl- (CA
15.139	15.015	15.235	247888	0.11	38626	0.12	6.42		Eicosane
15.415	15.235	15.535	731602	0.33	87462	0.27	8.36		5-Eicosene, (E)-
15.633	15.535	15.755	1014056	0.45	148303	0.46	6.84		TRICOSANE
15.981	15.755	16.035	1540150	0.69	222530	0.69	6.92		Pentadecane, 2,6,10,14-tetramethyl- (CA
16.139	16.035	16.335	4644448	2.08	590003	1.83	7.87		Decanoic acid (CAS)
16.395	16.335	16.475	744898	0.33	131937	0.41	5.65		Oxalic acid, cyclohexylmethyl tridecyl es
16.613	16.475	16.775	4847726	2.17	1296108	4.02	3.74		Tetradecane (CAS)
16.895	16.775	17.135	1649669	0.74	169259	0.53	9.75		Sulfurous acid, butyl decyl ester
17.270	17.135	17.415	1398732	0.63	171532	0.53	8.15		1H-INDENE, OCTAHYDRO-2,2,4,4,7,7
17.755	17.415	17.815	2305732	1.03	335302	1.04	6.88		Undecanoic acid (CAS)
17.991	17.815	18.075	3837466	1.72	357645	1.11	10.73		Tetradecane, 5-methyl- (CAS)
18.233	18.075	18.335	7067618	3.16	1098526	3.41	6.43		Tricosane (CAS)
18.395	18.335	18.515	1903957	0.85	273525	0.85	6.96		Dotriacontane, 1-iodo-
18.660	18.515	18.835	5358130	2.40	575439	1.79	9.31		Undecanoic acid (CAS)
18.961	18.835	18.975	2045764	0.92	338608	1.05	6.04		pentadecane
19.211	18.975	19.295	18817271	8.42	3922265	12.17	4.80		Heptadecane
19.400	19.295	19.635	5920451	2.65	403392	1.25	14.68		Dotriacontane (CAS)
19.738	19.635	19.875	5006756	2.24	829506	2.57	6.04		PHENOL, 2,4-BIS(1,1-DIMETHYLETH
20.033	19.875	20.175	4001387	1.79	332271	1.03	12.04		Carbonic acid, decyl tetradecyl ester
20.235	20.175	20.435	4905753	2.20	722191	2.24	6.79		Docosane (CAS)
20.495	20.435	20.635	3803231	1.70	526686	1.63	7.22		Cyclohexane, nonadecyl-
20.655	20.635	20.735	1458433	0.65	333975	1.04	4.37		2-Methyltetracosane
20.788	20.735	20.895	2655182	1.19	594570	1.84	4.47		Tetradecane, 3-methyl- (CAS)
21.142	20.895	21.355	19641743	8.79	2426018	7.53	8.10		Dodecanoic acid (CAS)
21.415	21.355	21.455	1946864	0.87	392201	1.22	4.96		Hexamethylene diacrylate
21.686	21.455	21.815	22399737	10.03	4208411	13.06	5.32		Hexadecane (CAS)
22.029	21.815	22.295	4304385	1.93	444137	1.38	9.69		Tridecanal (CAS)
22.589	22.355	22.695	5031963	2.25	695491	2.16	7.24		9-Octadecenoic acid (Z)- (CAS)
22.841	22.695	22.975	6570402	2.94	788588	2.45	8.33		2,6,10-TRIMETHYLPENTADECANE
23.079	22.975	23.135	3284196	1.47	866159	2.69	3.79		Ethyl tridecanoate
23.195	23.135	23.235	846109	0.38	199428	0.62	4.24		2-Methyltetracosane
23.465	23.235	23.815	33105353	14.82	2233131	6.93	14.82		Tridecanoic acid (CAS)
23.938	23.815	24.115	16184257	7.25	2449698	7.60	6.61		Ethyl tridecanoate
24.263	24.115	24.335	4639411	2.08	829511	2.57	5.59		Eicosane
24.447	24.335	24.535	3324019	1.49	575133	1.78	5.78		PENTACOSANE
24.620	24.535	24.715	2284372	1.02	409109	1.27	5.58		Tricosane (CAS)
24.874	24.715	24.995	3467900	1.55	759255	2.36	4.57		Tetradecanoic acid
			223379358	100.00	32232753	100.00			

Figure 8.4.3 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 310ºC, solvent H2O/E and 90% solvent content

8.4.4 GCMS for optimal process conditions Run: 310EW95



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.256	3.135	3.755	5529522	0.92	291416	0.43	18.97		2-Furanmethanol (CAS)
2	5.177	4.895	5.595	3279540	0.54	200160	0.29	16.38		4-Pentenoic acid
3	5.962	5.755	6.275	1961838	0.33	135753	0.20	14.68		Ethanone, 1-(1H-pyrrol-2-yl)- (CAS)
4	6.404	6.275	6.575	2032325	0.34	180877	0.27	11.24		1H-Pyrrole-2-carboxaldehyde (CAS)
5	6.655	6.575	6.815	644415	0.11	87963	0.13	7.33		3-Octanethiol, thiolacetate
6	7.394	7.255	7.615	907787	0.15	110263	0.16	8.23		Pentenoic acid, 4-oxo-, ethyl ester (CAS)
7	10.615	10.495	11.015	1844304	0.31	62481	0.09	29.52		Guanosine (CAS)
8	11.219	11.015	11.675	6268982	1.04	280436	0.41	22.36		2(5H)-Furanone, 5-butyldihydro-4-methyl
9	12.355	12.255	12.815	1553504	0.26	60929	0.09	25.50		1H-Pyrrole-2,5-dione, 3-ethyl-4-methyl- (C
10	12.905	12.815	13.055	882695	0.15	131328	0.19	6.72		Oxalic acid, 6-ethyloct-3-yl butyl ester
11	13.455	13.055	13.575	2565443	0.42	230655	0.34	11.11		BENZENEACETIC ACID
12	13.695	13.575	13.875	2862042	0.47	276312	0.41	10.36		Nonanoic acid (CAS)
13	14.123	14.035	14.255	1121977	0.19	153427	0.23	7.30		1H-Indole (CAS)
14	14.485	14.255	14.575	1658199	0.27	135255	0.20	12.26		Cyclohexanone, 2-(2-butynyl)- (CAS)
15	14.636	14.575	14.735	1545023	0.26	237062	0.35	6.52		Hexadecane, 1-iodo-
16	14.895	14.735	15.055	1664477	0.28	130473	0.19	12.76		Docosane (CAS)
17	15.443	15.255	15.575	2879336	0.48	305168	0.45	9.44		Pentadecanal-
18	15.711	15.575	15.795	5221697	0.86	561296	0.82	9.30		Benzenepropionic acid, 2-tetradecyl ester
19	15.835	15.795	15.955	3449825	0.57	423080	0.62	8.15		3,5-Dimethyldodecane
20	15.995	15.955	16.175	3877861	0.64	593073	0.87	6.54		HEXADECANE, 2,6,10,14-TETRAMET
21	16.321	16.175	16.475	9108696	1.51	990879	1.45	9.19		Decanoic acid (CAS)
22	16.634	16.475	16.795	15279188	2.53	2855788	4.19	5.35		Tetradecane (CAS)
23	16.908	16.795	16.975	3099662	0.51	373618	0.55	8.30		2-Tridecen-1-ol, (E)-
24	17.295	16.975	17.355	6819884	1.13	518406	0.76	13.16		Decahydro-1,1,4a,5,6-pentamethylnaphth
25	17.495	17.355	17.695	5077727	0.84	323100	0.47	15.72		Cyclohexanol, 2-(2-ethylhexyl)-
26	17.920	17.695	17.975	6785614	1.12	896954	1.32	7.57		9-Octadecenoic acid (Z)- (CAS)
27	18.077	17.975	18.135	9187292	1.55	1363251	2.00	6.89		2-Pyrrolidinecarboxylic acid-5-oxo-, ethyl
28	18.256	18.135	18.355	16434860	2.72	2214532	3.25	7.41		Heptadecane, 2,6,10,15-tetramethyl- (CA
29	18.821	18.355	19.015	63359373	10.49	2380185	3.49	26.62		9-Octadecenoic acid (Z)- (CAS)
30	19.235	19.015	19.395	42879303	7.10	6846298	10.04	6.26		Pentadecane
31	19.495	19.395	19.715	14113392	2.34	892721	1.31	15.81		Benzenepropenoic acid, alpha.,beta.-dim
32	19.897	19.715	20.035	43082365	7.13	4580242	6.72	9.41		Tetradecanoic acid, ethyl ester (CAS)
33	20.140	20.035	20.295	11455059	1.90	851272	1.25	13.46		3-Methyl-2-butenoic acid, 4-tridecyl ester
34	20.335	20.295	20.435	4288771	0.71	515726	0.76	8.31		Dodecanoic acid (CAS)
35	20.502	20.435	20.755	9714010	1.61	886665	1.30	10.96		a-Nonylcyclohexene
36	20.813	20.755	20.935	5426489	0.90	1087242	1.59	4.99		2-methyloctacosane
37	20.995	20.935	21.115	3066572	0.51	581061	0.85	5.28		Pentadecane, 3-methyl- (CAS)
38	21.291	21.115	21.575	31710674	5.25	3713221	5.45	8.54		Dodecanoic acid (CAS)
39	21.714	21.575	21.835	27304761	4.59	6558339	9.62	4.22		Hexadecane (CAS)
40	21.995	21.835	22.135	4536629	0.75	266784	0.39	17.00		Cyclohexene, 1-(1,1-dimethylethoxy)-4-m
41	22.220	22.135	22.395	1182097	0.20	171196	0.25	6.90		trans-2-Dodecenoic acid
42	22.508	22.395	22.935	39648113	6.57	2351434	3.45	16.86		Pentadecanoic acid (CAS)
43	23.036	22.935	23.295	17827288	2.95	1186822	1.74	15.02		9-Octadecenoic acid (Z)- (CAS)
44	23.450	23.295	23.515	36620255	6.06	3615768	8.24	6.52		Pentadecanoic acid, ethyl ester
45	23.587	23.515	23.715	33703171	5.58	4566811	6.70	7.38		9-Octadecenoic acid (Z)- (CAS)
46	23.791	23.715	23.875	21463788	3.55	3249302	4.77	6.61		Pentadecanoic acid, ethyl ester
47	23.901	23.875	24.135	13572588	2.25	1175390	1.72	10.55		n-Pentadecanol
48	24.302	24.135	24.395	19536999	3.24	2107339	3.09	9.27		Pentadecanoic acid (CAS)
49	24.483	24.395	24.675	28713383	4.75	3731221	5.47	7.70		n-Nonadecanol-1
50	24.745	24.675	24.915	6570211	1.09	729768	1.07	9.00		3-Methyl-1,4-diazabicyclo[4.3.0]nonan-2,
				603888935	100.00	68167097	100.00			

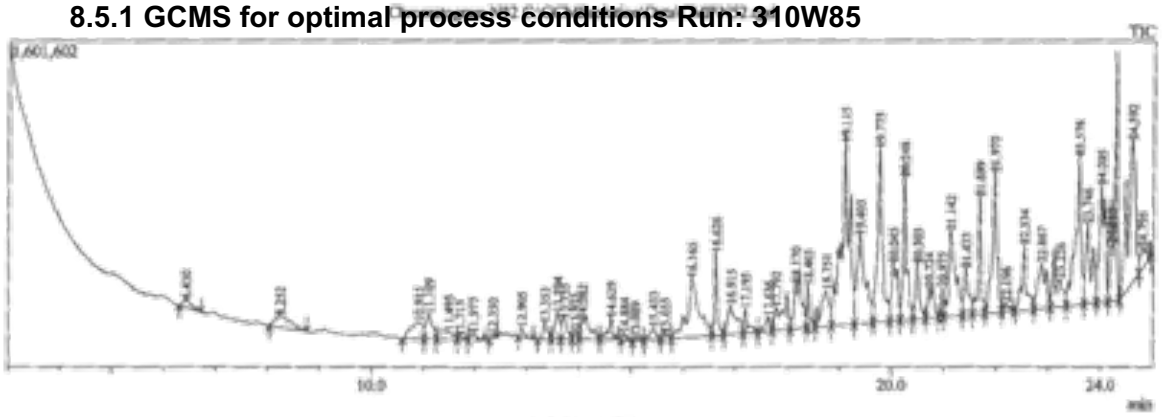
Figure 8.4.4 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 310ºC, solvent H2O/E and 95% solvent content

8.5 The effect of solvent type on the functional groups with respect to the optimal conditions.

The data for run 310EW75% temperature 310°C is presented in Figure 8.2.1

Figure 8.5.1: Run 310E75%
Figure 8.5.2: Run 310W75%

8.5.1 GCMS for optimal process conditions Run: 310W85

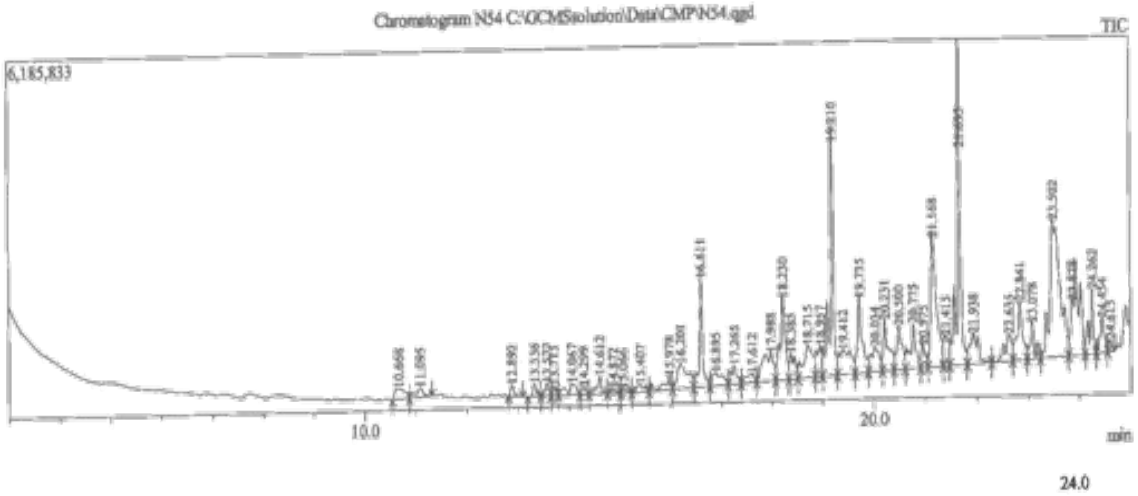


Peak Report TIC

	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
	6.430	6.295	6.715	440769	0.43	35047	0.29	12.58		1H-Pyrrole-2-carboxaldehyde (CAS)
	8.252	8.035	8.755	1157305	1.12	55390	0.46	20.89		Phenol, 4-methyl- (CAS)
	10.915	10.595	11.015	1344509	1.30	80547	0.66	16.69		Hexanoic acid, 1-methyloctyl ester (CAS)
	11.109	11.015	11.255	1109250	1.07	123384	1.01	9.00		Dodecane (CAS)
	11.495	11.255	11.655	822476	0.80	41985	0.35	19.59	V	Heptadecane (CAS)
	11.715	11.655	11.875	143975	0.14	18283	0.15	7.87	V	Dodecane, 4-methyl-
7	11.977	11.875	12.195	248984	0.24	34435	0.28	7.23	V	5-Hydroxymethyl-2,2,5-trimethyl-1,3-dio
8	12.350	12.275	12.435	111565	0.11	21351	0.18	5.23		4-(Ethylamino)-6-hydroxypyrimidine
9	12.905	12.835	13.135	244452	0.24	45077	0.37	5.42		Docosane (CAS)
10	13.353	13.215	13.475	532048	0.51	87421	0.72	6.09		Hexadecane (CAS)
11	13.594	13.475	13.635	851444	0.82	129726	1.07	6.56	V	Ether, hexyl t-butyl
12	13.735	13.655	13.875	835987	0.81	107762	0.89	7.76	V	(S)-2-Acetamido-2-methylsuccinic acid
13	13.935	13.875	14.015	301207	0.29	48943	0.40	6.15	V	HEXADECANE, 2,6,10,14-TETRAMET
14	14.082	14.015	14.415	1231806	1.19	92146	0.76	13.37	V	4-Pentenoic acid, 2-methyl-, heptadecyl es
15	14.629	14.415	14.755	645016	0.62	109773	0.90	5.88	V	Heptadecane
16	14.884	14.815	15.015	153988	0.15	35028	0.29	4.40		Eicosane
17	15.089	15.035	15.235	167880	0.16	20417	0.17	8.22		2,6,10-Trimethyltridecane
18	15.433	15.255	15.575	483152	0.47	65370	0.54	7.39	V	CYCLOPROPANE, NONYL-
19	15.655	15.575	15.775	229857	0.22	35016	0.29	6.56	V	1-Decanol, 2,2-dimethyl-
20	16.165	15.775	16.555	4686021	4.54	289006	2.38	16.21	V	Decanoic acid (CAS)
21	16.626	16.555	16.775	1607803	1.56	376475	3.09	4.27	V	Tetradecane (CAS)
22	16.915	16.775	17.155	1677583	1.62	141632	1.16	11.84	V	Fumaric acid, 2,4,4-trimethylpentyl but-3-
23	17.195	17.155	17.435	623240	0.60	114434	0.94	5.45	V	Hexadecane (CAS)
24	17.636	17.435	17.715	406126	0.39	72704	0.60	5.59		HENTRIACONTANE
25	17.792	17.715	18.055	1840468	1.78	112915	0.93	16.30	V	Undecanoic acid (CAS)
26	18.170	18.055	18.375	2724532	2.64	229393	1.89	11.88	V	1,2-Benzenedicarboxylic acid, dinethyl es
27	18.403	18.375	18.535	793735	0.77	204837	1.68	3.87	V	Nonadecane (CAS)
28	18.751	18.535	18.855	2080217	2.01	179966	1.45	11.82	V	Octadecanoic acid (CAS)
29	19.115	18.855	19.295	10298728	9.97	922563	7.58	11.16	V	Eicosane
30	19.403	19.295	19.655	4831466	4.68	429135	3.53	11.26	V	1-Dodecanamine, N,N-dimethyl- (CAS)
31	19.775	19.655	19.975	5798837	5.61	880501	7.24	6.59	V	PHENOL, 2,4-BIS(1,1-DIMETHYLETH
32	20.045	19.975	20.175	2198549	2.13	274946	2.26	8.00	V	Eicosane
33	20.248	20.175	20.415	3655683	3.54	716554	5.89	5.10	V	Eicosane
34	20.503	20.415	20.655	1536874	1.49	273446	2.25	5.62	V	Docosyl octyl ether
35	20.724	20.655	20.915	1178722	1.14	143572	1.18	8.21	V	Hexadecane, 2,6,10,14-tetramethyl- (CAS
36	20.975	20.915	21.015	437868	0.42	127984	1.05	3.42	V	Hexadecane, 2,6,10,14-tetramethyl- (CAS
37	21.142	21.015	21.375	4003917	3.88	418454	3.44	9.57	V	Dodecanoic acid (CAS)
38	21.433	21.375	21.555	1371903	1.33	249731	2.05	5.49	V	Hexamethylene diacrylate
39	21.699	21.555	21.795	2464304	2.39	569900	4.68	4.32	V	Hexadecane (CAS)
40	21.970	21.795	22.115	4516083	4.37	688714	5.66	6.56	V	Cedrane, 8-propoxy-
41	22.196	22.115	22.335	313524	0.30	42829	0.35	7.32	V	Tetradecane, 4-methyl- (CAS)
42	22.534	22.355	22.715	2096570	2.03	327669	2.69	6.40		Hexadecane, 2,6,10,14-tetramethyl- (CAS
43	22.867	22.715	23.035	2505270	2.42	218394	1.79	11.47	V	Hexadecane (CAS)
44	23.226	23.035	23.335	2174208	2.10	129738	1.07	16.76	V	Octadecane, 5-methyl-
45	23.578	23.335	23.675	5438217	5.26	743436	6.11	7.31	V	PENTACOSANE
46	23.746	23.675	23.915	3250147	3.15	377796	3.10	8.60	V	Hexadecane, 2,6,10,14-tetramethyl- (CAS
47	24.005	23.915	24.135	4597746	4.45	553156	4.55	8.31	V	1-Ethylcyclohexanol
48	24.215	24.135	24.355	5345565	5.17	365111	3.00	14.64	V	2,3,7-TRIMETHYLOCTANAL
49	24.592	24.355	24.715	7016416	6.79	701841	5.77	10.00		3-Methyl-1,4-diazabicyclo(4.3.0)nonan-2,
50	24.795	24.715	24.915	797389	0.77	108773	0.89	7.33	V	Hexadecane, 2-methyl- (CAS)
				103323359	100.00	12168604	100.00			

Figure 8.5.1 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 310ºC, solvent H2O and 85% solvent

8.5.2 GCMS for optimal process conditions Run: 310E85



Peak Report TIC

Peak#	R.Time		F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.668		10.875	2665582	1.00	187298	0.56	14.23		2-Piperidinone
2	11.095	10.875	11.315	1832578	0.69	165972	0.50	11.04	V	Dodecane (CAS)
3	12.892	12.815	13.095	1046943	0.39	199962	0.60	5.24		2-Hexyl-1-octanol
4	13.336	13.195	13.455	1077344	0.41	230035	0.69	4.68		Heptadecane, 8-methyl- (CAS)
5	13.577	13.455	13.655	1427071	0.54	225459	0.68	6.33	V	Ether, hexyl t-butyl
6	13.715	13.655	13.795	1148141	0.43	175045	0.52	6.56	V	Hexadecane, 2,6,10,14-tetramethyl- (CAS
7	14.067	13.795	14.215	2784052	1.05	193502	0.58	14.39	V	2-Isopropyl-5-methyl-1-heptanol
8	14.299	14.215	14.395	821072	0.31	142126	0.43	5.78	V	2-Isopropyl-5-methyl-1-heptanol
9	14.612	14.395	14.755	1971918	0.74	308631	0.92	6.39	V	Eicosane
10	14.872	14.755	15.015	619758	0.23	102446	0.31	6.05	V	Hexadecane, 2,6,10,14-tetramethyl- (CAS
11	15.066	15.015	15.235	514525	0.19	68868	0.21	7.47	V	Eicosane
12	15.407	15.235	15.575	1448633	0.55	129697	0.39	11.17		E,E,Z-1,3,12-Nonadecatriene-5,14-diol
13	15.978	15.575	16.035	2622322	0.99	242495	0.73	10.81	V	Hexadecane, 2,6,10,14-tetramethyl- (CAS
14	16.201	16.035	16.455	6446481	2.43	420778	1.26	15.32	V	Decanoic acid (CAS)
15	16.611	16.455	16.775	8659143	3.26	1896853	5.68	4.57	V	Tetradecane (CAS)
16	16.895	16.775	17.135	3264306	1.23	220966	0.66	14.77	V	Dodecane (CAS)
17	17.265	17.135	17.395	2741698	1.03	303542	0.91	9.03	V	1H-Indene, octahydro-2,2,4,4,7,7-hexame
18	17.612	17.395	17.695	1796738	0.68	147320	0.44	12.20	V	Hexadecane (CAS)
19	17.988	17.695	18.075	7498758	2.82	491885	1.47	15.24	V	Tetradecane, 5-methyl- (CAS)
20	18.230	18.075	18.335	10061573	3.79	1420145	4.26	7.08	V	Nonadecane (CAS)
21	18.385	18.335	18.515	3295055	1.24	427332	1.28	7.71	V	PENTACOSANE
22	18.715	18.515	18.855	7426895	2.80	569057	1.71	13.05	V	Undecanoic acid (CAS)
23	18.957	18.855	18.995	3796854	1.43	535703	1.61	7.09	V	Tetracosane (CAS)
24	19.210	18.995	19.295	21160296	7.97	4066090	12.18	5.20		Pentadecane
25	19.412	19.295	19.635	7110033	2.68	430327	1.29	16.52		Eicosane
26	19.735	19.635	19.895	8702103	3.28	1340985	4.02	6.49	V	PHENOL, 2,4-BIS(1,1-DIMETHYLETH
27	20.034	19.895	20.175	5142681	1.94	430855	1.29	11.94	V	Carbonic acid, eicosyl vinyl ester
28	20.231	20.175	20.395	5988600	2.25	881669	2.64	6.79	V	Docosane (CAS)
29	20.500	20.395	20.615	5697776	2.15	754492	2.26	7.55	V	(1-METHYLUNDECYL)CYCLOHEXA
30	20.775	20.615	20.915	5942844	2.24	696111	2.09	8.54	V	Eicosane (CAS)
31	20.975	20.915	21.055	2340082	0.88	456986	1.37	5.12	V	Pentadecane, 3-methyl- (CAS)
32	21.168	21.055	21.355	18708855	7.04	2262949	6.78	8.27	V	Dodecanoic acid (CAS)
33	21.415	21.355	21.475	3324109	1.25	533609	1.60	6.23	V	Hexamethylene diacrylate
34	21.695	21.475	21.815	25225643	9.50	4829083	14.47	5.22	V	Hexadecane (CAS)
35	21.938	21.815	22.275	5897078	2.22	538320	1.61	10.95	V	Cedrane, 8-propoxy-
36	22.635	22.275	22.695	4389978	1.65	459173	1.38	9.56	V	9-Octadecenoic acid (Z)- (CAS)
37	22.841	22.695	22.975	7900125	2.97	997168	2.99	7.92	V	Pentadecane, 2,6,10-trimethyl-
38	23.078	22.975	23.235	3906571	1.47	656168	1.97	5.95	V	Pentadecanoic acid, ethyl ester
39	23.502	23.235	23.795	33241230	12.52	2387787	7.15	13.92	V	9-Octadecenoic acid (Z)- (CAS)
40	23.878	23.795	24.115	15803759	5.95	1001143	3.00	15.79	V	1-Octadecene (CAS)
41	24.262	24.115	24.335	5592479	2.11	1016381	3.05	5.50	V	Docosane (CAS)
42	24.454	24.335	24.555	3653480	1.38	623715	1.87	5.86		PENTACOSANE
43	24.615	24.555	24.695	909212	0.34	207017	0.62	4.39	V	Tetratriacontane (CAS)

Figure 8.5.2 The total ion chromatogram of bio-oil from municipal sewage sludge HTL attained where the temperature was 310ºC, solvent ethanol and 85% solvent

8.6 Concentration of dominant compounds at different conditions

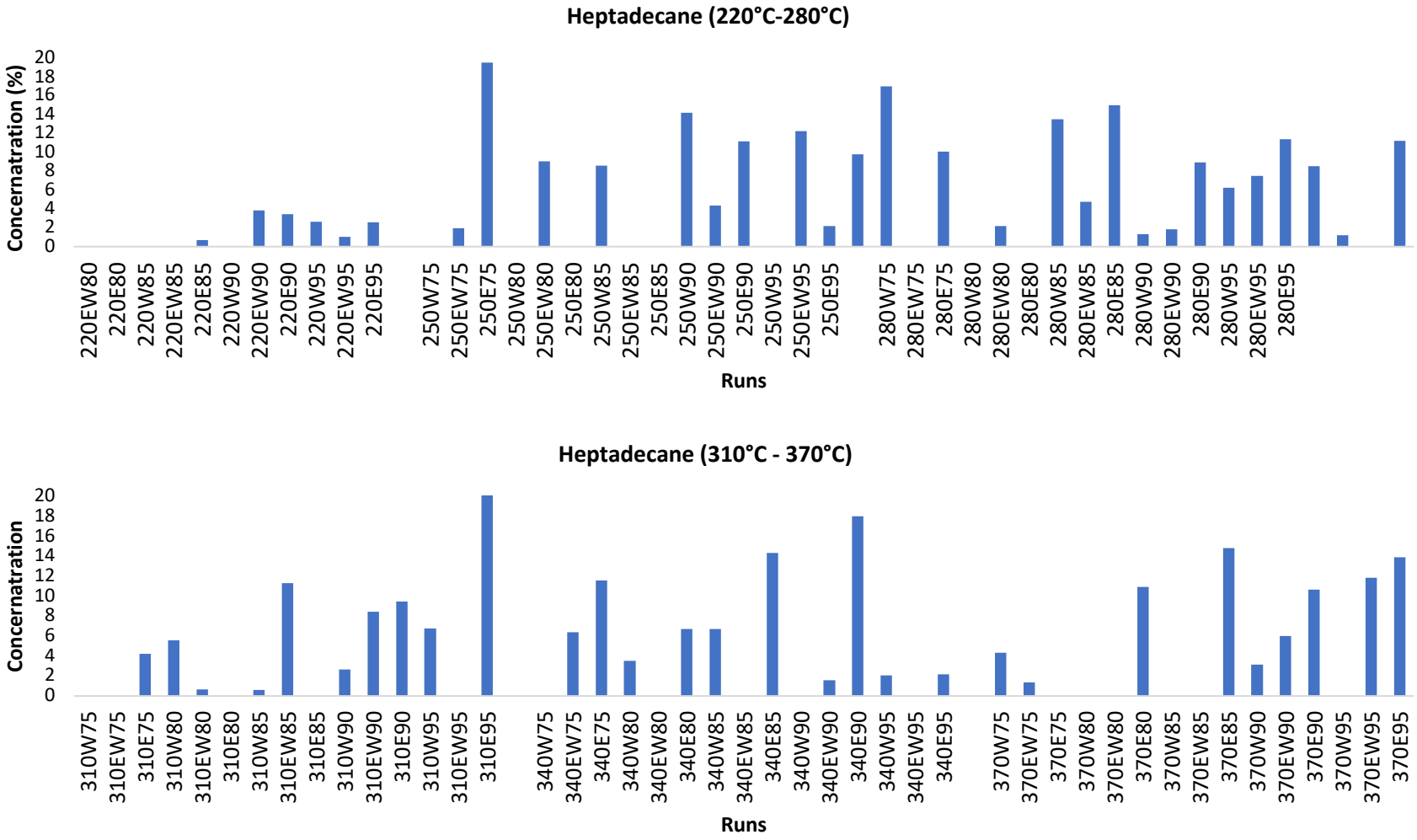


Figure 8.6.1 The concentration of heptadecane under different conditions

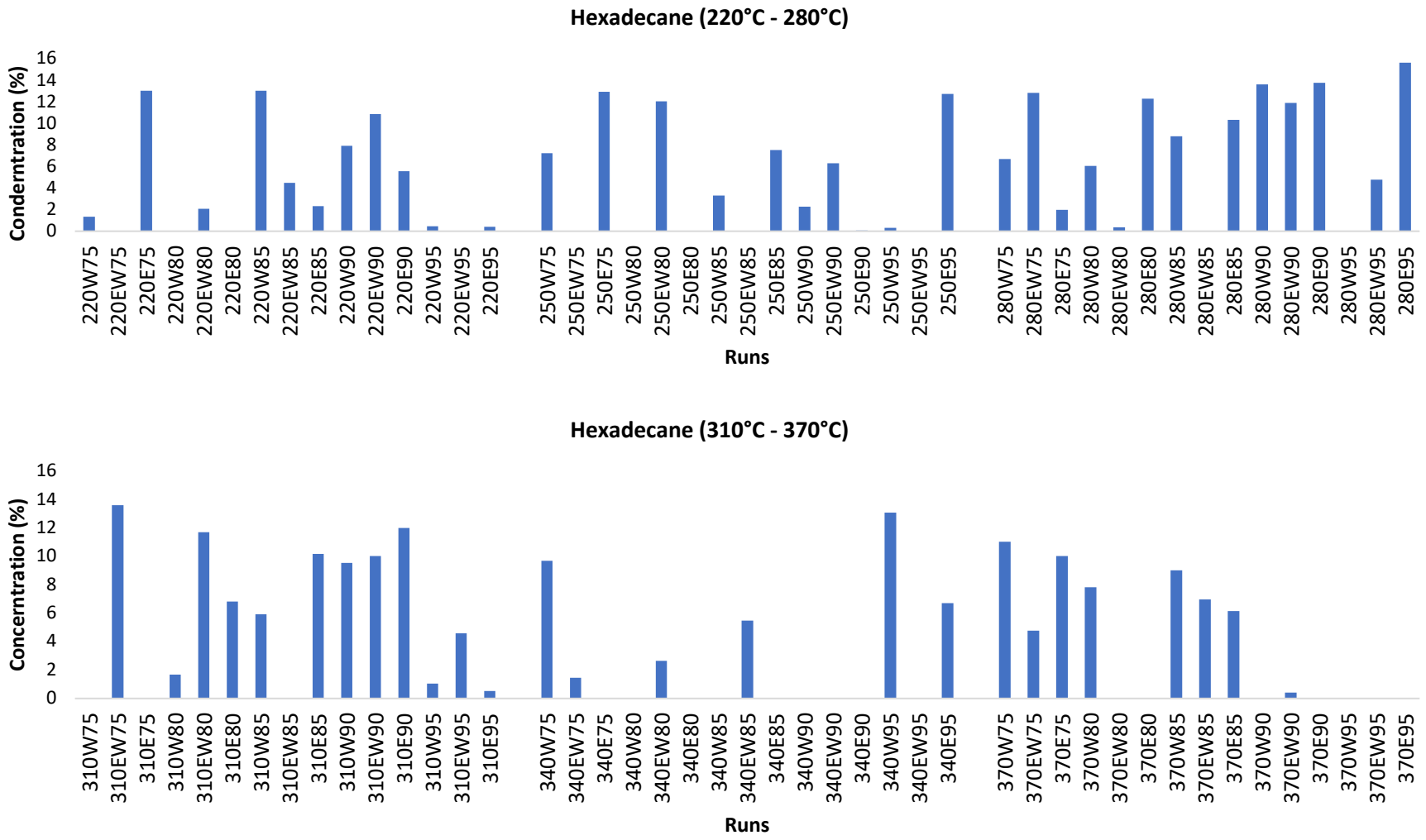


Figure 8.6.2 The concentration of hexadecane under different conditions

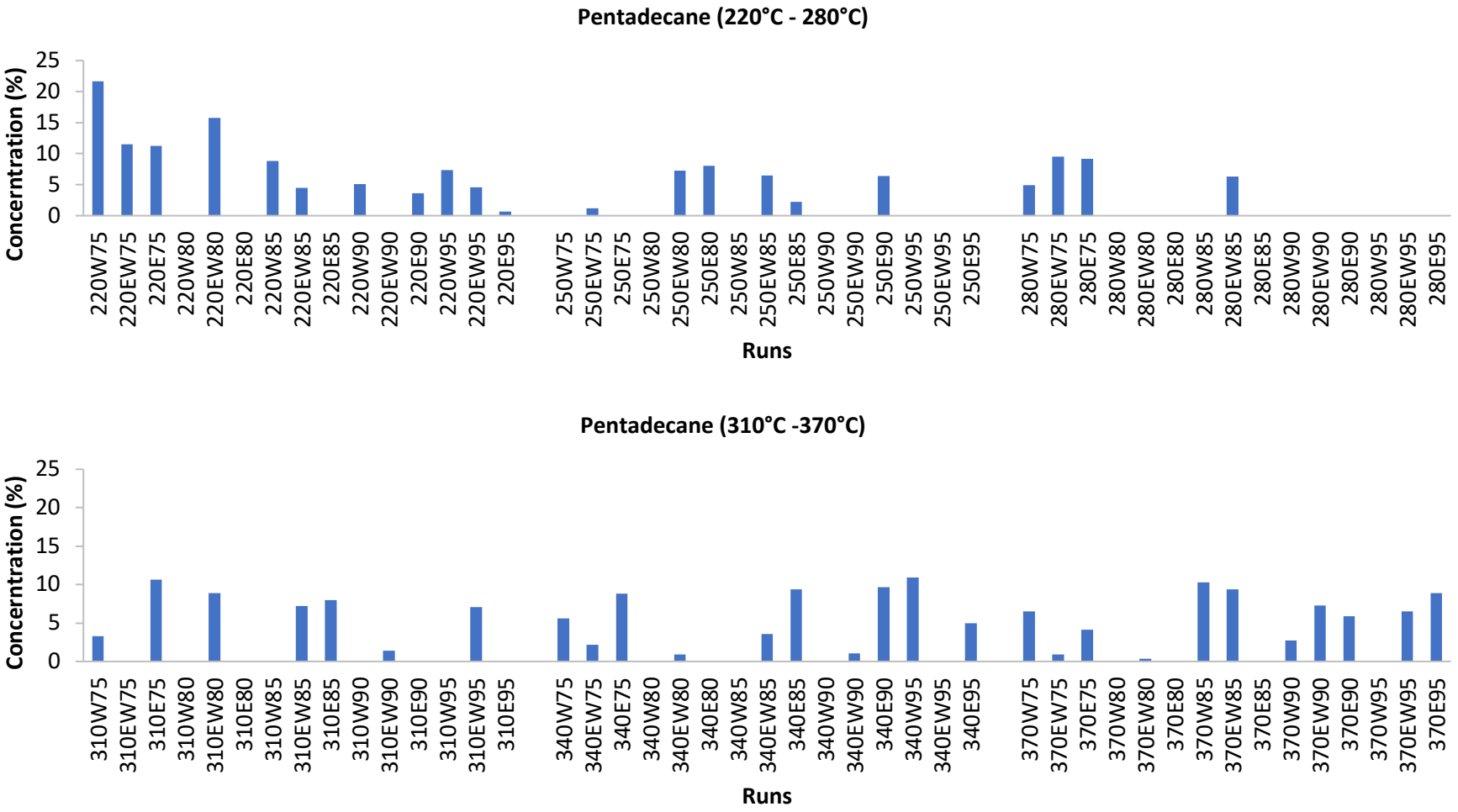


Figure 8.6.3 The concentration of pentadecane under different conditions

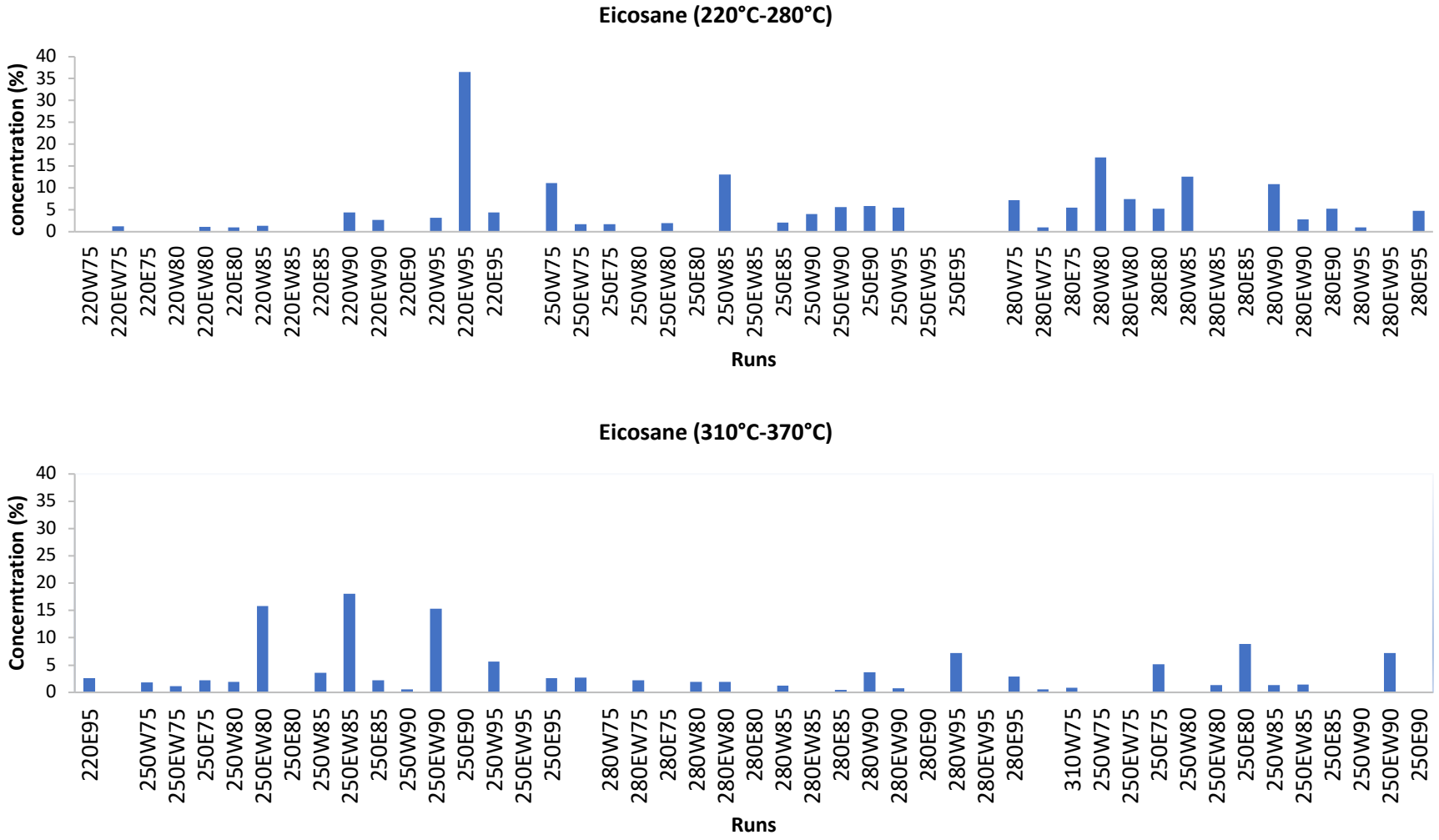


Figure 8.6.4 The concentration of eicosane under different conditions

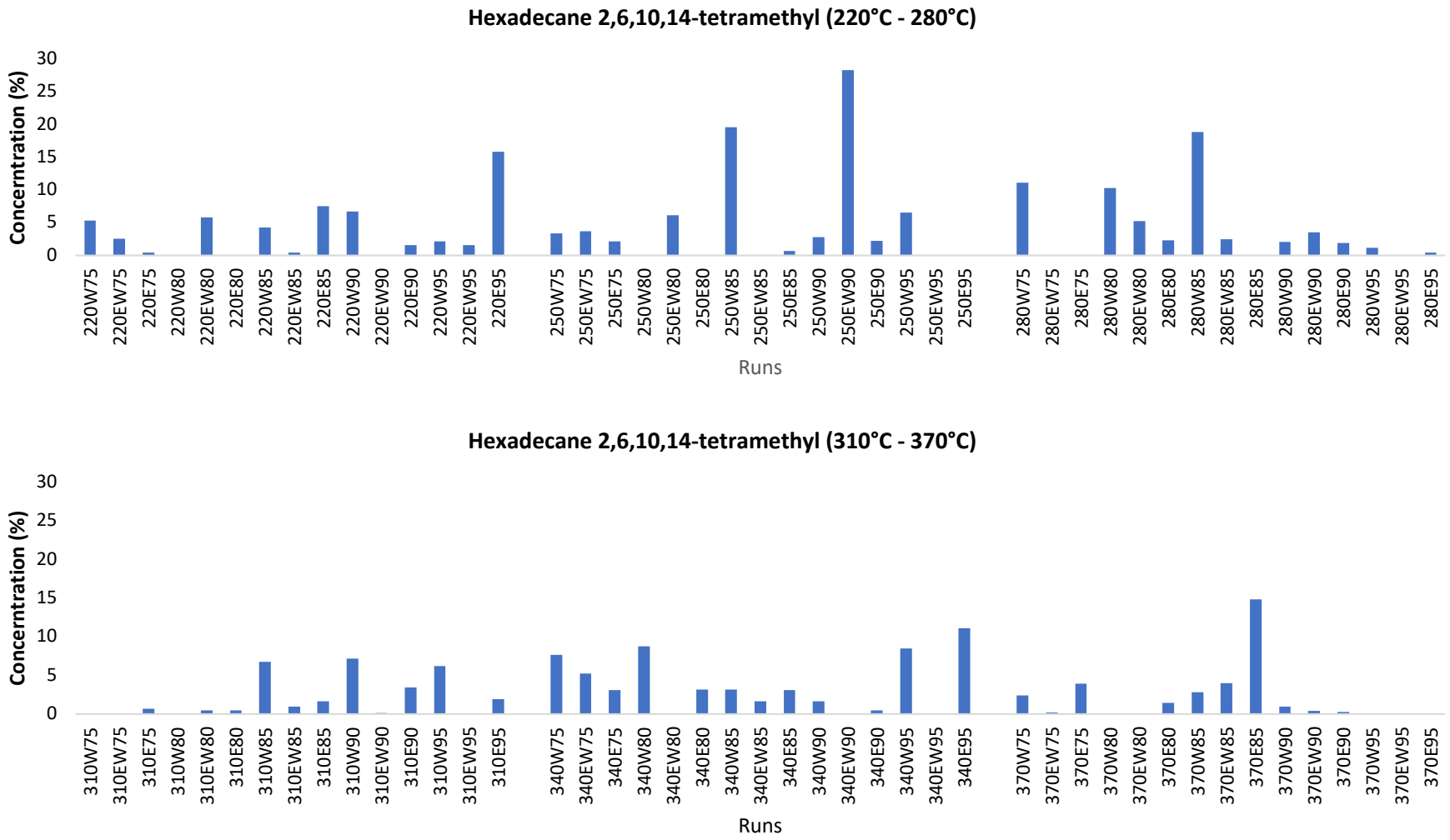


Figure 8.6.5 The concentration of hexadecane 2,6,10,14-tetramethyl under different conditions

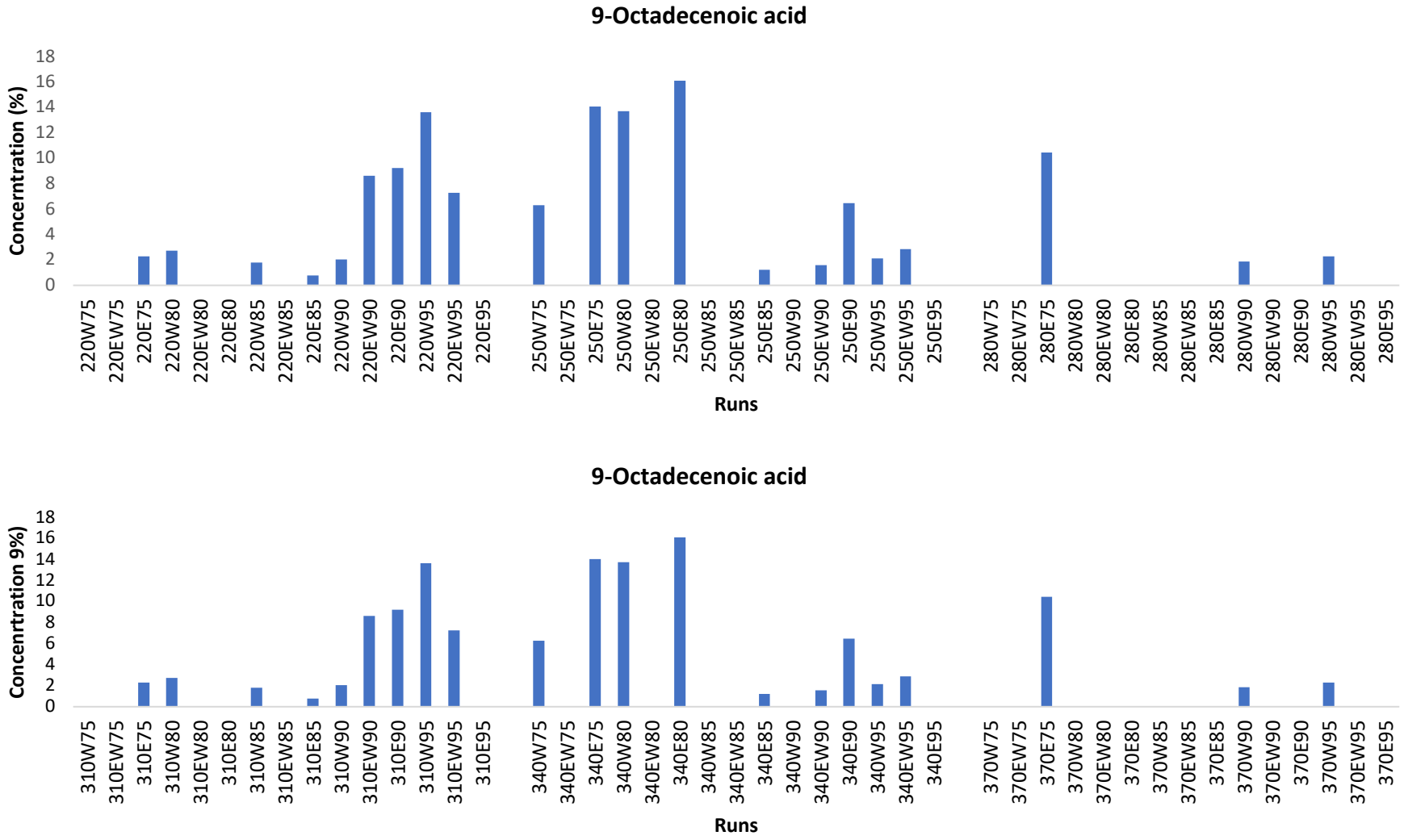


Figure 8.6.6 The concentration of 9-Octadecane under different conditions