



Energy and Resources Recovery from Gasified Screenings and Toxic Sludge

MSc (50/50) RESEARCH REPORT

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Abstract

Sludge and screenings management has been and is increasingly becoming a dilemma in recent decades due to increasing population and accumulation of toxins in wastewater sludge, caused by complex toxins in industrial, hospital, residential, agricultural and other effluents. Various sludge management options have been researched, ranging from incineration, thermochemical liquefaction, to pyrolysis and gasification.

This work proposes syngas, bio-oil and bio-char or char production through gasification of a mixture of sludge and screenings at different ratios of 25/75, 50/50 and 75/25. Triplicate samples of each ratio were produced from sludge and screenings that were collected from Olifantsfontein, Gauteng, South Africa. The analysis to find the toxins, metals resources in sludge, approximate analysis, CHNS and functional group analysis were aimed at finding if sludge is a good high energy matter. From a thermogravimetric analysis (TGA), the sampling and stopping temperatures during gasification were established. The overall best results of high syngas quality (high LHV, H_2 , CO and CH_4 contents) and high quality bio-oil (i.e. cleanest, with high crude oil equivalent bonds such as C_1 up to C_{36} and higher applicable bio-oil resources and chemical names obtained) was achieved by a 75/25 ratio, followed by a 50/50 ratio. The results also showed some possibility of biological and chlorinated hydrocarbon toxins such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) break down as well as reduction of sludge and screenings to about 32% of the initial mass.

The application of these results range from syngas application in power generation, to liquid fuel production through the Fischer-Tropsch synthesis (FTS). Char toxicity can be further analysed for its application in agriculture and as an adsorbent in other processes. Char can also be further analysed for metal extraction.

List of abbreviations and nomenclature

List of abbreviations and nomenclature in alphabetical order

Aerobic	That need oxygen to survive
Anaerobic	That do not need oxygen to survive
Anoxic	Without dissolved oxygen
BNR	Biological nutrient remover
BP-sludge	Belt-Pressed sludge
CHNS	Carbon, hydrogen, nitrogen and sulphur analysis
GC-MS	Gas chromatography - mass spectrometry
ERWAT	East Rand Water Care Company
Holding time	Time when temperature remains constant when the gas is collected
LHV	Lower Heating Value, a measure of the energy obtainable in fuel
LPG	Liquid Petroleum Gas
OPEC	Organization of Petroleum Exporting Countries
PAHs	Poly aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PST	Primary settling tank
RAS	Reverse activated sludge
RT	Retention time
SA	South Africa
TGA	Termogravimetric analysis
UJ	University of Johannesburg
US	United States of America
WAS	Waste activated sludge
WWTP	Wastewater treatment plant
WWTW	Wastewater treatment works

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Chapter 1. INTRODUCTION

1.1 Significance of specified problems

Sludge is a residue of wastewater, which is a mixture of primary mineral grains and fragments of biological and industrial materials (Fericelli, 2011). Screenings are the solids that flow within the wastewater body that include solids such as nappies, plastics, solids and solid sludge. Sludge toxicity is a current global challenge. Sludge and screenings are products of wastewater. Wastewater contains domestic and industrial wastes. Domestic sewage is more likely to have disease-causing microbes and it also contains harmful chemicals from house cleaning chemicals (Planetary Notions, 2002). Wastewater toxicants can result in health issues such as gastrointestinal disorders that are linked with viruses that are in sewage effluent. Detergents in washing powders can result in liver and kidney damage. Sewage water carries diseases such as giardiasis, amoebic dysentery and cholera (Planetary Notions, 2002).

Industrial waste can include heavy metals, organic compounds; mining waste, electroplating, metal processing, textile, battery manufacturing, petroleum refining, paint, pesticides, printing and waste from photographic industries. All the processes such as metal processing, petroleum refining, pesticide manufacturing are sources of heavy metals (Islam, et al., 2016). Metals such as chromium, nickel, copper, arsenic, cadmium, mercury and lead have been documented as hazardous elements (Islam, et al., 2016). The current and future generations' lives are at risk without clear screenings disposal guidelines. On the other hand, screenings have not been thoroughly investigated with regards to toxicity and energy contribution, although screenings are among the major toxicity and energy carriers in the wastewater treatment process.

Sludge and screenings are accumulating due to the population growth and urbanization. This phenomenon increases sludge cost (toxicity and disposal costs), the cost to process and transport the sludge is escalating as well (Lumley, et al., 2014). The sludge processing and disposal cost is estimated to be above 50% of the overall wastewater process cost. This is in addition to the challenge of rising wastewater treatment works (WWTWs) running costs. South Africa's economy is not growing as expected, meaning that the national treasury budget will continue to decline, and thus causing strain on municipalities' funds and therefore the running of WWTWs. There is therefore a growing need to improve every plant's energy balance and thus avoiding wastage of resources, with the aim of improving on financial savings.

South Africa has little liquid fuel energy generated locally. Most of the liquid fuel energy utilized in the country is imported. This trend exposes the country to foreign instabilities and exchange rates. There is therefore a growing need to protect the country from exposure to foreign instabilities, in order to protect local interests (businesses, political and academia).

1.2 Justification of the research

This research project was chosen because it responds to life threatening toxicity (biological), it attempts to deal with toxic chemicals in wastewater sludge, such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) that are a treat to the current public and to the generations to come. This topic also paves a way towards sustainable, green and renewable energy that the world is trying to adopt, by using toxic waste (sludge and screenings) which is a current global challenge.

This project is unique as it attempts to address two challenges (sludge and screenings disposal), in a resource beneficial way. Although current research on sludge is beneficiation driven, very little researched work focused on sludge and screenings for beneficiation. This means that screenings disposal with beneficiation potential has not been thoroughly looked at, especially with sludge in a mix.

Lumley et al. (2014) simulated various biomass feedstock (Wastewater sludge, pine wood, corn straw and municipal solid waste) for gasification to compare their energy values. Municipal solid waste is the closest biomass to screenings, meaning that its properties should be close to those of screenings. This generally means that screenings can be used as biomass, and therefore the research is possible.

Despite solving waste disposal challenges from the wastewater works, this solution can be extended to the Municipal solid waste disposal dilemma (Young, 2010). If this research is further developed, it can result in land conservation. This would be due to landfills not being fed at the same current rate with waste. This would be caused by the rechanneling of waste to resources recovery (Young, 2010) .

There is a potential for products from this research, finding applications as feedstock to the synthetic fuels production for vehicles and machines, and clean synthetic gas (syngas) can also be used directly in energy generation (Young, 2010). Bio-oil products can be used in the production of bio-diesel, wax, lubricants and chemicals. Further research in bio-char can result in the use of bio-char as an adsorbent in WWTW processes or as a fertilizer in the agricultural industry.

1.3 Contribution of the research

The results of this research can assist:

Wastewater treatment works (WWTW) in disposing their sludge and screenings safely and gaining income during that process through syngas, bio-oil and bio-char sales.

By providing locally produced gas, liquid energy and chemical process feedstock from wastewater waste (sludge and screenings). That process will help the country towards green economy, and also the use of locally produced sludge and screenings would be good for circular economy.

If further developed with clean syngas for power generation for WWTWs or plant sections and that will result in huge savings on escalating energy costs that are currently draining WWTWs.

If successful, the project will assist towards cost savings on plant maintenance (reduction of digestion systems such as heating, pumping and piping) and on the plant process (if digestion can be eliminated or reduced).

With informed decision around sludge treatment and disposal as well as screenings landfilling costs that include process installation, maintenance, process consumables and energy costs. Those costs can possibly be substituted by saleable syngas and potentially bio-toxic free soil nutrient for farmers.

With a new way of addressing challenges with methane venting to the atmosphere. This will be due to sludge methane being gasified with

syngas. With this solution, the problematic methane will be sold and used as an energy source in the syngas, thus protection our environment while creating revenue.

1.4 Practical applications of the proposed investigation

If this investigation was to be piloted, it could be used in wastewater treatment works (WWTW). The screenings (plastics, rags, papers and cloths) that are separated at the inlet of the plant can be mixed with raw sludge that settles at the primary settling tank (PST) and the activated sludge from the biological nutrient remover (BNR) reactor and clarifiers. The pre-digested sludge can go through the gasification process with screenings to yield syngas, bio-oil and bio-char.

This sludge process flow will save the sludge treating process costs. These costs include process installation, maintenance, process consumables and energy costs. The system or process arrangement would look like figure 1.1.

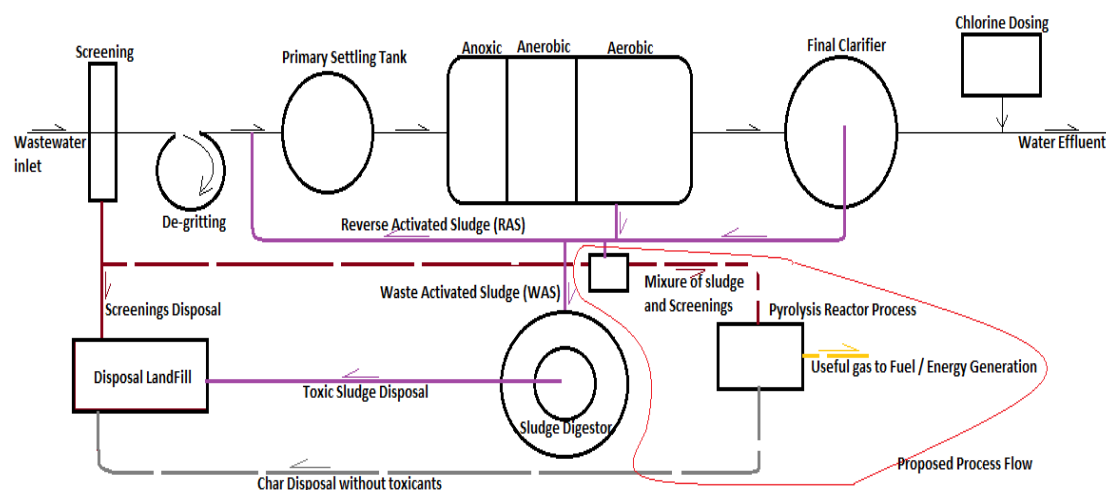


Fig 1. 1: Potential process flow from further development of this investigation

From figure 1.1, note the gas (for fuel and power generation) benefits that does not exist on the current plant configuration, there is also bio-oil and bio-char potential benefits.

The methane (CH_4) gas from sludge currently vented to the atmosphere will be used profitably. This potential process will result in numerous environmental and economic gains if further developed and implemented.

1.5 Problem statement

The current problems that triggered the investigation are:

The life threatening sludge toxicity (biological and chlorinated hydrocarbons) to the current public and to the generations to come. The accumulation in sludge and screenings production increases the cost of sludge handling such as sludge processing, transportation and disposal.

Tightening environmental regulations and public awareness on toxins in sludge render old disposal methods environmentally unfriendly. Public awareness means the freedom to dump any waste can be policed and reported by general public. Therefore, a need to meet tightening environmental regulations is becoming higher.

The current venting of methane to the atmosphere is loss of energy that wastewater treatment plants should take advantage of, in this rising electricity prices. There is a need to have a sludge disposal method that improves the wastewater treatment plant's energy balance.

The current and future ESKOM (South African electricity public utility, founded in 1923 as per the Electricity Act of 1922) challenges, the rising

fuel price and the reliance of South Africa on imported fuel and fuel sources, thus exposing the country to global dynamics (political and economic instabilities). These problems will affect power and energy consumers; therefore, a need exist to research alternative energy sources to avoid being victims to such challenges.

1.6 Research objectives

The objectives of this research study are therefore to:

- Determine if gasification can completely destroy toxins (biological and chlorinated hydrocarbons) in sludge and screenings and to see if gasification can completely eliminate the toxicity that ends up in landfills through sludge and screenings disposal.
- Determine bio-char elemental contents after gasification using total carbon, hydrogen, nitrogen and sulphur (CHNS) analysis, with the aim of seeing the elemental composition after gasification. This analysis will look for any remaining carbon and the possibility of polychlorinated biphenyls (PCBs) and poly aromatic hydrocarbons (PAHs) paralysis by gasification.
- Determine the amounts of syngas contents such as carbon monoxide (CO), hydrogen (H₂), methane (CH₄) and carbon dioxide (CO₂) at pyrolysis temperature of 400°C and at the gasification temperature of 1000°C in each experimental run of sludge/screenings ratio of 50/50, 75/25, 25/75, 100/0 and 0/100.
- Determine from the above results, the important gasification parameters such as: the gasification conditions (CO/(CO+H₂)), the

gas quality (H_2/CO), the syngas heating value ($LHV = 0.126 \times CO + 0.108 \times H_2 + 0.358 \times CH_4$) (Werle, 2015a) as per each sample run triplicated.

- Determine carbon chains (C_1 to C_{36}) in bio-oil and thus product diversity, bio-oil cleanliness (C-H and C-H-O bonds only) comparison by amount of particulates and bio-oil volume per sample run (based on sludge/screenings ratio) triplicated.

Chapter 2. LITERATURE REVIEW

2.1 Sludge and screenings production

Wastewater sludge and screenings originate from wastewater treatment process. Sludge is a residue generated during primary (physical and chemical), secondary (biological) and tertiary (often nutrient removal) treatment (Werle, 2013). Wastewater contains domestic and industrial wastes. Domestic waste contains dissolved and suspended impurities such as organic materials that rot, the example would be plant matter, plant nutrients and disease causing microbes such as bacteria, viruses, protozoa and fungi (Planetary Notions, 2002; SDWF, 2017). Industrial waste can have toxic organochlorine contaminants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and dioxins or furans as well as metals such as aluminum, iron, and zinc etc. (Bridle & Pritchard, 2004).

2.2 Sludge disposal and energy challenges

Until recently, sludge was considered as a valueless material that was disposed of on landfills or thrown into the ocean (Werle, 2013; Planetary Notions, 2002). The increase in human waste due to escalating population, tighter environmental regulations and environmental sustainability as driven by climate change policy as recognized in the Kyoto Protocol (Werle, 2015a) results in current disposal options environmentally unacceptable. Escalating population makes it expensive to process, transport and store sludge and screenings as the land is getting limited (Suzuki, et al., 1988; Kim & Parker, 2008). Sludge treatment, transportation and disposal is estimated at between 50 and 60% of the total wastewater treatment plant running costs (Chen, et al., 2014), while metals, chemicals and biological toxins increase the environmental cost. The toxins that are currently disposed will affect future generation's environment and life.

Despite the toxins and their effect on the current and future life, researchers like Kim and Parker (2007) have looked at the positive side to sludge management and disposal. This had been majorly driven by the increase in unused sludge that competes with useful land, researchers are looking at alternative sludge management options that focus on turning sludge into a useful resource. Indeed despite toxins (biological, chemical and metals) in sludge, sludge has 60-80% organic matter and that organic matter comprise of 20-30% crude protein, 6-35% fats and 8-15% carbohydrates (Kim & Parker, 2008). Kim and Parker looked at converting sludge to bio-oil (organic liquids and tar), gases and char through pyrolysis process (thermal decomposition of organic substance under oxygen-free conditions). The challenge was the low oil yield (Kim & Parker, 2008). The yield would amount to 0.5% of global crude oil supply per year (Slowikowski, 2017). German and Canadian researchers also proposed converting sludge into heavy oil through pyrolysis and thermochemical liquefaction (Suzuki, et al., 1988). These studies did not promise net positive energy output, due to their high energy demand (Suzuki, et al., 1988).

2.3 Sludge energy analysis parameters

The huge initial energy demand is also due to the drying of sludge. Sludge is predicted to have an initial moisture content of about 98% (Suzuki, et al., 1988). This moisture can be reduced to about 70-80% by mechanical dewatering (Chen, et al., 2014), also depending on the dewatering system's efficiency. After collection, samples are normally stored below 4°C to avoid bacterial development that further digests the sludge, and thus altering its properties. Moisture content affects the calorific value of sludge, therefore drying the sludge improves its energy value (Chen, et al., 2014).

The approximate analysis is used to determine the moisture content as per ASTM D4442-07, ash and volatile matter as per ASTM D1762-84. The ultimate analysis is used to determine the elements like C, H, N, S and O. A bomb calorimeter on

the other hand was used to determine the calorific value of dried sewage sludge. Also, according to the study conducted by Cai et al. (2009), sludge does have functional groups similar to those of hydrocarbons, this is another indicator why researchers like Kim and Parker (2007), Werle (2013, 2015a, b) and others keep investigating sludge for liquid and solid fuel extraction.

2.4 Research studies on sludge's energy contribution

As a result of energy resources (C-H bonds) in sludge, various researchers have looked at sludge's potential to power cars. The major challenge discovered is the sludge's low heating value (LHV) when processed through pyrolysis process for oil production (Planetary Notions, 2002) and syngas production (Lumley, et al., 2014). Another challenge of converting sludge into energy resource is that of its diversity (sludge production varies from time to time and properties are influenced by the wastewater treatment process employed). As a result of these challenges, it is difficult to predict its energy value according to Kim and Parker (2007) and LaFarre et al. (2001). Studies by Slowikowski (2017) show low energy values when converting sludge into bio-crude oil. For example a single person would produce 7.58 to 11.37 liters of bio-crude oil per year (Slowikowski, 2017). This is between 379 and 568.5 Mega liters of bio-crude oil per year for South African population (estimated at 50 000 000 people), compared to its 3.5 Terra liters of imported crude oil (SAMSA, 2017). This amounts only to less than 1% contribution to imported national energy, which is comparable to 0.5% globally (Slowikowski, 2017). Screenings on the other hand have a high plastic content and plastics have a higher energy value of about 21.3MJ/kg than 16.7MJ/kg of sludge (Lumley, et al., 2014).

2.5 Screenings to improve the sludge's energy value

Indeed, the 21MJ/kg of energy from screenings would improve the average energy if mixed with the 16MJ/kg from sludge. In summary, screenings can complement the sludge's low energy value and probably make the process profitable. Studies on "garbage to fuel and electricity" do not cover screenings and toxic sludge (Young, 2010). These studies therefore leave a knowledge gap in the research space where there is a need to deal with environmental issues (toxicity of sludge and screenings from WWTWs), land use and toxic waste disposal all at the same time. This project therefore aims at solving the environmental issues associated with screenings and toxic sludge disposal, while responding to the energy and fuel needs of the country and land conservation.

2.6 Researched sludge disposal options

Sludge in WWTPs globally is still a major issue, even more with the escalating sludge production rates due to urbanization and population growth. These sludge production rates impose limits on current disposal processes such as landfilling (too much toxins leach into the ground), land application and incineration (volumes to dispose increase despite burning), rendering them environmentally unfriendly. Landfilling competes with the country's productive land and sludge toxins might reach ground water. Land application on the other hand can result in the accumulation of harmful components and metals in the soil. Although incineration (burning or combustion) of sludge reduces sludge volume (Suzuki, et al., 1988) and stabilizes organic matter in the sludge, its gas emissions are not environmentally friendly (Kim & Parker, 2008) and it is an expensive disposal method as suggested by Suzuki and Nakamura (2008). Various sludge disposal methods have been proposed by researchers that include the following:

Thermochemical conversion

Lumley et al. (2014) simulated various thermochemical conversion processes (TCCs) technologies for sludge conversion into a beneficial resource. The technologies evaluated included hydrothermal carbonization, combustion, pyrolysis and gasification. Hydrothermal carbonization process occurs in non-oxygenated water at pressures up to 2MPa and temperatures up to 400°C and it transforms organic feedstock into carbonaceous char called hydro char or synthetic coal. This process removes oxygen, nitrogen and some hydrogen from carbon backbones, and thus a simpler carbon containing molecule then tends to polymerize into poly-aromatic, hydrophobic solid with hydrogen/carbon and oxygen/carbon ratios similar to those of lignite (brown coal). Synthetic coal can then be recovered as a precipitate and used as a solid fuel. It requires little to no energy for dewatering and low activation energies of hydrolysis reaction makes it occur at low temperatures (Lumley, et al., 2014). The challenge with this process is the increase of wastewater it generates and the creation of poly-aromatics that are toxic to the environment (Lumley, et al., 2014).

Combustion (Incineration)

Combustion involves burning sludge, pre-dried in a furnace to decompose organic material, concentrate ash and produce high temperature flue gases at 800-2000°C at atmospheric pressures. The problem with this method is its emissions into the air, soil and water, for example its emissions include fly ash, SO_x, NO_x, HCl, Hg, Cd, dioxins and Furans (Fericelli, 2011). Combustion or incineration has a long history as a waste stabilization mechanism (Lumley, et al., 2014). Furthermore heat exchange surfaces may be fouled by metals and alkali salts vaporized during combustion (Lumley, et al., 2014).

Pyrolysis process

Pyrolysis on the other hand, subjects sludge to temperatures between 450°C and 650°C in an anoxic environment. This process produces three fractions, a solid char, oil or water-miscible liquid (bio-oil) and combustible gas. The product partitions into each phase depend on the fuel composition and reactor conditions (Lumley, et al., 2014). This process is typical for maximum bio-oil yield for upgrading to transportation fuel. The problem with this process is that oil needs further upgrading into transportation fuel.

Gasification

Gasification on the other hand converts carbonaceous feedstock into a combustible synthesis gas or syngas by partial oxidation in a reducing atmosphere and at high temperatures (Werle, 2015b). This process produces syngas composed of H₂, CO, CH₄, CO₂, H₂O, N₂, minor species and tar (Crocker, 2018). Sludge gasification takes place close to atmospheric pressure from 700 to 1000°C (Lumley, et al., 2014).

The promising part about sludge gasification is the production of energy with low emissions, reduction of sludge to reusable fuel gas and non-leaching, low volume dry residue that which is easy to dispose (Fericelli, 2011). Syngas produced can be burnt as is or can be further processed into synthetic fuel, using Fischer-Tropsch synthesis (Crocker, 2018). Gasification process would save further processing infrastructure as its further processing is less complicated than that of bio-oil from the pyrolysis of sludge. Sludge processing undergoes physical and chemical processes in the presence of steam in an oxygen-lean environment (Fericelli, 2011). The chemical environment of gasifiers inhibits dioxin, furan, NO_x and SO_x formation.

Werle (2015a) predicted the calorific value of syngas by a lower heating value equation $LHV = 0.126 \times CO + 0.108 \times H_2 + 0.358 \times CH_4$.

This equation was developed from syngas constituents. Chen et al. (2014) used 5g sludge samples and dried them for 24h at 105°C. In case of sludge and screenings one could use 10g, ± 5 g screenings and ± 5 g sludge based on the selected ratio at hand. Drying from 80 to 10% moisture is estimated at consuming 75% of the total energy available in sludge (Lumley, et al., 2014). Therefore, drying with toxic waste such as screenings or garbage would be eliminating toxic waste while saving heating energy during the drying process.

2.7 Gasification feedstock

From the studies conducted previously, it is clear that the most important characteristic of sewage sludge when thermal application is considered as a disposal method is its energy (thermal) content or the heating value (Fericelli, 2011; Werle, 2015a). This property is used as a priority for evaluating the potential of sewage sludge. Lumley (2014) also evaluated the energy content of other gasification feedstock and has found that sludge has 16.7MJ/kg, while municipal solid waste leads at 21.3MJ/kg (similar to that of plastics as expected), pine wood was found to be 20,2MJ/kg while corn straw was sitting at 17.75MJ/kg (Lumley, et al., 2014). Although these findings show sludge to have the lowest energy content, its abundance and toxicity treat to society makes it the most worth researching. According to Fericelli (2011), cost studies have shown gasification as one of the thermal processes that consume less energy even though initial energy input is required. Emissions of dioxins, furans, mercury and other heavy metals, NO_x, N₂O and CO are significantly reduced as compared to combustion (Fericelli, 2011).

2.8 Gasification process

Finally, gasification can be defined as the production of gases with usable calorific value (Higman et al., 2008) and that is what separates burning from gasification as fumes ($\text{CO}_2 + \text{H}_2\text{O}$) from combustion (burning) have no usable calorific value. Various researches on gasification show the heat value as the main determinant of the potential of a biomass such as sludge. This energy value can be determined experimentally using a bomb calorimeter or approximate and ultimate analysis (Thipkhunthod, et al., 2005). According to the study on sewage sludge heating value predictions by Thipkhunthod et al. (2005), approximate analysis applies moisture content, volatile matter, fixed carbon contents while the ultimate analysis includes the assessment of the levels of carbon, hydrogen, oxygen, nitrogen and sulfur contents (Thipkhunthod, et al., 2005). For approximate analysis, details are available from ASTM D3172-89, for ultimate analysis details are available from ASTM D3176-89 and for the determination of the gross calorific value, one can consult ASTM D2015-85 (Thipkhunthod, et al., 2005).

2.9 Gasification in the reactor

Different studies conducted by Werle (2013) and Lumley et al. (2014) on sludge gasification agree on the inverse relationship between the energy content (LHV) of sludge, its moisture content, ash content and nitrogen. On the other hand, their results show direct proportionality between the energy content (LHV), the volatile matter, oxygen in sludge and carbon content. According to Werle (2015a) the air fuel ratio (air blown into the reactor to the supplied fuel) during gasification varies with syngas contents concentration. He discovered that the air fuel ratio ($\lambda = m_{air}/m_{fuel}$) of 0.18 gives optimum amounts of H_2 , CO and CH_4 which are the main syngas contents, and the lower amount of CO_2 which is the undesirable gas. This ratio provides the optimal oxygen for the optimal syngas

quality. Werle (2015a) suggested that the reaction of a gasification agent (blown air or steam) and carbon in the fuel (sludge or bio-solids):

$\text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2$ is endothermic ($-\Delta H$) i.e. absorbs heat energy, and the reaction of carbon monoxide and gasification air: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ is an exothermic reaction ($+\Delta H$), it rejects heat energy.

Therefore the composition of the syngas (gasification gas) changes with the amount of air supplied (gasification agent) into the reactor, i.e. the air-fuel ratio (Werle, 2015a). The following equation was used by Werle (2015a) to predict the lower heating value of the syngas (gasification gas) from syngas contents:

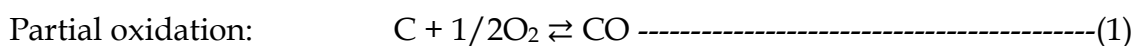
$\text{LHV} = 0.126 \times \text{CO} + 0.108 \times \text{H}_2 + 0.358 \times \text{CH}_4$. As a result, the highest LHV was achieved at the highest syngas concentration. From the lower heating value (LHV) equation, it is clear that methane (CH_4) has the highest influence on the heating value syngas from sludge gasification. Therefore, the best process would ensure the maximum production of methane, then carbon monoxide and Hydrogen in that order. Steam injection during the endothermic reaction showed the increase in LHV as it supported the generation of carbon monoxide (Lumley, et al., 2014). A perfect air fuel ratio ($\lambda = 0.18$), as proven by Werle (2013) in his study can maximize the production of CH_4 , CO and H_2 . Further heating the incoming air would also further increase the heating content (Werle, 2013).

Werle (2015) also indicated the negative impact caused by nitrogen (N_2) on the energy content of sludge. The higher the amount of air blown in, the lower is the heating value (Werle, 2013), and also the higher the nitrogen content in sludge, the lower is its energy content. This indicates that a nitrogen-rich sludge can be expected to have a corresponding low energy content. Since the sludge constituents vary by plant, by region i.e. based on what is being fed into the plant and by the process used in the wastewater treatment plant (WWTP), a great effort needs to be put on avoiding the generation of nitrates in the sludge, if it is to be

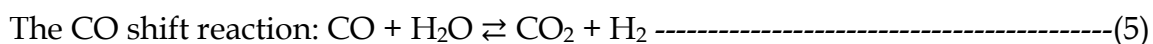
gasified. Further research can be focused on removing nitrogen from sludge before gasification process in order to increase or maintain its heating value (LHV). Lumley et al. (2014) declared that steam blown gasifiers produce the syngas with highest LHV of between 15-20MJ/kg energy, while oxygen blown gasifiers achieve syngas of 10-12MJ/kg LHV, accompanied with the cleanest gas with regards to tar. On the other hand a steam generator plant as well as oxygen generator will be respectively needed for these benefits (Lumley, et al., 2014).

2.10 Gasification reactions for reactor designs

On the previously mentioned reactors, one could expect the following reactions to occur during the gasification process of whether coal, coke or char. The principle chemical reactions involve carbon (C), carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water (H₂O) and methane (CH₄) (Higman et al., 2008). The equations that result in equilibrium syngas composition are the:



The reactions of major concern are complete (combustion reactions) reactions producing complete reaction products CO₂ and H₂O that will not burn further. These reactions are only necessary in very small scale to supply heat to the endothermic reactions. These reactions are:



Partial oxidation and water gas reaction reactions' balance is crucial for the successful gasification process (Higman et al., 2008). The general gasification reaction will therefore be:



Where: for gas, as pure as methane $m = 4$ and $n = 1$, hence $m/n = 4$ and for oil $m/n = 2$, hence $m = 2$ and $n = 1$.

2.11 Attempted gasification experiments

Werle (2013) on his gasification experiment used a gasifier to produce syngas that was later condensed to remove condensable matter. The gas was then passed through a set of filters to remove particulates. The clean gas was then flown into a gas analyzer.

Lumley et al. (2015) used four step gasification in his simulation. The steps involved drying (using syngas driven engine's exhaust gas heat), gasification (in a reactor and produced syngas, char and ash), gas cooling (cooling took place in a gas-to-gas heat exchanger) and cleaning (cleaning took place in a direct contact water scrubber to condense tars and remove acidic gases), and an engine generator (cool scrubbed syngas then drove the engine). The engine was simulated as a turbine calibrated to the equivalent spark ignition engine in ASPEN® simulator (Lumley, et al., 2014).

2.12 Gasification process products (syngas and residues)

In a nutshell, gasification produces syngas which is a mixture of carbon monoxide (CO), hydrogen (H₂), methane (CH₄), carbon dioxide (CO₂) and trapped carbon (C) in char. What makes gasification important is the versatility of syngas in terms of application, ease to clean and further process into more valuable liquid products such as synthetic fuels and chemicals. Fischer-Tropsch synthesis (FTS) is one example that turns syngas into liquid fuels and chemicals (Crocker, 2018). Various feedstock can be fed into this process, thus making room for bio-oil residues from sludge and screenings. Therefore, sludge and

screenings products will not be wasted due to the existence of such a process, where gasification products can be used as feedstock. Bio-oil from gasification condensates has concentrated C-H-O bonds already, as compared to biomass that needs gasification before the FTS.

2.13 Fischer Trop synthesis as applied in coal gasification

The Fischer-Tropsch synthesis (FTS) was invented by two German inventors, Franz Fischer and Hans Tropsch in the early 1920s. The process found significant applications during World War II as it assisted German war efforts by providing needed liquid hydrocarbons. After facing isolation, South Africa also used coal gasification to meet its hydrocarbon fuel and chemical needs (Crocker, 2018). As a result, the Sasol plants in South Africa present the most significant examples of commercialized FTS globally (Crocker, 2018). The Sasol process is fed by bituminous coal; natural gas is also used as supplementary feedstock. This process converts syngas to gasoline, olefins and a variety of other products. Figure 2.1 shows the FTS that generates products form syngas.

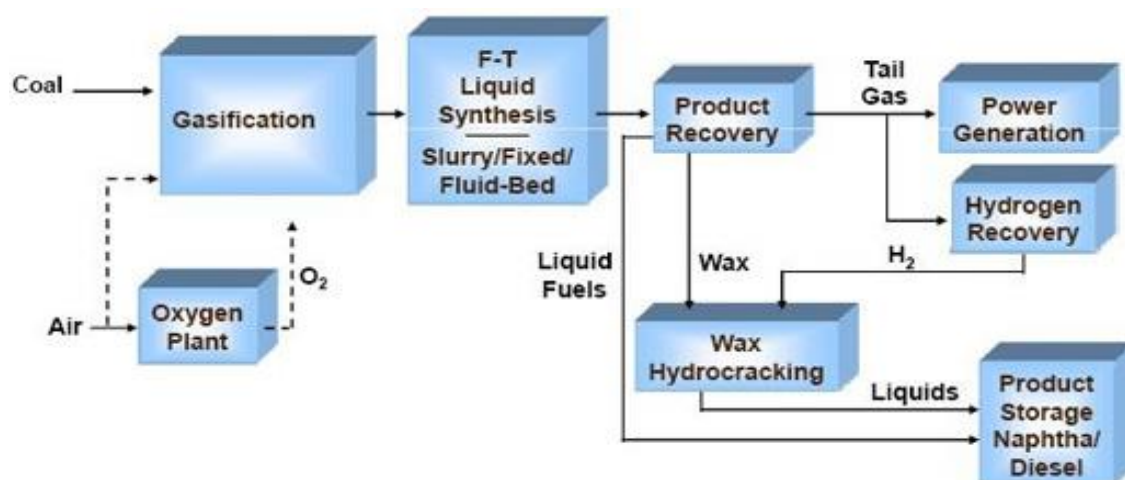
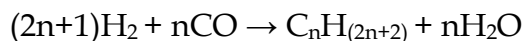


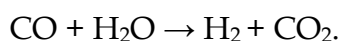
Fig 2. 1: Simplified FTS based production scheme (Crocker, 2018)

The basic reaction behind the FTS involves syngas conversion into hydrocarbons of various molecular weights, such as:



Where n is an integer i.e. if n = 1. Methane, an unwanted product or a lightweight product is generated; $3H_2 + CO \rightarrow CH_4 + H_2O$.

The aim is therefore to avoid n = 1 reaction and thus encourage the formation of heavier products according to Crocker (2018). The conditions for FTS are therefore chosen to maximize the formation of higher molecular weight hydrocarbon liquid fuels, which are higher value products. This process is also not immune to side reactions such the water-gas shift reaction:



According to Crocker (2018) it depends on the catalyst, the temperature of the process and process employed on which product is produced. The products range from methane to higher molecular paraffin and olefins, and lower molecular weight alcohols and organic acids are also formed. In theory, the FTS process is a condensation polymerization of carbon monoxide (CO) (Crocker, 2018).

2.14 Bio-oil resources extraction

As previously mentioned, pyrolysis was meant for bio-oil production. Low temperature volatile matter thus produces bio-oil, which means that gasification also can produce such residues if condensed. Lyu et al. (2015) used GC-MS techniques to characterize bio-oil from various feedstock. Lyu et al. (2015) also realized that feedstock and pyrolysis temperature affected bio-oil products yield and composition. This was in line with gasification drivers that are reactor conditions, and the gasification feed. From his studies it was concluded that higher pyrolysis temperatures favored the generation of small aldehydes and acids, accompanied by the reduction of phenols. The optimal temperature for

maximum furans and ketones yield was 520°C and 550°C respectively (Lyu, et al., 2015). According to Lyu (2015), low temperature pre-treatment of bio-oil resulted in high light weight compounds of bio-oils that are more useful and applicable in refining.

Table 2.1 shows carbon chains as found in crude oil, whose presence can be investigated in sludge and screenings condensate.

Table 2. 1: Hydrocarbon fractions from petroleum (Brown, et al., 2015)

Fraction	Size range of Molecules	Boiling point range (°C)	Application
Gas	C ₁ to C ₅	-160 to 30	Gaseous fuels (i.e. CH ₄ ; LPG) Production of H ₂
Straight -run gasoline	C ₅ to C ₁₂	30 to 200	Motor fuel (i.e. gasoline)
Kerosene fuel oil	C ₁₂ to C ₁₈	180 to 400	Diesel fuel, furnace fuel cracking
Lubricants	C ₁₆ to 20	350 and up	Lubricants (oil)
Paraffin	C ₂₀ and up	Low melting solids	Candles
Asphalt	C ₃₆ and up	Gummy residue	Surfacing roads

Table 2.1 shows correlation between crude oil carbon chains and sludge carbon chain resources that were found in the findings of Lyu (2015).

2.15 Current national energy challenges

Despite the abundance and accumulation of sludge and screenings in costly landfills, South Africa still relies on expensive imported energy (expensive due to shrinking rand value and reduction in crude oil quality). This reliance leaves the country's economy vulnerable to global developments. The statistics presented by Pricewaterhousecoopers adapted from the US energy information administration in 2010 showed that South Africa imports more than 50% of oil from the Middle East alone, and with other contributions from Nigeria, Angola, Russia and other countries. Figure 4.2 shows South Africa's reliance on imported energy.

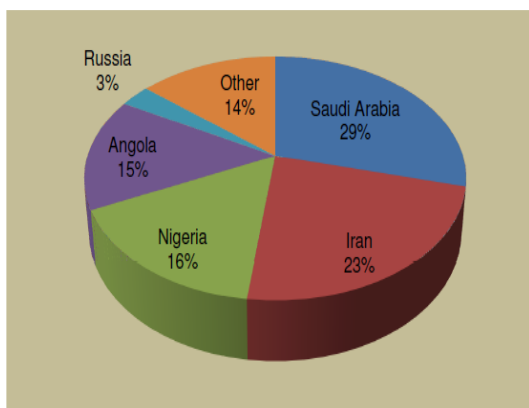


Fig 2. 2: SA's oil import by country of origin (SAMSA, 2017)

Synthetic fuels from coal gasification do not seem to replace the crude oil demand as they are expensive to produce, and thus their survival relies on crude oil price (Higman et al., 2008). The rising crude oil price (due to rigging complexities of depleting crude oil and low crude oil quality, i.e. crude becoming sour or with higher Sulphur content) and the finished product price hike (due to sour crude refining challenges) might make gasification process economically viable, which can benefit countries like South Africa. Projects such the one presented in this study might have a somehow energy saving potential, not only for the wastewater sector but for the country at large. Such projects have a potential of assisting South Africa towards its sustainability, green energy and clean environmental goals.

2.16 Possible metals beneficiation from sludge

Despite the energy and other resource recovery from sludge, precipitation also promises the possible extraction of metals from sludge. Literature search showed that precipitation of heavy metals from wastewater is possible with the use of lime, fly ash and carbon dioxide at a controlled pH. The study conducted by Chen et al. (2009) showed that lime, fly ash and carbon dioxide can precipitate heavy metals prevalent in sludge in the order of $\text{Cu} > \text{Cr} > \text{Pb} > \text{Zn}$.

Chapter 3. METHODS AND ANALYTICAL TECHNIQUES

3.1 Methods and experimental setup

3.1.1 Sludge generation and plant process

Sewage and screenings samples used in this study were collected from a single wastewater treatment plant in Olifantsfontein. The plant treats wastewater from Olifantsfontein, Tembisa Township and surrounding. Wastewater from residential areas mainly has nappies, food, washing soaps and human waste products. The industries that feed wastewater to the plant, supply products that vary from dairy products (high COD), glass (high in solids), soft drinks (low pH), chemicals (acids and ferric chloride), meat products (organic fat) etc. The screenings (mainly nappies, plastics, papers and human waste) are separated by screens at the head of works. After screening removal, the stream flows to degriters, where sand and bottle pieces are settled and removed.

After this stage, the stream reaches the primary settling tanks (PSTs), where the primary or raw sludge settles and is removed. The stream then continues to the anoxic, then anaerobic and to aerobic reactors and finally to clarifiers where biodegradable matter settles as sludge. Primary or raw sludge, sludge from the reactor and the sludge from clarifiers are fed into the dissolved air flotation unit (DAF) for sludge thickening. The thickened sludge is mixed with a flocculent (Polly at an average of 0.504% with respect to the thickened sludge) before dewatering at the belt-press. The belt-pressed sludge is then conveyed by a belt-conveyor onto a concrete slab, where farmers collect it for agricultural use. Finally, the treated water after clarifiers is passed through chlorine contact tanks for chlorination (dosing) before being discharged into the water stream that feeds to Hartebeespoort Dam. The effluent quality is governed by the National Water

Act 1998 (Act No 36 of 1998). Figure 3.1 shows the Olifantsfontein WWTW basic flow process.

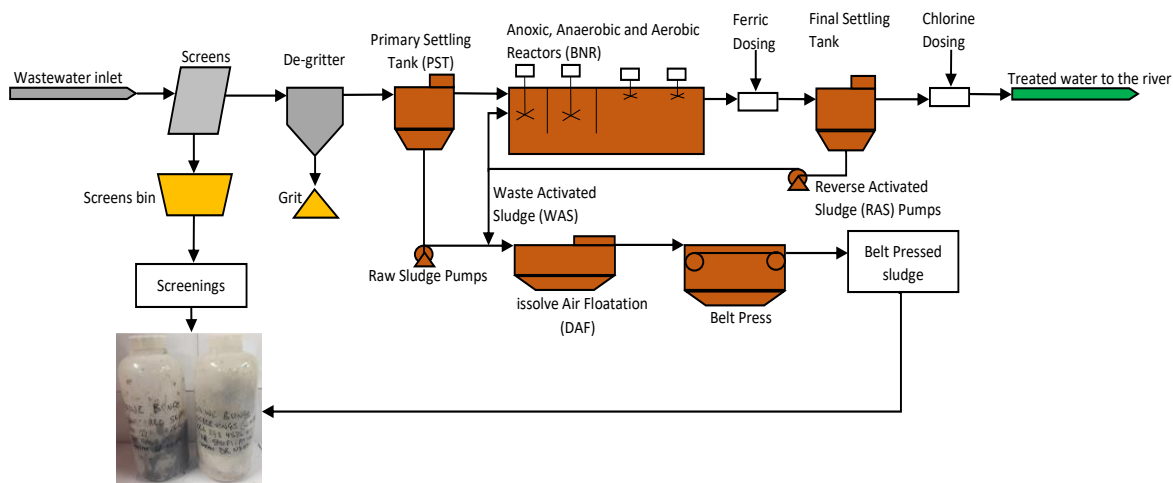


Fig 3. 1: Olifantsfontein WWTW plant process

3.1.2 Samples and sampling

In this study, a belt pressed sludge (BP-sludge) and screenings from Olifantsfontein wastewater treatment works (WWTW) in Olifantsfontein, in the Gauteng province of the Republic of South Africa was used. Two samples (one for sludge and another for screenings) were collected and delivered to Witwatersrand University in a cooler bag with ices that kept it at 0°C. The samples were stored in a cold room to avoid bacterial growth that would affect sludge properties. Before further processes and analysis, the sludge was dried at 105°C for 2 hours to achieve $\pm 83\%$ moisture removal. This is per the standard test method, ASTM D1762-84 for moisture content. This was done to improve the energy value as high moisture content reduces the fuel's energy value including that of sludge according (Lumley, et al., 2014; Molto, et al., 2013). The sampling process shown in figure 3.2 was followed during sampling and gasification.

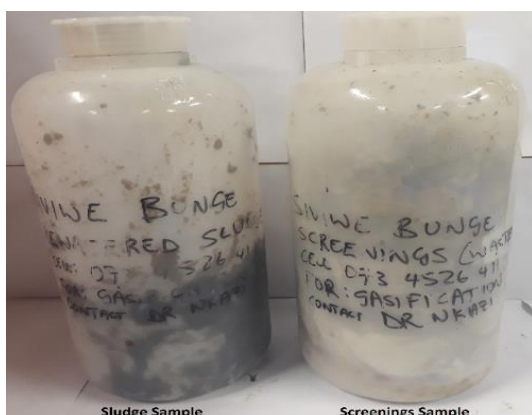
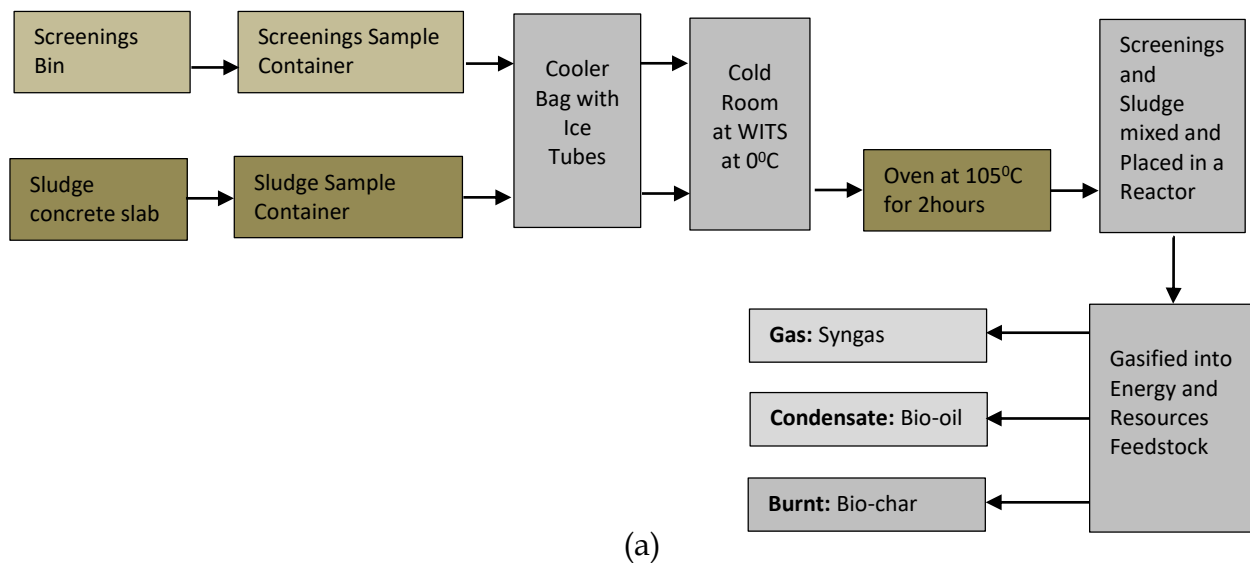


Fig 3. 2: Sampling process (a) and the samples (b) collected at Olifantsfontein WWTW

3.1.3 Gasification sample preparation and sampling

The equipment used during gasification was a horizontal, electrically heated fixed bed batch reactor (length: 790mm; diameter: 300mm; bore diameter: 60mm). The reactor consists of an enclosable tube of 50mm internal diameter and 1000mm length with attached aluminum square ends plates with taped M12 holes. The square end-plates were fitted onto the stainless steel tubes. One end-plate tube conveyed the purge gas (nitrogen) into the reactor while the second end-plate was attached to a U-tube shaped glass that was suited for bio-oil collection. The U-

tube was placed before the flow branched into the sampling chamber and to the volumetric flask. The volumetric flask was located under the fume hood, for fume extraction.

Figure 3.3 shows the experimental setup that was used.

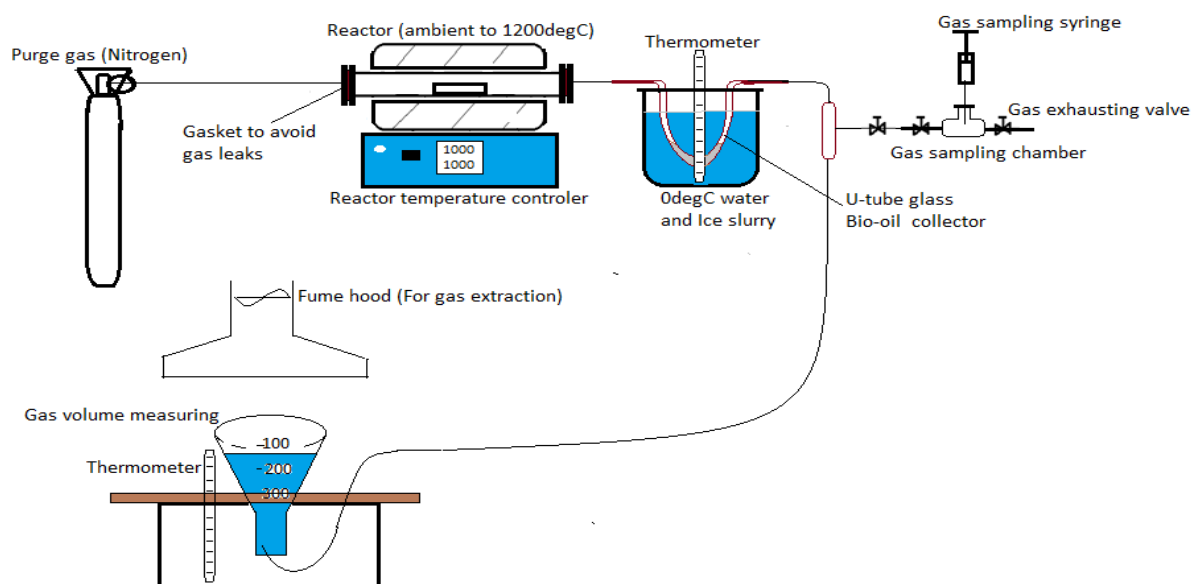


Fig 3. 3: Experimental setup

For each experimental run, the sludge of 50g was dried in an oven at 105°C for 2 hours. The sludge lost $\pm 83\%$ of moisture during the process to a final mass of $\pm 8.5\text{g}$. Detailed calculations are presented in annexure A. An applicable screenings proportion (to make the total sum of 17.5g) was added on a dry sample to achieve a sludge/screenings ratio of either: 0/100, 25/75, 50/50, 75/25 and 100/0. A mixture was then loaded in a reactor tube as shown in figure 3.4.



Fig 3. 4: A typical sludge and screenings sample loading in a reactor

The sample was then enclosed by bolting in the right end-plate. The glass U-tube section was then attached and dipped into the ice and salt slurry. The ice and salt slurry had a concentration of 0.016g/L (see annexure A). The mixture resulted in a temperature drop of up to -10°C in the glass tube. The aim of this procedure was to ensure that all gas components that are liquid at 0°C remain as liquid in the glass tube, for latter collection for bio-oil analysis.

The gas piping was then branched to a gas sampling chamber via a gas valve. The rest of the piping went to the volumetric flask, where the gas volume was measured by measuring the volume of displaced water at a known temperature. The temperature of the displaced water could be used to predict the amount of known dissolved species. The changes in absorbed gas would be minimal, due to negligible temperature change in displaced water reading. Absorbed gas amounts of different species of syngas in water was therefore ignored. Figure 3.5 shows the volumetric flask that was used to measure the gas volume per experimental run.



Fig 3. 5: Gas volume measuring method (a) and water volume measuring apparatus (b)

3.2 Analytical techniques

3.2.1 Approximate analysis

The approximate analysis was performed in sludge to identify the moisture content, volatile matter available and ash content.

3.2.2 Fuel properties of sludge

The elemental analysis was performed on the sludge to determine the amount of fuel (hydrocarbons) that can be retrieved for energy recovery and chemicals. The analysis was performed on a dry sludge basis, with the sludge dried at 105°C for 2 hours as per ASTM D1762-84. A Perking-Elmer CHNS analyzer was used to analyze dry sludge samples and gasification product (bio-char) at various ratios (50/50; 75/25; 25/75). The aim of the procedure was to identify the carbon amount changes due to resource recovery by gasification or resource addition if any from screenings addition.

3.2.3 Toxicants available in sludge

The toxicity analysis was performed on the sludge focusing on Olifantsfontein WWTW's prevalent toxicants. Various analyses were performed, such as the approximate analysis (moisture, ash content and volatile matter), microbiological analysis (pathogens) and for organochlorine toxicants such as PCBs and PAHs. The bio-char toxicity analysis was not performed due to the changes in the nature of sludge that did not meet the procedure requirements. Normally, the analysis procedures are suited for soils, sludge and watery sludge analysis. The small char volume was also disallowed by the toxicity analysis procedure.

3.2.4 Functional groups identification in the BP-sludge

A dried sludge sample of 10mg was analyzed on a Perkin-Elmer FT-IR spectrometer for functional groups identification in the BP-sludge. The aim of the analysis was to identify useful resources for energy and chemicals that can be obtained from sludge. Figure 3.6 shows the instrument that was used.



Fig 3. 6: Functional group identifying apparatus

3.2.5 Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was performed on the TGA analysis apparatus, developed by AS Solutions. Figure 3.7 shows a TGA instrument that was used during the analysis. TGA results are presented annexure B, while manipulated results graph is presented in figure 4.2.

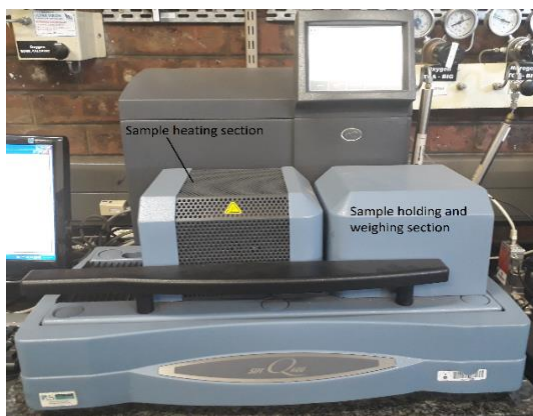


Fig 3. 7: TGA: Thermogravimetric analysis

The analysis aimed at identifying the critical temperatures for the pyrolysis and gasification of sludge and screenings combined and separated, and at determining the remaining char amounts.

3.2.6 Gas sampling and analysis

After setting up the reactor for an experiment, it was then started in order to heat up a sample from ambient ($\pm 22^{\circ}\text{C}$) to 400°C initially. The temperature was held at 400°C for 5 minutes, before sampling for pyrolysis gas species. Figure 3.8 (a) shows the gas sampling chamber, figure 3.8 (b) shows the gas sampling syringe that was used to take the sucked sample for injection into the GC-MS instrument (430-GC Gas Chromatogram) manufactured by Bruker as shown in figure 3.8 (c). The instrument used nitrogen as a purge gas and it analyzed gas species by their differences in conductivities.

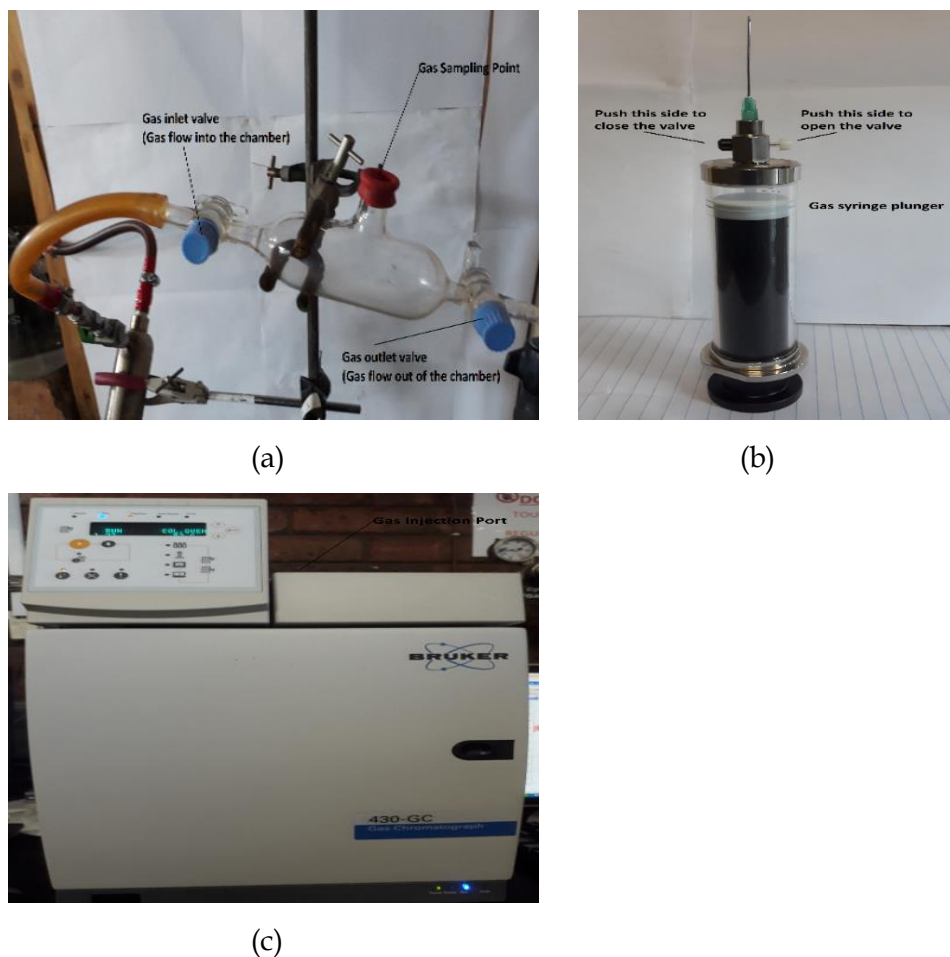


Fig 3. 8: Gas sampling chamber (a), gas syringe (b) and GC-MS analyzer (c)

The GC-MS analysis results were gas chromatograms with different peaks, area %, and retention times (RT) and peak positions. Gas standards for gas analysis were used to identify the gas species names for peaks obtained. The same sampling and analysis procedure was followed for gasification gas species after further temperature rise to 1000°C and another 5min holding time. This sampling stage targeted gasification species in sludge and screenings.

3.2.7 Bio-oil sampling and analysis

After the gasification process, the glass U-tube shown in figure 3.9(a) was removed and the liquid contents poured into small sample containers shown in figure 3.9(b). The containers had sample IDs for the ease of identification during

bio-oil analysis. The sample was sucked by a needle from containers and injected on the injection port as shown in figure 3.9(c). Bio-oil analysis was performed in a GC-MS Spectrometer (GCMS-QP2010) with molecule identifier (mass spectrometer). In order to identify and name species, two libraries were used (NIST.lib and Willey) to compare injected peak values to the standard known values from the libraries and so allocate the names. The GC system heated the liquid at 200°C to turn it into a gas, before being fed into the MS for species analysis and identification. The system then produced chromatograms with content names, their percentage areas, peak positions, and retention times.

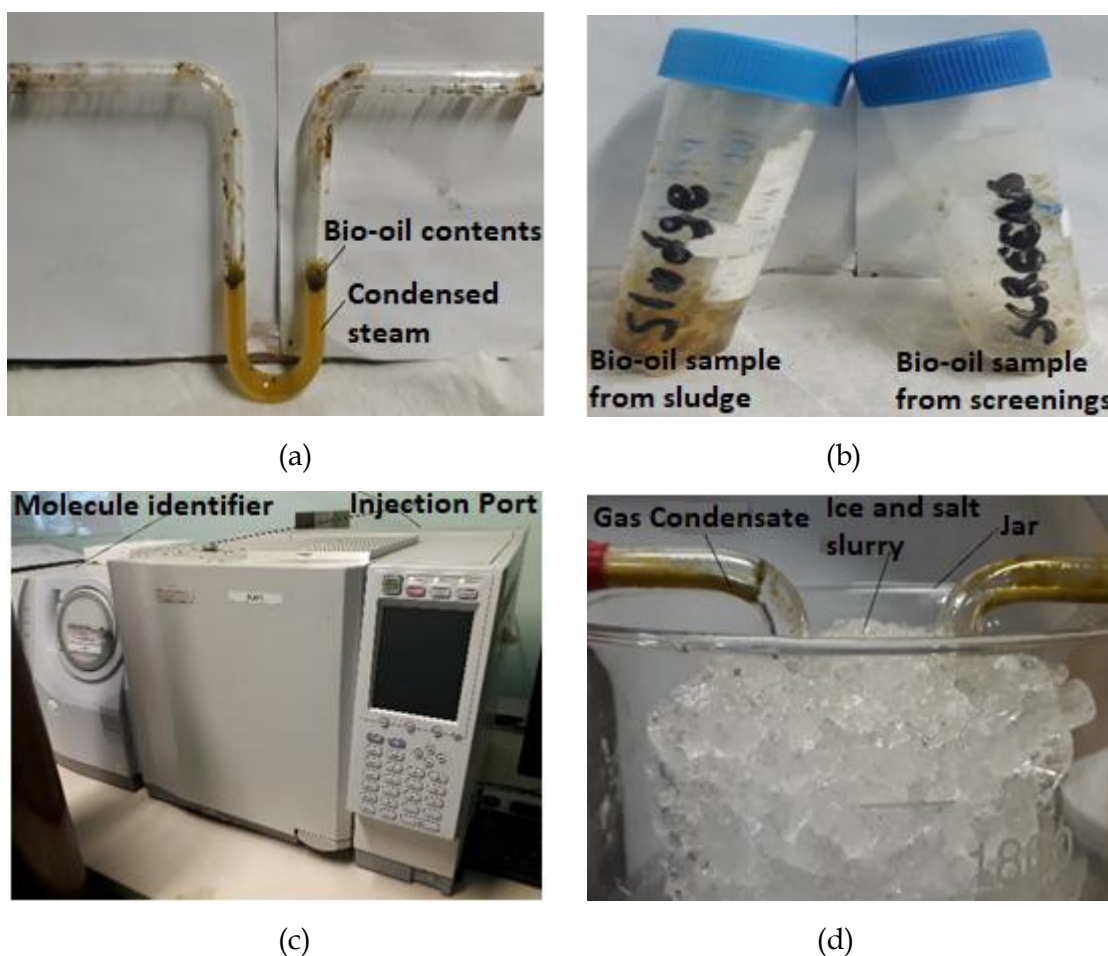


Fig 3. 9: Bio-oil U-tube (a), sludge and screenings samples (b), GCMS oil analyzer (c) and bio-oil condenser (d)

3.2.8 Bio-char sampling and analysis

After each experimental run, the reactor was cooled by forced convection using a cooling fan. After cooling, the char sample was collected. Sludge per screenings ratio samples were analyzed for elemental (CHNS, which is Carbon, Hydrogen, Nitrogen and Sulphur) composition at UJ: University of Johannesburg and the results are presented in table 4.7 of chapter 4.

Chapter 4. RESULTS AND DISCUSSION

4.1 Approximate analysis

Table 4.1 shows the approximate analysis results that give an indication of energy and resourcefulness of sludge. The results in table 4.1, column two are for Olifantsfontein belt press sludge, and are comparable to the results obtained in literature by Lumley (2014) and Werle (2013). According to literature studies, higher moisture and ash content reduce the energy value, while higher volatile matter results in higher energy value and gasification resources (Thipkhunthod, et al., 2005).

Table 4.1: Approximate analysis by method EL31A on the BP-sludge

Content	This work	Method	Lumley (2014)
% Water	83.9	EL31A	80
% Volatile matter	74.2	EL31A	71.3
% Total solids	16.1	EL31A	-
% Ash	25.8	EL31A	19.67

The approximate analysis results of sludge showed that water, volatile matter and ash contents were comparable to the sludge results used in literature specifically by Lumley (2014), as seen in table 4.1, column four. Moisture content of 83.9% to that of 80% and volatile matter of 74.2% to that of 71.35 from the literature, imply that the results of the sludge used in the study can be compared to that employed in literature. Therefore, Olifantsfontein sludge might have more resources than the sludge used by Lumley (2014).

4.2 Fuel properties of BP-sludge and bio-char

The fuel properties of BP-sludge and bio-char were analyzed and the results are summarized in table 4.2. Column two presents the fuel properties of sludge and confirmed the availability of carbon and hydrogen (basic building blocks of transportation fuels) in sludge. Column three, four and five present bio-char remaining fuel contents, after gasification to extract syngas and bio-oil.

Table 4.2: Fuel analysis (CHNS) results on the BP-sludge and bio-char

Element	Sludge only	Bio-char after gasification		
		50/50	75/25	25/75
% C	6.27	33.15	32.64	33.03
% H	6.27	0.00	0.00	0.00
% N	1.52	0.99	0.92	0.995
% S	0.00	2.41	2.40	2.42

Bio-char produced from sludge and screenings was more than five times carbon-rich than bio-char from sludge only. Hydrogen boiled away from bio-char as it is expected as it has a boiling point of -252.87°C . Results also show that some of the nitrogen also boiled away during gasification. This nitrogen was evidenced on bio-oil species that had nitrates. Sulphur also showed increase after the addition of screenings. The low zero value of sulphur on unmixed sludge might be due to its low amount that the instrument could not detect.

4.3 Toxicity analysis

Table 4.3 shows toxicity analysis results; biological and organic pollutants. Table 4.3 shows biological and chlorinated organic toxicants that were found in Olifantsfontein sludge with their limiting amounts as per regulations.

Table 4.3: BP-sludge toxicity analysis

Substance	Molecular formula	Amount (ppm)	Limiting amount (ppm)
Microbiological pollutants			
Salmonella enterica	Positive	-	
Organic pollutants			
Naphthalene (mg/kg)	C ₁₀ H ₈	<0.59	6
Acenaphthylene (mg/kg)	C ₁₂ H ₈	<0.91	6
Acenaphthene (mg/kg)	C ₁₂ H ₁₀	<0.86	6
Fluorene (mg/kg)	C ₁₃ H ₁₀	<0.77	6
Phenanthrene (mg/kg)	C ₁₄ H ₁₀	<0.84	6
Anthracene (mg/kg)	(C ₆ H ₄ CH) ₂	<0.80	6
Fluoranthene (mg/kg)	C ₁₆ H ₁₀	<0.89	6
Pyrene (mg/kg)	C ₁₆ H ₁₀	<0.52	6
Benzo(a)anthracene (mg/kg)	C ₁₈ H ₁₂	<0.67	6
Chrysens (mg/kg)	C ₁₈ H ₁₂	<1.10	6
Benzo(b)fluoranthene (mg/kg)	C ₂₀ H ₁₂	<0.89	6
Benzo(k)fluoranthene (mg/kg)	C ₂₀ H ₁₂	<0.84	6
Benzo(a)pyrene (mg/kg)	C ₂₀ H ₁₂	<0.91	6
Indeno(1;2;3-cd)pyrene (mg/kg)	C ₂₂ H ₁₂	<0.73	6
Dibenzo(a;h)anthracene (mg/kg)	C ₂₂ H ₁₄	<0.97	6
Benzo(ghi)pyrene (mg/kg)	C ₂₂ H ₁₂	<0.59	6

The results presented in Table 4.3 indicate that the Olifantsfontein BP-sludge sludge is within the accepted limits. From these results, it can be predicted that the char after gasification would be disposable without PCBs and PAHs exceeding regulatory limits.

4.4 Metal contents in sludge

The results on metal content in sludge were extracted from both the elemental and toxicity analysis results and were as presented in table 4.4.

Table 4.4: Metal characteristics of the BP-sludge

Metal	Amount	Limit (ppm)	Reference
Aluminum (mg/kg Al)	10959	10000-300000	EPA (annexure C)
Iron (mg/kg Fe)	7265	7000-550000	EPA (annexure C)
Zinc (mg/kg Zn) (Ann. I)	773	<2800	Sludge Guidelines

The amount of Al, Fe and Zn were below the limits set by relevant bodies in the environmental protection such as the United States' environmental protection agency (EPA) and South African sludge disposal guidelines. Refer to annexure C for environmental protection agency (EPA) guidelines. These results indicate that the sludge under review is safe to dispose or apply on an agricultural environment.

4.5 Functional group identification in the BP-sludge

The functional group analysis was performed in sludge to identify functional groups that can be applied in the production of liquid fuels, gaseous fuels and chemicals. Figure 4.1 shows the availability of the amine group, and fewer conjugate amides and small amounts of ketones, alkanes and alkenes. These results are in line with the findings of Cei et al. (2009) that showed that sludge has carbonyl, phosphate, and amine groups. Due to sludge diversity, one can expect functional groups to vary at least from plant to plant. A plant with efficient denitrification and phosphate removal processes will be expected to have low of such functional groups.

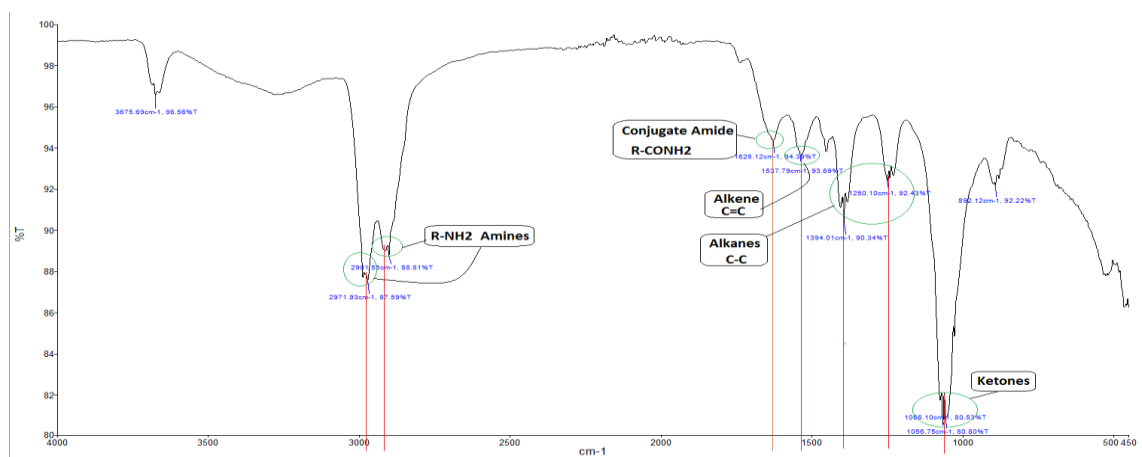


Fig 4.1: Functional groups in the analyzed BP-sludge

4.6 Thermogravimetric Analysis

Figure 4.2 shows the results of thermogravimetric analysis (TGA). As indicated in figure 4.2, most volatiles escaped at 540°C and the samples remained with ash content that varied between 32 and 8% at 1000°C. The first critical temperature was where most volatiles escaped and the second critical temperature was where no volatiles seemed to escape. All five samples with masses ranging between 10 and 15mg were analyzed to see their behavior as temperature rose from ±50°C to 1000°C.

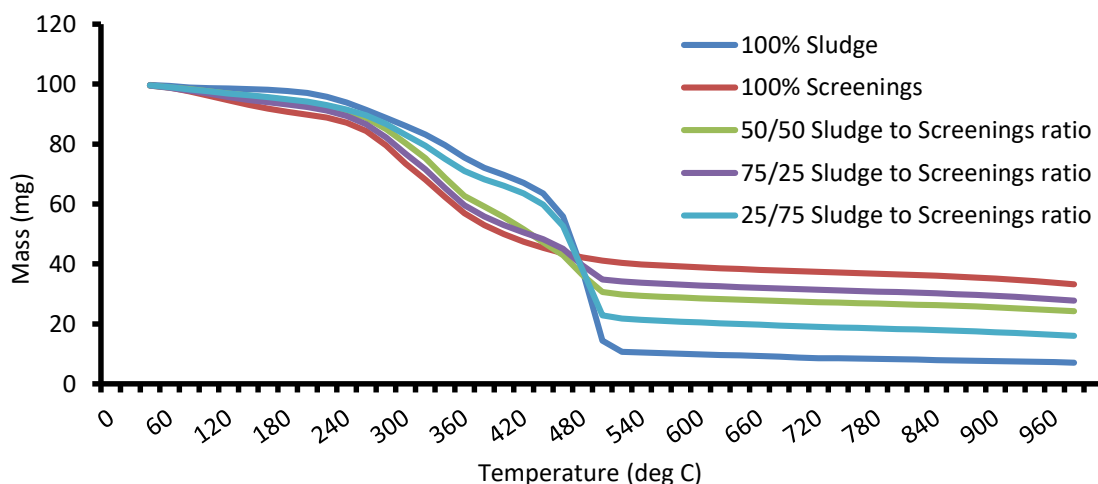


Fig 4.2: TGA: Thermogravimetric analysis results

These results imply that if one targets pyrolysis products, 540°C temperature would be an ideal optimum setting or that the optimum would be around 540°C. Although 540°C was the indicator of most volatile matter removal, screenings (100% screenings graph) could have started gasifying. Therefore, 400°C was used to target main pyrolysis products before any additional contents contributed by gasification. 540°C temperature is also in line with the boiling points of main crude oil fractions according to Crocker (2018) that are mostly below 500°C and that are targeted in sludge and screenings resources recovery.

Annexure B shows detailed TGA results per experimental run for sludge/screenings ratio of 50/50. The graph from the top left down, shows the sample weight loss, with increasing temperature (also presented in figure 4.2 for all samples). The graph starting just below it, is the heat flow in the TGA, while the third graph indicates the rate of change in sample weight.

Note also from table 2.1, chapter 2 that most suitable products for energy and chemical industry can be obtained from bio-oil products escaping at below 500°C. The screenings on the other hand remain with the highest amount of char volume than sludge, for disposal. The char from screenings is about four times the char that remains from sludge. These results need further investigation as 75/25 should be closer to 100/0 and also 25/100 closer to 0/100 due to sludge/screenings amount proportions.

4.7 Moisture content in BP-sludge and total gas produced

The experimental runs that were conducted in triplicate are individually shown in table 4.5. The average room temperature was 24°C, and the gas volume was measured at $\pm 21^\circ\text{C}$. The ice and salt slurry was kept below 0°C to condense all the heavy gas contents. The standard deviation for each ratio was calculated to be;

0.024ml for 25/75 ratios, 0.064ml for 50/50 and 0.009ml for 75/25. 0/100 and 100/0 ratios were implemented to assist in the interpretation of results trends.

Table 4.5: Details of experimental runs

Experiment	Total Mass (g)	Moisture Removed (%)	Sludge Mass (g)	Screenings Mass (g)	Gas Vol (l)	Duration Experiment (hours)
S1_50/50	17.5	83.0	8.75	8.75	7.357	6h06
S2_50/50	17.5	82.5	8.75	8.75	7.595	5h57
S3_50/50	17.5	84.0	8.75	8.75	7.120	5h24
S4_75/25	17.5	84.0	13.125	4.375	6.890	6h03
S5_75/25	17.5	84.0	13.125	4.375	6.850	5h54
S6_75/25	17.5	84.0	13.125	4.375	6.870	5h30
S7_25/75	17.5	84.0	4.375	13.125	8.375	6h02
S8_25/75	17.5	84.0	4.375	13.125	8.340	5h49
S9_25/75	17.5	84.0	4.375	13.125	8.270	5h25
S10_100/0	17.5	84.0	17.5	0.00	7.70	6h12
S11_0/100	17.5	0.00	0.00	17.5	7.510	5h54

Triplicate samples were created to improve results reliability. Triplicate samples made statistical validation to provide reliable data. Higher screenings ratio proved to have the higher gas volume on average that the rest of samples.

In addition, heating sludge for 1 hour more than the normal 2 hours proved to improve moisture loss by 1%. This investigation was done by drying three samples for 3 hours, to test for change in moisture removal. From these results, one can predict the optimum drying time to be 2 hours or less. 2 hour drying time is suggested by the standard (ASTM D1762-84). Further analysis of drying time vs moisture removal would be important in the optimization of the drying process for energy extraction from sludge. This optimum would be crucial for energy savings during the drying process.

4.8 Gasification gas volumes

The final average gas volumes showed that most gas can be generated from sludge per screenings ratio of 25/75, then 50/50 and lastly 75/25. It was evident that screenings produced more gas than sludge, making screenings the ideal feedstock for gas production. According to these finding, more gasification products can be expected from extra screenings feedstock than sludge only, since screenings are a product of crude oil. Figure 4.3 shows average gas volumes obtained per experimental run i.e. sludge per screenings ratio. These are averages of three samples per sludge/screenings ratio.

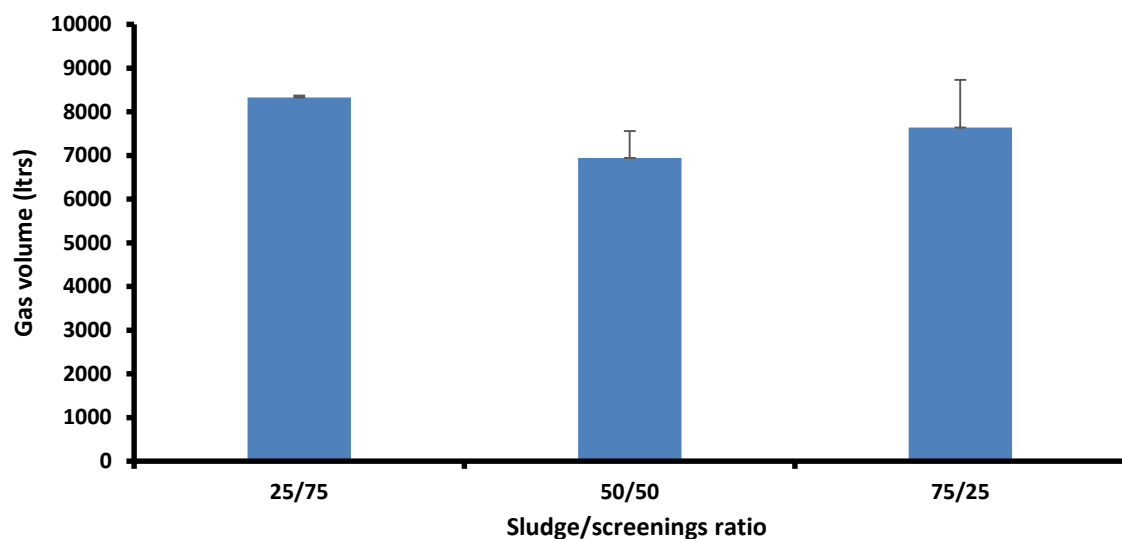


Fig 4.3: Final gas volume per sample run

The 25/5 sludge/screenings ratio showed highest gas volume with more repeating values, i.e. with lowest standard deviation, as shown by error bars. 75/25 ratio was the second highest, but with higher standard deviation than a 50/50 ratio that produced the lowest gas volume on average.

4.9 Syngas value of gasification products

Results from each gas sample, two samples per each experimental run, i.e. for pyrolysis at 400°C and gasification at 1000°C. The results from each gas injection into the GC-MS are presented in table 4.6

Table 4.6: Syngas contents per experimental run

Experiment	(Area %)				
	H ₂	CO	CH ₄	CO ₂	C ₂ H ₄
S1_50/50_Pyrolysis	82.85	3.91	5.72	0.22	0.00
S1_50/50_Gasification	68.72	13.93	0.06	0.44	0.00
S2_50/50_Pyrolysis	92.64	2.87	0.06	0.88	0.00
S2_50/50_Gasification	83.90	4.19	5.92	0.13	1.52
S3_50/50_Pyrolysis	92.64	2.87	0.06	0.88	0.00
S3_50/50_Gasification	83.90	4.19	5.92	0.13	1.52
S4_75/25_Pyrolysis	0.92	61.09	14.91	1.29	21.19
S4_75/25_Gasification	91.09	4.94	0.00	0.00	0.28
S5_75/25_Pyrolysis	0.97	67.12	1.52	2.05	21.19
S5_75/25_Gasification	90.27	4.72	0.91	0.00	0.28
S6_75/25_Pyrolysis	0.87	55.06	28.29	0.52	0.00
S6_75/25_Gasification	83.27	13.32	0.39	1.30	1.72
S7_25/75_Pyrolysis	9.02	67.10	18.11	1.65	0.00
S7_25/75_Gasification	6.10	55.46	13.11	3.95	12.62
S8_25/75_Pyrolysis	6.30	56.08	1.85	7.49	0.00
S8_25/75_Gasification	94.49	2.74	1.62	0.00	0.82
S9_25/75_Pyrolysis	0.00	50.34	0.00	10.23	14.93
S9_25/75_Gasification	90.64	4.61	3.66	0.00	0.80
S10_100/0_Pyrolysis	58.66	20.61	1.44	6.43	2.54
S10_100/0_Gasification	91.97	3.76	3.81	0.46	0.00
S11_0/100_Pyrolysis	31.19	31.09	24.34	2.28	0.00
S11_0/100_Gasification	29.70	16.38	41.96	3.11	0.00

According to literature by various researchers such Werle (2013), Higman et al. (2008), Crocker (2018), syngas is generally made up of H₂, CO, CH₄, CO₂ and other small species. Pyrolysis gas samples (taken at 400°C) and gasification samples (taken at 1000°C) were analyzed in the GC-MS instrument. The analysis results were gas chromatograms that showed peaks of various gas species and a table indicating each gas against its area percent (A%). The A% is the amount of that specie in the analyzed sample. This presentation focuses on hydrogen (H₂),

carbon monoxide (CO) and methane (CH₄). Area percentages for each specie at pyrolysis and gasification were presented to analyze amounts of various syngas components. The gasification species at pyrolysis and gasification per experimental run were added. Those sums were averaged, and their standard deviations plotted as error bars.

More calculations were performed based on the amounts measured by the GC-MS. The aim of the calculations was to identify gasification conditions CO/(CO+CO₂) of the reactor used, i.e. to find if the reactor was gasifying or combusting. The second calculation aimed at measuring hydrogen in relation to carbon monoxide H₂/CO or syngas quality, as a normal practice in gas to liquid (GTL) processes. These results aimed at informing on hydrogen amount as the most needed resource in liquid fuel production. The third calculation was aimed at predicting the syngas energy value (LHV) from the equation ($LHV = 0.126 \times H_2 + 0.108 \times CO + 0.358 \times CH_4$) derived by Werle (2013). All these calculations were performed per sample run for both pyrolysis and gasification, i.e. two samples (pyrolysis and gasification sample) per experimental run.

Syngas (H₂, CO and CH₄) amounts were analyzed for pyrolysis and gasification. The summed results were then averaged for three samples, standard deviations and coefficient of variations were calculated. The results are summarized in figure 4.4, 4.5 and 4.6, with averages and standard deviations as error bars. The average for three same sample runs was calculated to find the highest amount of gas out of three gas ratios; 25/75, 50/50 and 75/25. The standard deviation and coefficient of variation for each triplicate were calculated to find least scattered data for reliable results, i.e. precise and accurate data.

The hydrogen (H₂) content in the synthetic gas was analyzed and the results are summarized in figure 4.4.

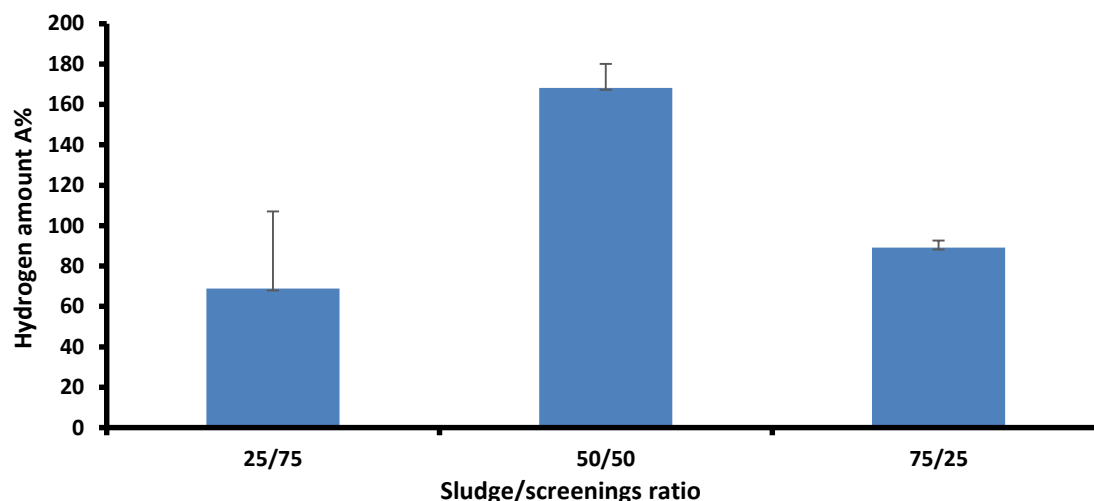


Fig 4.4: Hydrogen yield per experimental run

The highest average hydrogen (H_2) production was achieved at a 50/50 ratio: the average of 168A%, the standard deviation of 5.66A% and the coefficient of variation of 3.37% were achieved. The overall highest score was achieved by a ratio of 75/25, due to its lowest standard deviation of 1.41A% and lowest coefficient of variation of 1.57%, even though its average was lower at 88A%.

The carbon monoxide (CO) content in the synthetic gas was also analyzed and the results are summarized in figure 4.5.

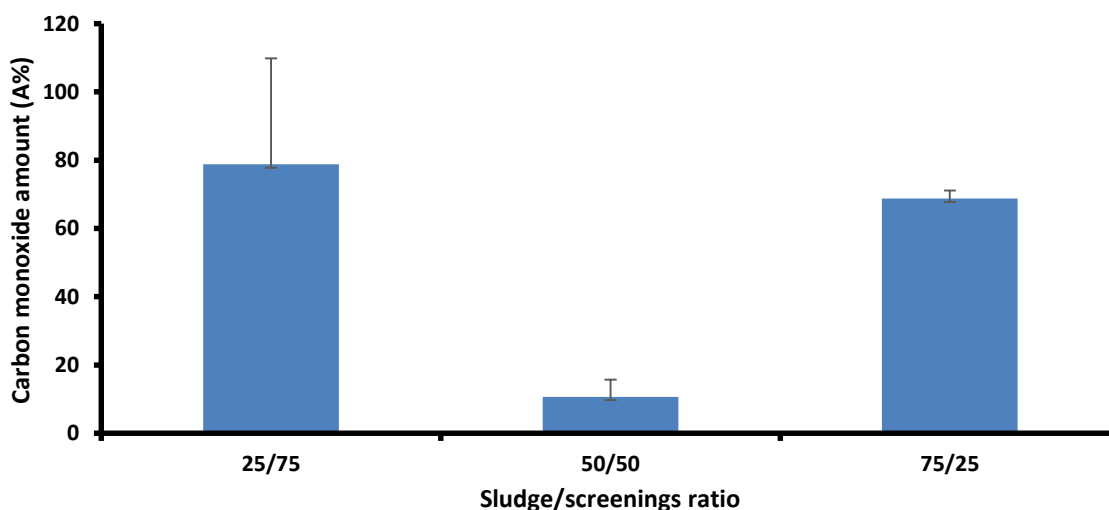


Fig 4.5: Carbon monoxide yield per experimental run

The most carbon monoxide (CO) production data was achieved at a 75/25 ratio: the average of 71A%, the standard deviation of 2.38A% and the coefficient of variation of 6.84% were achieved. The second highest was a ratio of 25/75, that achieved the higher average than 75/25 of 77.5A%, a lower standard deviation of 5.08A% and also a lower coefficient of variation of 20%.

The methane (CH₄) content in the synthetic gas was analyzed and the results are summarized in figure 4.6.

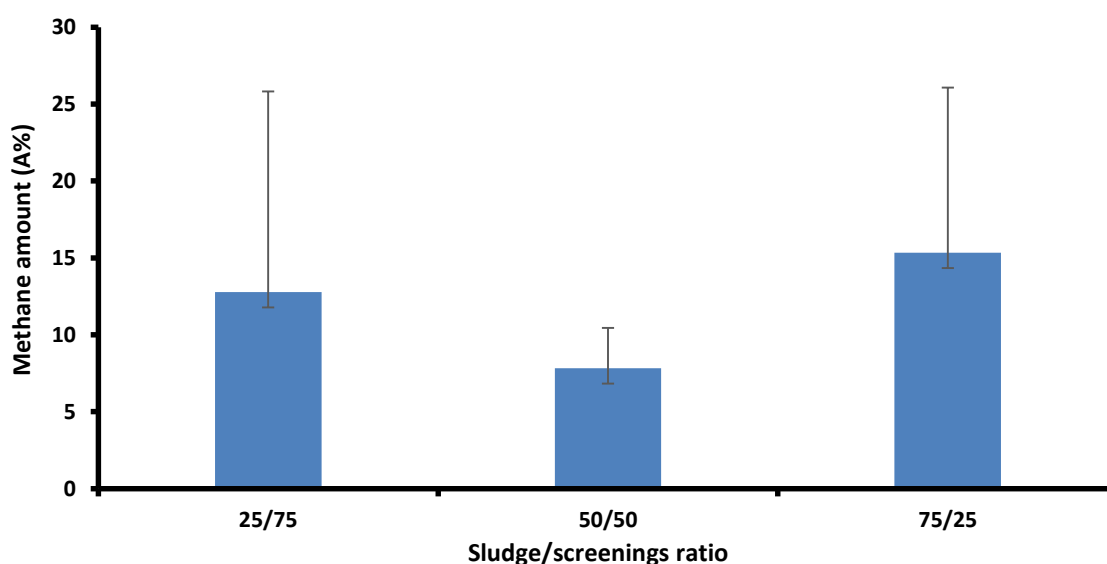


Fig 4.6: Methane yield per experimental run

The highest methane (CH₄) average production was achieved at a 75/25 ratio: at the average of 15.34A%, the standard deviation of 10.72A% and the coefficient of variation of 33.87% were achieved, while the second highest ratio was 50/50, that achieved the lowest average of 12.78A%, but better standard deviation of 2.62A% and a coefficient of variation of 17.68% respectively.

The lower heating value (LHV) or the energy value of the gas products was predicted by the equation adopted from Werle (2015).

From the equation: ($LHV = 0.126 \times H_2 + 0.108 \times CO + 0.358 \times CH_4$) it is clear that the greatest contributor to syngas or gasification gas's LHV is methane at about three times. Figure 4.7 shows results that predict the energy value of the gas species obtained. The lower heating value (LHV) of the syngas was analyzed and the results are summarized in figure 4.7.

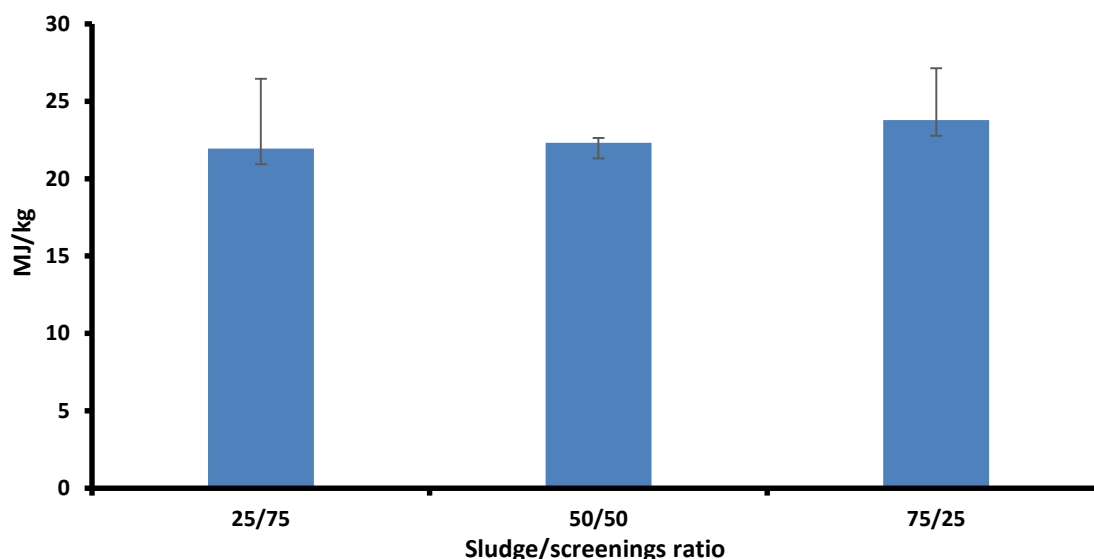


Fig 4.7: Lower heating value (LHV) of syngas per experimental run

The highest average calculated lower heating value results were achieved at a 50/50 ratio, with the second highest average achieved as 22.31A%, the standard deviation of 0.31A% and the coefficient of variation of 1.67%. On the other hand, the overall second highest ratio was 75/25, that achieved a highest average of 23.78A%, standard deviation of 3.35A% and a coefficient of variation of 8.50%.

Gasification conditions, calculated by $CO/(CO+CO_2)$ are emphasized in literature (Higman et al., 2008) as they refer to the generation of gasification products such as carbon monoxide (CO) in comparison to combustion, i.e. the generation of CO_2 . Figure 4.4 shows gasification conditions for all experiments conducted in a fixed bed batch reactor, the aim of the figure is to determine if the reactor was gasifying as opposed to combusting in each experimental run.

The gasification conditions $\text{CO}/(\text{CO}+\text{CO}_2)$ of the synthetic gas were analyzed and the results are summarized in figure 4.8.

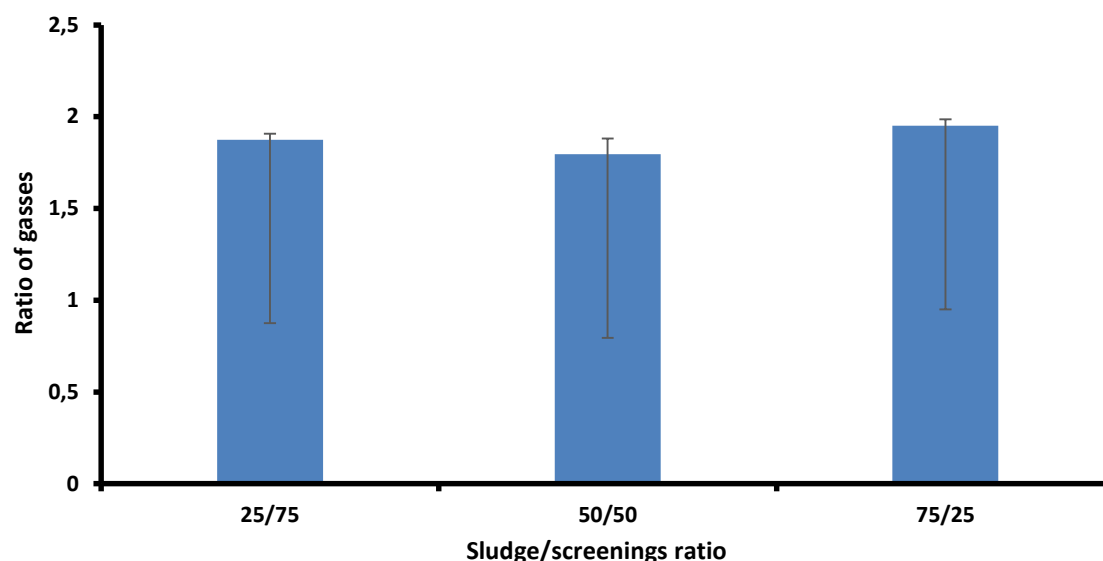


Fig 4.8: Reactor gasification conditions ($\text{CO}/(\text{CO}+\text{CO}_2)$) per experimental run

Better gasification conditions $\text{CO}/(\text{CO}+\text{CO}_2)$ were achieved at the ratio of 25/75, with the highest average of 1.87, the standard deviation of 0.032 and the coefficient of variation of 1.13%. The second overall best ratio was 75/25, at the average of 1.95, standard deviation of 0.035 and a coefficient of variation of 2.73%.

According to petroleum literature by Crocker (2018), hydrogen is a major petroleum product, as it drives many refining processes such as de-sulphurization process that removes Sulphur from petroleum products. Fuels need more carbon and hydrogen in their molecular structure, making carbon and hydrogen the main fuel components. Figure 4.9 shows hydrogen to carbon ratios on various experimental runs. Figure 4.8 measures the extent to which the reactor produces CO as opposed to CO_2 . Figure 4.9 on the other hand predicts or measures the amount of hydrogen produced in relation to CO per experimental run.

Gasification literature (Crocker, 2018) puts emphasis on H_2/CO as a measure of syngas quality. On the other hand, crude oil refining puts emphasis on H_2/HC as a measure crude oil quality in crude oil refining. Both measures indicate the importance of hydrogen in liquid fuel energy production (Higman et al., 2008). Figure 4.9 measures the crucial liquid fuel feedstock contents in relation to one another for liquid fuel production stoichiometry and for other hydrogen application processes. The gas quality with regards to hydrogen production in relation to the production of carbon monoxide was analyzed and the results are summarized in figure 4.9.

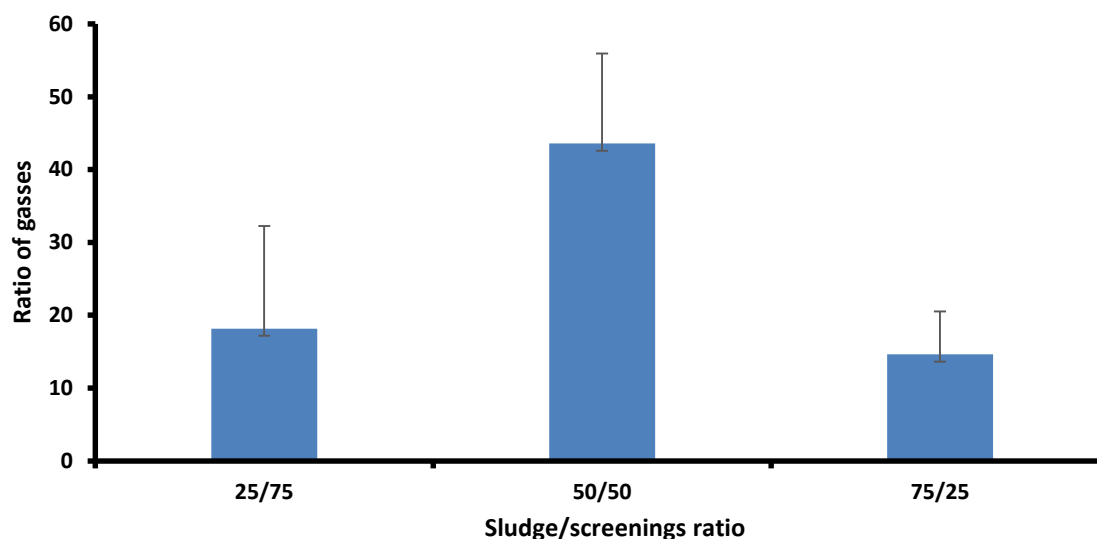


Fig 4.9: Syngas quality (H_2/CO) per experimental run

Better gas quality (H_2/CO) was achieved at the ratio of 50/50, with the average of 43.58, the standard deviation of 12.34 and the coefficient of variation of 13.88%, while the second promising ratio was 75/25, at the average of 14.62A%, standard deviation of 5.91A% and a coefficient of variation of 21.85%.

Although combustion is not a preferred reaction for gasification products, a controlled amount of it generates heat that assists in endothermic reactions during gasification.

A scoring criteria was used to simplify the selection of the better performing sludge/screenings ratio in terms of average, standard deviation and the coefficient of variation for each syngas property presented in figure 4.4 to figure 4.9. The highest average of the three ratios was given 3 points, the second was given 2 and the last one was given 1 point. On the other hand, the lowest standard deviation was given 3 points, the second lowest was given 2 and the highest was given 1 point, the same process as with the case of standard deviation was applied on the coefficient of variation. Table 4.7 shows syngas results summary for the five syngas properties of interest in this study that are the H₂, CO, and CH₄ production, gasification condition, syngas quality and syngas energy value.

Table 4.7: Overall syngas scoring results

Syngas Value	75/25			25/75			50/50		
	Av	STD	COV	Av	STD	COV	Av	STD	COV
H ₂ production	2	3	3	1	1	1	3	2	2
CO production	2	3	3	3	2	2	1	1	1
CH ₄ production	3	2	2	2	1	1	1	3	3
Gasification Conditions	3	2	2	2	3	3	1	1	1
Syngas Quality	1	3	2	2	1	1	3	2	3
Syngas energy value	3	2	2	1	1	1	2	3	3

Note from table 4.7 that best leaders are highlighted, while best finishers, the ones with 1 point less the highlighted, are blocked. The results table presented in table 4.7 aimed at simplifying the choice of the quality syngas producing ratio of the three ratios; 25/75, 50/50 and 75/25. From the syngas results summary, it was clear that 75/25 achieved most syngas qualities, followed by 50/50 ratio.

4.10 Bio-oil value products

4.10.1 Bio-oil cleanliness

Bio-oil samples were analyzed and results were chromatograms with names of species. Sample results were very diverse, with few species common in few samples at various amounts. Due to such diversity, all useful products were added together and compared with impurities that were also grouped in order to achieve a significant amount. Figure 4.10 shows bio-oil contents and trace elements or impurities. Most impurities were identified at a 25/75 followed by 25/75, 50/50 ratio proved to have least impurities.

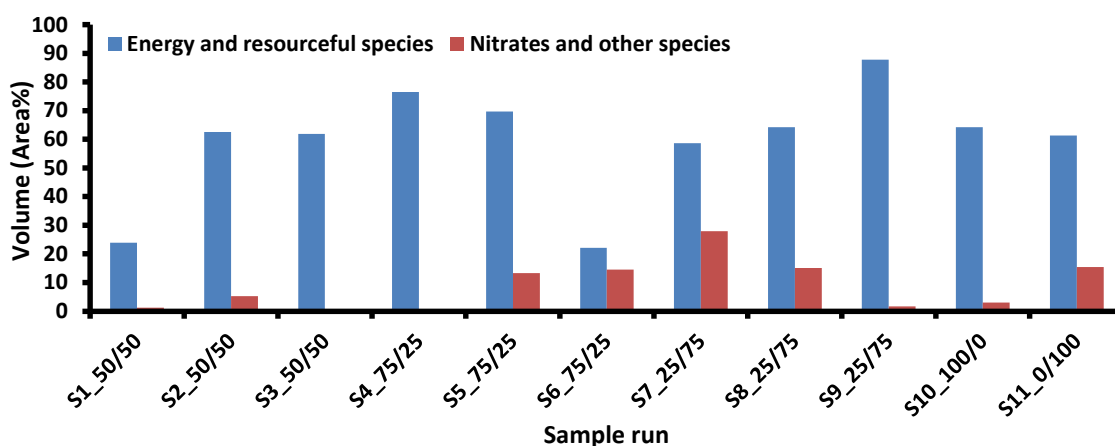


Fig 4.10: Bio-oil cleanliness results

Note the highest nitrates level was testified during the 25/75 ratio sample. An effort to reduce nitrogen will improve the quality and amount of reusable resources and energy in sludge.

4.10.2 Bio-oil carbon chains for liquid fuels

Hydrocarbon molecules with carbon (C), hydrogen (H) and oxygen (O) atoms were considered. Only molecules with area% of one (species amount to the overall amount analyzed by the GC-MS) and above were considered in those C-H-O and C-H molecules. The bio-oil analysis per sample showed that about 89% of hydrocarbons extracted are between C₃ and C₂₀. According to petroleum

fractions applications (Crocker, 2018), C_4 to C_{20} carbon chains can be processed into gas (C_1 to C_5), gasoline (C_5 to C_{12}), diesel (C_{12} to C_{18}), and lubricants (C_{20} and up). Longer carbon chains of C_{36} and above can be used in tar production. This means that useful petroleum products exist in sludge and screenings.

Figure 4.11 shows the percentages of carbon chain ranges per sample analyzed. The aim of this analysis was to find potential products in each sludge to screenings ratio to see which mix can give which products.

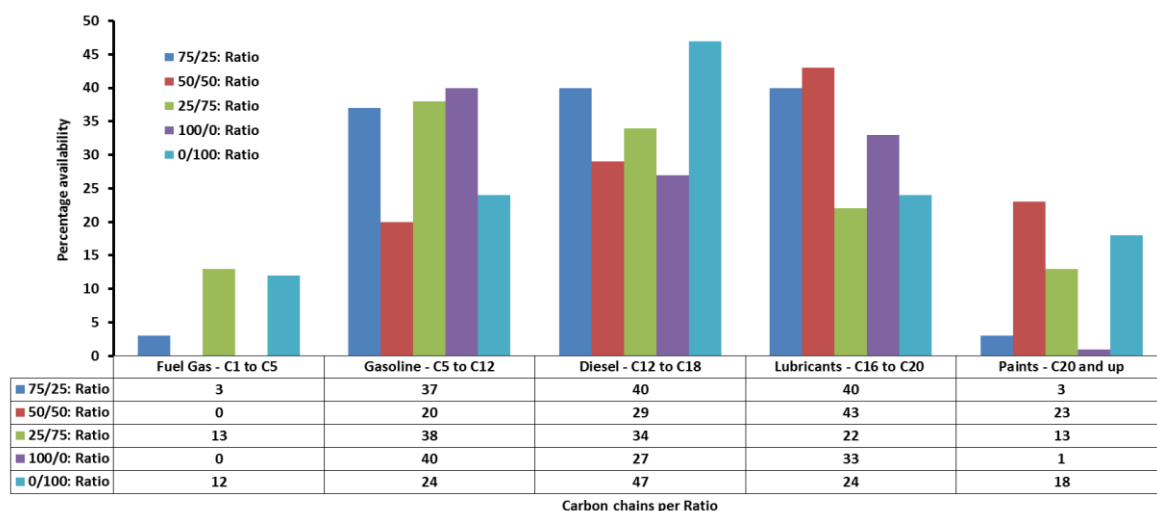


Fig 4.11: C_1 up to C_{36} chain bonds in each sludge/screenings ratio

The results in figure 4.11 showed that gas products (i.e. methane, LPG etc.) are more prevalent in screenings as proved by Young (2010) on a similar resource such as municipal solid waste (MSW). This is in line with other findings in this study, where screenings rich samples (25/75 ratio) produced highest gas volumes, gasification hydrogen and methane. Screenings rich ratios (25/75 and 0/100) also proved to have a range of petroleum resources (from gas to heavy residue chains). Sludge rich ratios (75/25 and 100/0) proved to be rich in gasoline, diesel and lubricant chains. 50/50 ratio proved to be rich in lubricants.

4.10.3 Chemical resources recovered from bio-oil

From bio-oil experimental results, the ratio that achieved the highest amount (A%) of bio-oil applicable resources C-H and C-H-O bonds was determined. The results are presented in figure 4.13.

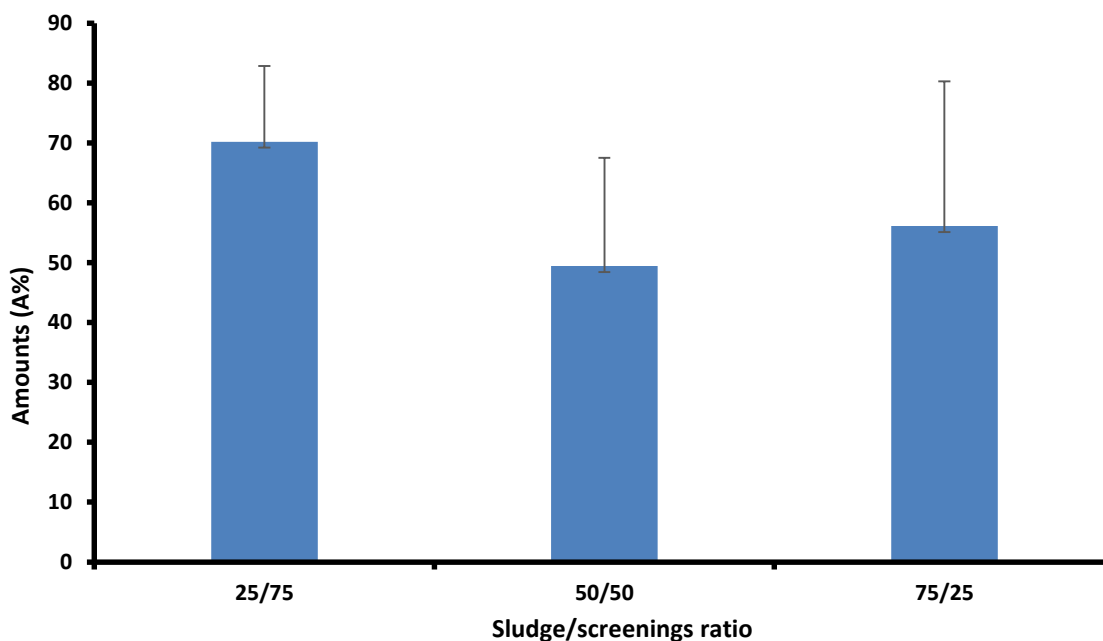


Fig 4.12: Bio-oil per sludge/screenings ratio

From figure 4.12 it is clear that 25/75 produced the highest applicable bio-oil average amount of 70.2A% at the lowest standard deviation of 12.62A%. The second highest average bio-oil amount was achieved by a 75/25 ratio at 56.12A% and at the standard deviation of 24.19A%. These C-H and C-H-O resources need further processing into various products and chemicals of interest.

4.10.4 Chemical amounts in each sludge/screenings ratio

Figure 4.13 shows chemical resources amount and compares exact chemical specie per ratio, i.e. how much of each specie came out in each of the 25/75, 50/50 and 75/25 sludge/screenings ratios.

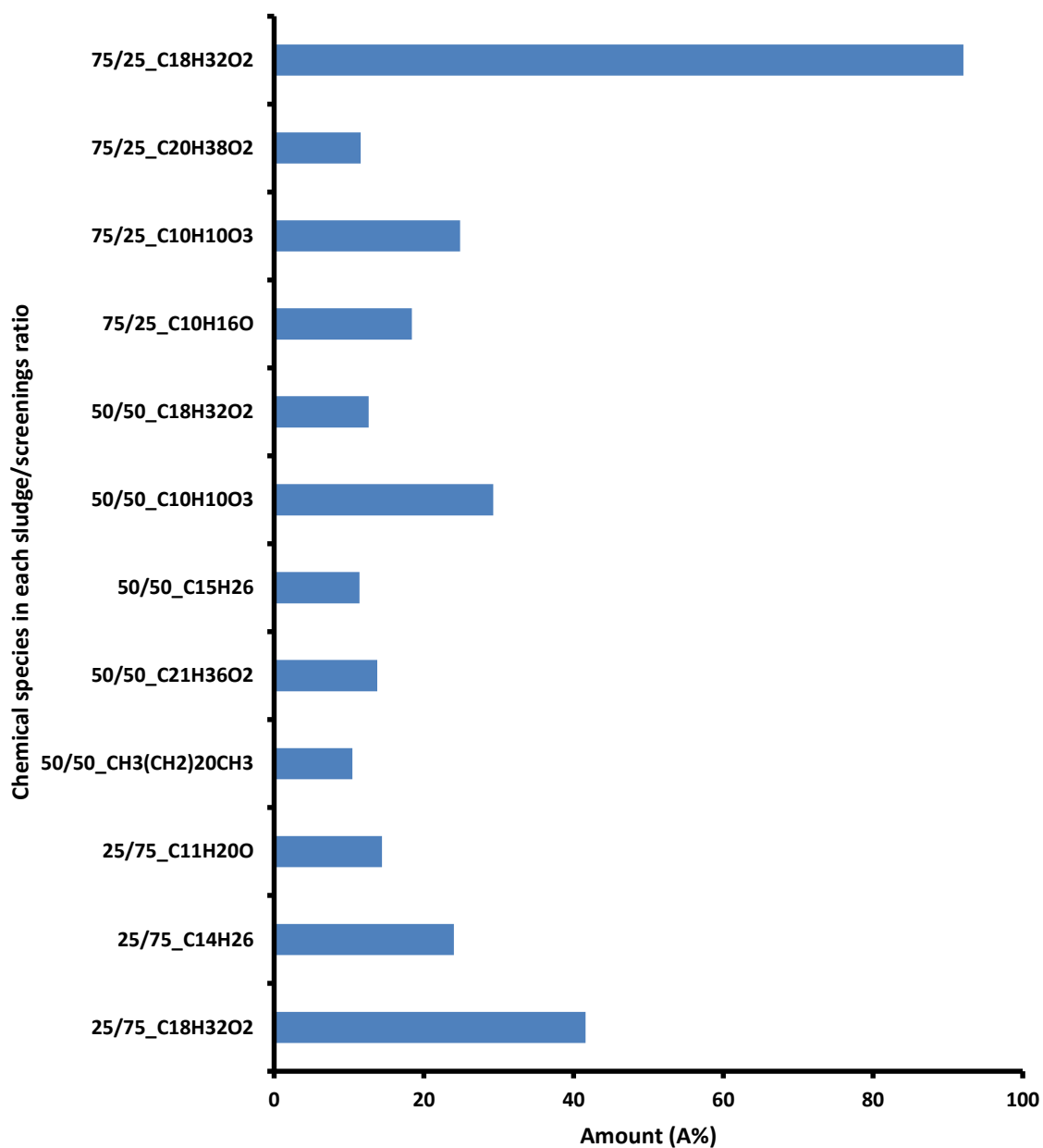


Fig 4.13: Chemical species in each sludge/screenings ratio

Although most chemicals species showed minor amounts (A%) from the GC-MS analysis, few were more frequent in significant amounts. 75/25 ratio excelled in producing significant amounts of linoleic acid ($C_{18}H_{32}O_2$) at 92A% (Pubchem, 2005; Ren, et al., 2012), this same acid was the highest in the 25/75 ratio at 42A%. 25/75 was the second highest producer of high amounts of the same species. 2-

Isopropyl-5-Methyl clohexanol or mentol was at 41.61A% and the third one was 2-Propenal or 3-(4-Hydroxy-3-methoxyphenyl)prop-2-enal (C₁₀H₁₀O) which was shared among 75/25 and 50/50 ratios (Jing-Pei, et al., 2010). Refer to annexure D for a detailed summary of resources and chemicals that were obtained at various ratios. These species are similar to bio-oil species obtained from other literature on sledge and biomass pyrolysis and gasification such as by Jing-Pei et al. (2010) and Ren S. et al. (2012).

4.10.4 Bio-oil contents summary

Bio-oil results were analyzed in summary table to find the best ratio applicable to achieve high quality bio-oil with most applicable products, least impurities, highest difference between impurities and applicable products or chemical resources as well as highest c-bonds for fuel production and chemicals production. Table 4.8 shows results that indicate the best sludge/screenings ratio to achieve some important bio-oil properties.

Table 48: Bio-oil contents per experimental run

Bio-oil Value	75/25		25/75		50/50	
	Av(A%)	Score	Av(A%)	Score	Av(A%)	Score
Bio-oil applicable contents	56.00	2	70.00	3	49.33	1
Bio-oil impurities	9.33	2	15.00	1	2	3
Variance	83.33	2	78.57	1	95.95	3
Highest usable chemicals	50.12	2	70.2	3	49.43	1
Highest repeat chemical species	146.86	3	80.01	2	77.42	1
Bio-oil amounts Of C ₁ to > C ₂₀ bonds	24.60	2	21.40	1	25.60	3

From table 4.8 it is clear that ratio 50/50 produced most bio-oil properties, followed by 75/25 and lastly was 25/75. Carbon chain bonds were almost the

same as between 21 and 26A%. This is due to the ratios being productive more of a certain range of c-chains that the other, which turns to almost level up in overall.

4.11 Gas and bio-oil results summary

Table 4.9 summarizes and simplifies the sludge per screenings ratios for syngas and bio-oil results. The table was derived from scoring the sludge per screenings ratios on syngas and bio-oil qualities, as one (1) for the least and three (3) for the best. The highest sum was the indicator of superior qualities. The aim was to identify the most resourceful ratio under gasification for both syngas and bio-oil production.

Table 4.9: Per ratio syngas and bio-oil results summary

Bio-oil Value	75/25 Score	25/75 Score	50/50 Score
H ₂ production	8	3	7
CO production	8	7	3
CH ₄ production	7	4	7
Gasification Conditions	7	8	3
Syngas Quality	6	4	8
Syngas energy value	7	3	8
Bio-oil applicable contents	2	3	1
Bio-oil impurities Variance	2	1	3
Highest usable chemicals	2	3	1
Highest repeat chemical species	3	2	1
Bio-oil amounts Of C ₁ to > C ₂₀ bonds	2	1	3
Total score	54	39	45

For both syngas and bio-oil properties, 75/25 at 54 points was the overall leader, followed by 50/50 ratio at 45 and lastly 25/75 at 39 points. Although these are the preliminary studies towards sludge/screenings gasification, it can be deduced that an optimum might be around 60/40. Future studies can look for the optimum, before designing a reactor for syngas and bio-oil production. Another benefit from these findings is that more sludge is needed per each available amount of screenings, which is fortunately in line with sludge/screenings production in the wastewater treatment environment.

4.12 Sludge and char toxicity analysis results

After gasification, the remaining char was collected and analyzed for remaining elements such C, H, N and S that are relevant to energy. Figure 4.12 shows the nature of char that remained after gasification of various sludge per screenings ratios.

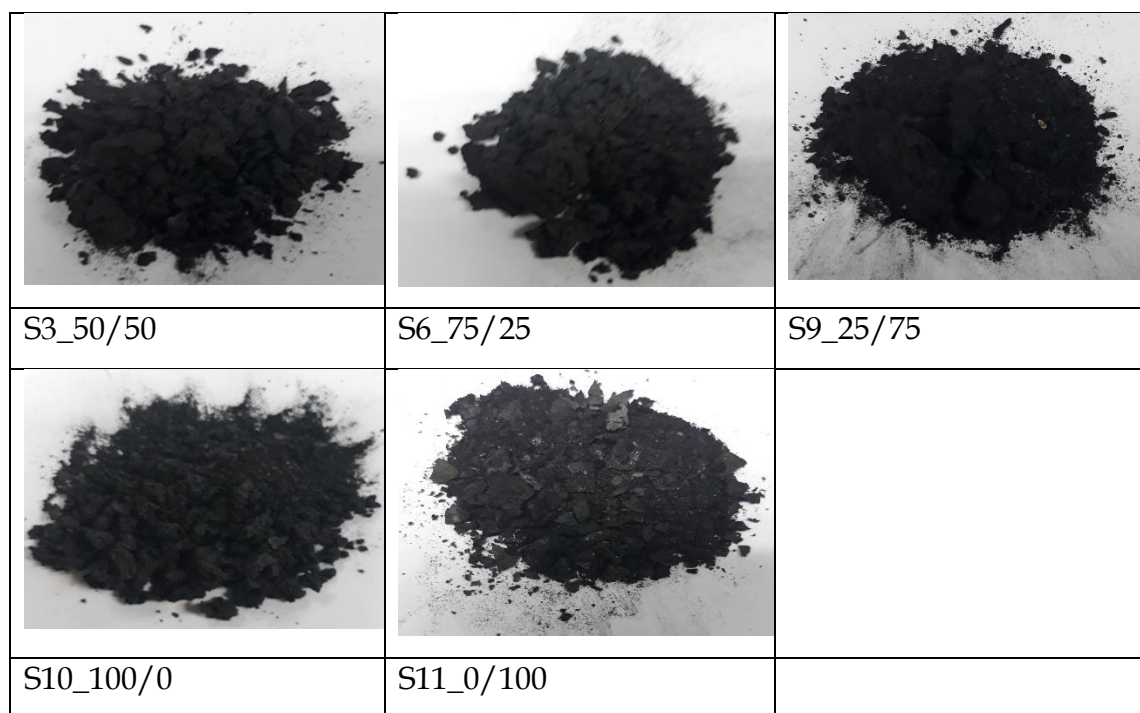


Fig 4.14: Post gasification char per sludge/screenings ratio

The results presented in table 4.10 showed the absence of hydrogen, equal presence of Sulphur and more carbon after gasification.

Table 4.10: Fuel analysis results on BP-sludge and bio-char

Element	Sludge only	Bio-char after gasification		
		50/50	75/25	25/75
% C	6.27	33.15	32.64	33.03
% H	6.27	0.00	0.00	0.00
% N	1.52	0.99	0.92	0.995
% S	0.00	2.42	2.41	2.40

The absence of hydrogen might mean that gasification broke PCBs and PAHs to some extent into bio-oil products and gas products that were analyzed during its GC-MS analysis. If all hydrogen escaped from sludge, that might imply the possibility of a complete paralysis PAHs and PCBs in sludge as these toxins are made up of C-H-x atoms. PCBs for instance have the name and a molecular formula 2, 3', 4, 4', 5-Pentachlorobiphenyl and $C_{12}H_5Cl_5$ that involve H-atoms that disappeared in the char analysis results. This might be a clear indicator of the breaking down of organic pollutants by gasification.

Literature has proven that biological pollutants such as *salmonella enterica* in sludge dies at about 40°C (SDWF, 2017). Temperature in this study reached 1000°C, which is a way beyond a temperature this pathogen can withstand. It can be concluded that biological toxicants are also destroyed by gasification.

Toxicity analysis of sludge itself proved to be safe for environment according to the disposable limits for agriculture (refer to South African sludge management guidelines. This means that the char was safe to dispose with additional advantage of weight reduction of about 68%.

4.13 Metal content in sludge and bio-char analysis results

The results of the metal content in sludge analysis showed that the metal levels in gasified sludge were below the environmental limits. Metals studied were aluminum (Al), zinc (Zn) and iron (Fe). This choice of selection was due to their popularity in the sludge from the studied WWTW sludge. The results showed that the sludge was safe to use on agricultural applications with respect to metal content.

Chapter 5. CONCLUSIONS

With results from triplicated samples at 25/75, 50/50 and 75/25 sludge/screenings ratio, the most overall gas, liquid energy and resources or chemicals benefiting ratio was established to be a 75/25 ratio, followed by a 50/50 ratio. Further studies would look for the optimum point between 50/50 and 75/25. The higher sludge/screenings ratio that promise higher quality beneficiation resources is a fortunate finding as sludge is produced at a higher ratio than screenings. The results also promise consistency, as the scoring considered lowest standard deviation, as well as the lowest coefficient of variation.

The approximate and CHNS analysis showed that the Olifantsfontein BP-sludge is comparable in properties to other sludge reviewed in literature. The absence of hydrogen in char's CHNS analysis results might mean the paralysis of PCBs and PAHs in addition to the destruction of biological toxins by the processes' high temperatures. Further analysis of bio-char to justify such a possibility which might mean that gasification destroys both toxins (biological and organochlorine) in sludge. On the other hand, the presence of carbon in bio-char after gasification can be further investigated for its potential application as an adsorbent in other processes. This carbon might mean that bio-char can be a saleable resource as an adsorbent, despite its potential use in agriculture.

Similar functional groups to those in literature were found during the functional group analysis of the BP-sludge. The thermogravimetric analysis (TGA) of the BP-sludge also showed that 540°C is an ideal temperature for extracting pyrolysis products in sludge and screenings, while 1000°C would be ideal for gasification, with a potential of reducing sludge/screenings mass by up to 68%. This mass reduction could result in significant disposal cost savings.

Chapter 6. RECOMMENDATIONS AND FUTURE WORK

For further development of the study, the following activities and studies can be conducted in future.

6.1 Toxicity analysis in bio-char

Complete toxicity analysis in bio-char from sludge to prove the possibility of polychlorinated biphenyls (PCBs) and poly aromatic hydrocarbons (PAHs) complete destruction by hydrogen removal during gasification. This will give guarantees with respect to the use of sludge for agricultural purposes.

6.2 CHNS analysis and LVH of sludge per plant

Total carbon, hydrogen, nitrogen and sulphur (CHNS) analysis and energy value (LHV) analysis of sludge per ERWAT plant will assist in identifying high energy potential sludge for a pilot plant. The lower heating value (LHV) will tell which plant produces sludge with the highest energy.

6.3 Mass and energy balance

Mass and energy balance of the entire gasification pilot plant needs to be conducted to identify the amount of sludge and screenings needed to produce a certain amount of syngas and bio-oil or saleable resources as presented in figure 4.11. This study will enable investors to see if there are potential returns in investing in such a development.

6.4 Pyrolysis and gasification pilot plant manufacturing

From the study presented in the previous chapters, a pilot scale plant is proposed that can produce gas to the volume that can drive an engine and bio-oil to a volume that can be processed into diesel, gasoline and useful chemical resources (lubricants, tar etc.).

6.5 Syngas collection and application in power generation

From the results presented in this study, syngas test to drive a gas engine to generate electricity is proposed. A high energy value syngas can drive a power generating engine (generator) and produce electricity that can pull some parts of the plant out of the grid. This will thus be a cost saving on electricity.

6.6 Syngas to liquid processing by Fischer-Tropsch synthesis

The syngas produced in this experiment can be further treated (cleaned) and processed through a Fischer-Tropsch synthesis into energy (bio-diesel and bio-gasoline) and chemical resources.

6.7 Bio-oil cleaning and cracking into useful products feedstock

Bio-oil produced in this study can also be processed through fractionation into various bio-fuel products. This can follow a similar process followed in coal gasification and conversion into liquid fuels.

6.8 Bio-char's potential as an adsorbent in other WWTW processes

Bio-char can also be investigated further with respect to its potential to be used as an adsorbent in water and other wastewater treatment processes. Clean bio-char can also be used as fertilizer in the farming industry.

6.9 Metal extraction from bio-char

Heavy metal extraction from bio-char can be further investigated as that can be an additional resource from sludge and screenings gasification process, while making sludge and screenings agro-user friendly.

REFERENCES

- Bridle, T. & Pritchard, D., 2004. *Energy and nutrient recovery from sewage sludge via pyrolysis*. [Online] Available at: https://www.researchgate.net/publication/8146909_Energy_and_nutrient_recovery_from_sewage_sludge_via_pyrolysis [Accessed 02 January 2018].
- Brown et al., 2015. *Chemistry, The Central Science*. 13th ed. Edinburg: PEARSON.
- Chen et al., 2014. Microwave Drying of Wastewater Sewage Sludge. *Clean Energy Technologies*, 2(3), pp. 282-286.
- Crocker, M., 2018. *FISCHER-TROPSCH SYNTHESIS*. [Online] Available at: https://www.netl.doe.gov/research/coal/energysystems/gasification/gasifipedia/ft_synthesis [Accessed 03 February 2018].
- Fericelli, P., 2011. *Comparison of Sludge Treatment by Gasification vs. Incineration*. Medellin, Colombia, LACCEI, pp. 55-116.
- Higman et al., 2008. *Gasification: Chapter 11, Gasification*. 1st ed. Toronto: Elsevier Inc..
- Islam, S. et al., 2016. Total and dissolved metals in the industrial wastewater: A case study from Dhaka Metropolitan, Bangladesh.. *Environmental Nanotechnology, Monitoring & Management*, 5(1), pp. 74-80.
- Jing-Pei, C. et al., 2010. Fractionation and identification of organic nitrogen species from bio-oil produced by fast pyrolysis of sewage sludge. *Bioresource Technology*, Volume 101, pp. 7648-7652.
- Kim, Y. & Parker, W., 2008. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. *Bioresource Technology*, 99(5), pp. 1409-1416.
- Lumley et al., 2014. Techno-economic analysis of wastewater sludge gasification: A decentralised urban perspective. *BIORESOURCETECHNOLOGY*, Volume 161, pp. 385-394.
- Lyu et al., 2015. Estimation and comparison of bio-oil components from different pyrolysis conditions. *Frontiers in Energy Research*, pp. 1-11.
- Molto, J., Barneto, A., Ariza, J. & Conesa, J., 2013. Gas production during the pyrolysis and gasification of biological and physico-chemical sludges from oil refinery. *JOURNAL OF ANALYTICAL AND APPLIED PYROLYSIS*, 103(1), pp. 167-172.
- Planetary Notions, 2002. *Effects of Dumping Sewage Water Directly into the Sea: A Project by Students in Saida, Lebanon*. [Online] Available at: <http://www.gobiidae.com/PN/dumpingsewage.html> [Accessed 05 January 2018].
- Pubchem, 2005. *U.S. National Library of Medicine, National Center for Biotechnology Information*. [Online] Available at: <https://pubchem.ncbi.nlm.nih.gov/search/#query=C10H10O3> [Accessed 05 January 2018].
- Ren, S. et al., 2012. Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet. *Journal of Analytical and Applied Pyrolysis*, Volume 94, pp. 163-169.
- SAMSA, 2017. *Offshore Oil and Gas - Industry Profile*. [Online] Available at:

- https://www.samsa.org.za/sites/samsa.org.za/files/industry_profile_offshore_oil_and_gas_0.pdf [Accessed 05 February 2018].
- SDWF, 2017. *Disease Causing Micro-organisms*. [Online] Available at: <https://www.safewater.org/fact-sheets-1/2017/1/23/disease-causing-microorganisms>
- Slowikowski, M., 2017. *From Feces To Fuel: Our Cars Could Soon Be Powered By Human Waste*. [Online] Available at: <https://oilprice.com/Energy/Energy-General/From-Feces-To-Fuel-Our-Cars-Could-Soon-Be-Powered-By-Human-Waste.html> [Accessed 10 January 2018].
- Suzuki, A. et al., 1988. Conversion of Sewage Sludge to Heavy Oil by Direct Thermochemical Liquefaction. *ELSEVIER*, 21(3), pp. 288-291.
- Thipkhunthod et al., 2005. Predicting the heating value of sewage sludges in Thailand from proximate and ultimate analysis. *ELSEVIER*, Volume 85, pp. 849-857.
- Werle, S., 2013. Sewage Sludge Gasification: Theoretical and Experimental Investigation. *Environmental Protection Engineering*, 39(2), pp. 25-32.
- Werle, S., 2015a. Gasification of a Dried Sewage Sludge in a Laboratory Scale Fixed Bed Reactor. *Energies*, 8(8), pp. 8562-8572.
- Werle, S., 2015b. Sewage Sludge to Energy Management in Eastern Europe: A Polish Perspective. *DE GRUYTER*, 22(3), pp. 459-469.
- Young, G., 2010. *Municipal Solid Waste to Energy Conversion Processes: Economic, Technical, and Renewable Comparison*. 1st ed. New Jersey: Wiley & Sons.

ANNEXURES

ANNEXURE: A Basic Calculations

A1: Moisture Content as per ASTM D 1762-84

Wet sludge = 50g

Dry sludge = 8.5g

$$\% \text{ Moisture lost} = \frac{\text{Wet sludge} - \text{Dry sludge}}{\text{Wet sludge}} \times 100 = \frac{50 - 8.5}{50} \times 100 = 83\%$$

A2: Preferred sludge / screenings ratio

Total sample mass = 17.5g

$50/50$: *Sludge* = $0.5 \times 17.5 = 8.75g$; *Screenings* = $0.5 \times 17.5 = 8.75g$

$75/25$: *Sludge* = $0.75 \times 17.5 = 13.125g$; *Screenings* = $0.25 \times 17.5 = 4.375g$

$25/75$: *Sludge* = $0.25 \times 17.5 = 4.375g$; *Screenings* = $0.75 \times 17.5 = 13.125g$

$100/0$: *Sludge* = $1 \times 17.5 = 17.5g$; *Screenings* = $0 \times 17.5 = 0g$

$0/100$: *Sludge* = $0 \times 17.5 = 0g$; *Screenings* = $1 \times 17.5 = 17.5g$

A3: Gas volume measured

Gas volume = *Total water volume displaced from a jar in ml*

A4: Salt in water concentration (in a salt slurry)

Crucible mass = 1.013g

Ice volume = 1850ml

$$\text{Ice volume (m}^3\text{)} = 1850 \times \left(\frac{1m}{1000m}\right)^3 = 1.85 \times 10^{-3}m^3$$

$$\text{Ice mass (kg)} = \rho V = 1000 \times 1.85 \times 10^{-3} = 1.85kg$$

$$\text{Total mass (kg)} = \text{Crucible} + \text{Salt} = 31.358g$$

$$\text{Salt mass (kg)} = \text{Total mass} - \text{Crucible mass} = 31.358 - 1.013 = 30.345g$$

Salt concentration was:

$$\text{Concentration} = \frac{\text{Mass of solute (g)}}{\text{Volume of solvent (l)}} = \frac{30.435}{1850 \times 10^{-3}} = 16.02g/l$$

A5: Mass Reduction from BP-Sludge to Bio-char

BP-sludge mass = 50g

Dries BP-sludge mass = 8.5g

Bio-char = 7.8g (*highest*)

Sample mass = 17.5g

$$\% \text{ Mass reduced} = \frac{\text{Sample mass} - \text{char mass}}{\text{Sample mass}} \times 100 = \frac{17.5 - 7.8}{17.5} \times 100 = 55.4\%$$

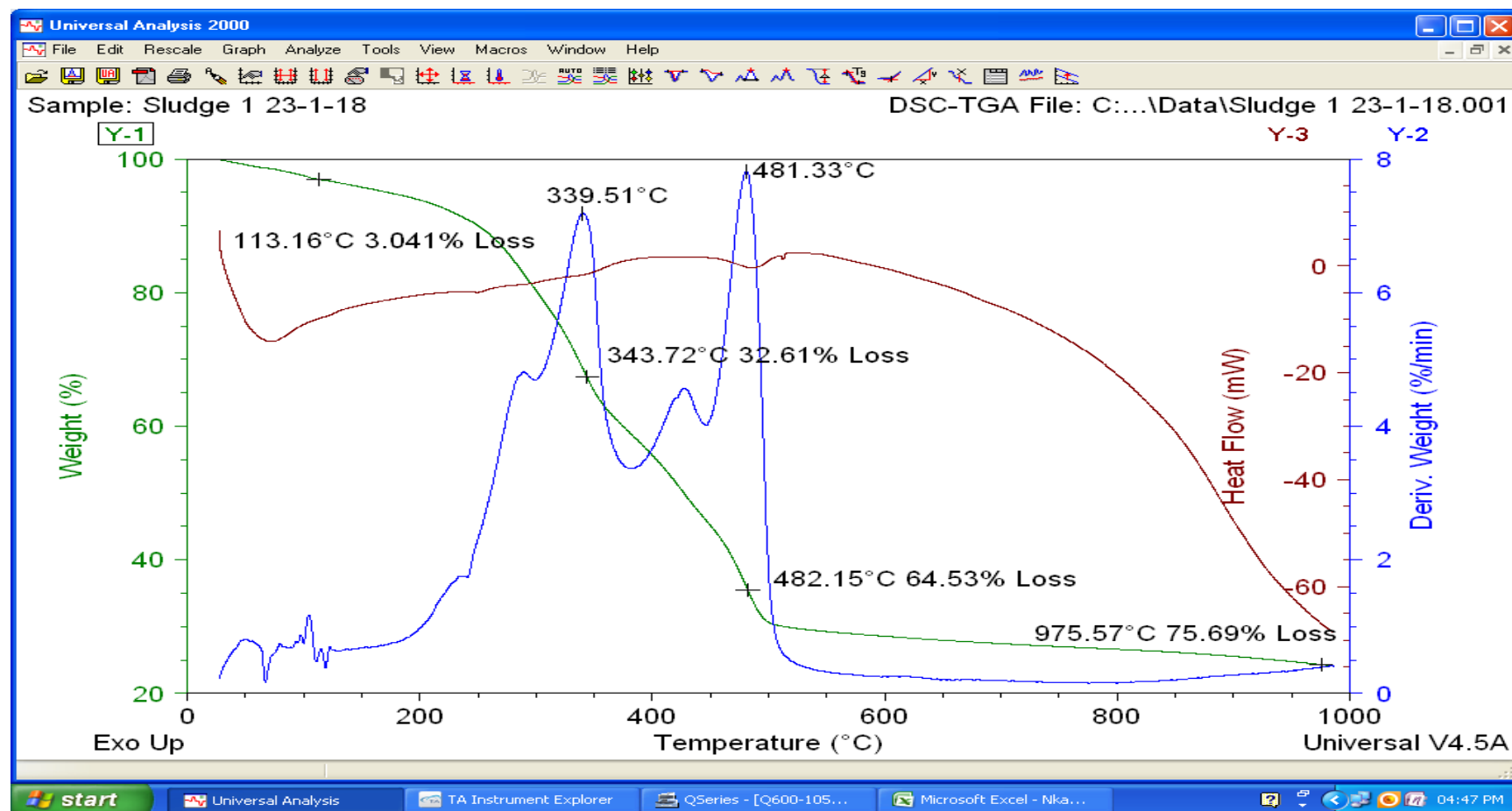
A6: Percentage Polymer in the BP-Sludge

Sludge flow rate = 516.30kg/h

Polymer to sludge ratio = 5.07kg/Ton

Belt Press speed = 1.73m/min

$$\% \text{ Polymer in sludge} = \frac{\text{Polymer}}{\text{Sludge} + \text{Polymer}} \times 100 = \frac{5.07}{1000 + 5.07} \times 100 = 0.504\%$$

ANNEXURE: B: Thermogravimetric Analysis Curves

ANNEXURE: C: Environmental Protection Agency (EPA) Metals in Sludge Limits

METALS LIMITS

PERMISSIBLE LIMITS FOR METALS

METAL	Primary Drinking Water Standard (MCL) ⁸ mg/l	Secondary Drinking Water Standard mg/l	Hazardous Waste Screening Criteria (TCLP) mg/kg	TCLP Hazardous Waste Limit mg/l	Common Range in Soils ⁶ mg/kg	Livestock Water Quality ⁶ mg/l	Surface Water Quality mg/l	Land Application of Sewage Sludge ppm
Aluminum (Al)		0.05-0.20			10,000-300,000	5.0		
Arsenic (As)	0.05		100	5.0	1-50; ⁹ 1-40 ¹⁰	0.5	0.04	75
Antimony (Sb)	0.006							
Barium (Ba)	2.0		2000	100.0	100-3,000 ¹⁰		1.0	
Beryllium (Be)	0.004							
Cadmium (Cd)	0.005		20	1.0	0.01-0.7	0.5	0.02	85
Chromium (Cr)	0.1		100	5.0	1-1,000; 5-3,000 ¹⁰	1.0	0.05	3,000
Copper (Cu)	1.3 ⁹	1.0			2-100	0.5	1.0	4,300
Iron (Fe)		0.3			7,000-550,000			
Lead (Pb)	0.015 ⁹		100	5.0	2-200	0.05	0.10	840
Manganese (Mn)		0.05			20-3,000			
Mercury (Hg)	0.002		4	0.2	0.01-0.3	0.01	0.002	57
Nickel (Ni)					5-500	1.0		420
Selenium (Se)	0.05		20	1.0	0.1-2.0	0.1	0.01	100
Silver (Ag)		0.1	100	5.0	0.01-5.0		0.05	
Thallium (Tl)	0.002							
Zinc (Zn)		5.0			10-300	25.0	5.0	

Compiled by: Brent L. Balentine 7/95 (Direction of Everett Wilson)

Revised by: Everett Wilson and Carl Solomon

ANNEXURE: D: Bio-oil Analysis Main Results**Table D1: (S1_50/50) Bio-oil results**

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area%
3Beta-Methyl-Trans-Hexahydi	C ₁₀ H ₁₀ O ₃	178.187	12.138	1
2-Mthylhexacosane	C ₂₇ H ₅₆	380.745	13.123	1
Heneicosane	C ₂₁ H ₄₄	296.583	13.745	1.13
2-Nonen-1-ol	C ₉ H ₁₈ O	142.242	13.881	1.03
Tetracontane	C ₄₀ H ₈₂	563.096	14.612	2.25
9,12-Octadecadienoic acid, methyl ester	C ₁₉ H ₃₄ O ₂	294.472	15.419	1.22
9-Octadecadienoic acid, methyl (E)-	C ₁₈ H ₃₄ O ₂	282.461	15.727	2.86
9,12-Octadecadienoic acid (Z,Z), methyl	C ₁₉ H ₃₄ O ₂	294.479	15.911	1.88
Hexacosane	C ₆₀ H ₁₂₂	843.636	16.462	1.04
Docosane (CAS)	CH ₃ (CH ₂) ₂₀ CH ₃	310.61	18.266	10.44
TOTAL:				23.85

Table D2: (S2_50/50) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area %
E,E,Z-1,3,12-Nonadecanenatriene-5,14-diol	C ₁₉ H ₃₄	294.472	13.917	1.38
E,E,Z-1,3,12-Nonadecatriene-5,14-diol	C ₁₉ H ₃₄ O ₂	294.472	15.251	2.08
9,12-Octadecadien-1 -ol, (Z,Z)	C ₁₈ H ₃₄ O	266.469	15.741	2.03
Tetracontane	C ₄₀ H ₈₂	563.096	18.019	5.34
Ethyl linoleate	C ₂₀ H ₃₆ O ₂	308.506	18.780	2.11
7,10,13-Eicosatrienoic acid, methyl ester	C ₂₁ H ₃₆ O ₂	320.517	19.451-24.033	13.75
4,8,13-Cyclotetradecatriene-1,3-diol,1,5	C ₂₀ H ₃₄ O ₂	306.49	19.733	4.45
7-Octylidenebicyclo[4.1.0]heptane	C ₁₅ H ₂₆	206.373	21.201-22.286	11.37
.alpha.-Humulene (CAS)	C ₁₅ H ₂₄	204.357	21.858	2.22
(-)-Caryophyllene oxide	C ₁₅ H ₂₀ O	220.356	24.611	2.87
Heptacosane	C ₂₇ H ₅₆	380.745	25.679	2.47
9,12-Octadecanoic acid (Z,Z)-(CAS)	C ₁₀ H ₂₀ O ₂	172.682	26.177-27.281	3.76
9,12-Octadecadienoic acid (Z,Z)-	C ₁₈ H ₃₂ O ₂	280.4455	26.762	2.32
Tricyclo[20.8.0.0(7,16)]tricontane, 1(22)	C ₃₀ H ₅₂ O ₂	444.744	28.344	3.33
Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)	C ₂₀ H ₃₈ O ₂	310.514	29.009	3.05
TOTAL:				62.53

Table D3: (S3_50/50) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area %
9,12-Octadecanoic acid (Z,Z)-	C ₁₈ H ₃₂ O ₂	280.4455	18.965	12.62
2,8-Dioxatricyclo[5.3.0.0(3,9)]decane	C ₈ H ₁₂ O ₂	140.17968	19.686	4.74
METHYL ESTER OF RICINOLEIC ACID	C ₁₉ H ₃₆ O ₃	312.487	20.756	1.14
Tricyclo[20.8.0.0(7,16)]triacontane(22)	C ₁₀ H ₁₀ O ₃	142.242	21.325-28.627	29.24
Ethyl linoleate	C ₂₀ H ₃₆ O ₂	308.506	23.143-28.986	5.51
9,12-Octadecadienoic acid (Z,Z)-(CAS)	C ₁₀ H ₂₀ O ₂	172.682	24.470	1.99
03027205002 FLAVONE 4'-OH,5-OH,7	C ₁₅ H ₁₀ O ₂	222.239	25.352	1.15
4-Isopropyl-1-methyl-3-methylenecyclohex	C ₁₁ H ₁₈	150.261	26.993	2.07
Bombykol	C ₁₆ H ₃₀ O	238.415	27.833	1.80
Kioganal II	C ₁₈ H ₃₂ O	264.453	28.827	1.64
TOTAL:				61.9

Table D4: (S4_75/25) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area %
Oxirane, tetradecyl-	C ₁₆ H ₃₂ O	240.4247	15.688	1.01
Linoelaidic acid	C ₁₈ H ₃₂ O ₂	280.452	18.882-19.730	13.37
METHYL ESTER OF RICINOLEIC ACID	C ₁₉ H ₃₆ O ₃	312.487	20.730	2.43
9,12-Octadecadienoic acid (Z,Z)-(CAS)	C ₁₀ H ₂₀ O ₂	172.682	24.470	4.16
Tricyclo[20.8.0.0(7,16)]triacontane(22)	C ₁₀ H ₁₀ O ₃	142.242	22.992-28.363	9.32
(R)-(-)-14-Methyl-8-hexadecyn-1-ol	C ₁₇ H ₃₂ O	252.442	16.096-28.143	8.86
(Z)-18-Octadec-9-enolide	C ₁₈ H ₃₂ O ₂	280.4455	26.861	28.24
3-OXABICYCLO[4.1.0]HEPTAN-2-ON	C ₁₇ H ₂₀ O ₄	288.343	27.260	3.44
8,11 -Octadecadienoic acid, methyl ester	C ₁₉ H ₃₄ O ₂	294.4721	28.772	5.65
TOTAL:				76.48

Table D5: (S5_75/25) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area %
Pentanoic acid, 3,3-dimethyl-4-semicarba	C ₇ H ₁₄ O	130.185	12.844	2.02
[1,1'-Bicyclopropyl]-2-octanoic acid 2'-hexane	C ₂₁ H ₃₈ O ₂	322.533	13.252	2.27
Hexadecane, 2,6,11,15-tetramethyl- (CAS)	C ₂₀ H ₄₂	282.556	14.594	3.11
2-Undecenal (CAS)	C ₁₁ H ₂₀ O	168.28	16.655	14.38
9-Octadecanal, (Z)- (CAS)	C ₁₈ H ₃₄ O	266.469	16.830	1.75
1,9-Tetradecadiene (CAS)	C ₁₄ H ₂₆	194.35624	17.693	24.02
METHYL ESTER OF RICINOLEIC ACID	C ₁₉ H ₃₆ O ₃	312.487	20.637	2.29
2-Isopropyl-5-methyl-1-heptanol	C ₁₁ H ₂₄ O	172.312	21.475	1.94
2-Hexyl-1-decanol	C ₁₆ H ₃₄ O	242.447	22.301	1.38
Muskolactone	C ₁₅ H ₂₈ O ₂	240.382	26.695	8.13
OXACYCLOHEXADECANE-2,13-DIO	C ₅ H ₄ O ₂	96.085	26.911	1.17
5,10-Dioxatricyclo[7.1.0.0(4,6)-]decane	C ₈ H ₁₂ O ₂	140.182	27.115	1.54
Z5-DECENYLACETATE	C ₁₂ H ₂₂ O ₂	198.306	27.835	5.74
TOTAL:				69.74

Table D6: (S6_75/25) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area%
2-Furanmethanol (CAS)	C ₅ H ₆ O ₂	98.0999	4.620	1.72
Tetradecane (CAS)	C ₁₄ H ₃₀	198.394	13.540	2.94
Cyclopropaneoctanoic acid, 2-[[2-(2-ethyl	C ₁₁ H ₂₀ O ₂	184.279	13.759	1.01
Tetradecane (CAS)	C ₁₄ H ₃₀	198.394	14.639	2.77
9,12-Octadecadienoic acid (Z,Z)-(CAS)	C ₁₀ H ₂₀ O ₂	172.682	26.795	8.44
3A,6,6,9A-TETRAMETHYLDODECAN	C ₁₆ H ₂₈ O	236.393	27.055	1.79
Tricyclo[20.8.0.0(7,16)]triacontane(22)	C ₁₀ H ₁₀ O ₃	142.242	27.290	2.28
Cyclopentene, 3-heptyl-	C ₁₁ H ₂₈	152.281	28.254	1.18
Total:				22.13

Table D7: (S7_25/75) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area%
ETHENE, (2-METHOXYETHOXY)	C ₅ H ₁₀ O ₂	102.132	4.509	1.48
2(3H)-Furanone,dihydro- (CAS)	C ₅ H ₁₀ O ₂	100.1158	5.686	1.90
4-AMINOBUTANOIC ACID HYDRO	C ₄ H ₈ O ₃	104.105	6.037	1.12
Napthalene (CAS)	C ₁₀ H ₈	128.174	8.753	1.50
Trans-5,6-Epoxydecane	C ₁₀ H ₂₀ O	156.2652	9.338	2.14
Hexanoic acid, methyl ester (CAS)	C ₇ H ₁₄ O ₂	130.1849	11.555	1.05
1-Dodecanol (CAS)	CH ₃ (CH ₂) ₁₀ CH ₂ OH	186.339	13.473	1.20
2(S),3(S)-(Isopropylidenedioxy)-4(R)-(2)	C ₁₅ H ₂₀ O ₅	280.32	13.756	1.51
2-Ethyl-1-dodecanol	C ₁₄ H ₃₀ O	214.393	14.661	2.32
Linoelaidic acid	C ₁₈ H ₃₂ O ₂	280.452	18.435	44.41
TOTAL:				58.63

Table D8: (S8_25/75) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area%
2(3H)-Furanone, dihydro- (CAS)	C ₄ H ₄ O ₂	84.074	5.682	1.61
1-(Propa-1',2'-dienyl)-2,2,6,6,-tetrauteri	C ₁₁ H ₁₆ O	164.244	6.029	1.17
Naphtalene (CAS)	C ₁₀ H ₈	128.174	8.751	1.47
trans-5,6-Epoxydecane	C ₁₀ H ₂₀ O	156.2652	9.336	2.13
Hexanoic acid, methyl ester (CAS)	C ₇ H ₁₄ O ₂	130.1849	11.548	1.01
Tetradecane (CAS)	C ₁₄ H ₃₀	198.394	12.420	1.00
2,4,6-Cycloheptatrien-1-one-3,5,-bisitrim	C ₁₃ H ₂₂	250.484	12.784	1.17
Bicyclo[2.2.1]heptan-2-one, 4,7,7-trimethyl	C ₁₀ H ₁₆ O	152.237	13.755-18.684	18.4
Dococosane (CAS)	C ₂₂ H ₄₆	310.61	14.652	2.60
Cyclododecanone, 2-methylene- (CAS)	C ₁₂ H ₂₂	182.303	16.135	7.04
Linoelaidic acid	C ₁₈ H ₃₂ O ₂	280.452	18.439	26.61
TOTAL:				64.21

Table D9: (S9_25/75) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area%
2-Methyltetracosane	C ₂₅ H ₅₂	352.691	14.664	1.22
Linoelaidic acid	C ₁₈ H ₃₂ O ₂	280.452	18.006	21.07
8,11-Eicosanoic acid, methyl ester (C)	C ₂₁ H ₃₈ O ₂	322.533	18.861	3.84
9,12-Octadecanoic acid (Z,Z)-	C ₁₈ H ₃₂ O ₂	280.4455	19.270	7.84
1,4-METHANONAPHTHALENE, 6,7-	C ₁₅ H ₂₆	206.373	21.084	1.30
9,12-Octadecadienoic acid (Z,Z)-(CAS)	C ₁₀ H ₂₀ O ₂	172.682	21.825-23.801	2.77
(R)-(-)-14-Methyl-8-hexadecyn-1-ol	C ₁₇ H ₃₂ O	252.442	22.393-28.159	9.72
1H-Indene, 1-hexadecycloctahydro- (CAS)	C ₁₇ H ₃₂ O	252.442	22.975	1.70
Tricyclo[20.8.0.0(7,16)]triacontane(22)	C ₁₀ H ₁₀ O ₃	142.242	23.305-27.317	24.84
TRISPIRO[4.2.4.2.4.2]HENEICOSAN	C ₂₁ H ₃₆	288.519	27.535	1.93
Ethanol,2-(9,12-octadecadienyloxy)- (2)	C ₂₀ H ₃₈ O ₂	310.514	28.376-28.816	11.53
TOTAL:				87.76

Table D10: (S10_100/0) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area%
Naphthalene (CAS)	C ₁₀ H ₈	128.174	8.721	1.35
1-Hexadecanol (CAS)	C ₁₆ H ₃₄ O	102.177	13.424-17.725	9.76
1-Heptadecanol (CAS)	C ₁₇ H ₃₆ O	256.474	14.445	1.63
PHENANTHRENE	C ₁₄ H ₁₀	178.234	15.812	1.52
Oxacycloheptadec-8-en-2-one (CAS)	C ₁₆ H ₂₈ O ₂	252.3923	18.061	2.29
9-Octadecanal, (Z)- (CAS)	C ₁₈ H ₃₄ O	266.469	18.721	7.35
Cyclooctacosane	C ₂₈ H ₅₆	392.756	19.663	4.41
1-Heptacosanol (CAS)	C ₂₇ H ₅₆ O	396.744	20.634	2.82
Heptanedoic acid, 2,4-dimethyl-	C ₁₁ H ₂₀ O ₄	216.2741	21.999	1.32
1-Dodecanol, 2-octyl-	C ₂₀ H ₄₂ O	298.555	23.150	1.51
[1,1'-Bicyclopropyl]-2-octanoic acid, 2'-h	C ₂₁ H ₃₈ O ₂	322.533	23.779	1.31
9,12-Octadecadienoic acid (Z,Z)-(CAS)	C ₁₈ H ₃₂ O ₂	172.682	26.495-27.416	24.25
Ethyl linoleate	C ₂₀ H ₃₆ O ₂	308.506	26.734	1.74
1-Oxaspiro[2.5]octan-4-one, 2,2-dimethyl	C ₉ H ₁₄ O ₂	154.209	27.054	1.38
Cyclopentane, 2-(1-hydroxy-2-propyl)-1	C ₁₀ H ₂₀ O	156.2652	27.100	1.56
TOTAL:				64.2

Table D11: (S11_0/100) Bio-oil results

Name	Chemical Formula	Mw (g/mol)	Retention Time	Area%
Cyclopentanone	C ₅ H ₁₀ O	84.12	3.114	4.41
1,3-CYCLOPENTADIENE, 5-(1-METHYL)	C ₈ H ₁₂ O ₂	140.182	4.134	2.01
Acetic acid	CH ₃ COOH	60.052	4.643	1.18
Butanoic acid (CAS)	C ₁₄ H ₈ O ₂	88.1051	5.271	1.18
1-Limonene	C ₁₀ H ₁₆	136.238	6.461	2.02
9H-Fluorene (CAS)	C ₁₃ H ₁₀	166.219	13.648	1.92
1,4-Benzenediol,2,6-bis(1,1-dimethylethyl)	C ₁₄ H ₂₂ O ₂	222.3233	13.999	1.30
1-Hexadecanol (CAS)	C ₁₆ H ₃₄ O	242.447	14.485	1.22
Eicosane, 7-hexyl-	C ₂₆ H ₅₄	366.718	14.663	1.22
2-Methyltetracosane	C ₂₅ H ₅₂	352.691	15.742	1.70
Isogeraniol (CAS)	C ₁₀ H ₁₈ O	154.253	16.380	1.82
1-Pentadecanol (CAS)	C ₁₅ H ₃₂ O	228.42	16.733	1.79
10-Undecynoic acid, methyl ester (CAS)	C ₁₂ H ₂₂ O ₂	198.3019	17.079	1.43
9-Octadecen-1-ol, (Z)- (CAS)	C ₁₈ H ₃₆ O	268.4778	18.115	13.20
Z-7-Hexadecenal	C ₁₆ H ₃₀ O	238.415	18.798-21.386	15.13
Oxirane, hexadecyl-	C ₁₈ H ₃₆ O	268.4778	19.692	8.46
Carbonic acid, eicosyl vinyl ester	C ₂₃ H ₄₄ O ₃	368.5937	20.661	1.36
TOTAL:				61.35